CUET UG Chemistry Sample Paper - 18

Duration: 1 Hour **Maximum Marks: 250**

Instructions

- This paper contains a total of 50 Multiple Choice Questions.
- Each correct answer carries **+5 marks**.
- Each incorrect answer carries **-1 mark**.
- No negative marking for unattempted questions.

Q1. Arrange the following in increasing order of their osmotic pressure (assuming molarities are equal):

I. Glucose II. $MgCl_2$ III. $NaCl$ IV. $Al_2(SO_4)_3$

(A) I < III < II < IV

(B) IV < II < III < I

(C) I < II < III < IV

(D) III < I < II < IV

Q2. The value of Henry's Law constant K_H is:

(A) Greater for gases with higher solubility.

(B) Greater for gases with lower solubility.

(C) Constant for all gases at all temperatures.

(D) Not related to the nature of the gas.

Q3. An unknown solute is dissolved in water. If the Van't Hoff factor (i) is found to be 2.74, the solute is most likely:

(A) $NaCl$

(B) $CaCl_2$

(C) $AlCl_3$

(D) Glucose

Q4. According to Raoult's Law, the relative lowering of vapor pressure for a solution containing a non-volatile solute is equal to:

(A) Mole fraction of the solvent.

(B) Mole fraction of the solute.

(C) Molality of the solution.

(D) Molarity of the solution.

Q5. For an ideal solution, which of the following is correct?

(A) $\Delta H_{\text{mix}} > 0, \Delta V_{\text{mix}} = 0$

(B) $\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} > 0$

(C) $\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$

(D) $\Delta G_{\text{mix}} = 0$

Q6. How much charge (in Faraday) is required to reduce 1 mole of MnO_4^- to Mn^{2+}?

(A) 1 F

(B) 3 F

(C) 5 F

(D) 2 F

Q7. The limiting molar conductivity of an electrolyte A_2B is given by:

(A) $\lambda^\circ_A + \lambda^\circ_B$

(B) $2\lambda^\circ_A + \lambda^\circ_B$

(C) $\lambda^\circ_A + 2\lambda^\circ_B$

(D) $1/2\lambda^{\circ}_{A} + \lambda^{\circ}_{B}$

Q8. In a Hydrogen-Oxygen fuel cell, the reaction occurring at the cathode is:

(A) $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

(B) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(C) $H^+ + e^- \rightarrow 1/2H_2$

(D) $Zn \rightarrow Zn^{2+} + 2e^-$

Q9. The Nernst equation for the electrode reaction $M^{n+} + ne^- \rightarrow M$ at 298 K is:

(A) $E = E^{\circ} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$

(B) $E = E^{\circ} + \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$

(C) $E = E^{\circ} - \frac{n}{0.059} \log[M^{n+}]$

(D) $E = E^{\circ} - 0.059 \log[M^{n+}]$

Q10. Which of the following batteries is a secondary cell?

(A) Dry cell

(B) Mercury cell

(C) Lead storage battery

(D) Leclanché cell

Q11. If the E°_{cell} for a reaction is negative, then:

(A) $\Delta G^{\circ} < 0, K_c > 1$

(B) $\Delta G^{\circ} > 0, K_c < 1$

(C) $\Delta G^{\circ} = 0, K_c = 1$

(D) $\Delta G^{\circ} > 0, K_c > 1$

Q12. For a first-order reaction, the time taken for 75% completion is:

(A) Twice the half-life ($t_{1/2}$).

(B) Thrice the half-life ($t_{1/2}$).

(C) Equal to the half-life ($t_{1/2}$).

(D) Four times the half-life ($t_{1/2}$).

Q13. The rate constant for a reaction is $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}. The order of the reaction is:

(A) Zero

(B) First

(C) Second

(D) Third

Q14. According to the Arrhenius equation, a plot of $\ln k$ vs $1/T$ gives a straight line with slope:

(A) E_a/R

(B) $-E_a/R$

(C) A/R

(D) $-R/E_a$

Q15. For a zero-order reaction, the unit of the rate constant is:

(A) s^{-1}

(B) mol L^{-1} s^{-1}

(C) L mol^{-1} s^{-1}

(D) mol L^{-1}

Q16. If the concentration of reactant is doubled and the rate of reaction quadruples, the order of reaction is:

(A) 0

(B) 1

(C) 2

(D) 3

Q17. Lanthanoid contraction is due to:

(A) Perfect shielding of 4f electrons.

(B) Poor shielding of 4f electrons.

(C) Increase in nuclear charge.

(D) Both (B) and (C).

Q18. Which of the following ions is colorless in aqueous solution?

(A) Ti^{3+}

(B) V^{3+}

(C) Sc^{3+}

(D) Fe^{2+}

Q19. The highest oxidation state shown by transition elements is:

(A) +7

(B) +8

(C) +6

(D) +5

Q20. The magnetic moment of a divalent ion ($Z = 25$) in aqueous solution is:

(A) 2.84 BM

(B) 3.87 BM

(C) 5.92 BM

(D) 4.90 BM

Q21. The IUPAC name of $[Co(NH_3)_5Cl]Cl_2$ is:

(A) Pentaamminechlorocobalt (III) chloride

(B) Pentaaminechloridocobalt (III) chloride

(C) Chloridopentaamminecobalt (III) chloride

(D) Pentaamminechloridocobalt (II) chloride

Q22. Which of the following complexes shows linkage isomerism?

(A) $[Co(NH_3)_5Cl]SO_4$

(B) $[Co(NH_3)_5(NO_2)]Cl_2$

(C) $[Cr(H_2O)_6]Cl_3$

(D) $[Fe(en)_3]Cl_3$

Q23. According to Crystal Field Theory, the sequence of ligands in the spectrochemical series is:

(A) $Cl^- < F^- < OH^- < CN^-$

(B) $CN^- < OH^- < F^- < Cl^-$

(C) $F^- < Cl^- < CN^- < OH^-$

(D) $OH^- < CN^- < Cl^- < F^-$

Q24. The hybridization and shape of $[Ni(CN)_4]^{2-}$ are:

(A) sp^3, Tetrahedral

(B) dsp^2, Square Planar

(C) sp^3d^2, Octahedral

(D) d^2sp^3, Octahedral

Q25. The number of geometrical isomers for $[Pt(NH_3)_2Cl_2]$ is:

(A) 2

(B) 3

(C) 4

(D) 0

Q26. Which of the following is an outer orbital complex?

(A) $[Fe(CN)_6]^{3-}$

(B) $[Mn(CN)_6]^{3-}$

(C) $[CoF_6]^{3-}$

(D) $[Co(NH_3)_6]^{3+}$

Q27. Which of the following will react fastest with aqueous KOH?

(A) CH_3Cl

(B) CH_3CH_2Cl

(C) $(CH_3)_2CHCl$

(D) $(CH_3)_3CCl$

Q28. Finkelstein reaction is used for the preparation of:

(A) Alkyl fluorides

(B) Alkyl iodides

(C) Alkyl chlorides

(D) Alkyl bromides

Q29. An S_N2 reaction at an asymmetric carbon of a compound always gives:

(A) A mixture of diastereomers.

(B) A racemic mixture.

(C) A single stereoisomer with inverted configuration.

(D) A single stereoisomer with retained configuration.

Q30. Wurtz reaction of methyl iodide yields:

(A) Methane

(B) Ethane

(C) Propane

(D) Butane

Q31. Lucas reagent is a mixture of:

(A) HCl + anhydrous $ZnCl_2$

(B) H_2SO_4 + $KMnO_4$

(C) Pd/$BaSO_4$

(D) Na/liquid NH_3

Q32. Reimer-Tiemann reaction of phenol with $CHCl_3$ and NaOH gives:

(A) Salicylic acid

(B) Salicylaldehyde

(C) Benzene

(D) Benzoic acid

Q33. Phenol is more acidic than ethanol because:

(A) Phenoxide ion is resonance stabilized.

(B) Ethoxide ion is resonance stabilized.

(C) Phenol has a higher molecular weight.

(D) Phenol contains an $-OH$ group.

Q34. Propan-1-ol and Propan-2-ol can be distinguished by:

(A) Oxidation followed by Iodoform test.

(B) Fehling's test.

(C) Tollen's test.

(D) Bromine water.

Q35. Williamson synthesis is used to prepare:

(A) Alcohols

(B) Ketones

(C) Ethers

(D) Aldehydes

Q36. Which of the following does NOT undergo Aldol condensation?

(A) CH_3CHO

(B) CH_3COCH_3

(C) HCHO

(D) CH_3CH_2CHO

Q37. Cannizzaro reaction is given by:

(A) Formaldehyde

(B) Acetaldehyde

(C) Acetone

(D) Propionaldehyde

Q38. The most reactive towards nucleophilic addition among the following is:

(A) HCHO

(B) CH_3CHO

(C) CH_3COCH_3

(D) $PhCOCH_3$

Q39. The reduction of an aldehyde to a hydrocarbon using Zn-Hg/HCl is known as:

(A) Wolff-Kishner reduction

(B) Clemmensen reduction

(C) Rosenmund reduction

(D) Stephen reduction

Q40. Tollen's reagent is:

(A) Ammoniacal silver nitrate.

(B) Alkaline $KMnO_4$.

(C) $SnCl_2/HCl$.

(D) $I_2/NaOH$.

Q41. Which of the following carboxylic acids is the strongest?

(A) CH_3COOH

(B) $ClCH_2COOH$

(C) $Cl_2CHCOOH$

(D) FCH_2COOH

Q42. The correct order of basic strength of methyl substituted amines in aqueous solution is:

(A) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(B) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(C) $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

(D) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

Q43. Gabriel Phthalimide synthesis is used for the preparation of:

(A) Primary aliphatic amines

(B) Primary aromatic amines

(C) Secondary amines

(D) Tertiary amines

Q44. Aniline reacts with $NaNO_2$ + HCl at 0–5°C to give:

(A) Chlorobenzene

(B) Benzene diazonium chloride

(C) Nitrobenzene

(D) Phenol

Q45. Hinsberg's reagent is:

(A) Benzene sulphonyl chloride

(B) Benzene sulphonic acid

(C) Phenyl isocyanide

(D) Nitrous acid

Q46. Which of the following is a non-reducing sugar?

(A) Glucose

(B) Fructose

(C) Lactose

(D) Sucrose

Q47. The linkage present in proteins is:

(A) Glycosidic linkage

(B) Peptide linkage

(C) Phosphodiester linkage

(D) Ester linkage

Q48. Deficiency of Vitamin K in the human body leads to:

(A) Increase in blood clotting time

(B) Decrease in blood clotting time

(C) Night blindness

(D) Sterility

Q49. On denaturation of proteins, which structure remains intact?

(A) Primary

(B) Secondary

(C) Tertiary

(D) Quaternary

Q50. In DNA, the base Guanine pairs with:

(A) Adenine

(B) Cytosine

(C) Thymine

(D) Uracil

Detailed Solutions

Q1.

Solution

Concept: Osmotic pressure (π) is a colligative property and depends on the number of solute particles in solution. It is given by:

$$\pi = i \cdot C \cdot R \cdot T$$

where i is the Van't Hoff factor. For equal molar concentrations, $\pi \propto i$.

Solution: We compare the Van't Hoff factor (i) for each substance:

- **Glucose:** Non-electrolyte, does not dissociate $\implies i = 1$
- **NaCl:** Dissociates into Na^+ and Cl^- $\implies i = 2$
- **$MgCl_2$:** Dissociates into Mg^{2+} and $2Cl^-$ $\implies i = 3$
- **$Al_2(SO_4)_3$:** Dissociates into $2Al^{3+}$ and $3SO_4^{2-}$ $\implies i = 5$

Thus, increasing order of osmotic pressure (based on increasing i):

$$\text{Glucose} < \text{NaCl} < MgCl_2 < Al_2(SO_4)_3$$

Answer: (A)

Q2.

