CUET UG Chemistry Sample Paper - 13

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. 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
(D) Not related to the solubility of gases

Q2. If the Van't Hoff factor for a solute is 0.5, the solute undergoes:

(A) Dissociation
(B) Association
(C) No change
(D) Complete ionization

Q3. An ideal solution is formed when its components:

(A) Have zero heat of mixing
(B) Have zero volume change on mixing
(C) Obey Raoult's Law over the entire range of concentration
(D) All of the above

Q4. The osmotic pressure of a solution is given by the relation:

(A) $P = CRT$

(B) $P = C/RT$

(C) $P = RC/T$

(D) $P = RT/C$

Q5. In the electrolysis of aqueous $CuSO_4$ using copper electrodes, the reaction at the anode is:

(A) $Cu^{2+} + 2e^- \longrightarrow Cu$

(B) $Cu \longrightarrow Cu^{2+} + 2e^-$

(C) $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

(D) $SO_4^{2-} \longrightarrow SO_2 + O_2 + 2e^-$

Q6. The molar conductivity of a strong electrolyte:

(A) Increases linearly with $\sqrt{C}$

(B) Decreases linearly with $\sqrt{C}$

(C) Is independent of concentration

(D) Increases with increase in concentration

Q7. How many Coulombs are required for the oxidation of 1 mol of H_2O to O_2?

(A) 96500 C

(B) 193000 C

(C) 48250 C

(D) 386000 C

Q8. The Nernst equation for the electrode reaction $M^{n+} + ne^- \longrightarrow M$ is:

(A) $E = E^0 - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$

(B) $E = E^0 + \frac{RT}{nF}\ln[M^{n+}]$

(C) Both A and B

(D) $E = E^0 - \frac{RT}{nF}\ln[M^{n+}]$

Q9. Which of the following is a secondary cell?

(A) Dry cell

(B) Mercury cell

(C) Lead storage battery

(D) Fuel cell

Q10. According to Kohlrausch law, the limiting molar conductivity of CH_3COOH is:

(A) $\Lambda^0_{CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$

(B) $\Lambda^0_{CH_3COONa} - \Lambda^0_{HCl} + \Lambda^0_{NaCl}$

(C) $\Lambda^0_{CH_3COONa} + \Lambda^0_{NaCl} - \Lambda^0_{HCl}$

(D) $\Lambda^0_{HCl} + \Lambda^0_{NaCl} - \Lambda^0_{CH_3COONa}$

Q11. For a reaction $A + B \rightarrow C$, doubling the concentration of A quadruples the rate, but doubling B has no effect. The rate law is:

(A) $Rate = k[A][B]$

(B) $Rate = k[A]^2$

(C) $Rate = k[A]^2[B]$

(D) $Rate = k[A][B]^2$

Q12. The unit of rate constant for a zero-order reaction is:

(A) s^{-1}

(B) $mol\, L^{-1}\, s^{-1}$

(C) $L\, mol^{-1}\, s^{-1}$

(D) $L^2\, mol^{-2}\, s^{-1}$

Q13. The half-life of a first-order reaction is 69.3 seconds. The rate constant is:

(A) $0.01\, s^{-1}$

(B) $0.1\, s^{-1}$

(C) $1.0\, s^{-1}$

(D) $10\, s^{-1}$

Q14. Activation energy of a chemical reaction can be determined by:

(A) Determining the rate constant at standard temperature

(B) Determining the rate constants at two different temperatures

(C) Determining probability of collision

(D) Using catalyst

Q15. In a pseudo-first-order reaction:

(A) One reactant is present in large excess

(B) Both reactants are in equal concentration

(C) The reaction is actually zero order

(D) The rate is independent of temperature

Q16. Which of the following ions is paramagnetic?

