MH 12 CHEMISTRY Question and Solutions

Time Allowed :3 Hours	**Maximum Marks :**70	**Total questions :**34

General Instructions

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1. **Section A**: Q. No. 1 contains **Ten** multiple choice type of questions carrying **One** mark each. Only the first attempt will be considered for evaluation. Q. No. 2 contains **Eight** very short answer type of questions carrying **One** mark each.
2. **Section B**: Q. No. 3 to Q. No. 14 are **Twelve** short answer type -I questions carrying **Two** marks each. (Attempt any **Eight**)
3. **Section C**: Q. No. 15 to Q. No. 26 are **Twelve** short answer type -II questions carrying **Three** marks each. (Attempt any **Eight**)
4. **Section D**: Q. No. 27 to Q. No. 31 are **Five** long answer type of questions carrying **Four** marks each. (Attempt any **Three**)
5. Use of log table is allowed. Use of calculator is not allowed.
6. Figures to the right indicate full marks.
7. **Given data**:
    (i) R = 8.314 J/K/mol
    (ii) Atomic mass Na = 23
    (iii) K_f for water = 1.86 K kg mol^{-1}
    (iv) 1F = 96500C
    (v) $N_A = 6.022 \times 10^{23}$

SECTION - A

Directions: Select and write the correct answer for the following multiple choice type questions.

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1. Schottky defect is NOT observed in _______.

(A) NaCl

(B) KCl

(C) AgBr

(D) NiO

Correct Answer: (C) AgBr

Solution: Step 1: Understand the types of defects. A Schottky defect is a vacancy defect in crystalline solids where a pair of oppositely charged ions are missing from the lattice, maintaining overall electrical neutrality. It is common in highly ionic compounds where the cation and anion are of similar size (e.g., NaCl, KCl). A Frenkel defect is a defect where an ion (usually the smaller cation) is displaced from its lattice position to an interstitial site. This is common in crystals with a large size difference between the cation and anion.
Step 2: Analyze the options. - NaCl and KCl are classic examples of compounds showing Schottky defects. - AgBr is a unique case that shows both Schottky and Frenkel defects. However, it is most commonly cited as an example of a Frenkel defect because the Ag^+ ion is small and can easily move to an interstitial site. Therefore, among the given choices, AgBr is the compound where the Frenkel defect is more prominent and Schottky defect is not the primary defect observed.

Quick Tip

To identify crystal defects: - **Schottky Defect:** Think ”similar size” ions (e.g., Na^+/Cl^-). This defect decreases the density of the crystal. - **Frenkel Defect:** Think ”large size difference” (e.g., small Ag^+/large Br^-). Density remains unchanged.

2.

The freezing point of 0.1m aqueous solution of urea, if K_f for water is 1.86 K kg mol^{-1} is _______.

(A) $1.86\,°\text{C}$

(B) $-1.86\,°\text{C}$

(C) $0.186\,°\text{C}$

(D) $-0.186\,°\text{C}$

Correct Answer: (D) $-0.186\,°\text{C}$

Solution: Step 1: Identify the formula for depression in freezing point. The depression in freezing point (ΔT_f) is calculated using the formula:

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

where i is the van't Hoff factor, K_f is the molal freezing point depression constant, and m is the molality of the solution.

Step 2: Determine the value of the van't Hoff factor (i). Urea ($CO(NH_2)_2$) is a non-electrolyte, meaning it does not dissociate into ions in solution. Therefore, its van't Hoff factor is $i = 1$.

Step 3: Calculate the depression in freezing point (ΔT_f).

$$\Delta T_f = (1) \cdot (1.86 \text{ K kg mol}^{-1}) \cdot (0.1 \text{ m}) = 0.186 \text{ K or } 0.186\,°\text{C}$$

Step 4: Calculate the new freezing point of the solution. The freezing point of pure water is $0\,°\text{C}$. The freezing point of the solution is the freezing point of the pure solvent minus the depression.

$$\text{Freezing Point}_{\text{solution}} = \text{Freezing Point}_{\text{water}} - \Delta T_f$$

$$\text{Freezing Point}_{\text{solution}} = 0\,°\text{C} - 0.186\,°\text{C} = -0.186\,°\text{C}$$

Quick Tip

For colligative properties, always check if the solute is an electrolyte or non-electrolyte to determine the van't Hoff factor (i). For non-electrolytes like urea, glucose, and sucrose, $i = 1$. For electrolytes like NaCl, $i = 2$.

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3. Ozone layer is depleted by _______.

(A) NO

(B) NO_2

(C) NO_3

(D) N_2O_5

Correct Answer: (A) NO

Solution: Step 1: Recall the mechanism of ozone depletion. The ozone layer is depleted by free radical catalysts. The most well-known are chlorine radicals (from CFCs) and nitric oxide radicals.

Step 2: Analyze the role of nitric oxide (NO). Nitric oxide, often produced by the exhaust of supersonic jets in the stratosphere, acts as a catalyst in a cycle that converts ozone (O_3) to oxygen (O_2). The catalytic cycle is as follows:

$$\mathrm{NO}(g) + \mathrm{O_3}(g) \rightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

$$\mathrm{NO_2}(g) + \mathrm{O}(g) \rightarrow \mathrm{NO}(g) + \mathrm{O_2}(g)$$

The NO molecule is regenerated in the second step, allowing it to destroy thousands more ozone molecules.

Quick Tip

Remember that ozone depletion involves **catalytic cycles**. The active species (like Cl· or NO) is regenerated, which is why a small amount can cause significant damage to the ozone layer.

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4. When excess of $AgNO_3$ is added to a complex, one mole of AgCl is precipitated. The formula of complex is _______.

(A) $[CoCl_2(NH_3)_4]Cl$

(B) $[CoCl(NH_3)_5]Cl_2$

(C) $[CoCl_3(NH_3)_3]$

(D) $[Co(NH_3)_6]Cl_3$

Correct Answer: (A) $[CoCl_2(NH_3)_4]Cl$

Solution: Step 1: Understand precipitation in coordination compounds. When silver nitrate ($AgNO_3$) is added to a solution of a coordination complex, it only reacts with the halide ions that are outside the coordination sphere (the square brackets). These are known as counter-ions. Ions inside the coordination sphere are covalently bonded to the central metal atom and do not dissociate.

Step 2: Relate the amount of precipitate to the number of counter-ions. The problem states that one mole of silver chloride (AgCl) is precipitated per mole of the complex. This means there must be exactly one chloride ion (Cl^-) available as a counter-ion in the formula.

Step 3: Examine the given formulas. - (A) $[CoCl_2(NH_3)_4]Cl$: Has one Cl^- outside the brackets. Will precipitate 1 mole of AgCl. - (B) $[CoCl(NH_3)_5]Cl_2$: Has two Cl^- outside the brackets. Will precipitate 2 moles of AgCl. - (C) $[CoCl_3(NH_3)_3]$: Has zero Cl^- outside the brackets. Will precipitate 0 moles of AgCl. - (D) $[Co(NH_3)_6]Cl_3$: Has three Cl^- outside the brackets. Will precipitate 3 moles of AgCl.

Based on this analysis, formula (A) is the correct answer.

Quick Tip

Think of the square brackets in a coordination compound as a protective box. Reagents like $AgNO_3$ can only react with the ions that are *outside* this box. The number of moles of AgCl formed directly tells you the number of Cl^- ions outside the brackets.

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5. The value of Δn_g for the oxidation of 4 mole of sulphur dioxide to sulphur trioxide is _______.