Solution

Concept: **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 present above the surface of the liquid or solution. The most common mathematical form is:

$$P = K_H \cdot \chi$$

Where:

- P = Partial pressure of the gas.
- K_H = Henry's Law constant.
- χ = Mole fraction of the gas in the solution (a measure of solubility).

Solution: To understand the relationship between K_H and solubility, we rearrange the formula for mole fraction (χ):

$$\chi = \frac{P}{K_H}$$

From this equation, it is evident that at a constant partial pressure (P), the solubility (χ) is **inversely proportional** to the Henry's Law constant (K_H):

$$\chi \propto \frac{1}{K_H}$$

[Image showing table of Henry's Law constants for different gases at various temperatures]
Analysis: 1. **Inverse Relationship:** A higher value of K_H means that for a given pressure, a smaller amount of gas will dissolve in the liquid. Therefore, **gases with lower solubility have higher K_H values**. 2. **Temperature Dependence:** K_H is not a universal constant; it depends on the nature of the gas and the solvent. Furthermore, K_H increases with an increase in temperature, which explains why the solubility of gases decreases as temperature rises.
Analysis of options:

- **(A):** Incorrect. Higher solubility corresponds to a lower K_H.
- **(B):** Correct. Lower solubility corresponds to a higher K_H.
- **(C):** Incorrect. K_H varies with the nature of the gas and temperature.
- **(D):** Incorrect. K_H is a characteristic property of the specific gas-solvent pair.

Conclusion: Because the Henry's Law constant acts as a resistance factor to dissolution in the mathematical model, a larger constant mathematically necessitates a lower mole fraction of the gas in the liquid phase.

Answer: (B)

Q3.

Solution

Concept: The **Van't Hoff factor (i)** represents the ratio of the actual concentration of particles produced when a substance is dissolved to the concentration of the substance as calculated from its mass. For electrolytes, i is related to the degree of dissociation (α) and the number of ions (n) produced per formula unit:

$$i = 1 + \alpha(n - 1)$$

If dissociation is complete ($\alpha = 1$), then $i = n$. If dissociation is partial, i will be slightly less than n.

Solution: We calculate the theoretical maximum value of n (the number of ions) for each given solute:

- **(A) $NaCl$:** Dissociates into Na^+ and Cl^-. $n = 2$. Therefore, i should be ≤ 2.
- **(B) $CaCl_2$:** Dissociates into Ca^{2+} and $2Cl^-$. $n = 3$. Therefore, i should be ≤ 3.
- **(C) $AlCl_3$:** Dissociates into Al^{3+} and $3Cl^-$. $n = 4$. Therefore, i should be ≤ 4.
- **(D) Glucose ($C_6H_{12}O_6$):** A non-electrolyte; it does not dissociate. $n = 1$. Therefore, $i = 1$.

Analysis: The observed Van't Hoff factor is **$i = 2.74$**. 1. This value is greater than 2, so it cannot be $NaCl$ or Glucose. 2. This value is less than 3, but close to it, which is typical for an electrolyte like **$CaCl_2$** ($n = 3$) that has undergone significant but perhaps not perfect dissociation in a real solution. 3. While $AlCl_3$ ($n = 4$) could technically result in $i = 2.74$ if dissociation were very low, in standard chemistry problems, the observed i is usually slightly less than the theoretical maximum n of the correct electrolyte.

Conclusion: Since 2.74 is just below the theoretical maximum of 3, the solute is most likely Calcium Chloride, as real-world inter-ionic attractions usually make the observed i slightly lower than the number of ions produced.

Answer: (B)

Q4.

Solution

Concept: **Raoult's Law** for a solution containing a non-volatile solute states that the partial vapor pressure of a solvent in a solution is directly proportional to its mole fraction. When a non-volatile solute is added to a pure solvent, the vapor pressure of the solvent decreases because the solute particles occupy some of the surface area, hindering the escape of solvent molecules into the gas phase.

Mathematical Derivation: Let P° be the vapor pressure of the pure solvent and P_s be the vapor pressure of the solution. According to Raoult's Law:

$$P_s = P^\circ \cdot \chi_{\text{solvent}}$$

Since the sum of mole fractions is 1 ($\chi_{\text{solvent}} + \chi_{\text{solute}} = 1$), we can substitute $\chi_{\text{solvent}} = 1 - \chi_{\text{solute}}$:

$$P_s = P^\circ(1 - \chi_{\text{solute}})$$

$$P_s = P^\circ - P^\circ \cdot \chi_{\text{solute}}$$

Rearranging to find the **Relative Lowering of Vapor Pressure (RLVP)**:

$$P^\circ - P_s = P^\circ \cdot \chi_{\text{solute}}$$

$$\frac{P^\circ - P_s}{P^\circ} = \chi_{\text{solute}}$$

Analysis of options:

- **(A) Mole fraction of the solvent:** Incorrect. The vapor pressure *of the solution* is proportional to the mole fraction of the solvent, but the *lowering* is proportional to the solute.
- **(B) Mole fraction of the solute:** Correct. As derived above, RLVP is exactly equal to the mole fraction of the non-volatile solute.
- **(C) Molality of the solution:** Incorrect. While other colligative properties like ΔT_b use molality, RLVP uses mole fraction.
- **(D) Molarity of the solution:** Incorrect.

Conclusion: Relative lowering of vapor pressure is a colligative property that directly measures the ratio of solute particles to the total particles in the mixture, which is by definition the mole fraction of the solute.

Answer: (B)

Q5.

Solution

Concept: An **ideal solution** is a solution that obeys **Raoult's Law** over the entire range of concentration and at all temperatures. In such solutions, the intermolecular forces of attraction between the solute-solute ($A - A$) and solvent-solvent ($B - B$) molecules are nearly identical to the solute-solvent ($A - B$) molecules.

Properties of Ideal Solutions: Because the molecular environments do not change significantly upon mixing:

- **Enthalpy of Mixing ($\Delta H_{\text{mix}} = 0$):** No heat is absorbed or evolved when the components are mixed. The energy required to break $A - A$ and $B - B$ bonds is exactly balanced by the energy released in forming $A - B$ bonds.
- **Volume of Mixing ($\Delta V_{\text{mix}} = 0$):** The total volume of the solution is exactly equal to the sum of the volumes of the individual components. There is no expansion or contraction upon mixing.

Thermodynamic Considerations: While enthalpy and volume changes are zero, other thermodynamic parameters for a spontaneous mixing process are:

- **Entropy of Mixing (ΔS_{mix}):** Always **positive** ($\Delta S_{\text{mix}} > 0$) because randomness increases.
- **Gibbs Free Energy of Mixing (ΔG_{mix}):** Always **negative** ($\Delta G_{\text{mix}} < 0$) for the process to be spontaneous.

Analysis of options:

- **(A)** $\Delta H_{\text{mix}} > 0$**:** Incorrect. This indicates an endothermic process (non-ideal solution with positive deviation).
- **(B)** $\Delta V_{\text{mix}} > 0$**:** Incorrect. This indicates expansion (non-ideal solution with positive deviation).
- **(C)** $\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$**:** Correct. These are the defining physical criteria for ideality.
- **(D)** $\Delta G_{\text{mix}} = 0$**:** Incorrect. If $\Delta G = 0$, the system would be at equilibrium and no mixing would occur; for mixing to happen, ΔG must be less than zero.

Conclusion: Ideal solutions are characterized by the perfect substitution of molecular interactions, resulting in no net change in heat or total volume during the mixing process.

Answer: (C)

Q6.

Solution

Concept: According to **Faraday's First Law of Electrolysis**, the amount of charge required for the oxidation or reduction of a substance is directly proportional to the number of electrons exchanged in the balanced chemical half-reaction.

- The charge of 1 mole of electrons is equal to **1 Faraday (1 F)**.
- Total Charge (Q) = $n \times F$, where n is the number of moles of electrons.

Solution: 1. **Determine the Oxidation State of Mn in MnO_4^-:** Let the oxidation state of Manganese be x. Oxygen is usually -2.

$$x + 4(-2) = -1$$

$$x - 8 = -1 \implies x = +7$$

2. **Determine the Oxidation State of Mn in the Product:** The product is Mn^{2+}, so its oxidation state is **+2**.
3. **Write the Reduction Half-Reaction:** The change in oxidation state from +7 to +2 requires the gain of 5 electrons.

$$MnO_4^- + 8H^+ + \mathbf{5e^-} \rightarrow Mn^{2+} + 4H_2O$$

4. **Calculate the Charge:** From the balanced equation, 1 mole of MnO_4^- requires **5 moles of electrons** for complete reduction. Since 1 mole of electrons carries a charge of 1 F:

$$\text{Charge required} = 5 \times 1 \text{ F} = 5 \text{ F}$$

Analysis of options:

- **(A) 1 F:** Incorrect (requires 1 mole of electrons).
- **(B) 3 F:** Incorrect (this would be for reduction to MnO_2).
- **(C) 5 F:** Correct.
- **(D) 2 F:** Incorrect.

Conclusion: The reduction of the Manganese center from a +7 oxidation state to a +2 state necessitates the transfer of five electrons per ion; therefore, five Faradays of electricity are required per mole of reactant.

Answer: (C)

Q7.

Solution

Concept: The relationship between the limiting molar conductivity of an electrolyte and its constituent ions is governed by **Kohlrausch's Law of Independent Migration of Ions**.
The law states that the limiting molar conductivity (Λ_m°) of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte.
Solution: For an electrolyte with the general formula A_xB_y, the dissociation in an aqueous solution is represented as:

$$A_xB_y \rightarrow xA^{y+} + yB^{x-}$$

According to Kohlrausch's Law:

$$\Lambda_m^\circ(A_xB_y) = x\lambda_{A^{y+}}^\circ + y\lambda_{B^{x-}}^\circ$$

Where:

- λ_A° and λ_B° are the limiting molar conductivities of the individual ions.
- x and y are the stoichiometric coefficients of the ions.

1. **Identify the stoichiometry for A_2B:** The electrolyte A_2B dissociates as follows:

$$A_2B \rightarrow 2A^+ + B^{2-}$$

2. **Apply the Law:** Since there are **2 moles of cation A** and **1 mole of anion B** produced per mole of electrolyte:

$$\Lambda_m^\circ(A_2B) = 2\lambda_A^\circ + \lambda_B^\circ$$

Analysis of options:

- **(A):** Incorrect. Only accounts for one A ion.
- **(B):** Correct. Matches the stoichiometric ratio 2 : 1.
- **(C):** Incorrect. This would be for an electrolyte of type AB_2.
- **(D):** Incorrect. This is a common confusion with equivalent conductivity definitions.

Conclusion: Because each formula unit of A_2B releases two A ions and one B ion into the solution, their total contribution to the conductivity at infinite dilution is the sum of their individual molar conductivities multiplied by their respective coefficients.

Answer: (B)

Q8.

Solution

Concept: A **Hydrogen-Oxygen fuel cell** is a galvanic cell that converts the chemical energy of the combustion of hydrogen directly into electrical energy. It consists of porous carbon electrodes containing catalysts (like Platinum or Palladium) and an aqueous electrolyte (usually concentrated KOH or $NaOH$).

- **Anode:** Where oxidation (loss of electrons) occurs.
- **Cathode:** Where reduction (gain of electrons) occurs.

[Image of hydrogen-oxygen fuel cell diagram showing anode, cathode, and electrolyte]
Solution: In an alkaline fuel cell, the reactions at the electrodes are as follows:
1. **At Anode (Oxidation):** Hydrogen gas is oxidized to water by reacting with hydroxide ions from the electrolyte.

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$$

This corresponds to option (A), which is the **anodic** reaction.
2. **At Cathode (Reduction):** Oxygen gas is reduced in the presence of water to form hydroxide ions.

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

This corresponds to option (B), which is the **cathodic** reaction.
Overall Cell Reaction: Summing the two half-reactions gives the net reaction of water formation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Analysis of options:

- **(A):** Incorrect. This is the oxidation half-reaction occurring at the anode.
- **(B):** Correct. This is the reduction half-reaction occurring at the cathode.
- **(C):** Incorrect. This is the reduction of protons, typical of a standard hydrogen electrode in acidic medium.
- **(D):** Incorrect. This is the oxidation of zinc, which occurs in a Dry Cell or Daniell Cell.