(A) Sc^{3+}

(B) Cu^{+}

(C) Zn^{2+}

(D) Cr^{3+}

Q17. Lanthanoid contraction is responsible for the fact that:

(A) Zr and Y have same radius

(B) Zr and Nb have same radius

(C) Zr and Hf have same radius

(D) Zr and Zn have same radius

Q18. The highest oxidation state shown by transition elements is:

(A) +7

(B) +8

(C) +6

(D) +5

Q19. When $K_2Cr_2O_7$ is heated with conc. HCl, the gas evolved is:

(A) O_2

(B) Cl_2

(C) CrO_2Cl_2

(D) HCl

Q20. The IUPAC name for $K_3[Fe(CN)_6]$ is:

(A) Potassium ferricyanide

(B) Potassium hexacyanoferrate(II)

(C) Potassium hexacyanoferrate(III)

(D) Tri-potassium hexacyanoiron(III)

Q21. Which of the following exhibits linkage isomerism?

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

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

(C) $[Pt(NH_3)_2Cl_2]$

(D) $[Fe(H_2O)_6]Cl_3$

Q22. 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) $OH^- < F^- < Cl^- < CN^-$

Q23. The hybridization and shape of $[Ni(CO)_4]$ are:

(A) sp^3, tetrahedral

(B) dsp^2, square planar

(C) sp^3d^2, octahedral

(D) d^2sp^3, octahedral

Q24. The spin-only magnetic moment of $[MnBr_4]^{2-}$ is:

(A) 5.92 BM

(B) 4.90 BM

(C) 3.87 BM

(D) 1.73 BM

Q25. Which complex is used as an anti-cancer agent?

(A) Mer-platin

(B) Cis-platin

(C) Trans-platin

(D) Zeise's salt

Q26. Which of the following will react fastest with aqueous KOH?

(A) CH_3Cl

(B) CH_3CH_2Cl

(C) $(CH_3)_2CHCl$

(D) $(CH_3)_3CCl$

Q27. Finkelstein reaction involves the use of:

(A) NaI in dry acetone

(B) AgF in water

(C) Cl_2 in UV light

(D) PCl_5

Q28. 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

Q29. Wurtz-Fittig reaction is used to prepare:

(A) Alkanes

(B) Alkenes

(C) Alkylarenes

(D) Aryl halides

Q30. Lucas reagent is a mixture of:

(A) HCl + anhydr. $ZnCl_2$

(B) HCl + Hydrated $ZnCl_2$

(C) $HNO_3 + H_2SO_4$

(D) $Pd + BaSO_4$

Q31. Which of the following is most acidic?

(A) Phenol

(B) *o*-Nitrophenol

(C) *m*-Nitrophenol

(D) *p*-Nitrophenol

Q32. Reimer-Tiemann reaction involves the formation of:

(A) Salicylaldehyde

(B) Salicylic acid

(C) Benzaldehyde

(D) Benzoic acid

Q33. Aspirin is obtained by the reaction of salicylic acid with:

(A) CH_3OH

(B) $(CH_3CO)_2O$

(C) CH_3Cl

(D) CH_3CHO

Q34. Phenol is distilled with Zn dust to give:

(A) Benzene

(B) Toluene

(C) Benzaldehyde

(D) Benzoic acid

Q35. Which of the following will not give Aldol condensation?

(A) CH_3CHO

(B) CH_3COCH_3

(C) C_6H_5CHO

(D) CH_3CH_2CHO

Q36. Cannizzaro reaction is given by:

(A) Aldehydes with α-hydrogen

(B) Aldehydes without α-hydrogen

(C) Ketones with α-hydrogen

(D) Only aromatic aldehydes

Q37. The correct order of reactivity of $PhCHO$, CH_3CHO and CH_3COCH_3 towards nucleophilic addition is:

(A) $CH_3CHO > PhCHO > CH_3COCH_3$

(B) $PhCHO > CH_3CHO > CH_3COCH_3$

(C) $CH_3COCH_3 > CH_3CHO > PhCHO$

(D) $CH_3CHO > CH_3COCH_3 > PhCHO$

Q38. Tollen's reagent is:

(A) Alkaline $KMnO_4$

(B) Ammoniacal silver nitrate

(C) Ammoniacal cuprous chloride

(D) $I_2/NaOH$

Q39. Carboxylic acids have higher boiling points than aldehydes of comparable molecular mass due to:

(A) Hydrogen bonding
(B) Formation of dimers
(C) More polar nature
(D) Both A and B

Q40. Which acid is the strongest?