(A) -2

(B) 2

(C) -4

(D) 4

Correct Answer: (A) -2

Solution: Step 1: Write the balanced chemical equation for the reaction. The standard balanced equation for the oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) is:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

This equation shows the reaction for 2 moles of SO_2. The question asks for 4 moles of SO_2, so we multiply the entire equation by 2:

$$4SO_2(g) + 2O_2(g) \rightleftharpoons 4SO_3(g)$$

Step 2: Calculate Δn_g. The change in the number of moles of gas (Δn_g) is the difference between the total moles of gaseous products and the total moles of gaseous reactants.

$$\Delta n_g = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})$$

From our balanced equation: - Moles of gaseous products = 4 mol (from $4SO_3$) - Moles of gaseous reactants = 4 mol (from $4SO_2$) + 2 mol (from $2O_2$) = 6 mol

Step 3: Substitute the values to find Δn_g.

$$\Delta n_g = 4 - 6 = -2$$

Quick Tip

To find Δn_g, always start with a balanced chemical equation for the specific quantities mentioned. Then, carefully sum the stoichiometric coefficients of all gaseous products and subtract the sum of the coefficients of all gaseous reactants.

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6. One dimensional nanostructure amongst the following is _______.

(A) Nanoparticles

(B) Nanotubes

(C) Nanofilms

(D) Nanorods

Correct Answer: (B) Nanotubes (and (D) Nanorods)

Solution: Step 1: Understand the dimensionality of nanostructures. Nanostructures are classified based on the number of dimensions that are not confined to the nanoscale range (typically 1-100 nm). - **0D (Zero-dimensional):** All three dimensions are at the nanoscale. Example: Nanoparticles (quantum dots). - **1D (One-dimensional):** Two dimensions are at the nanoscale, while the third is larger, creating an elongated structure. Examples: Nanotubes, nanorods, nanowires. - **2D (Two-dimensional):** One dimension is at the nanoscale, while the other two are larger, creating a sheet-like structure. Example: Nanofilms (graphene). - **3D (Three-dimensional):** None of the dimensions are confined to the nanoscale. These are bulk materials made of nanoscale components.

Step 2: Classify the options. - (A) Nanoparticles are 0D. - (B) Nanotubes are 1D. - (C) Nanofilms are 2D. - (D) Nanorods are 1D. Both Nanotubes and Nanorods fit the description of a one-dimensional nanostructure.

Quick Tip

Think of the "D" as the number of "free" or large dimensions. - 0D: A point (all small) → Nanoparticles. - 1D: A line (long in one direction) → Nanotubes, nanorods. - 2D: A plane (large in two directions) → Nanofilms.

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7. Which formula co-relates degree of dissociation and concentration of electrolyte?

(A) $c = \sqrt{\frac{K_a}{\alpha}}$

(B) $\alpha = \sqrt{\frac{K_a}{c}}$

(C) $c = \sqrt{K_a \alpha}$

(D) $c = \sqrt{\frac{\alpha}{K_a}}$

Correct Answer: (B) $\alpha = \sqrt{\frac{K_a}{c}}$

Solution: Step 1: State Ostwald's Dilution Law. This law relates the dissociation constant (K_a) of a weak electrolyte, its degree of dissociation (α), and its concentration (c).

Step 2: Derive the relationship. Consider a weak monoprotic acid HA dissociating in solution:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

Initial concentration: $c \quad 0 \quad 0$ Equilibrium concentration: $c(1-\alpha) \quad c\alpha \quad c\alpha$

The acid dissociation constant, K_a, is given by:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

For a weak electrolyte, the degree of dissociation α is very small, so we can approximate $1 - \alpha \approx 1$.

$$K_a \approx c\alpha^2$$

Step 3: Rearrange the formula to solve for α.

$$\alpha^2 = \frac{K_a}{c} \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{c}}$$

This shows that the degree of dissociation is inversely proportional to the square root of the concentration.

Quick Tip

Ostwald's Dilution Law is a cornerstone for understanding weak electrolytes. The key approximation is $1 - \alpha \approx 1$, which simplifies the math and leads directly to the relationship $\alpha = \sqrt{K_a/c}$.

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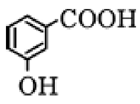
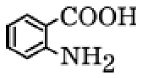
8. The highest acidic compound among the following is _______.

(a)

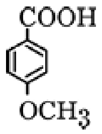


(b)



(c)

(d)



(A) o-Hydroxybenzoic acid

(B) o-Aminobenzoic acid

(C) Benzoic acid

(D) p-Methoxybenzoic acid

Correct Answer: (A) o-Hydroxybenzoic acid (Salicylic acid)

Solution: Step 1: Analyze the effect of substituents on the acidity of benzoic acid. Acidity is determined by the stability of the conjugate base (carboxylate anion, -COO$^-$).

Electron-withdrawing groups (EWGs) stabilize the anion and increase acidity.

Electron-donating groups (EDGs) destabilize the anion and decrease acidity.

Step 2: Evaluate each compound. - **(C) Benzoic acid:** This is our reference compound. - **(A) o-Hydroxybenzoic acid (Salicylic acid):** The -OH group is an EWG via its inductive effect (-I) but an EDG via resonance (+R). However, at the ortho position, the conjugate base is significantly stabilized by intramolecular hydrogen bonding between the -OH proton and the -COO$^-$ group. This is a powerful stabilizing effect known as the ”ortho effect,” making it much more acidic than benzoic acid. - **(B) o-Aminobenzoic acid:** The -NH$_2$ group is a strong EDG via resonance (+R), which destabilizes the conjugate base and decreases acidity. - **(D) p-Methoxybenzoic acid:** The -OCH$_3$ group at the para position is a strong EDG via resonance (+R), destabilizing the conjugate base and making it less acidic than benzoic acid.

Step 3: Compare the acidities. Due to the strong stabilization from intramolecular hydrogen bonding, o-hydroxybenzoic acid is the most acidic compound among the choices. The general order is: (A) ¿ (C) ¿ (D) ¿ (B).

Quick Tip

When comparing substituted benzoic acids, look for the ”ortho effect.” Ortho substituents, especially those capable of hydrogen bonding (like -OH, -NH$_2$), can have a surprisingly large impact on acidity due to steric hindrance and intramolecular H-bonding that stabilizes the conjugate base.

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9. The formula used to calculate molar conductivity of an electrolyte is _______.

(A) $\Lambda = \frac{1000c}{k}$

(B) $c = \frac{1000\Lambda}{k}$

(C) $\Lambda = \frac{1000k}{c}$

(D) $k = \frac{1000}{\Lambda c}$

Correct Answer: (C) $\Lambda = \frac{1000k}{c}$

Solution: Step 1: Define the terms. - **Molar conductivity** **(**Λ_m**):** The conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. - **Conductivity (k**

or κ): The conductance of a solution of 1 cm length with a cross-sectional area of 1 cm^2. Its unit is S cm^{-1}. - **Concentration (c):** The amount of electrolyte in moles per liter (mol L^{-1}).
Step 2: Relate the terms. Molar conductivity is defined as the conductivity divided by the molar concentration:

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

However, the units must be consistent. Typically, k is in S cm^{-1} and c is in mol L^{-1}. To make them compatible, we must convert the volume from Liters to cm^3 (since 1 L = 1000 cm^3).

$$\Lambda_m(\text{S cm}^2\text{mol}^{-1}) = \frac{k(\text{S cm}^{-1})}{c(\text{mol L}^{-1})} \times \frac{1000(\text{cm}^3)}{1(\text{L})}$$

$$\Lambda_m = \frac{1000k}{c}$$

Quick Tip

The "1000" in the molar conductivity formula is a unit conversion factor, not a fundamental constant. It's used specifically when concentration is in mol/L and conductivity is in S/cm. Always be mindful of the units you are given and the units you need.

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10. Which of the following is a secondary amine?