Conclusion: In the H_2-O_2 fuel cell, oxygen is the species being reduced at the cathode, accepting electrons to produce hydroxide ions in the alkaline environment.

Answer: (B)

Q9.

Solution

Concept: The **Nernst equation** relates the reduction potential of an electrochemical cell (or half-cell) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing oxidation and reduction.
For a general reduction half-reaction:

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

The Nernst equation at any temperature T is:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

Solution: 1. **Simplify for Pure Solids:** The concentration of a pure solid metal $[M]$ is taken as unity (1).

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

2. **Convert to Common Logarithm ($\log_{10}$):** Use the conversion factor 2.303.

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

3. **Apply Standard Conditions (298 K):** At $T = 298$ K, $R = 8.314$ J K^{-1} mol^{-1}, and $F = 96487$ C mol^{-1}. The value of the constant term $\frac{2.303RT}{F} \approx 0.0591$ V. The equation becomes:

$$E = E^\circ - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Analysis of options:

- **(A):** Correct. Matches the derived standard form at 298 K.
- **(B):** Incorrect. The sign before the log term should be negative when using the reciprocal of the ion concentration.
- **(C):** Incorrect. The factor n should be in the denominator, not the numerator.
- **(D):** Incorrect. It omits the n factor entirely.

Conclusion: By substituting the physical constants at 298 K into the thermodynamic derivation, the reduction potential is found to decrease linearly with the logarithm of the reciprocal of the metal ion concentration.

Answer: (A)

Q10.

Solution

Concept: Electrochemical cells are classified into two main types based on their rechargeability:

- **Primary Cells:** The reaction occurs only once. After use over a period of time, the battery becomes dead and cannot be reused or recharged (e.g., Dry cell, Mercury cell).
- **Secondary Cells:** These can be recharged by passing an electric current through them in the opposite direction. They can be used again and again (e.g., Lead storage battery, Nickel-Cadmium cell).

Analysis of Options:

- **(A) Dry cell:** A primary cell commonly used in torches and transistors. The chemical reaction is irreversible.
- **(B) Mercury cell:** A primary cell used in low-current devices like hearing aids and watches. It provides a constant voltage but cannot be recharged.
- **(C) Lead storage battery:** A **secondary cell** used in automobiles and inverters. During discharge, it acts as a voltaic cell, and during charging, it acts as an electrolytic cell.
- **(D) Leclanché cell:** Another name for the standard Dry cell. It is a primary cell.

Chemistry of Lead Storage Battery: The rechargeability is due to the reversible nature of the electrode reactions:

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

On charging, these reactions are reversed, restoring the original reactants.

Conclusion: Because the chemical reactions in a lead storage battery can be reversed by an external electrical source, it is classified as a secondary cell, unlike the other options which are discarded after a single discharge cycle.

Answer: (C)

Q11.

Solution

Concept: The spontaneity of a redox reaction and its extent of completion are governed by the relationships between the standard cell potential (E°_{cell}), the standard Gibbs free energy change (ΔG°), and the equilibrium constant (K_c).

Relationship 1: E°_{cell} and ΔG° The standard Gibbs free energy is related to the standard cell potential by the equation:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

Where:

- n = Number of moles of electrons transferred.
- F = Faraday's constant (96485 C mol^{-1}).

Since n and F are always positive, the sign of ΔG° is opposite to the sign of E°_{cell}.

- If $E^\circ_{\text{cell}} < 0$ (negative), then $\mathbf{\Delta G^\circ > 0}$ (positive).

Relationship 2: ΔG° and K_c The standard Gibbs free energy is related to the equilibrium constant by:

$$\Delta G^\circ = -RT \ln K_c \quad \text{or} \quad E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K_c$$

For a reaction where ΔG° is positive (or E°_{cell} is negative):

- $\ln K_c$ must be negative, which means $\mathbf{K_c < 1}$.

Analysis of options:

- **(A):** Incorrect. This describes a spontaneous reaction ($E^\circ_{\text{cell}} > 0$).
- **(B):** Correct. A negative E°_{cell} implies a non-spontaneous reaction under standard conditions, characterized by a positive ΔG° and an equilibrium that favors reactants ($K_c < 1$).
- **(C):** Incorrect. This describes a system at equilibrium under standard conditions ($E^\circ_{\text{cell}} = 0$).
- **(D):** Incorrect. $\Delta G^\circ > 0$ and $K_c > 1$ are mathematically inconsistent with each other.

Conclusion: A negative standard cell potential indicates that the reaction is non-spontaneous in the forward direction; thermodynamically, this requires a positive change in free energy and an equilibrium constant less than unity.

Answer: (B)

Q12.

Solution

Concept: For a **first-order reaction**, the rate of reaction depends on the concentration of only one reactant. Two key features of first-order kinetics are:

- The integrated rate equation: $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$
- The half-life ($t_{1/2}$) is constant and independent of the initial concentration: $t_{1/2} = \frac{0.693}{k}$

Solution: We can solve this using the relationship between concentration and time intervals:
1. **First Half-life ($t_{1/2}$):** The concentration reduces from 100% to 50%. Time taken = $1 \times t_{1/2}$.
2. **Second Half-life ($t_{1/2}$):** The remaining 50% concentration reduces by half again (to 25%). Total completion = 100% − 25% = 75%. Total time taken = $t_{1/2} + t_{1/2} = 2 \times t_{1/2}$.
Mathematical Verification: Using the integrated rate equation for 75% completion ($[A]_t = 0.25[A]_0$):

$$t_{75\%} = \frac{2.303}{k} \log \frac{[A]_0}{0.25[A]_0} = \frac{2.303}{k} \log 4$$

$$t_{75\%} = \frac{2.303}{k} (2 \log 2) = 2 \left(\frac{2.303 \log 2}{k} \right)$$

Since $t_{1/2} = \frac{2.303 \log 2}{k}$:

$$t_{75\%} = 2 \times t_{1/2}$$

Analysis of options:

- **(A):** Correct. Two half-lives are required to reach 25% remaining reactant (which is 75% completion).
- **(B):** Incorrect. Three half-lives would result in 87.5% completion.
- **(C):** Incorrect. One half-life is 50% completion.
- **(D):** Incorrect.

Conclusion: In first-order kinetics, each successive half-life reduces the remaining concentration by half; therefore, to consume three-quarters of the starting material, the reaction must proceed through exactly two half-life periods.

Answer: (A)

Q13.

Solution

Concept: The **order of a reaction** can be directly identified by the units of its rate constant (k). The general formula for the units of the rate constant is:

$$\text{Units of } k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$$

Where n is the overall order of the reaction.

Solution: We compare the given units of $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} with the general formula:

- **For Zero Order ($n = 0$):** Units = $(\text{mol L}^{-1})^{1-0}\ \text{s}^{-1} = \text{mol L}^{\mathbf{-1}}\ \text{s}^{\mathbf{-1}}$
- **For First Order ($n = 1$):** Units = $(\text{mol L}^{-1})^{1-1}\ \text{s}^{-1} = (\text{mol L}^{-1})^{0}\ \text{s}^{-1} = \text{s}^{\mathbf{-1}}$
- **For Second Order ($n = 2$):** Units = $(\text{mol L}^{-1})^{1-2}\ \text{s}^{-1} = (\text{mol L}^{-1})^{-1}\ \text{s}^{-1} = \text{L mol}^{\mathbf{-1}}\ \text{s}^{\mathbf{-1}}$
- **For Third Order ($n = 3$):** Units = $(\text{mol L}^{-1})^{1-3}\ \text{s}^{-1} = (\text{mol L}^{-1})^{-2}\ \text{s}^{-1} = \text{L}^{\mathbf{2}}\ \text{mol}^{\mathbf{-2}}\ \text{s}^{\mathbf{-1}}$

Analysis: The units provided in the question are L mol^{-1} s^{-1} (which can also be written as M^{-1} s^{-1}). This matches the calculated units for a **second-order reaction**.

Conclusion: The numerical value of the rate constant is irrelevant for determining the order in this context; the presence of "Litre" and "inverse mole" in the units signifies that the rate depends on the square of the concentration.

Answer: (C)

Q14.

Solution

Concept: The **Arrhenius equation** describes the dependence of the rate constant (k) of a chemical reaction on the absolute temperature (T). It is expressed as:

$$k = A \cdot e^{-E_a/RT}$$

Where:

- k = Rate constant
- A = Arrhenius factor (Frequency factor)
- E_a = Activation energy
- R = Gas constant (8.314 J K^{-1} mol^{-1})
- T = Absolute temperature (in Kelvin)

Solution: To linearize the equation, we take the natural logarithm (ln) on both sides:

$$\ln k = \ln(A \cdot e^{-E_a/RT})$$

Using the property $\ln(ab) = \ln a + \ln b$:

$$\ln k = \ln A + \ln(e^{-E_a/RT})$$

Since $\ln(e^x) = x$:

$$\ln k = \ln A - \frac{E_a}{RT}$$

This can be rearranged into the form of a straight-line equation ($y = mx + c$):

$$\underbrace{\ln k}_{y} = \underbrace{\left(-\frac{E_a}{R}\right)}_{m} \cdot \underbrace{\frac{1}{T}}_{x} + \underbrace{\ln A}_{c}$$

Analysis: By comparing the rearranged equation to $y = mx + c$:

- The variable on the y-axis is $\ln k$.
- The variable on the x-axis is $1/T$.
- The **slope (m)** of the line is $-\mathbf{E_a/R}$.
- The y-intercept (c) is $\ln A$.

Conclusion: The negative sign in the slope indicates that as the inverse of temperature increases (meaning temperature itself decreases), the rate constant decreases. The magnitude of this steepness is determined by the ratio of activation energy to the gas constant.

Answer: (B)

Q15.

Solution

Concept: The **rate of a reaction** is defined as the change in concentration of a reactant or product per unit time (Rate = $\frac{d[A]}{dt}$). For a reaction of the n^{th} order, the rate law is expressed as:

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

Where k is the rate constant and n is the order of the reaction.

Solution: For a **zero-order reaction** ($n = 0$), the rate of the reaction is independent of the concentration of the reactants:

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

Since $[A]^0 = 1$, we have:

$$\text{Rate} = k$$

This means the units of the rate constant (k) are identical to the units of the rate of reaction.

Dimensional Analysis: The units of Rate are:

$$\frac{\text{Concentration}}{\text{Time}} = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{\mathbf{-1}}\ \text{s}^{\mathbf{-1}}$$

General Formula Method: The units for a rate constant of order n can be calculated using:

$$\text{Units} = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$$

Substituting $n = 0$:

$$\text{Units} = (\text{mol L}^{-1})^{1-0}\ \text{s}^{-1} = \text{mol L}^{\mathbf{-1}}\ \text{s}^{\mathbf{-1}}$$

Analysis of options:

- **(A) s^{-1}:** Units for a **first-order** reaction.
- **(B) $\text{mol L}^{-1}\ \text{s}^{-1}$:** Correct. Matches the units for a zero-order reaction.
- **(C) $\text{L mol}^{-1}\ \text{s}^{-1}$:** Units for a **second-order** reaction.
- **(D) mol L^{-1}:** Units for concentration, not a rate constant.

Conclusion: In a zero-order reaction, the speed at which the reaction progresses remains constant regardless of how much reactant is present; therefore, the rate constant carries the same units as the rate itself.

Answer: (B)

Q16.