(A) CH_3COOH
(B) $ClCH_2COOH$
(C) $Cl_2CHCOOH$
(D) Cl_3CCOOH

Q41. The correct order of basicity of amines in gaseous phase is:

(A) $3^o > 2^o > 1^o > NH_3$
(B) $1^o > 2^o > 3^o > NH_3$
(C) $NH_3 > 1^o > 2^o > 3^o$
(D) $2^o > 1^o > 3^o > NH_3$

Q42. Gabriel phthalimide synthesis is used to prepare:

(A) Primary aliphatic amines
(B) Primary aromatic amines
(C) Secondary amines
(D) Tertiary amines

Q43. Hinsberg reagent is:

(A) Benzene sulphonyl chloride

(B) Benzene sulphonic acid

(C) Benzamide

(D) Chlorobenzene

Q44. Aniline on reaction with $NaNO_2$ and HCl at 0°C gives:

(A) Benzene

(B) Benzene diazonium chloride

(C) Phenol

(D) Nitrobenzene

Q45. Which of the following is a non-reducing sugar?

(A) Glucose

(B) Fructose

(C) Sucrose

(D) Maltose

Q46. The linkage present in proteins is:

(A) Glycosidic linkage

(B) Peptide linkage

(C) Phosphodiester linkage

(D) Hydrogen linkage

Q47. Deficiency of Vitamin D causes:

(A) Scurvy

(B) Rickets

(C) Night blindness

(D) Beri-beri

Q48. On denaturation, which structure of protein remains intact?

(A) Primary
(B) Secondary
(C) Tertiary
(D) Quaternary

Q49. In DNA, the complementary base pair of Guanine is:

(A) Adenine
(B) Cytosine
(C) Thymine
(D) Uracil

Q50. Which of the following statements is incorrect regarding Raoult's Law for a binary solution of two volatile liquids A and B?

(A) For an ideal solution, $\Delta H_{mixing} = 0$.
(B) If $P_{total} > P_A^0 \chi_A + P_B^0 \chi_B$, the solution shows positive deviation.
(C) In positive deviation, A-B interactions are stronger than A-A or B-B interactions.
(D) Minimum boiling azeotropes are formed by solutions showing large positive deviation.

Detailed Solutions

Q1.

Solution

Concept: According to **Henry's Law**, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. The mathematical relationship is expressed as:

$$P = K_H \cdot \chi$$

Where:

- P is the partial pressure of the gas.
- χ is the mole fraction of the gas in the solution (a measure of solubility).
- K_H is the **Henry's law constant**.

Solution: To understand the relationship between K_H and solubility (χ), we rearrange the formula at a constant pressure (P):

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

From this expression, it is evident that at a given pressure, the mole fraction (χ) is **inversely proportional** to the Henry's law constant (K_H):

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

This inverse relationship implies:

- **Higher K_H value:** Corresponds to a **lower solubility** of the gas in the solvent.
- **Lower K_H value:** Corresponds to a **higher solubility** of the gas in the solvent.

Note: K_H is a function of the nature of the gas and the temperature. As temperature increases, K_H increases, which explains why gases are generally less soluble in liquids at higher temperatures.

Answer: (B)

Q2.