(A) Cyclohexylamine

(B) Isopropylamine

(C) Diphenylamine

(D) N, N-Dimethylaniline

Correct Answer: (C) Diphenylamine

Solution: Step 1: Define the classes of amines. Amines are classified based on the number of alkyl or aryl groups directly bonded to the nitrogen atom. - **Primary (1°) amine:** One carbon group attached to nitrogen (general formula $R\text{-}NH_2$). - **Secondary (2°) amine:** Two carbon groups attached to nitrogen (general formula $R_2\text{-}NH$). - **Tertiary (3°) amine:** Three carbon groups attached to nitrogen (general formula $R_3\text{-}N$).
Step 2: Classify each option. - **(A) Cyclohexylamine:** The nitrogen is attached to one cyclohexyl group. It is a primary amine ($C_6H_{11}\text{-}NH_2$). - **(B) Isopropylamine:** The nitrogen

is attached to one isopropyl group. It is a primary amine ($(CH_3)_2CH\text{-}NH_2$). - **(C) Diphenylamine:** The nitrogen is attached to two phenyl groups. It is a secondary amine ($(C_6H_5)_2NH$). - **(D) N, N-Dimethylaniline:** The nitrogen is attached to one phenyl group and two methyl groups, for a total of three carbon groups. It is a tertiary amine. Therefore, diphenylamine is the secondary amine.

Quick Tip

To quickly classify an amine, count the number of hydrogen atoms attached to the nitrogen. Two H's = Primary. One H = Secondary. Zero H's = Tertiary. (This trick works for simple, non-quaternary amines).

Q. 2. Answer the following questions :

2.1 Write the structural formula of N, N-dimethylethanamine.

Solution: The name indicates an ethanamine parent structure ($CH_3CH_2NH_2$). The "N, N-dimethyl" prefix means that two methyl groups (CH_3) replace the two hydrogens on the nitrogen atom. This results in a tertiary amine.

$$CH_3CH_2N(CH_3)_2$$

2.2 Write the reagents used for the reduction of carbonyl group in Clemmensen's reduction.

Solution: The reagents for the Clemmensen reduction are **Zinc amalgam (Zn-Hg)** and **concentrated Hydrochloric acid (conc. HCl)**.

Quick Tip

This reaction is used to reduce aldehydes and ketones to alkanes under acidic conditions. For base-sensitive compounds, the Wolff-Kishner reduction (N_2H_4, KOH/ethylene glycol) is used instead.

2.3 Write the IUPAC name of isoprene.

Solution: The structure of isoprene is CH_2=C(CH_3)CH=CH_2. The longest carbon chain containing the double bonds has 4 carbons (a butadiene). Numbering from the end that gives the substituents the lowest number, we find a methyl group on carbon 2. Therefore, the IUPAC name is **2-methylbuta-1,3-diene**.

2.4 The rate law equation for A → Product, is rate = k[A]^x. What is the effect of increase in concentration of 'A' on rate of reaction, if x ¡ 0?

Solution: When the order of the reaction with respect to a reactant is negative (x ¡ 0), the rate of the reaction is inversely proportional to the concentration of that reactant. Therefore, if the concentration of 'A' is increased, the rate of the reaction will **decrease**.

2.5 What is the molality of an aqueous solution of KBr having freezing point -3.72°C (K$_f$ for water is 1.86 K kg mol^{-1})?

Solution: Step 1: Find the depression in freezing point (ΔT_f).

$$\Delta T_f = T_{f(\text{pure})} - T_{f(\text{solution})} = 0°\text{C} - (-3.72°\text{C}) = 3.72°\text{C}$$

Step 2: Determine the van't Hoff factor (i). KBr is a strong electrolyte that dissociates into two ions: KBr → K^+ + Br^-. So, $i = 2$. **Step 3:** Use the freezing point depression formula to find molality (m).

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

$$m = \frac{\Delta T_f}{i \cdot K_f} = \frac{3.72}{2 \times 1.86} = \frac{3.72}{3.72} = 1.0\,\text{m}$$

The molality of the solution is **1.0 mol kg^{-1}**.

2.6 Write the balanced chemical equation, when excess of ammonia is treated with chlorine.

Solution: When ammonia is in excess, it reacts with chlorine to produce nitrogen gas and ammonium chloride. The balanced overall equation is:

$$8NH_3(\text{excess}) + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Quick Tip

Be careful with the limiting reactant. If chlorine were in excess, the product would be the explosive nitrogen trichloride (NCl_3).

2.7 Write the number of donor atoms present in EDTA, during formation of complex.

Solution: EDTA (Ethylenediaminetetraacetic acid) is a hexadentate ligand. It has six donor atoms that can bond to a central metal ion: two nitrogen atoms and four oxygen atoms from the deprotonated carboxyl groups. So, the number of donor atoms is **6**.

2.8 Write the names of the metal elements in brass alloy.

Solution: Brass is an alloy primarily made of **Copper (Cu)** and **Zinc (Zn)**.

Quick Tip

Remember the composition of common copper alloys: - **Brass:** Copper + Zinc - **Bronze:** Copper + Tin

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SECTION - B

Directions: Attempt any EIGHT of the following questions.

Q. 3. Derive the relation between half life and rate constant for a first order reaction.

Solution: Step 1: Start with the integrated rate law for a first-order reaction. The integrated rate law relates the initial concentration of a reactant, $[\text{A}]_0$, to its concentration at any time t, $[\text{A}]_t$, for a rate constant k.

$$\ln \frac{[\text{A}]_0}{[\text{A}]_t} = kt$$

Alternatively, in base-10 logarithm form:

$$k = \frac{2.303}{t} \log_{10} \frac{[\text{A}]_0}{[\text{A}]_t}$$

Step 2: Define half-life ($t_{1/2}$). Half-life is the time required for the concentration of a reactant to decrease to half of its initial value. At $t = t_{1/2}$, the concentration $[\text{A}]_t = \frac{1}{2}[\text{A}]_0$.

Step 3: Substitute the half-life condition into the integrated rate law. Using the natural logarithm form:

$$\ln \frac{[\text{A}]_0}{\frac{1}{2}[\text{A}]_0} = k \cdot t_{1/2}$$

Step 4: Simplify the equation. The $[\text{A}]_0$ terms cancel out:

$$\ln(2) = k \cdot t_{1/2}$$

Step 5: Solve for half-life ($t_{1/2}$). Since $\ln(2) \approx 0.693$:

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

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

This is the relation between the half-life and the rate constant for a first-order reaction. It shows that the half-life is constant and independent of the initial concentration of the reactant.

Quick Tip

A key feature of first-order reactions is their constant half-life. This is why radioactive decay, a first-order process, is described by a half-life (e.g., Carbon-14 has a half-life of 5730 years) regardless of how much material you start with.

Q. 4. (a) State Henry's law. (b) Define: Osmotic pressure

Solution: (a) Henry's Law 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 surface of the liquid. Mathematically, this is expressed as:

$$p = K_H \cdot x$$

where: - p is the partial pressure of the gas in the vapor phase. - x is the mole fraction of the gas dissolved in the liquid. - K_H is the Henry's law constant, which is specific to the gas and solvent at a given temperature.

(b) Osmotic Pressure Osmotic pressure (π) is a colligative property defined as the minimum external pressure that must be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane. It is the pressure required to stop the process of osmosis. The osmotic pressure of a dilute solution is given by the van't Hoff equation:

$$\pi = iCRT$$

where: - i is the van't Hoff factor. - C is the molar concentration of the solution. - R is the ideal gas constant. - T is the absolute temperature in Kelvin.

Q. 5. Write the differences between lanthanoids and actinoids.

Solution: The key differences between lanthanoids and actinoids are summarized below:

Property	Lanthanoids	Actinoids
Differentiating Electron	Enters the 4f orbital.	Enters the 5f orbital.
Binding Energy	The 4f electrons have a high binding energy and are held tightly by the nucleus.	The 5f electrons have a lower binding energy and are more loosely bound.
Shielding Effect	The 4f electrons have a poor shielding effect.	The 5f electrons have an even poorer shielding effect than 4f electrons.
Oxidation States	The most common oxidation state is +3. A few elements also show +2 and +4 states.	They show a wide range of variable oxidation states (e.g., from +3 to +7) because the 5f, 6d, and 7s orbitals have comparable energies.
Radioactivity	All are non-radioactive, except for Promethium (Pm).	All are radioactive.
Complex Formation	They have a lesser tendency to form complexes.	They have a greater tendency to form complexes due to their higher charge and smaller ion size.
Basicity	Their compounds are generally less basic.	Their compounds are more basic.