Solution

Concept: The **order of a reaction** is the power to which the concentration of a reactant is raised in the rate law expression. For a general reaction where the rate depends on one reactant A, the rate law is:

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

Where:

- k = Rate constant
- $[A]$ = Molar concentration of reactant
- n = Order of the reaction

Solution: Let the initial rate be R_1 and the initial concentration be $[A]_1$.

$$R_1 = k[A]_1^n \quad \text{— (Equation 1)}$$

According to the problem, the concentration is doubled ($[A]_2 = 2[A]_1$) and the rate quadruples ($R_2 = 4R_1$).

$$R_2 = k[2A_1]^n$$

$$4R_1 = k \cdot 2^n \cdot [A]_1^n \quad \text{— (Equation 2)}$$

Mathematical Calculation: Divide Equation 2 by Equation 1:

$$\frac{4R_1}{R_1} = \frac{k \cdot 2^n \cdot [A]_1^n}{k \cdot [A]_1^n}$$

$$4 = 2^n$$

We know that 4 can be written as 2^2:

$$2^2 = 2^n$$

Equating the exponents:

$$n = 2$$

Solution

Analysis of options:

- **(A) 0:** If $n = 0$, the rate would remain unchanged ($2^0 = 1$).
- **(B) 1:** If $n = 1$, the rate would double ($2^1 = 2$).
- **(C) 2:** Correct. The rate increases by the square of the concentration change ($2^2 = 4$).
- **(D) 3:** If $n = 3$, the rate would increase eightfold ($2^3 = 8$).

Conclusion: Since the rate of reaction increases by a factor of four when the concentration is doubled, the mathematical relationship shows a second-order dependency on the reactant concentration.

Answer: (C)

Q17.

Solution

Concept: **Lanthanoid contraction** refers to the steady decrease in the atomic and ionic radii of the lanthanoid elements (from Lanthanum to Lutetium) with an increase in their atomic number. This phenomenon has a significant impact on the chemistry of the post-lanthanoid elements (5d series).

Cause of Lanthanoid Contraction: Two main factors contribute to this effect:

1. **Poor Shielding Effect of 4f Electrons:** As we move along the lanthanoid series, electrons are added to the $4f$ subshell. The shape of the f-orbitals is very diffused, which results in **poor shielding** of the outer electrons from the nuclear charge. The $4f$ electrons do not effectively "block" the pull of the nucleus.

2. **Increase in Nuclear Charge:** With each successive element, the atomic number (number of protons) increases by one. This increases the positive charge of the nucleus.

Analysis: Because the $4f$ electrons shield the nucleus poorly, they cannot compensate for the increasing nuclear charge. As a result, the effective nuclear charge (Z_{eff}) experienced by the outer electrons increases, pulling the electron cloud closer to the nucleus and causing the atom to shrink.

Analysis of options:

- **(A):** Incorrect. $4f$ shielding is notoriously poor, not perfect.
- **(B):** Correct, but incomplete on its own.
- **(C):** Correct, but incomplete on its own.
- **(D):** **Correct.** The contraction is the result of the combined effect of the increasing nuclear pull and the inability of the $4f$ electrons to shield that pull effectively.

Conclusion: Lanthanoid contraction is a cumulative effect where the steady rise in nuclear charge, paired with the diffuse nature of the $4f$ orbitals, leads to a greater-than-expected reduction in atomic size.

Answer: (D)

Q18.

Solution

Concept: The color of transition metal ions in aqueous solution is generally due to **$d - d$ transitions**. When light falls on these ions, electrons in the lower-energy d-orbitals absorb specific wavelengths of visible light and jump to higher-energy d-orbitals.
For an ion to exhibit color:

- It must have **partially filled d-orbitals** (i.e., d^1 to d^9 configuration).
- If the d-orbitals are completely empty (d^0) or completely filled (d^{10}), no $d - d$ transitions are possible, and the ion is typically **colorless**.

Solution: We determine the electronic configuration of each ion's d-subshell:

- **(A) Ti^{3+}:** Atomic number of Ti is 22. Ti = $[Ar]3d^2 4s^2 \rightarrow Ti^{3+} = [Ar]\mathbf{3d^1}$ (Partially filled, **Purple/Violet**)
- **(B) V^{3+}:** Atomic number of V is 23. V = $[Ar]3d^3 4s^2 \rightarrow V^{3+} = [Ar]\mathbf{3d^2}$ (Partially filled, **Green**)
- **(C) Sc^{3+}:** Atomic number of Sc is 21. Sc = $[Ar]3d^1 4s^2 \rightarrow Sc^{3+} = [Ar]\mathbf{3d^0}$ (Empty d-orbital, **Colorless**)
- **(D) Fe^{2+}:** Atomic number of Fe is 26. Fe = $[Ar]3d^6 4s^2 \rightarrow Fe^{2+} = [Ar]\mathbf{3d^6}$ (Partially filled, **Pale Green**)

Analysis: Scandium ($Z = 21$) loses all three of its valence electrons to form the Sc^{3+} ion. This results in a stable noble gas configuration ($[Ar]$) with no electrons left in the $3d$ subshell. Without d-electrons, there is no possibility of electronic excitation within the visible spectrum.
Conclusion: Because Scandium(III) possesses a d^0 configuration, it lacks the necessary electrons to undergo the energy transitions that produce visible color, rendering its aqueous solution clear and colorless.

Answer: (C)

Q19.

Solution

Concept: Transition elements (d-block) exhibit variable oxidation states because of the small energy difference between $(n-1)d$ and ns orbitals. This allows electrons from both subshells to participate in bond formation. The maximum oxidation state generally increases up to the middle of a series and then decreases.

Analysis of the Series:

- **3d Series:** The maximum oxidation state is **+7**, exhibited by Manganese (Mn) in compounds like $KMnO_4$.
- **4d and 5d Series:** Heavier transition elements can reach even higher states due to the increased stability of higher oxidation states down a group.
- **Ruthenium** (Ru) and **Osmium** (Os) can achieve an oxidation state of **+8** in their tetroxides (RuO_4 and OsO_4).

Solution: While +7 is a very common high oxidation state (especially in introductory chemistry focusing on the $3d$ series), the absolute highest oxidation state known for transition elements in the periodic table is **+8**.

Analysis of options:

- **(A) +7:** This is the maximum for the $3d$ series (Manganese).
- **(B) +8:** This is the maximum for the entire d-block (Osmium and Ruthenium).
- **(C) +6:** Common for Chromium and Tungsten, but not the highest.
- **(D) +5:** Common for Vanadium, but not the highest.

Conclusion: Although most common transition metals peak at +7, the heavy metals Osmium and Ruthenium are capable of losing or sharing eight electrons to reach the +8 state, making it the highest possible for the group.

Answer: (B)

Q20.

Solution

Concept: The **magnetic moment (μ)** of transition metal ions is primarily determined by the number of unpaired electrons in their d-subshell. This is calculated using the **spin-only formula**:

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

Where:

- n = Number of unpaired electrons.
- BM = Bohr Magneton (unit of magnetic moment).

Solution: 1. **Identify the element:** The atomic number $Z = 25$ corresponds to **Manganese (Mn)**.
2. **Electronic configuration of neutral Mn:** Mn = $[Ar]3d^5 4s^2$
3. **Electronic configuration of divalent ion (Mn^{2+}):** A divalent ion has a +2 charge, meaning it loses 2 electrons from the outermost $4s$ orbital. $Mn^{2+} = [Ar]3d^5$
4. **Count unpaired electrons (n):** In the $3d^5$ configuration, according to Hund's Rule, each of the five d-orbitals contains one electron. Therefore, **n = 5**.
5. **Calculate the Magnetic Moment:**

$$\mu = \sqrt{5(5+2)}$$

$$\mu = \sqrt{5 \times 7} = \sqrt{35}$$

Since $\sqrt{36} = 6$, $\sqrt{35}$ must be slightly less than 6.

$$\mu \approx 5.916 \text{ BM} \approx \mathbf{5.92} \text{ BM}$$

Analysis of options:

- **(A) 2.84 BM:** Corresponds to $n = 2$.
- **(B) 3.87 BM:** Corresponds to $n = 3$.
- **(C) 5.92 BM:** Correct. Corresponds to $n = 5$.
- **(D) 4.90 BM:** Corresponds to $n = 4$.

Conclusion: Manganese(II) possesses a half-filled d-subshell with five unpaired electrons; applying the spin-only formula yields a magnetic moment of approximately 5.92 BM, indicating a high-spin state.

Answer: (C)

Q21.

Solution

Concept: To name a coordination compound correctly according to **IUPAC rules**, we follow these steps:

(a) Name the cation first, then the anion.

(b) Within the coordination sphere, name the ligands in **alphabetical order**.

(c) Use Greek prefixes (di, tri, tetra, penta, hexa) to indicate the number of each ligand.

(d) For neutral/cationic complexes, the metal name remains unchanged.

(e) The oxidation state of the metal is indicated by a **Roman numeral** in parentheses.

Solution: 1. **Identify Ligands and their counts:**

- Five NH_3 groups: **Pentaammine** (Note the double 'm' in ammine).
- One Cl inside the bracket: **Chlorido** (Anionic ligands end in '-o').

2. **Calculate the Oxidation State of Cobalt (Co):** Let the oxidation state of Co be x. NH_3 is neutral (charge = 0). Cl is anionic (charge = -1). The total charge of the complex must balance the two chloride ions outside ($2 \times -1 = -2$), so the coordination sphere has a +2 charge.

$$x + 5(0) + 1(-1) = +2$$

$$x - 1 = +2 \implies \mathbf{x = +3}$$

3. **Alphabetical Ordering:** "Ammine" (starts with 'a') comes before "Chlorido" (starts with 'c').
4. **Construct the Name: Pentaammine + chlorido + cobalt(III) + chloride** (the counter ion).
Analysis of options:

- **(A):** Incorrect. Uses "chloro" instead of the current IUPAC recommendation "chlorido".
- **(B):** **Correct.** Follows all naming conventions, including the correct oxidation state and the "chlorido" suffix.
- **(C):** Incorrect. The ligands are not in alphabetical order.
- **(D):** Incorrect. The oxidation state is wrong (+2 instead of +3).

Conclusion: By strictly applying IUPAC priority and oxidation state calculations, we identify the complex as a cobalt(III) center coordinated by five ammine ligands and one chlorido ligand, balanced by two chloride counter-ions.

Answer: (B)

Q22.

Solution

Concept: **Linkage isomerism** occurs in coordination compounds containing **ambidentate ligands**. An ambidentate ligand is a group that possesses two or more different donor atoms but coordinates to the central metal ion through only one of them at a time.
Common ambidentate ligands include:

- NO_2^-: Can bind via Nitrogen (nitrito-N) or Oxygen (nitrito-O).
- SCN^-: Can bind via Sulfur (thiocyanato-S) or Nitrogen (isothiocyanato-N).
- CN^-: Can bind via Carbon (cyanido-C) or Nitrogen (isocyanido-N).

Solution: We examine each complex for the presence of an ambidentate ligand:

- **(A)** $\mathbf{[Co(NH_3)_5Cl]SO_4}$**:** Contains NH_3 and Cl^-. Neither is ambidentate. This complex shows **ionization isomerism** with $[Co(NH_3)_5SO_4]Cl$.
- **(B)** $\mathbf{[Co(NH_3)_5(NO_2)]Cl_2}$**:** Contains the **$NO_2^-$** group. Since NO_2^- is ambidentate, it can exist as:
  (a) $[Co(NH_3)_5(NO_2)]Cl_2$ (Nitro isomer - Yellow)
  (b) $[Co(NH_3)_5(ONO)]Cl_2$ (Nitrito isomer - Red)

  This is a classic example of **linkage isomerism**.
- **(C)** $\mathbf{[Cr(H_2O)_6]Cl_3}$**:** Contains H_2O and Cl^-. This typically shows **hydrate isomerism**.
- **(D)** $\mathbf{[Fe(en)_3]Cl_3}$**:** Contains ethylenediamine (en), a bidentate ligand. This complex shows **optical isomerism** but not linkage isomerism.

Conclusion: Linkage isomerism is specifically tied to the mode of attachment of a ligand; because the nitrite ion can bond through either nitrogen or oxygen, the cobalt complex containing it can exist in two distinct structural forms.

Answer: (B)

Q23.