Solution

Concept: The **Van't Hoff factor** (i) is a measure of the effect of a solute on colligative properties. It is defined as the ratio of the observed (experimental) value of a colligative property to the calculated (theoretical) value.
Mathematically, it is expressed as:

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Solution: The value of i indicates the behavior of the solute in the solvent:

- $i > 1$**:** Indicates **dissociation** (e.g., $NaCl \rightarrow Na^+ + Cl^-$, where $i \approx 2$). The number of particles increases.
- $i = 1$**:** Indicates **no change** (non-electrolytes like glucose or urea). The number of particles remains the same.
- $i < 1$**:** Indicates **association** (e.g., acetic acid in benzene forms dimers). The number of particles decreases.

Analysis of the given value: Since the given Van't Hoff factor is 0.5, which is **less than 1**, the solute particles must be joining together in the solution. This process is known as **association**.
A factor of 0.5 specifically suggests that two molecules are associating to form a single unit (dimerization), such as:

$$2A \rightarrow A_2$$

Conclusion: A Van't Hoff factor of 0.5 signifies that the solute undergoes association.

Answer: (B)

Q3.

Solution

Concept: An **ideal solution** is a theoretical model of a solution where the intermolecular interactions between the unlike molecules ($A-B$) are exactly the same as the interactions between the like molecules ($A-A$ and $B-B$).

Solution: For a binary solution to be classified as ideal, it must satisfy the following criteria:

(a) **Obedience to Raoult's Law:** The solution must obey Raoult's Law ($P_{total} = P_A^0\chi_A + P_B^0\chi_B$) over the entire range of concentration and at all temperatures.

(b) **Enthalpy of Mixing (ΔH_{mix}):** There should be no heat absorbed or evolved during the mixing of the components.

$$\Delta H_{mix} = 0$$

(c) **Volume Change on Mixing (ΔV_{mix}):** The total volume of the solution must be exactly equal to the sum of the volumes of the individual components.

$$\Delta V_{mix} = 0$$

Analysis of options:

- **(A):** Correct. No heat change occurs ($A-B$ bonds are as stable as $A-A$ and $B-B$).
- **(B):** Correct. No expansion or contraction occurs upon mixing.
- **(C):** Correct. This is the fundamental definition of an ideal solution.
- **(D):** Since all the above conditions are necessary characteristics of an ideal solution, this is the correct choice.

Examples: Benzene and Toluene, n-hexane and n-heptane, Bromoethane and Chloroethane.

Answer: (D)

Q4.

Solution

Concept: Osmotic pressure (π or P) is the minimum pressure that must be applied to a solution to prevent the inward flow of its pure solvent across a semi-permeable membrane. It is a colligative property, meaning it depends on the number of solute particles in the solution.

Solution: For a dilute solution, the osmotic pressure follows the van 't Hoff equation, which is analogous to the ideal gas law ($PV = nRT$).

1. **The Equation:**

$$\pi \cdot V = n \cdot R \cdot T$$

Where:

- π (or P) is the osmotic pressure.
- V is the volume of the solution in liters.
- n is the number of moles of solute.
- R is the gas constant.
- T is the absolute temperature (in Kelvin).

2. **Deriving the Concentration Relation:** By rearranging the equation to solve for pressure:

$$P = \frac{n}{V} \cdot R \cdot T$$

Since molar concentration (C or M) is defined as the number of moles per unit volume ($C = n/V$), we can substitute it into the equation:

$$P = C \cdot R \cdot T$$

Analysis of options:

- **(A)** $P = CRT$**:** Correct. This represents the direct proportionality between pressure, concentration, and temperature.
- **(B), (C), (D):** Incorrect. These are mathematically incorrect rearrangements of the physical law.

Conclusion: The osmotic pressure is directly proportional to the molarity (C) of the solution at a given temperature.

Answer: (A)

Q5.

Solution

Concept: Electrolysis involving **active electrodes** (like copper) differs from electrolysis using inert electrodes (like platinum). In the case of active electrodes, the electrode material itself participates in the chemical reaction rather than just providing a surface for the discharge of ions from the electrolyte.