Q. 6. Write anomalous behaviour of oxygen with respect to : (i) Atomicity (ii) Oxidation state (iii) Magnetic property (iv) Nature of hydrides.

Solution: Oxygen shows anomalous behaviour compared to other elements in Group 16 (S, Se, Te) due to its small atomic size, high electronegativity, and the absence of d-orbitals.

(i) **Atomicity:** Oxygen is a diatomic molecule (O_2) connected by a double bond, whereas other elements like sulfur and selenium are polyatomic solids (e.g., S_8, Se_8) with puckered ring structures.

(ii) Oxidation state: Due to its high electronegativity, oxygen typically shows a -2 oxidation state. It also shows -1 (peroxides) and +2 (with fluorine, OF_2). Other elements in the group show +2, +4, and +6 oxidation states in addition to -2, due to the presence of vacant d-orbitals.

(iii) Magnetic property: Dioxygen (O_2) is paramagnetic because its molecular orbital diagram shows two unpaired electrons in the antibonding π^* orbitals. The other elements in the group are diamagnetic in their standard states.

(iv) Nature of hydrides: Water (H_2O), the hydride of oxygen, is a liquid at room temperature due to strong intermolecular hydrogen bonding. The hydrides of other group members (H_2S, H_2Se) are gases with much lower boiling points because they lack hydrogen bonding.

Q. 7. What is the action of : (i) Liquid bromine in acetic acid on anisole. (ii) Soda-lime on sodium acetate?

Solution: (i) Liquid bromine in acetic acid on anisole: This reaction is the bromination of anisole (methoxybenzene). The methoxy group ($-OCH_3$) is an activating and ortho, para-directing group. Acetic acid is a polar solvent that facilitates the reaction. The major product is p-bromoanisole due to less steric hindrance compared to the ortho position.

$$\text{Anisole} + \text{Br}_2 \xrightarrow{\text{CH}_3\text{COOH}} \text{p-Bromoanisole} + \text{HBr}$$

(ii) Soda-lime on sodium acetate: This is a decarboxylation reaction. When sodium acetate is heated with soda-lime (a mixture of NaOH and CaO), it loses a molecule of carbon dioxide to form methane.

$$\text{CH}_3\text{COONa} + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} \text{CH}_4 + \text{Na}_2\text{CO}_3$$

Q. 8. Calculate the work done in kJ in a reaction, if volume of the reactant decreases from 8 dm^3 to 4 dm^3 against 43 bar pressure. [1 dm^3 bar = 100J]

Solution: Step 1: Identify the given values. Initial volume (V_1) = 8 dm^3 Final volume (V_2) = 4 dm^3 External pressure (P_{ext}) = 43 bar

Step 2: Calculate the change in volume (ΔV).

$$\Delta V = V_2 - V_1 = 4\,\text{dm}^3 - 8\,\text{dm}^3 = -4\,\text{dm}^3$$

Step 3: Calculate the work done (W) in dm^3 bar. The formula for pressure-volume work is $W = -P_{ext}\Delta V$.

$$W = -(43\,\text{bar}) \times (-4\,\text{dm}^3) = 172\,\text{dm}^3 \cdot \text{bar}$$

Step 4: Convert the work done to Joules (J). Using the given conversion factor (1 dm^3 bar = 100 J):

$$W = 172 \times 100\,\text{J} = 17200\,\text{J}$$

Step 5: Convert the work done to kiloJoules (kJ). Since 1 kJ = 1000 J:

$$W = \frac{17200}{1000}\,\text{kJ} = 17.2\,\text{kJ}$$

The work done is **17.2 kJ**.

Q. 9. Explain ionization isomers with suitable example in complexes.

Solution: Definition: Ionization isomers are coordination compounds that have the same overall composition but produce different ions when dissolved in a solvent (usually water). This type of isomerism arises when a counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

Example: The pair $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ are ionization isomers.

- **$[Co(NH_3)_5SO_4]Br$**: When dissolved in water, it dissociates to give the complex ion $[Co(NH_3)_5SO_4]^+$ and the bromide ion Br^-. The presence of Br^- can be confirmed by adding a solution of silver nitrate ($AgNO_3$), which will form a pale yellow precipitate of silver bromide ($AgBr$).

- **$[Co(NH_3)_5Br]SO_4$**: When dissolved in water, it dissociates to give the complex ion $[Co(NH_3)_5Br]^{2+}$ and the sulfate ion $SO_4{}^{2-}$. The presence of $SO_4{}^{2-}$ can be confirmed by adding a solution of barium chloride ($BaCl_2$), which will form a white precipitate of barium sulfate ($BaSO_4$).

Q. 10. Write preparation of glucose from sucrose.

Solution: Glucose can be prepared in the laboratory by the hydrolysis of sucrose (cane sugar). **Procedure:** Sucrose is boiled with a dilute solution of a mineral acid, such as hydrochloric acid (HCl) or sulfuric acid (H_2SO_4), for about two hours. The acid acts as a catalyst for the hydrolysis reaction. **Reaction:** During this process, one molecule of sucrose breaks down to give one molecule of glucose and one molecule of fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{H}^+\text{or Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The resulting solution contains an equimolar mixture of glucose and fructose. Glucose is less soluble in ethanol than fructose, so adding ethanol to the cooled solution causes glucose to crystallize out, while fructose remains dissolved.

Quick Tip

This hydrolysis reaction is also called the ”inversion of cane sugar” because sucrose is dextrorotatory (rotates plane-polarized light to the right), but the resulting mixture of glucose (dextrorotatory) and fructose (levorotatory) is overall levorotatory. The enzyme used for this is called invertase.

Q. 11. How many coulombs of electricity is required to produce 1g of sodium metal by reduction of sodium ion?

Solution: Step 1: Write the reduction half-reaction for sodium.

$$\text{Na}^+ + e^- \rightarrow \text{Na}$$

This equation shows that 1 mole of electrons is required to produce 1 mole of sodium metal.

Step 2: Relate moles to mass and charge. - Molar mass of Na = 23 g/mol. - Charge of 1 mole of electrons = 1 Faraday (F) = 96500 Coulombs (C).

Step 3: Set up the proportion. From the stoichiometry, 96500 C of electricity are required to produce 23 g of Na. We need to find the charge (Q) required for 1 g of Na.

$$\frac{96500\,\text{C}}{23\,\text{g Na}} = \frac{Q}{1\,\text{g Na}}$$

Step 4: Solve for Q.

$$Q = \frac{96500\,\text{C}}{23} \approx 4195.65\,\text{C}$$

Approximately **4196 C** of electricity is required.

Quick Tip

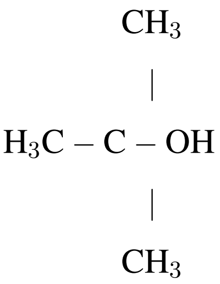
Remember Faraday's first law of electrolysis: The mass of a substance deposited at an electrode is directly proportional to the quantity of electricity passed. The constant of proportionality involves the molar mass and the number of electrons in the reaction.

Q. 12. Write the structural formula and IUPAC name of the alcohol having molecular formula $C_4H_{10}O$ which does not undergo oxidation under normal condition.

Solution: An alcohol that does not undergo oxidation under normal conditions must be a **tertiary alcohol**. This is because a tertiary alcohol has no hydrogen atom attached to the carbinol carbon (the carbon atom bonded to the -OH group).

For the molecular formula $C_4H_{10}O$, the tertiary alcohol is 2-methylpropan-2-ol.