Solution

Concept: The **Spectrochemical Series** is an empirical series of ligands arranged in order of their ability to cause **crystal field splitting** (Δ) of d-orbitals in a coordination complex.

- **Weak Field Ligands:** Cause small splitting (e.g., halides, OH^-).
- **Strong Field Ligands:** Cause large splitting (e.g., CN^-, CO, en).

Solution: The generally accepted order for common ligands in the spectrochemical series is:

$$I^- < Br^- < SCN^- < Cl^- < S^{2}- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN$$

To solve this specific question, we extract the ligands provided: **Cl^-**, **F^-**, **OH^-**, and **CN^-**.

(a) **Halides:** $I^- < Br^- < Cl^- < F^-$. (Note: Small, more electronegative ions like F^- cause more splitting than Cl^-).

(b) **Hydroxide:** OH^- follows the halides in the series.

(c) **Cyanide:** CN^- is one of the strongest field ligands due to its π-acidic character.

Comparing these, the sequence is:

$$Cl^- < F^- < OH^- < CN^-$$

Analysis of options:

- **(A):** Correct. It matches the increasing order of field strength.
- **(B):** Incorrect. This is almost the exact reverse order.
- **(C):** Incorrect. F^- is a stronger field ligand than Cl^-.
- **(D):** Incorrect. CN^- is much stronger than halides.

Conclusion: The ability of a ligand to split d-orbitals increases as we move from large, polarizable halide ions like chloride to oxygen-donor ligands like hydroxide, and peaks with carbon-donor π-acceptor ligands like cyanide.

Answer: (A)

Q24.

Solution

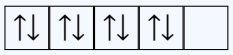
Concept: The hybridization and geometry of coordination complexes are explained by **Valence Bond Theory (VBT)**. The shape depends on the coordination number and the nature of the ligands (strong field vs. weak field).

- **Strong Field Ligands (e.g., CN^-):** Cause pairing of electrons in the d-orbitals, often leading to inner orbital complexes.
- **Weak Field Ligands (e.g., Cl^-):** Do not cause pairing, often leading to outer orbital complexes.

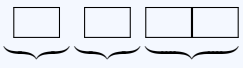
Solution: 1. **Oxidation State of Ni:** Let the oxidation state of Ni be x. Cyanide (CN^-) has a charge of -1.

$$x + 4(-1) = -2 \implies x = +2$$

Nickel is in the **+2** oxidation state.
2. **Electronic Configuration:** Atomic number of Ni = 28. Ni = $[Ar]3d^8 4s^2$ $Ni^{2+} = [Ar]3d^8 4s^0$
3. **Effect of Ligand (CN^-):** Since CN^- is a **strong field ligand**, it forces the two unpaired electrons in the $3d$ orbitals to pair up. This clears one $3d$ orbital.

3d configuration after pairing: 

4. **Hybridization:** With one $3d$ orbital, one $4s$ orbital, and two $4p$ orbitals available, the metal undergoes **dsp^2 hybridization** to accommodate 4 pairs of electrons from the 4 CN^- ligands.

Hybrid orbitals:  $\implies dsp^2$

5. **Shape and Magnetic Property:**

- **Shape:** Complexes with dsp^2 hybridization are **Square Planar**.
- **Magnetic Property:** Since all electrons are paired, it is **diamagnetic**.

Solution

Analysis of options:

- **(A):** Incorrect. This would be the case for $[NiCl_4]^{2-}$ where Cl^- is a weak field ligand.
- **(B):** **Correct.** Strong field cyanide leads to pairing and square planar geometry.
- **(C) & (D):** Incorrect. These are for coordination number 6 (Octahedral).

Conclusion: In the presence of the strong field cyanide ligand, the d-electrons of Ni^{2+} are redistributed to vacate an inner d-orbital, resulting in dsp^2 hybridization and a square planar spatial arrangement.

Answer: (B)

Q25.

Solution

Concept: Geometrical isomerism occurs in coordination compounds when the same ligands can be arranged in different spatial positions relative to each other. For a coordination number of 4, two geometries are possible: **Tetrahedral** and **Square Planar**.

- **Tetrahedral complexes** (sp^3) do not show geometrical isomerism because all four positions are adjacent to each other.
- **Square planar complexes** (dsp^2) of the type MA_2B_2 (where M is the metal and A, B are monodentate ligands) show geometrical isomerism.

Solution: 1. **Identify the Metal and Geometry:** Platinum (Pt^{2+}) with a coordination number of 4 typically forms **square planar** complexes due to its position in the 5d series and the resulting high crystal field splitting.
2. **Identify the Isomers:** The complex $[Pt(NH_3)_2Cl_2]$ is of the type MA_2B_2. It exists in two forms:

- **Cis-isomer:** The two identical ligands (e.g., two NH_3 groups) are adjacent to each other (90° angle). This specific isomer is known as **Cisplatin**, a famous anti-cancer drug.
- **Trans-isomer:** The two identical ligands are opposite to each other (180° angle).

3. **Calculation:** There are exactly **2** geometrical isomers for this coordination environment.
Analysis of options:

- **(A) 2:** Correct.
- **(B) 3:** Incorrect (this would require a complex of type $MABCD$).
- **(C) 4:** Incorrect.
- **(D) 0:** Incorrect (true only for tetrahedral or MA_4/MA_3B types).

Conclusion: Because Platinum(II) enforces a square planar geometry, the two ammine and two chloride ligands can be arranged either on the same side or on opposite sides of the central atom, resulting in two distinct geometrical isomers.

Answer: (A)

Q26.

Solution

Concept: The distinction between **inner orbital** and **outer orbital** complexes is based on which d-orbitals are used for hybridization (d^2sp^3 vs. sp^3d^2). This is primarily determined by the strength of the ligand:

- **Strong Field Ligands (SFL):** Such as CN^- or NH_3 (usually), cause pairing of electrons in the $(n-1)d$ subshell. This vacates the inner d-orbitals, forming an **inner orbital complex** (d^2sp^3).
- **Weak Field Ligands (WFL):** Such as F^- or Cl^-, cannot cause pairing. The $(n-1)d$ electrons remain unpaired, and the metal uses the outer nd orbitals for bonding, forming an **outer orbital complex** (sp^3d^2).

Solution Analysis:

- **(A) $[Fe(CN)_6]^{3-}$:** Fe^{3+} is $3d^5$. CN^- is a **strong field ligand**. It forces pairing, leaving inner $3d$ orbitals available. It is an **inner orbital complex**.
- **(B) $[Mn(CN)_6]^{3-}$:** Mn^{3+} is $3d^4$. CN^- is a **strong field ligand**. It forces pairing of $3d$ electrons to vacate the inner orbitals. It is an **inner orbital complex**.
- **(C) $[CoF_6]^{3-}$:** Co^{3+} is $3d^6$. **F^- is a weak field ligand.** It cannot force the pairing of electrons in the $3d$ subshell. Consequently, the $3d$ orbitals remain occupied by unpaired electrons, and the complex uses the $4d$ orbitals for hybridization (sp^3d^2). This is an **outer orbital complex**.
- **(D) $[Co(NH_3)_6]^{3+}$:** Co^{3+} is $3d^6$. NH_3 acts as a **strong field ligand** with Co^{3+}, causing pairing and vacating the inner $3d$ orbitals. It is an **inner orbital complex**.

Conclusion: Because the fluoride ion is a weak field ligand, it lacks the energy to reorganize the $3d$ electrons of the Cobalt(III) ion; the metal is therefore forced to utilize its outer $4d$ shell for bonding, resulting in a high-spin, outer orbital configuration.

Answer: (C)

Q27.

Solution

Concept: The reaction of alkyl halides with aqueous KOH is a **nucleophilic substitution reaction** where the OH^- ion replaces the halide ion (Cl^-). The mechanism and rate depend on the structure of the alkyl group:

- S_N1 **Mechanism:** Favored by tertiary (3°) alkyl halides. The rate depends on the stability of the carbocation intermediate.
- S_N2 **Mechanism:** Favored by primary (1°) and methyl halides. The rate depends on the lack of steric hindrance.

Solution Analysis: In aqueous medium, the substitution of tertiary alkyl halides is generally much faster than that of primary or secondary ones because they proceed via the **S_N1 mechanism**, which involves the formation of a highly stable carbocation.
1. **(A) CH_3Cl (Methyl chloride):** Reacts via S_N2. Very fast for S_N2, but slower than 3° in polar protic solvents. 2. **(B) CH_3CH_2Cl (Ethyl chloride):** Primary (1°) alkyl halide. Reacts via S_N2. 3. **(C) $(CH_3)_2CHCl$ (Isopropyl chloride):** Secondary (2°) alkyl halide. Can react via S_N1 or S_N2. 4. **(D) $(CH_3)_3CCl$ (tert-Butyl chloride):** **Tertiary (3°) alkyl halide.**
Why (D) is fastest: When $(CH_3)_3CCl$ reacts with aqueous KOH, it readily ionizes to form the **tert-butyl carbocation** $(CH_3)_3C^+$. This carbocation is highly stabilized by the inductive effect ($+I$) and hyperconjugation from three methyl groups. Because the formation of this stable intermediate is the rate-determining step, 3° halides react the most rapidly in these conditions.
Conclusion: Tertiary alkyl halides provide the most stable carbocation intermediate in an aqueous environment, allowing the reaction to proceed through the S_N1 pathway with the lowest activation energy compared to primary or secondary alternatives.

Answer: (D)

Q28.

Solution

Concept: The **Finkelstein reaction** is a classic organic reaction used for the synthesis of alkyl iodides. It is a type of **nucleophilic substitution reaction** (specifically S_N2) known as a halogen exchange reaction.

Reaction Details: In this reaction, an alkyl chloride or alkyl bromide reacts with **sodium iodide (NaI)** in the presence of **dry acetone**.

$$R - X + NaI \xrightarrow{\text{dry acetone}} R - I + NaX$$

(Where $X = Cl$ or Br)

Role of Acetone: The use of dry acetone is crucial for the success of this reaction.

- Sodium iodide (NaI) is soluble in acetone.
- However, the by-products formed, sodium chloride ($NaCl$) and sodium bromide ($NaBr$), are **insoluble** in acetone and precipitate out.
- According to **Le Chatelier's Principle**, the constant precipitation of the by-product shifts the equilibrium in the forward direction, ensuring a high yield of the alkyl iodide.

Analysis of options:

- **(A) Alkyl fluorides:** These are prepared using the **Swarts reaction** (using metallic fluorides like AgF, Hg_2F_2).
- **(B) Alkyl iodides:** Correct. This is the primary purpose of the Finkelstein reaction.
- **(C) Alkyl chlorides:** Generally prepared by direct chlorination or from alcohols.
- **(D) Alkyl bromides:** Generally prepared by direct bromination or from alcohols.

Conclusion: The Finkelstein reaction leverages the unique solubility of halide salts in organic solvents to drive the exchange of a chloride or bromide for an iodide, making it the standard laboratory method for producing alkyl iodides.

Answer: (B)

Q29.

Solution

Concept: The **S_N2 mechanism** (Substitution Nucleophilic Bimolecular) is a concerted, single-step process. In this reaction, the nucleophile attacks the electrophilic carbon atom from the side opposite to the leaving group (backside attack).

Stereochemical Outcome: Because the nucleophile must approach from the side exactly opposite to the bond being broken:

(a) The transition state involves the carbon atom being partially bonded to both the incoming nucleophile and the outgoing leaving group.

(b) As the leaving group departs, the remaining three groups on the carbon atom "flip" over to the other side, much like an umbrella being turned inside out in a strong wind.

(c) This phenomenon is known as **Walden Inversion**.

Analysis of the Asymmetric Carbon: When the reaction occurs at an asymmetric (chiral) carbon:

- The spatial arrangement of the groups is reversed.
- If the starting material is a single pure enantiomer (e.g., the '*R*' isomer), the product will be the '*S*' isomer (assuming the priority of the nucleophile is similar to that of the leaving group).
- Unlike the S_N1 mechanism, which forms a carbocation and leads to racemization (a mixture of isomers), the S_N2 process is **stereospecific**.