Structural Formula:



$$\begin{array}{c} CH_3 \\ | \\ H_3C - C - OH \\ | \\ CH_3 \end{array}$$

IUPAC Name: The longest carbon chain containing the -OH group has three carbons (propane). The -OH group is on carbon 2, and a methyl group is also on carbon 2. Therefore, the name is **2-methylpropan-2-ol**.

Quick Tip

The reactivity of alcohols to oxidation is a key way to distinguish them: - **Primary (1°) alcohols** oxidize to aldehydes, then to carboxylic acids. - **Secondary (2°) alcohols** oxidize to ketones. - **Tertiary (3°) alcohols** resist oxidation under normal conditions.

Q. 13. Identify 'A' and 'B' in the following reaction and rewrite the complete reaction :

$$CH_3\text{-}CH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} A \xrightarrow[\text{-KBr}]{\text{alcoholic KCN}} B$$

Solution: Step 1: First reaction (Propene to A) This is the addition of HBr to propene in the presence of peroxide. This follows the **anti-Markovnikov's rule** (Kharasch effect), where the negative part of the addendum (Br^-) attaches to the carbon atom with more hydrogen atoms.

$$\underset{\text{Propene}}{CH_3\text{-}CH{=}CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{(A) 1-bromopropane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}Br}$$

So, **A is 1-bromopropane**.

Step 2: Second reaction (A to B) This is a nucleophilic substitution reaction where 1-bromopropane reacts with alcoholic potassium cyanide (KCN). The cyanide ion (CN^-) displaces the bromide ion (Br^-).

$$\underset{\text{(A) 1-bromopropane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}Br} + KCN\ (\text{alc.}) \rightarrow \underset{\text{(B) Butanenitrile}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CN} + KBr$$

So, **B is Butanenitrile**.

Complete Reaction:

$$CH_3\text{-}CH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} CH_3\text{-}CH_2\text{-}CH_2\text{-}Br \xrightarrow[\text{-KBr}]{\text{alcoholic KCN}} CH_3\text{-}CH_2\text{-}CH_2\text{-}CN$$

Quick Tip

The addition of HBr to an alkene can yield two different products. Without peroxide, it follows Markovnikov's rule (electrophilic addition). In the presence of peroxide, it follows a free-radical mechanism, leading to the anti-Markovnikov product. This effect is specific to HBr.

Q. 14. Write the reaction for the preparation of : (i) acetaldehyde by Rosenmund reaction. (ii) benzaldehyde by Gatterman-Koch formylation.

Solution: (i) Rosenmund Reaction for Acetaldehyde This reaction involves the catalytic hydrogenation of an acid chloride to an aldehyde. The catalyst is poisoned to prevent further reduction of the aldehyde to an alcohol.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow{\text{Pd/BaSO}_4\text{,S or quinoline}} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

(ii) Gatterman-Koch Formylation for Benzaldehyde This reaction introduces a formyl group (-CHO) onto an aromatic ring. Benzene is treated with carbon monoxide and hydrogen chloride in the presence of a catalyst mixture of anhydrous aluminum chloride and cuprous chloride.

$$\underset{\text{Benzene}}{C_6H_6} + CO + HCl \xrightarrow[\text{High Pressure}]{\text{Anhydrous AlCl}_3/\text{CuCl}} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

Quick Tip

Named reactions are important shortcuts in organic synthesis. Rosenmund reduction is a classic way to get aldehydes from acid chlorides, while Gatterman-Koch is a key method for formylating aromatic rings.

SECTION - C

Directions: Attempt any EIGHT of the following questions.

Q. 15. Write the general electronic configuration of 3d series. Draw the structures of sulphuric acid and thiosulphuric acid.

Solution: Part 1: General Electronic Configuration of 3d Series The 3d series consists of elements from Scandium (Sc, Z=21) to Zinc (Zn, Z=30). The differentiating electron enters the 3d orbital. The general electronic configuration for the elements of the 3d series is:

$$[\text{Ar}]\,3d^{1-10}\,4s^{1-2}$$

where [Ar] represents the core configuration of Argon.

Part 2: Structures of Sulphuric Acid and Thiosulphuric Acid

- **Sulphuric Acid (H_2SO_4)**: Sulphur is the central atom, bonded to two hydroxyl (-OH) groups and two oxygen atoms via double bonds. It has a tetrahedral geometry around the sulphur atom.
- **Thiosulphuric Acid ($H_2S_2O_3$)**: The structure is similar to sulphuric acid, but one of the doubly-bonded oxygen atoms is replaced by a sulphur atom.

Quick Tip

To draw structures of oxoacids, first determine the central atom (usually the least electronegative). Then, attach the required number of -OH groups corresponding to the number of acidic protons, and finally, satisfy the octet of the central atom using double bonds with the remaining oxygen atoms.

Q. 16. Define conjugate acid-base pair. The hydroxyl ion concentration in aqueous solution of NaOH is 2 $\times$ 10^{-4} mol dm^{-3}. Calculate pH of the solution.

Solution: Part 1: Definition of Conjugate Acid-Base Pair A conjugate acid-base pair consists of two species that differ from each other by the presence of a single proton (H^+). When a Brønsted-Lowry acid donates a proton, the species that remains is its conjugate base. When a Brønsted-Lowry base accepts a proton, the species formed is its conjugate acid. Example: In the reaction $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$, HCl is the acid and Cl^- is its conjugate base. H_2O is the base and H_3O^+ is its conjugate acid.
Part 2: Calculation of pH Step 1: Given Information Hydroxyl ion concentration, $[OH^-]$ = 2 $\times$ 10^{-4} mol dm^{-3}.
Step 2: Calculate pOH The pOH is the negative logarithm of the hydroxyl ion concentration.

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{pOH} = -\log_{10}(2 \times 10^{-4})$$

$$\text{pOH} = -(\log_{10} 2 + \log_{10} 10^{-4})$$

$$\text{pOH} = -(0.3010 - 4) = 3.699$$

Step 3: Calculate pH The sum of pH and pOH at 298 K (25°C) is 14.

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 3.699 = 10.301$$

The pH of the solution is **10.301**.

Quick Tip

Always remember the fundamental relationship $\text{pH} + \text{pOH} = 14$ for aqueous solutions at 25°C. If you are given $[H^+]$, find pH first. If you are given $[OH^-]$, find pOH first, then convert to pH.

Q. 17. What is atom economy? Explain any two applications of nanomaterials.

Solution: Part 1: Atom Economy Atom economy is a concept in green chemistry that measures the efficiency of a chemical reaction in converting reactants into the desired product. It is calculated as the ratio of the formula weight of the desired product to the sum of the formula weights of all reactants, multiplied by 100.

$$\%\,\text{Atom Economy} = \frac{\text{Formula weight of desired product}}{\text{Sum of formula weights of all reactants}} \times 100$$

A higher atom economy means less waste is generated.

Part 2: Applications of Nanomaterials

- **Catalysis:** Nanoparticles have a very high surface area-to-volume ratio, which makes them extremely efficient catalysts. For example, gold nanoparticles are used as catalysts in various industrial processes, and platinum nanoparticles are used in catalytic converters in automobiles to reduce harmful emissions.
- **Medicine and Drug Delivery:** Nanomaterials can be designed to target specific cells or tissues in the body. For instance, nanoparticles can be loaded with drugs and functionalized to bind only to cancer cells, delivering the therapeutic agent directly to the tumor while minimizing damage to healthy surrounding tissues.

Quick Tip

Atom economy is a theoretical measure of reaction efficiency, unlike percentage yield, which is an experimental measure. A reaction can have a 100% yield but a very low atom economy if it produces many unwanted byproducts.

Q. 18. What is peptide bond? How is it formed? Write the name and formula of the reagent used to convert alkylhalide to nitroalkane.

Solution: Part 1: Peptide Bond and its Formation A peptide bond is a covalent chemical bond formed between two amino acid molecules. It is an amide-type bond (-CO-NH-).
Formation: It is formed when the carboxyl group (-COOH) of one amino acid reacts with the amino group (-NH_2) of another amino acid. This is a condensation (or dehydration) reaction, where a molecule of water is eliminated. The resulting molecule is a dipeptide.
Part 2: Reagent for Alkyl Halide to Nitroalkane Conversion To convert an alkyl halide to a nitroalkane, the reagent used is **silver nitrite**. - **Name:** Silver Nitrite - **Formula:** $AgNO_2$
The reaction is:

$$\underset{\text{Alkyl Halide}}{\text{R-X}} + \underset{\text{Silver Nitrite}}{\text{AgNO}_2} \rightarrow \underset{\text{Nitroalkane}}{\text{R-NO}_2} + \text{AgX}$$

Quick Tip

The nitrite ion (NO_2^-) is an ambident nucleophile, meaning it can attack from two different sites (N or O). Using silver nitrite ($AgNO_2$), where the Ag-O bond is more covalent, favors attack from the nitrogen atom, forming a nitroalkane (R-NO_2). Using an ionic nitrite like $NaNO_2$ favors attack from the oxygen, forming an alkyl nitrite (R-O-N=O).

Q. 19. (a) Write the reactions for the action of following reagents on phenol : (i) Nitrating mixture (ii) Zinc dust (b) What is the action of phosphorous pentachloride on ethyl methyl ether?

Solution: (a) Reactions on Phenol

(i) **Nitrating mixture (conc. HNO_3 + conc. H_2SO_4)**: The -OH group of phenol is highly activating. Reacting phenol with a nitrating mixture results in the substitution of nitro groups at the ortho and para positions, forming 2,4,6-trinitrophenol (Picric acid).

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc. } H_2SO_4} C_6H_2(NO_2)_3OH + 3H_2O$$

(ii) **Zinc dust**: When phenol is heated with zinc dust, it undergoes dehydroxylation (removal of the -OH group) to form benzene.

$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$$

(b) Action of PCl_5 on Ethyl Methyl Ether When ethyl methyl ether ($CH_3OC_2H_5$) is heated with phosphorus pentachloride (PCl_5), the ether linkage breaks, and both alkyl groups are converted into their corresponding alkyl chlorides.

$$CH_3OC_2H_5 + PCl_5 \xrightarrow{\Delta} CH_3Cl + C_2H_5Cl + POCl_3$$

Quick Tip

The reaction of ethers with PCl_5 is a useful method for preparing alkyl halides. The C-O bonds on both sides of the ether oxygen are cleaved. Remember that phenol's reaction with zinc dust is a classic reduction that converts it back to its parent arene.

Q. 20. (a) Write the formula to calculate EAN. (b) Explain formation of $[CO(NH_3)_6]^{3+}$ complex ion with respect to : (i) Type of hybridisation (ii) Magnetic property

Solution: (a) Formula for EAN (Effective Atomic Number)

$$\text{EAN} = Z - X + Y$$

where: - Z = Atomic number of the central metal atom. - X = Number of electrons lost during the formation of the metal ion from its atom. - Y = Number of electrons donated by the ligands.

(b) Formation of $[Co(NH_3)_6]^{3+}$ Step 1: Determine the oxidation state and electron configuration of Cobalt. Cobalt (Co) has Z = 27. Its configuration is [Ar] $3d^7$ $4s^2$. In the complex, NH_3 is neutral, so the oxidation state of Co is +3. Co^{3+} has the configuration [Ar] $3d^6$.

Step 2: Consider the ligand and its effect. Ammonia (NH_3) is a strong-field ligand. It causes the pairing of the 3d electrons of Co^{3+}. The six electrons in the 3d orbitals will pair up in three orbitals.

Step 3: Determine hybridisation and magnetic property.

(i) Type of hybridisation: For the formation of six coordinate bonds with six NH_3 molecules, the Co^{3+} ion uses two empty 3d orbitals, one 4s orbital, and three 4p orbitals. This results in **d^2sp^3** hybridisation, forming an inner orbital or low-spin octahedral complex.

(ii) Magnetic property: Since all six 3d electrons are paired up due to the strong-field ligand, there are no unpaired electrons. Therefore, the complex is **diamagnetic**.

Quick Tip

The strength of the ligand determines whether a complex will be inner orbital (low-spin) or outer orbital (high-spin). Strong-field ligands like NH_3 and CN^- force electrons to pair up, using inner d-orbitals for hybridisation. Weak-field ligands like H_2O and Cl^- do not, leading to the use of outer d-orbitals.

Q. 21. (a) Calculate spin only magnetic moment of M^{2+} ion. [atomic number of M = 26] (b) Write condensed electronic configuration of Gadolinium [Z = 64].

Solution: (a) Spin-Only Magnetic Moment Calculation Step 1: Identify the element and its ion. The element M with atomic number Z = 26 is Iron (Fe). We need to find the magnetic moment for the M^{2+} ion, which is Fe^{2+}.

Step 2: Write the electronic configurations. Fe (Z=26): [Ar] $3d^6$ $4s^2$ Fe^{2+}: [Ar] $3d^6$

Step 3: Determine the number of unpaired electrons (n). In the $3d^6$ configuration, the electrons are distributed among the five d-orbitals. Following Hund's rule, there will be one pair and four unpaired electrons. So, n = 4.

Step 4: Calculate the magnetic moment (μ). The formula for spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ Bohr Magnetons (BM).

$$\mu = \sqrt{4(4+2)} = \sqrt{4 \times 6} = \sqrt{24} \approx 4.90\,\text{BM}$$

(b) Condensed Electronic Configuration of Gadolinium Gadolinium (Gd) has an atomic number Z = 64. Its configuration is an exception to the Aufbau principle due to the stability of the half-filled 4f subshell. The condensed electronic configuration is:

$$[\text{Xe}]\, 4f^7\, 5d^1\, 6s^2$$

Quick Tip

For calculating magnetic moment, the key is to correctly determine the number of unpaired electrons. For f-block elements like Gadolinium, remember the special stability associated with the half-filled f^7 configuration, which can lead to an electron occupying the 5d orbital instead of the 4f.

Q. 22. (a) Write the reducing agents used to convert Fe_2O_3 to 'Fe' in the reduction zone of blast furnace. (b) Write chemical equations involved in : (i) Carbylamine reaction for ethylamine. (ii) Hoffmann Bromamide degradation for acetamide.

Solution: (a) Reducing Agents in Blast Furnace In the reduction zone of a blast furnace, the primary reducing agent for converting iron oxides (like Fe_2O_3) to molten iron (Fe) is **carbon monoxide (CO)**. Carbon (in the form of coke) also acts as a reducing agent at higher temperatures.

(b) Chemical Equations

(i) **Carbylamine Reaction for Ethylamine:** This is a test for primary amines. Ethylamine is heated with chloroform ($CHCl_3$) and alcoholic potassium hydroxide (KOH) to form ethyl isocyanide, which has a foul smell.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + CHCl_3 + 3KOH\ (\text{alc.}) \xrightarrow{\Delta} \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$

(ii) **Hoffmann Bromamide Degradation for Acetamide:** This reaction converts an amide to a primary amine with one less carbon atom. Acetamide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Quick Tip

The Carbylamine test is specific to primary amines (both aliphatic and aromatic) and is a reliable way to distinguish them from secondary and tertiary amines. The Hoffmann degradation is a step-down reaction, crucial for synthesis where the carbon chain needs to be shortened by one atom.

Q. 23. (a) Explain Cannizzaro's reaction with the help of benzaldehyde. (b) Write the reaction for the conversion of cyclohexene to adipic acid.