Analysis of options:

- **(A):** Incorrect. Diastereomers require at least two chiral centers.
- **(B):** Incorrect. This is the typical outcome of an S_N1 reaction.
- **(C):** **Correct.** The backside attack ensures that the product has a configuration opposite to the reactant.
- **(D):** Incorrect. Retention of configuration is rare and usually involves a double inversion or specific neighboring group participation.

Conclusion: The S_N2 reaction is characterized by a "back-to-front" substitution; consequently, if the reaction site is a chiral center, the geometry of that center is strictly inverted, yielding a single stereoisomeric product.

Answer: (C)

Q30.

Solution

Concept: The **Wurtz reaction** is a coupling reaction used in organic chemistry to prepare higher alkanes from alkyl halides. In this reaction, two molecules of an alkyl halide react with sodium metal in the presence of **dry ether**.

General Equation:

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

The reaction involves the coupling of two alkyl groups (R) to form a symmetrical alkane with double the number of carbon atoms present in the starting alkyl halide.

Solution Analysis: The starting material given is **methyl iodide** (CH_3I).

- The alkyl group (R) is a methyl group (CH_3-).
- When two methyl groups couple, they form a two-carbon chain.

Chemical Equation:

$$2CH_3I + 2Na \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaI$$

The product $CH_3 - CH_3$ is **ethane**.

Analysis of options:

- **(A) Methane:** Cannot be prepared by the Wurtz reaction as it requires at least two carbon atoms to form a C-C bond.
- **(B) Ethane:** Correct. Coupling of two methyl groups ($C_1 + C_1$) yields ethane (C_2).
- **(C) Propane:** Produced if a mixture of methyl iodide and ethyl iodide is used (though this yields a mixture of products).
- **(D) Butane:** Produced if ethyl iodide is used as the starting material.

Conclusion: The Wurtz reaction acts as a "molecular joiner," pairing up the alkyl fragments of the halide; since methyl iodide contains a single carbon, the resulting alkane must contain exactly two carbons, identifying the product as ethane.

Answer: (B)

Q31.

Solution

Concept: The **Lucas reagent** is used in organic chemistry to distinguish between primary (1°), secondary (2°), and tertiary (3°) alcohols. The test is based on the difference in reactivity of these alcohols with hydrogen halides via an S_N1 mechanism.
Composition: The Lucas reagent consists of a solution of **concentrated hydrochloric acid (HCl)** and **anhydrous zinc chloride ($ZnCl_2$)**.

- HCl provides the chloride nucleophile.
- Anhydrous $ZnCl_2$ acts as a **Lewis acid catalyst**, coordinating with the oxygen of the alcohol to make the $-OH$ group a better leaving group.

The Lucas Test (Observations): When the reagent is added to an alcohol, the corresponding alkyl chloride is formed, which is insoluble in the reagent and causes **turbidity** (cloudiness).

- **Tertiary alcohols:** React immediately to produce turbidity.
- **Secondary alcohols:** Produce turbidity within 5–10 minutes.
- **Primary alcohols:** Do not produce turbidity at room temperature (may react upon heating).

Analysis of options:

- **(A) HCl + anhydrous $ZnCl_2$:** Correct. This is the definition of Lucas reagent.
- **(B) H_2SO_4 + $KMnO_4$:** This is an oxidizing mixture, often Baeyer's reagent (though that is usually alkaline $KMnO_4$).
- **(C) Pd/$BaSO_4$:** Known as **Lindlar's catalyst**, used for partial hydrogenation of alkynes.
- **(D) Na/liquid NH_3:** Used in **Birch reduction** of aromatic rings or alkynes.

Conclusion: Lucas reagent effectively catalyzes the substitution of the hydroxyl group for a chloride ion; because anhydrous zinc chloride significantly weakens the C-O bond, it allows for a quick diagnostic test based on the speed of the resulting solution's clouding.

Answer: (A)

Q32.

Solution

Concept: The **Reimer-Tiemann reaction** is a classic organic chemistry method used for the *ortho*-formylation of phenols. It involves the introduction of an aldehyde group ($-CHO$) onto the aromatic ring, primarily at the position adjacent to the hydroxyl group.

Solution: When phenol is treated with **chloroform** ($CHCl_3$) in the presence of an aqueous alkali like **sodium hydroxide** ($NaOH$), the following steps occur:

(a) **Generation of Carbene:** $NaOH$ reacts with $CHCl_3$ to generate the highly reactive electrophile, **dichlorocarbene** (: CCl_2).

(b) **Electrophilic Attack:** The dichlorocarbene attacks the phenoxide ion (formed from phenol in the basic medium) at the *ortho* position.

(c) **Hydrolysis:** The intermediate substituted with $-CHCl_2$ undergoes alkaline hydrolysis to form an unstable geminal diol, which loses water to become an aldehyde.

(d) **Acidification:** Final protonation yields the phenolic aldehyde.

Analysis of options:

- **(A) Salicylic acid:** Formed in the **Kolbe-Schmitt reaction** (using CO_2) or if *carbon tetrachloride* (CCl_4) is used in the Reimer-Tiemann reaction.
- **(B) Salicylaldehyde: Correct.** This is the major product formed when $CHCl_3$ is used.
- **(C) Benzene:** Phenol is converted to benzene using zinc dust.
- **(D) Benzoic acid:** Formed via oxidation of toluene or benzaldehyde, not this reaction.

Conclusion: The reaction uses the electrophilic nature of dichlorocarbene to substitute the phenol ring, resulting in the formation of 2-hydroxybenzaldehyde, commonly known as salicylaldehyde.

Answer: (B)

Q33.

Solution

Concept: The acidity of a compound depends on the stability of its conjugate base. A more stable conjugate base corresponds to a stronger parent acid. When an acid loses a proton (H^+), it forms a negatively charged ion:

- **Phenol → Phenoxide ion** ($C_6H_5O^-$)
- **Ethanol → Ethoxide ion** ($CH_3CH_2O^-$)

Solution: The difference in acidity is explained by the distribution of the negative charge on the oxygen atom:
1. **Phenoxide Ion Stability:** In the phenoxide ion, the negative charge on the oxygen is in conjugation with the π-electrons of the benzene ring. This allows the charge to be delocalized over the ortho and para positions of the ring through **resonance**. Delocalization spreads the charge over a larger volume, making the ion highly stable.
2. **Ethoxide Ion Stability:** In the ethoxide ion, the negative charge is localized on the oxygen atom. Furthermore, the ethyl group (CH_3CH_2-) exerts an **inductive effect ($+I$)**, which pushes electron density toward the already negative oxygen, destabilizing the ion.

Analysis of options:

- **(A) Phenoxide ion is resonance stabilized:** Correct. This stabilization makes phenol much more willing to lose a proton compared to ethanol.
- **(B) Ethoxide ion is resonance stabilized:** Incorrect. Ethoxide has no π-system for resonance; it is actually destabilized by induction.
- **(C) Phenol has a higher molecular weight:** Incorrect. Molecular weight does not directly determine acidity.
- **(D) Phenol contains an −OH group:** Incorrect. Both molecules contain an $-OH$ group, so this does not explain the difference in their properties.

Conclusion: Phenol is significantly more acidic than ethanol because the resulting phenoxide ion can distribute its negative charge into the aromatic ring via resonance, a stabilizing feature that is entirely absent in the ethoxide ion.

Answer: (A)

Q34.

Solution

Concept: To distinguish between two different alcohols, we often rely on their oxidation products. Primary and secondary alcohols yield different types of carbonyl compounds:

- **Primary alcohols** (1°)**:** Oxidize to aldehydes, which can further oxidize to carboxylic acids.
- **Secondary alcohols** (2°)**:** Oxidize to ketones.

Solution Analysis: Let's look at the specific alcohols in the question:

(a) **Propan-1-ol** ($CH_3CH_2CH_2OH$)**:** A primary alcohol. Upon oxidation (using $K_2Cr_2O_7$ or $KMnO_4$), it forms **Propanal** (CH_3CH_2CHO).

(b) **Propan-2-ol** ($CH_3CH(OH)CH_3$)**:** A secondary alcohol. Upon oxidation, it forms **Propanone** (Acetone, CH_3COCH_3).

Now, we apply the **Iodoform Test** to these products:

- The Iodoform test is positive for compounds containing a **methyl keto group** (CH_3CO-) or alcohols that can be oxidized to a methyl keto group (like $CH_3CH(OH)-$).
- **Propanone** (from Propan-2-ol) contains the CH_3CO- group. It reacts with $I_2/NaOH$ to give a **yellow precipitate** of Iodoform (CHI_3).
- **Propanal** (from Propan-1-ol) does *not* have a methyl keto group (it is CH_3CH_2CHO) and thus gives a negative Iodoform test.

Analysis of options:

- **(A):** Correct. Oxidation converts them to an aldehyde and a ketone, respectively, where only the ketone (from Propan-2-ol) yields a positive Iodoform test.
- **(B) & (C):** Incorrect. Fehling's and Tollen's tests distinguish aldehydes from ketones, but both alcohols themselves do not react directly with these reagents.
- **(D):** Incorrect. Bromine water is used to detect unsaturation (double/triple bonds) or phenols/anilines, not to distinguish between these saturated alcohols.

Conclusion: Propan-2-ol is a "secondary methyl alcohol" which, upon oxidation, generates a methyl ketone capable of forming the characteristic yellow iodoform precipitate, whereas Propan-1-ol does not.

Answer: (A)

Q35.

Solution

Concept: The **Williamson ether synthesis** is one of the most widely used laboratory methods for the preparation of symmetrical and unsymmetrical **ethers**. It is a nucleophilic substitution reaction, specifically following an S_N2 mechanism.

Reaction Details: In this reaction, an **alkyl halide** is reacted with a **sodium alkoxide**.

$$R - X + R' - ONa \longrightarrow R - O - R' + NaX$$

Mechanism and Limitations:

(a) The alkoxide ion ($R'O^-$) acts as a nucleophile and attacks the alkyl halide ($R - X$) from the backside, displacing the halide ion.

(b) For the best yield of ethers, the alkyl halide should be **primary** (1°).

(c) If a tertiary (3°) alkyl halide is used, the alkoxide (which is also a strong base) prefers to act as a base rather than a nucleophile, leading to **elimination** and the formation of an alkene instead of an ether.

Analysis of options:

- **(A) Alcohols:** Prepared by hydration of alkenes or reduction of carbonyls, but not via Williamson synthesis.
- **(B) Ketones:** Prepared by oxidation of secondary alcohols or Friedel-Crafts acylation.
- **(C) Ethers: Correct.** This is the specific product of the reaction between an alkoxide and an alkyl halide.
- **(D) Aldehydes:** Prepared by oxidation of primary alcohols or Rosenmund reduction.

Conclusion: By utilizing an alkoxide ion as a nucleophile to attack an alkyl halide, the Williamson synthesis allows for the precise construction of an ether linkage, provided that steric hindrance on the halide is kept to a minimum to avoid competing elimination.

Answer: (C)

Q36.

Solution

Concept: Aldol condensation is a characteristic reaction of aldehydes and ketones that possess at least one **α-hydrogen** atom.

- The α-carbon is the carbon atom directly attached to the carbonyl group ($C = O$).
- Hydrogen atoms attached to this α-carbon are called α-hydrogens.
- In the presence of a dilute alkali (like $NaOH$), these hydrogens are acidic enough to be removed, forming an enolate ion which then attacks another carbonyl molecule.

Solution Analysis: We must check each option for the presence of α-hydrogens:

- **(A) CH_3CHO (Acetaldehyde):** The carbonyl carbon is attached to a methyl group. It has **three** α-hydrogens. It undergoes Aldol condensation.
- **(B) CH_3COCH_3 (Acetone):** The carbonyl carbon is attached to two methyl groups. It has **six** α-hydrogens. It undergoes Aldol condensation.
- **(C) HCHO (Formaldehyde):** The carbonyl carbon is attached only to two hydrogen atoms. There is no carbon atom adjacent to the carbonyl group; therefore, it has **zero α-hydrogens**.
- **(D) CH_3CH_2CHO (Propionaldehyde):** The carbon adjacent to the carbonyl group ($-CH_2-$) has **two** α-hydrogens. It undergoes Aldol condensation.