Solution: (a) Cannizzaro's Reaction The Cannizzaro reaction is a redox disproportionation reaction given by aldehydes that **do not have an α-hydrogen atom**. When heated with a concentrated alkali solution (like 50% NaOH), one molecule of the aldehyde is reduced to an alcohol, and another molecule is oxidized to the salt of a carboxylic acid. **Example with Benzaldehyde:** Benzaldehyde (C_6H_5CHO) has no α-hydrogen. When two molecules of benzaldehyde are treated with concentrated NaOH, one is reduced to benzyl alcohol, and the other is oxidized to sodium benzoate.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \text{conc. NaOH} \xrightarrow{\Delta} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

(b) Conversion of Cyclohexene to Adipic Acid This conversion is achieved by the strong oxidation of cyclohexene. The double bond is cleaved, and the carbons of the double bond are oxidized to carboxylic acid groups. A common oxidizing agent for this is alkaline potassium permanganate ($KMnO_4$) followed by acidification, or hot concentrated nitric acid (HNO_3).

$$\underset{\text{Cyclohexene}}{C_6H_{10}} \xrightarrow[\text{heat}]{\text{alk. KMnO}_4} \underset{\text{Adipic acid}}{HOOC - (CH_2)_4 - COOH}$$

Quick Tip

A key way to remember the Cannizzaro reaction is "No alpha, Can't aldol". Aldehydes without alpha-hydrogens undergo Cannizzaro; those with alpha-hydrogens undergo the Aldol condensation in the presence of a dilute base.

Q. 24. Define zero order reaction. A reaction takes place in two steps : (i) NO(g) + Cl_2(g) → $NOCl_2$(g) (ii) $NOCl_2$(g) + NO(g) → 2NOCl(g). Write the overall reaction and identify the reaction intermediate.

Solution: Definition: Zero-Order Reaction A zero-order reaction is a chemical reaction wherein the rate of reaction does not depend on the concentration of the reactants. The rate is constant over time. Rate = $k[\text{Reactant}]^0$ = k, where k is the rate constant.

Reaction Analysis Step 1: Write the overall reaction. To get the overall reaction, add the elementary steps and cancel out species that appear on both sides.

$$\text{Step 1: } NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$$

$$\underline{\text{Step 2: } NOCl_2(g) + NO(g) \rightarrow 2NOCl(g)}$$

$$\text{Overall: } 2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

Step 2: Identify the reaction intermediate. A reaction intermediate is a species that is formed in one step of a reaction and consumed in a subsequent step. It does not appear in the overall balanced equation. In this mechanism, **$NOCl_2$(g)** is formed in Step 1 and consumed in Step 2. Therefore, $NOCl_2$ is the reaction intermediate.

Quick Tip

Intermediates are transient species that are part of the reaction mechanism but are not final products. Catalysts, on the other hand, are consumed in one step and regenerated in a later step, so they also don't appear in the overall equation but are present at the beginning and end.

Q. 25. ΔH for formation of ethane gas is -84.4 kJ at 300 K. Calculate ΔU for the reaction.

Solution: Step 1: Write the balanced chemical equation for the formation of ethane. Ethane (C_2H_6) is formed from its constituent elements in their standard states: solid carbon (graphite) and hydrogen gas (H_2).

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$$

Step 2: Use the relationship between enthalpy change (ΔH) and internal energy change (ΔU).

$$\Delta H = \Delta U + \Delta n_g RT$$

where: - Δn_g = (moles of gaseous products) - (moles of gaseous reactants) - R = Ideal gas constant (8.314 J K^{-1} mol^{-1}) - T = Absolute temperature in Kelvin

Step 3: Calculate Δn_g.

$$\Delta n_g = (1) - (3) = -2\,\text{mol}$$

Step 4: Rearrange the formula and solve for ΔU.

$$\Delta U = \Delta H - \Delta n_g RT$$

Given: - $\Delta H = -84.4$ kJ = -84400 J - $\Delta n_g = -2$ mol - R = 8.314 J K^{-1} mol^{-1} - T = 300 K

$$\Delta U = -84400\,\text{J} - (-2\,\text{mol} \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times 300\,\text{K})$$

$$\Delta U = -84400\,\text{J} - (-4988.4\,\text{J})$$

$$\Delta U = -84400 + 4988.4 = -79411.6\,\text{J}$$

Step 5: Convert ΔU to kJ.

$$\Delta U = -79.4116\,\text{kJ} \approx -79.41\,\text{kJ}$$

Quick Tip

Pay close attention to units. Since R is in J/K·mol, it's best to convert ΔH to Joules for the calculation and then convert the final answer back to kiloJoules. Also, remember that Δn_g only includes gaseous species.

Q. 26. Mention the types of polymers formed on the basis of intermolecular forces. Write any two uses of low density polyethylene.

Solution: Part 1: Types of Polymers Based on Intermolecular Forces Based on the magnitude of intermolecular forces, polymers are classified into four types:

1. **Elastomers:** These polymers have the weakest intermolecular forces, which allow them to be stretched. The polymer chains are held together by weak van der Waals forces. Example: Buna-S, Neoprene.
2. **Fibres:** These polymers have strong intermolecular forces, such as hydrogen bonding or dipole-dipole interactions. These strong forces lead to close packing of chains and give them high tensile strength. Example: Nylon-6,6, Terylene.
3. **Thermoplastics:** These polymers have intermolecular forces that are intermediate between elastomers and fibres. They can be repeatedly softened by heating and hardened by cooling. Example: Polyethylene, PVC.

4. **Thermosetting Polymers:** These polymers form extensive cross-links between chains when heated, leading to a hard, infusible, and insoluble mass. They cannot be remolded once set. Example: Bakelite, Urea-formaldehyde resin.

Part 2: Uses of Low-Density Polyethylene (LDPE) Low-density polyethylene is a chemically inert and flexible material. Two common uses are:

1. **Packaging Film:** It is widely used to make plastic bags, grocery bags, and packaging films.
2. **Insulation for Wires and Cables:** Its flexibility and excellent electrical insulation properties make it suitable for insulating electrical wires and cables.

Quick Tip

A simple way to remember the polymer types by force: Elastomers are weak and stretchy (rubber bands), Fibres are strong and thread-like (clothing), Thermoplastics can be reshaped with heat (plastic bottles), and Thermosetting polymers set permanently with heat (pot handles).

SECTION - D

Directions: Attempt any THREE of the following questions.

Q. 27. (a) An element with molar mass 27 g/mol forms a cubic unit cell with edge length 405 pm. If density of the crystal is 2.7 g cm^{-3}, identify the type of unit cell. (b) Derive the equation of Raoult's law for binary solution containing non-volatile solute.

Solution: (a) Identifying the Type of Unit Cell Step 1: List the given information. - Molar mass (M) = 27 g/mol - Edge length (a) = 405 pm = 405 $\times$ 10^{-10} cm = 4.05 $\times$ 10^{-8} cm - Density (ρ) = 2.7 g cm^{-3} - Avogadro's number (N$_A$) = 6.022 $\times$ 10^{23} mol^{-1}

Step 2: Use the formula for the density of a unit cell. The density is related to the molar mass and unit cell dimensions by the formula:

$$\rho = \frac{z \cdot M}{a^3 \cdot N_A}$$

where 'z' is the number of atoms per unit cell.

Step 3: Rearrange the formula to solve for z.

$$z = \frac{\rho \cdot a^3 \cdot N_A}{M}$$

Step 4: Substitute the values and calculate z.

$$z = \frac{(2.7\,\text{g cm}^{-3}) \cdot (4.05 \times 10^{-8}\,\text{cm})^3 \cdot (6.022 \times 10^{23}\,\text{mol}^{-1})}{27\,\text{g mol}^{-1}}$$

$$z = \frac{(2.7) \cdot (66.43 \times 10^{-24}) \cdot (6.022 \times 10^{23})}{27}$$

$$z = \frac{108.0}{27} = 4$$

Step 5: Identify the unit cell type. Since the number of atoms per unit cell (z) is 4, the unit cell is a **face-centred cubic (FCC)** unit cell.