Special Note: Aldehydes like formaldehyde ($HCHO$) and benzaldehyde (C_6H_5CHO) which lack α-hydrogens do not undergo Aldol condensation; instead, they undergo the **Cannizzaro reaction** when treated with concentrated alkali.
Conclusion: Because formaldehyde consists only of a carbonyl group bonded to hydrogen atoms, it lacks the alpha-carbon necessary to host the acidic protons required for the Aldol pathway.

Answer: (C)

Q37.

Solution

Concept: The **Cannizzaro reaction** is a redox (disproportionation) reaction characteristic of aldehydes that **lack an α-hydrogen atom**.

- In the presence of a **concentrated alkali** (like 50% $NaOH$ or KOH), one molecule of the aldehyde is reduced to an alcohol, while another molecule is oxidized to the salt of a carboxylic acid.
- Aldehydes with α-hydrogens undergo Aldol condensation instead.

Solution Analysis: We examine the structure of each option to check for the presence of α-hydrogens (hydrogens on the carbon adjacent to the $C = O$ group):

- **(A) Formaldehyde ($HCHO$):** The carbonyl carbon is bonded only to hydrogen atoms. There is no α-carbon, hence **no α-hydrogens**. It undergoes the Cannizzaro reaction.

$$2HCHO + NaOH(\text{conc.}) \rightarrow CH_3OH + HCOONa$$

- **(B) Acetaldehyde (CH_3CHO):** Contains a methyl group adjacent to the carbonyl. It has **three α-hydrogens** and undergoes Aldol condensation.
- **(C) Acetone (CH_3COCH_3):** A ketone with **six α-hydrogens**. It undergoes Aldol condensation.
- **(D) Propionaldehyde (CH_3CH_2CHO):** The α-carbon (CH_2) has **two α-hydrogens**. It undergoes Aldol condensation.

Conclusion: Formaldehyde is the simplest aldehyde and lacks the alpha-carbon necessary for enolization; thus, it follows the Cannizzaro pathway where it simultaneously acts as both an oxidizing and reducing agent to form methanol and a formate salt.

Answer: (A)

Q38.

Solution

Concept: The reactivity of carbonyl compounds (aldehydes and ketones) toward **nucleophilic addition** is governed by two main factors:

(a) **Electronic Factor (Inductive Effect):** Alkyl groups are electron-donating ($+I$ effect). They increase the electron density on the carbonyl carbon, making it less electrophilic (less "hungry" for a nucleophile).

(b) **Steric Factor (Steric Hindrance):** Larger groups around the carbonyl carbon physically block the approach of the incoming nucleophile, increasing the activation energy of the reaction.

Solution Analysis: We compare the structures of the given compounds based on these factors:

- **(A) HCHO (Formaldehyde):** Has two small hydrogen atoms. There is **minimal steric hindrance** and **no $+I$ effect** to reduce the positive charge on the carbon. It is the most reactive.
- **(B) CH_3CHO (Acetaldehyde):** Has one methyl group. The methyl group adds steric bulk and slightly reduces the electrophilicity of the carbon via the $+I$ effect. It is less reactive than formaldehyde.
- **(C) CH_3COCH_3 (Acetone):** Has two methyl groups. This increases steric hindrance and further reduces the positive charge on the carbonyl carbon through two $+I$ effects. Ketones are generally less reactive than aldehydes.
- **(D) $PhCOCH_3$ (Acetophenone):** Has a large phenyl ring and a methyl group. The phenyl ring offers significant steric hindrance. Additionally, the carbonyl group is in resonance with the benzene ring, which greatly stabilizes the carbonyl carbon and reduces its electrophilic character.

Reactivity Order: $HCHO > CH_3CHO > CH_3COCH_3 > PhCOCH_3$
Conclusion: Formaldehyde stands out as the most reactive because its carbonyl carbon is flanked only by tiny hydrogen atoms; this lack of steric crowding and electronic stabilization leaves the carbon highly exposed and intensely electrophilic compared to its substituted counterparts.

Answer: (A)

Q39.

Solution

Concept: Aldehydes and ketones can be reduced to their corresponding alkanes (hydrocarbons) by converting the carbonyl group ($> C = O$) into a methylene group ($> CH_2$). This can be achieved through two primary name reactions depending on the conditions:

- **Clemmensen Reduction:** Uses acidic conditions.
- **Wolff-Kishner Reduction:** Uses basic conditions.

Solution Analysis: The reagent specified in the question is **zinc amalgam and concentrated hydrochloric acid (Zn-Hg/HCl)**.

- **(A) Wolff-Kishner reduction:** Uses **hydrazine** (NH_2NH_2) followed by heating with a strong base like KOH in a high-boiling solvent like ethylene glycol.
- **(B) Clemmensen reduction: Correct.** This reaction specifically uses **Zn-Hg** and **conc. HCl**. It is particularly useful for compounds that are stable toward acids.
- **(C) Rosenmund reduction:** Used to reduce an **acid chloride** to an **aldehyde** using $H_2/Pd - BaSO_4$. It does not produce a hydrocarbon.
- **(D) Stephen reduction:** Used to reduce a **nitrile** to an **aldehyde** using $SnCl_2/HCl$ followed by hydrolysis.

Chemical Equation (Clemmensen):

$$R - CHO \xrightarrow{\text{Zn-Hg/conc. HCl}} R - CH_3 + H_2O$$

Conclusion: The use of zinc amalgam in an acidic environment is the hallmark of the Clemmensen reduction; this method effectively strips the oxygen from the carbonyl carbon to yield a saturated hydrocarbon.

Answer: (B)

Q40.

Solution

Concept: Tollen's reagent is a mild oxidizing agent used primarily to distinguish between aldehydes and ketones. It is an aqueous solution containing the diamminesilver(I) complex ion, $[Ag(NH_3)_2]^+$.

Solution Analysis: Tollen's reagent is prepared by adding a few drops of sodium hydroxide to silver nitrate solution to form silver oxide, which is then dissolved by adding dilute ammonia. This resulting solution is known as **ammoniacal silver nitrate**.

- **Reaction with Aldehydes:** Aldehydes are easily oxidized to carboxylate ions. During this process, the Ag^+ ions in the reagent are reduced to metallic silver (Ag), which deposits on the inner wall of the test tube, creating a "silver mirror."

$$R - CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow R - COO^- + 2Ag(s) + 4NH_3 + 2H_2O$$

- **Reaction with Ketones:** Ketones generally do not react with Tollen's reagent (except for α-hydroxy ketones), making this a definitive test for the aldehyde functional group.

Analysis of options:

- **(A) Ammoniacal silver nitrate: Correct.** This is the chemical identity of Tollen's reagent.
- **(B) Alkaline $KMnO_4$:** Known as **Baeyer's reagent**, used for testing unsaturation.
- **(C) $SnCl_2/HCl$:** Used in the **Stephen reduction** to convert nitriles to aldehydes.
- **(D) $I_2/NaOH$:** Reagent for the **Iodoform test**, used to detect methyl ketones or specific alcohols.

Conclusion: Tollen's reagent relies on the high reduction potential of silver ammine complexes to selectively oxidize aldehydes; the formation of a literal silver coating on the glass provides a clear, visual confirmation of the aldehyde group.

Answer: (A)

Q41.

Solution

Concept: The acidity of carboxylic acids is primarily determined by the stability of the resulting carboxylate ion ($RCOO^-$). This stability is influenced by the electronic effects of the substituents attached to the α-carbon:

- **Inductive Effect ($-I$):** Electron-withdrawing groups (EWGs) like halogens pull electron density away from the carboxylate group, dispersing the negative charge and stabilizing the ion. This **increases** acidity.
- **Number of Substituents:** More EWGs lead to a stronger cumulative $-I$ effect and higher acidity.
- **Electronegativity:** For a single substituent, a more electronegative atom ($F > Cl > Br > I$) exerts a stronger $-I$ effect.

Solution Analysis: We evaluate the substituents in each option:

- **(A) CH_3COOH (Acetic acid):** The methyl group is electron-donating ($+I$), which destabilizes the carboxylate ion. It is the weakest acid in this list.
- **(B) $ClCH_2COOH$ (Chloroacetic acid):** One chlorine atom exerts a $-I$ effect, increasing acidity relative to acetic acid.
- **(C) $Cl_2CHCOOH$ (Dichloroacetic acid):** Two chlorine atoms exert a combined, powerful $-I$ effect. This stabilizes the carboxylate ion much more than a single halogen.
- **(D) FCH_2COOH (Fluoroacetic acid):** One fluorine atom is more electronegative than one chlorine atom, making it more acidic than option (B), but **less** acidic than option (C) because the quantity of EWGs usually outweighs a single step in electronegativity.

Acidity Order: $Cl_2CHCOOH > FCH_2COOH > ClCH_2COOH > CH_3COOH$

Conclusion: While fluorine is the most electronegative element, the presence of two chlorine atoms in dichloroacetic acid creates a significantly stronger cumulative electron-withdrawing effect, leading to superior stabilization of the conjugate base and thus making it the strongest acid provided.

Answer: (C)

Q42.

Solution

Concept: The basicity of amines in the aqueous phase is not determined by a single factor, but by the interplay of three competing effects:

(a) **Inductive Effect (+*I*):** Methyl groups are electron-donating, increasing electron density on the Nitrogen atom, which increases basicity ($3^\circ > 2^\circ > 1^\circ$).

(b) **Solvation (Hydration) Effect:** In water, the protonated amine (conjugate acid) is stabilized by hydrogen bonding with water molecules. Smaller ions with more hydrogens are better solvated and thus more stable ($1^\circ > 2^\circ > 3^\circ$).

(c) **Steric Hindrance:** Bulkier methyl groups around the Nitrogen atom hinder the approach of a proton (H^+), reducing basicity ($1^\circ > 2^\circ > 3^\circ$).

Solution Analysis: For **methyl-substituted** amines, the net result of these combined effects leads to a specific experimental order:

- The **secondary amine** ($(CH_3)_2NH$) is the strongest base because it strikes the perfect balance between the inductive effect and solvation.
- The **primary amine** (CH_3NH_2) comes next because its conjugate acid is very well solvated, despite having only one +*I* group.
- The **tertiary amine** ($(CH_3)_3N$) follows; although it has the strongest +*I* effect, it is poorly solvated and highly sterically hindered.
- **Ammonia** (NH_3) is the weakest as it lacks any electron-donating methyl groups.

Experimental Order for Methyl Amines:

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

(Numerical code trick: **213** for Methyl, where the numbers represent the degree of the amine).
Note: For *ethyl* substituted amines, the order changes to **231** ($2^\circ > 3^\circ > 1^\circ$) because the larger ethyl groups make the +*I* effect more dominant over the solvation effect compared to methyl groups.
Conclusion: In an aqueous environment, the basicity of methylamines is a "tug-of-war" between electron donation and water stabilization; the dimethylamine molecule wins because it provides enough electron density without sacrificing too much hydration.

Answer: (A)

Q43.

Solution

Concept: The **Gabriel Phthalimide synthesis** is a very important laboratory method used specifically for the preparation of **primary amines**. It involves the nucleophilic substitution (S_N2) of an alkyl halide by the phthalimide anion.

Reaction Steps:

(a) **Formation of Potassium Phthalimide:** Phthalimide is treated with ethanolic KOH to form potassium phthalimide.

(b) **Alkylation:** The potassium salt reacts with a primary alkyl halide ($R - X$) to form N-alkylphthalimide. This step is an S_N2 reaction.

(c) **Hydrolysis:** The N-alkylphthalimide is then hydrolyzed (using $NaOH$ or hydrazine) to yield the pure **primary aliphatic amine** and phthalic acid.

Why it is limited to Aliphatic Amines:

- To prepare **aromatic** primary amines (like aniline), we would need to use an aryl halide (like chlorobenzene) in the second step.
- However, aryl halides **do not undergo nucleophilic substitution** (S_N2) with the phthalimide anion under ordinary conditions because of the partial double-bond character of the $C - X$ bond and electronic repulsion from the benzene ring.

Analysis of options:

- **(A) Primary aliphatic amines: Correct.** This is the primary use of this synthesis.
- **(B) Primary aromatic amines:** Cannot be prepared because aryl halides are unreactive toward the phthalimide anion.
- **(C) & (D) Secondary/Tertiary amines:** This method is specifically designed to prevent "over-alkylation," ensuring only a primary amine is formed.

Conclusion: Gabriel Phthalimide synthesis is a "clean" method for producing primary amines because the nitrogen atom is protected within the phthalimide ring, preventing multiple alkylations; however, its reliance on S_N2 chemistry restricts its utility to aliphatic groups.

Answer: (A)

Q44.

Solution

Concept: The reaction of a primary aromatic amine with nitrous acid (generated in situ from $NaNO_2$ and HCl) at low temperatures is known as the **Diazotization reaction**.

Solution Analysis: When aniline ($C_6H_5NH_2$) is treated with a mixture of sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl) at a cold temperature (0–5°C), it forms **benzene diazonium chloride**.

Reaction Equation:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{–}5^\circ C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Key Points:

- **Temperature Control:** The temperature must be kept between 0–5°C. If the temperature rises, the diazonium salt becomes unstable and decomposes, reacting with water to form phenol.
- **Stability:** Benzene diazonium salts are relatively stable at low temperatures due to the resonance stabilization of the diazonium group with the benzene ring.

Analysis of options:

- **(A) Chlorobenzene:** This is formed if the diazonium salt is further treated with $CuCl/HCl$ (Sandmeyer reaction).
- **(B) Benzene diazonium chloride: Correct.** This is the direct product of diazotization.
- **(C) Nitrobenzene:** Requires different nitration conditions (conc. $HNO_3 + H_2SO_4$).
- **(D) Phenol:** Formed if the reaction mixture is warmed above 10°C.

Conclusion: Diazotization is a fundamental transformation in synthetic organic chemistry; by keeping the reaction chilled, the highly reactive amine group is converted into a versatile diazonium leaving group, serving as a gateway to numerous other aromatic compounds.

Answer: (B)

Q45.

Solution

Concept: The **Hinsberg test** is a chemical method used to distinguish between primary (1°), secondary (2°), and tertiary (3°) amines. The test relies on the reaction of amines with the **Hinsberg reagent**.

Solution Analysis: Hinsberg's reagent is chemically known as **benzene sulphonyl chloride** ($C_6H_5SO_2Cl$).

How the test works:

(a) **Primary amines (1°):** React to form an N-alkylbenzene sulphonamide. Because this sulfonamide has an acidic hydrogen attached to the nitrogen, it is **soluble in alkali** ($NaOH$).

(b) **Secondary amines (2°):** React to form an N,N-dialkylbenzene sulphonamide. This product lacks an acidic hydrogen and is **insoluble in alkali**.

(c) **Tertiary amines (3°):** Do not react with the reagent under normal conditions as they lack a hydrogen atom on the nitrogen to displace the chloride.

Analysis of options:

- **(A) Benzene sulphonyl chloride: Correct.** This is the chemical name for Hinsberg's reagent.
- **(B) Benzene sulphonic acid:** This is the hydrolyzed product of the reagent, not the reagent itself.
- **(C) Phenyl isocyanide:** This is the foul-smelling product of the **Carbylamine test**, used to detect primary amines.
- **(D) Nitrous acid:** Used in the **Diazotization reaction** to distinguish aliphatic and aromatic amines.

Conclusion: Benzene sulphonyl chloride acts as the Hinsberg reagent by forming sulfonamide derivatives whose varying solubility in basic solutions allows for the clear identification of an amine's degree of substitution.

Answer: (A)

Q46.

Solution

Concept: Sugars are classified as **reducing** or **non-reducing** based on their ability to reduce Tollen's reagent or Fehling's solution.

- **Reducing Sugars:** Contain a free (or potentially free) **aldehyde** or **ketone** group. In cyclic structures, this means they have a free **hemiacetal** or **hemiketal** group (an $-OH$ group attached directly to the anomeric carbon).
- **Non-reducing Sugars:** The aldehydic or ketonic groups are involved in forming a glycosidic bond between two monosaccharide units. They lack a free hemiacetal/hemiketal group.

Solution Analysis: We examine the structures of the given carbohydrates:

- **(A) Glucose:** A monosaccharide with a free aldehyde group (aldose). It is a **reducing sugar**.
- **(B) Fructose:** A monosaccharide with a free ketone group (ketose). Although ketones are generally not reducing, α-hydroxy ketones like fructose can isomerize to aldehydes in basic reagents. It is a **reducing sugar**.
- **(C) Lactose:** A disaccharide (Milk sugar) made of Glucose and Galactose. The anomeric carbon of the glucose unit is free. It is a **reducing sugar**.
- **(D) Sucrose:** A disaccharide (Table sugar) made of Glucose and Fructose. The glycosidic linkage is formed between the **C1 of α-D-glucose** and the **C2 of β-D-fructose**. Since both anomeric carbons are involved in the bond, there is no free hemiacetal group. It is a **non-reducing sugar**.

Analysis of options:

- **(A), (B), (C):** All have free functional groups that can reduce copper(II) or silver(I) ions.
- **(D): Correct.** Sucrose does not react with Tollen's or Fehling's reagents because its reactive centers are locked in a bond.

Conclusion: Sucrose is the most common example of a non-reducing sugar because the linkage between its two components consumes the aldehyde and ketone functionalities of both glucose and fructose, respectively, preventing any further oxidation reactions.

Answer: (D)

Q47.

Solution

Concept: Proteins are high-molecular-weight polymers (polyamides) made up of α-amino acids. These amino acids are joined together by a specific type of covalent bond known as a **peptide bond** or **peptide linkage**.

Solution Analysis: A peptide linkage is formed through a condensation reaction between the carboxyl group ($-COOH$) of one amino acid and the amino group ($-NH_2$) of the next amino acid, with the elimination of a water molecule.

- The resulting group is an amide linkage: $-CO-NH-$.
- When two amino acids combine, they form a dipeptide; many such linkages result in a polypeptide or protein.

Analysis of options:

- **(A) Glycosidic linkage:** Found in **carbohydrates** (polysaccharides) like starch, cellulose, and sucrose, joining monosaccharide units.
- **(B) Peptide linkage: Correct.** This is the fundamental structural linkage that holds amino acid chains together in proteins.
- **(C) Phosphodiester linkage:** Found in **nucleic acids** (DNA and RNA), joining the 3' carbon of one sugar to the 5' carbon of another via a phosphate group.
- **(D) Ester linkage:** Found in **lipids** (triglycerides) and some polymers like polyesters.

Conclusion: The peptide linkage is a robust amide bond that defines the primary structure of proteins; it is through the specific sequence of these bonds that proteins achieve their diverse functional shapes and biological roles.

Answer: (B)

Q48.

Solution

Concept: **Vitamin K** (Phylloquinone/Menaquinone) is a fat-soluble vitamin that plays a critical role in the synthesis of several proteins required for **blood coagulation** (clotting). It acts as a co-factor for the enzyme that carboxylates specific glutamic acid residues in clotting factors II (prothrombin), VII, IX, and X.

[Image of Vitamin K role in blood clotting cascade]

Solution Analysis: When the body is deficient in Vitamin K, the liver cannot produce functional clotting factors. This results in a significant physiological change:

- **Blood Clotting Time:** The time it takes for blood to thicken and stop flowing from a wound **increases**. This can lead to excessive bleeding (hemorrhage) even from minor injuries.

Analysis of options:

- **(A) Increase in blood clotting time: Correct.** Without Vitamin K, the coagulation cascade is delayed, lengthening the time required to form a stable clot.
- **(B) Decrease in blood clotting time:** Incorrect. This would mean faster clotting, which is not a result of Vitamin K deficiency.
- **(C) Night blindness:** Caused by the deficiency of **Vitamin A**.
- **(D) Sterility:** Often associated with the deficiency of **Vitamin E** (Tocopherol) in some animal models, as it maintains reproductive health.

Conclusion: Vitamin K is essential for the activation of prothrombin; its absence disrupts the body's internal sealing mechanism, making "increased clotting time" the primary clinical indicator of its deficiency.

Answer: (A)

Q49.

Solution

Concept: Denaturation is a process in which a protein loses its native conformation (shape) due to physical or chemical changes, such as changes in temperature, pH, or the addition of certain chemicals.

Solution Analysis: Proteins are organized into four levels of structure:

(a) **Primary** (1°)**:** The linear sequence of amino acids held together by strong covalent **peptide bonds**.

(b) **Secondary** (2°)**:** Local folding into α-helices and β-pleated sheets, stabilized by hydrogen bonds.

(c) **Tertiary** (3°)**:** The overall 3D shape stabilized by various interactions (disulfide bridges, ionic bonds, hydrophobic interactions).

(d) **Quaternary** (4°)**:** The arrangement of multiple polypeptide chains.

During denaturation, the relatively weak bonds (hydrogen bonds, ionic bonds, and van der Waals forces) responsible for the secondary, tertiary, and quaternary structures are disrupted. This causes the protein to unfold and lose its biological activity.

However, the **primary structure**—the specific sequence of amino acids—remains **intact** because the covalent peptide bonds are strong enough to withstand the conditions that cause denaturation.

Analysis of options:

- **(A) Primary: Correct.** The amino acid sequence is preserved as peptide bonds are not broken during denaturation.
- **(B), (C), (D):** Incorrect. These higher-order folds are lost as the protein "uncoils" into a random string.

Conclusion: Denaturation is a structural "unfolding" rather than a chemical breakdown; while the complex 3D architecture collapses, the fundamental chemical identity defined by the primary sequence of amino acids remains perfectly preserved.

Answer: (A)

Q50.

Solution

Concept: In the double-helix structure of DNA, the nitrogenous bases on opposite strands are linked by hydrogen bonds. This pairing follows the **Chargaff's Rule of Base Pairing**, which ensures that a purine always pairs with a pyrimidine to maintain a constant distance between the two strands.

Solution Analysis: There are four nitrogenous bases in DNA: Adenine (A), Guanine (G), Cytosine (C), and Thymine (T). The specific pairing rules are:

- **Adenine (A)** pairs with **Thymine (T)** via **two** hydrogen bonds ($A = T$).
- **Guanine (G)** pairs with **Cytosine (C)** via **three** hydrogen bonds ($G \equiv C$).

Analysis of options:

- **(A) Adenine:** Pairs with Thymine in DNA (or Uracil in RNA).
- **(B) Cytosine: Correct.** Guanine and Cytosine are complementary bases. The triple hydrogen bond between them makes this pairing slightly stronger than the A-T pair.
- **(C) Thymine:** Pairs with Adenine in DNA.
- **(D) Uracil:** Found in **RNA** instead of Thymine; it pairs with Adenine.

Conclusion: Base pairing in DNA is highly specific; Guanine identifies Cytosine as its partner through a precise arrangement of three hydrogen bond donors and acceptors, ensuring the genetic code is copied with high fidelity.

Answer: (B)

Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	A	2	B	3	B	4	B	5	C
6	C	7	B	8	B	9	A	10	C
11	B	12	A	13	C	14	B	15	B
16	C	17	D	18	C	19	B	20	C
21	B	22	B	23	A	24	B	25	A
26	C	27	D	28	B	29	C	30	B
31	A	32	B	33	A	34	A	35	C
36	C	37	A	38	A	39	B	40	A
41	C	42	A	43	A	44	B	45	A
46	D	48	B	48	A	49	A	50	B