(b) Derivation of Raoult's Law for a Solution with a Non-Volatile Solute Step 1: State Raoult's Law. Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction. For a component 1, $P_1 \propto x_1$, or $P_1 = P_1^0 x_1$, where P_1^0 is the vapour pressure of the pure component.

Step 2: Consider a binary solution with a non-volatile solute. Let the solvent be component 1 and the non-volatile solute be component 2. The vapour pressure of the solution will only be due to the solvent, as the solute does not contribute to the vapour. Therefore, the vapour pressure of the solution (P_{solution}) is equal to the partial vapour pressure of the solvent (P_1).

$$P_{\text{solution}} = P_1 = P_1^0 x_1 \quad \cdots (1)$$

Step 3: Define the lowering of vapour pressure. The lowering of vapour pressure (ΔP) is the difference between the vapour pressure of the pure solvent (P_1^0) and the vapour pressure of the solution (P_{solution}).

$$\Delta P = P_1^0 - P_{\text{solution}}$$

Substituting equation (1):

$$\Delta P = P_1^0 - P_1^0 x_1 = P_1^0 (1 - x_1)$$

Step 4: Relate to the mole fraction of the solute. For a binary solution, the sum of the mole fractions is 1: $x_1 + x_2 = 1$. Therefore, $1 - x_1 = x_2$. Substituting this into the equation for ΔP:

$$\Delta P = P_1^0 x_2$$

Step 5: Derive the expression for relative lowering of vapour pressure. The relative lowering of vapour pressure is the ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent.

$$\frac{\Delta P}{P_1^0} = \frac{P_1^0 x_2}{P_1^0}$$

$$\frac{\Delta P}{P_1^0} = x_2$$

This equation, $\frac{P_1^0 - P_{\text{solution}}}{P_1^0} = x_2$, is the mathematical expression of Raoult's law for a solution containing a non-volatile solute. It shows that the relative lowering of vapour pressure is equal to the mole fraction of the solute.

Quick Tip

For unit cell calculations, ensure all units are consistent before plugging them into the formula (e.g., convert pm to cm). For Raoult's law, remember that a non-volatile solute lowers the vapour pressure of the solvent because it reduces the fraction of solvent molecules at the surface available to escape into the vapour phase.

Q. 28. (a) State whether entropy change is positive or negative in the following examples : (i) Melting of ice (ii) Vaporisation of a liquid (b) Explain 'common ion effect' with example.

Solution: (a) Entropy Change Entropy is a measure of the randomness or disorder of a system.

(i) **Melting of ice**: This is a phase transition from a highly ordered solid state to a less ordered liquid state. The disorder increases, so the entropy change (ΔS) is **positive**.

(ii) **Vaporisation of a liquid**: This is a phase transition from a less ordered liquid state to a highly disordered gaseous state. The disorder increases significantly, so the entropy change (ΔS) is **positive**.

(b) Common Ion Effect The common ion effect is the suppression of the dissociation of a weak electrolyte upon the addition of a strong electrolyte that contains an ion in common with the weak electrolyte. **Example:** Consider the dissociation of the weak acid, acetic acid

(CH_3COOH):

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

If we add sodium acetate (CH_3COONa), a strong electrolyte, it dissociates completely into Na^+ and CH_3COO^- ions. This increases the concentration of the common ion, acetate (CH_3COO^-). According to Le Chatelier's principle, the equilibrium of the acetic acid dissociation will shift to the left to counteract this increase, thus reducing the ionization of acetic acid.

Quick Tip

Entropy generally increases as a substance goes from solid to liquid to gas. The common ion effect is a direct application of Le Chatelier's principle to ionic equilibria, crucial for understanding buffer solutions and solubility.

Q. 29. Draw a neat and labelled diagram of a lead accumulator cell. Write the overall reactions taking place at cathode and anode during discharging of the cell.

Solution: Lead Accumulator Cell A lead accumulator is a secondary (rechargeable) cell. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as the cathode. The electrolyte is an aqueous solution of sulphuric acid (about 38% H_2SO_4).

Reactions during Discharging:

- **Anode (Oxidation):** The lead anode is oxidized to lead(II) sulfate.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

- **Cathode (Reduction):** The lead dioxide cathode is reduced to lead(II) sulfate.

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

Overall Cell Reaction: Adding the anode and cathode half-reactions gives the overall reaction:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

Quick Tip

A useful mnemonic for electrode reactions is ”An Ox” (Anode is Oxidation) and ”Red Cat” (Reduction at Cathode). Note that during the discharge of a lead-acid battery, both electrodes become coated with lead(II) sulfate, and the concentration of the sulfuric acid electrolyte decreases.

Q. 30. (a) Define a unit cell. Which colour is shown by NaCl crystal due to formation of F-centre? (b) Why does fluorine show anomalous behaviour in ‘17 group’ elements?

Solution: (a) Unit Cell and F-centre

- **Unit Cell Definition:** A unit cell is the smallest repeating structural unit of a crystalline solid. When repeated in three dimensions, it generates the entire crystal lattice.
- **Colour due to F-centre:** When an NaCl crystal is heated in an atmosphere of sodium vapour, it develops a **yellow** colour. This is due to the formation of F-centres, which are anionic sites occupied by unpaired electrons. These electrons absorb energy from the visible region of light and get excited, imparting colour to the crystal.

(b) Anomalous Behaviour of Fluorine Fluorine, the first member of Group 17, shows anomalous behaviour compared to other halogens. This is due to its:

1. **Small atomic size:** It is the smallest atom in its group.
2. **Highest electronegativity:** It is the most electronegative element in the periodic table.
3. **Low F-F bond dissociation enthalpy:** Due to repulsion between the lone pairs on the small fluorine atoms.
4. **Absence of d-orbitals:** In its valence shell, which restricts it to an oxidation state of -1 and prevents it from forming polyhalide ions or expanding its octet.

Quick Tip

The anomalous properties of the first element in any p-block group (like Fluorine) are a consistent trend. The main reasons are always small size, high electronegativity, and the non-availability of d-orbitals.

Q. 31. (a) Write salient features of SN^2 mechanism. (b) What is the action of following reagents on bromomethane : (i) bromobenzene (ii) mercurous fluoride

Solution: (a) Salient Features of SN^2 Mechanism

- It is a single-step, concerted mechanism where bond breaking and bond formation occur simultaneously.
- It follows second-order kinetics, i.e., the rate is proportional to the concentration of both the substrate and the nucleophile: Rate = k[Alkyl Halide][Nucleophile].
- The attack of the nucleophile occurs from the side opposite to the leaving group (backside attack).
- It results in a complete inversion of the stereochemical configuration, known as Walden inversion.
- The reactivity order for alkyl halides is governed by steric hindrance: CH_3X ¿ 1° ¿ 2° ¿ 3°.

(b) Reactions of Bromomethane

(i) **Bromobenzene (in presence of Na/dry ether):** This is the Wurtz-Fittig reaction. Bromomethane reacts with bromobenzene in the presence of sodium metal in dry ether to form toluene.

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + \underset{\text{Bromomethane}}{CH_3Br} + 2Na \xrightarrow{\text{dry ether}} \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaBr$$

(ii) **Mercurous fluoride (Hg_2F_2):** This is a halogen exchange reaction known as the Swarts reaction, used for the synthesis of alkyl fluorides. Bromomethane reacts with mercurous fluoride to form fluoromethane.

$$2CH_3Br + Hg_2F_2 \rightarrow 2CH_3F + Hg_2Br_2$$

Quick Tip

For substitution reactions, SN^2 means ”substitution, nucleophilic, bimolecular.” Think ”backside attack” and ”inversion.” For preparing specific alkyl halides, remember the Swarts reaction (using metal fluorides) for fluoroalkanes and the Finkelstein reaction (using NaI/acetone) for iodoalkanes.