Solution: When aqueous $CuSO_4$ is electrolyzed using copper electrodes:

- **At the Cathode (Reduction):** Copper ions (Cu^{2+}) from the solution move toward the cathode, gain electrons, and are deposited as metallic copper.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

- **At the Anode (Oxidation):** Since copper is an "active" metal, it is easier for the copper atoms of the anode to lose electrons than it is for SO_4^{2-} ions or H_2O molecules to be oxidized. Consequently, the copper anode dissolves into the solution as copper ions.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Analysis of options:

- **(A):** This represents the **cathode** reaction (reduction).
- **(B):** This represents the **anode** reaction (oxidation) where the copper electrode dissolves.
- **(C):** This reaction (oxidation of water) would occur if **inert electrodes** (like Pt) were used.
- **(D):** This is not a standard electrochemical reaction for sulphate ions in this context.

Conclusion: The anode reaction is the oxidation of copper metal into copper ions.

Answer: (B)

Q6.

Solution

Concept: The variation of molar conductivity (Λ_m) with concentration (C) for a strong electrolyte is described by the **Debye-Huckel-Onsager equation**:

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

Where:

- Λ_m is the molar conductivity at a given concentration.
- Λ_m° is the **limiting molar conductivity** (at infinite dilution).
- A is a constant that depends on the type of electrolyte, solvent, and temperature.
- C is the molar concentration.

Solution: 1. **Behavior of Strong Electrolytes:** Strong electrolytes are completely ionized at all concentrations. However, at higher concentrations, the inter-ionic attractions are strong, which reduces the mobility of ions. 2. **Effect of Dilution:** As the solution is diluted (concentration C decreases), the ions move further apart, inter-ionic attractions decrease, and the molar conductivity increases. 3. **Mathematical Relationship:** The equation $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$ is in the form of a straight line equation ($y = mx + c$), where:

- $y = \Lambda_m$
- $x = \sqrt{C}$
- Slope (m) = $-A$ (Negative slope)
- Intercept (c) = Λ_m°

4. **Analysis of options:**

- **(A):** Incorrect. While the relationship is with $\sqrt{C}$, the value of Λ_m *decreases* as $\sqrt{C}$ increases (concentration increases).
- **(B):** Correct. The plot of Λ_m against $\sqrt{C}$ is a straight line with a negative slope. Thus, molar conductivity **decreases linearly** as the square root of concentration increases.
- **(C) & (D):** Incorrect. Molar conductivity is highly dependent on concentration and always increases upon dilution (decreasing concentration).

Answer: (B)

Q7.

Solution

Concept: The quantity of electricity required for an electrolytic process is related to the number of electrons transferred in the redox reaction. According to **Faraday's First Law of Electrolysis**, the charge (Q) is given by:

$$Q = n \cdot F$$

Where:

- n is the number of moles of electrons transferred per mole of substance.
- F is Faraday's constant ($\approx 96500\, C/mol$).

Solution: 1. **The Half-Reaction:** The oxidation of water (H_2O) to oxygen (O_2) occurs at the anode. The balanced electrochemical equation is:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

From this equation, we see that 4 moles of electrons are required to produce 1 mole of O_2 from 2 moles of H_2O.

2. **Calculation for 1 mole of H_2O:** Dividing the entire equation by 2 to find the requirement for 1 mole of H_2O:

$$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

Thus, $n = 2$ moles of electrons are required for the oxidation of 1 mole of H_2O.

3. **Total Charge (Q):**

$$Q = n \times F$$

$$Q = 2 \times 96500\, C$$

$$Q = 193000\, C$$

Conclusion: The oxidation of 1 mole of water requires 193000 C of electricity.

$\boxed{\textbf{Answer: (B)}}$

Q8.

Solution

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

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

Solution: 1. **The General Form:** The Nernst equation for the potential (E) of an electrode is given by:

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

Where Q is the reaction quotient, defined as the ratio of the activity of products to the activity of reactants.

$$Q = \frac{[M(s)]}{[M^{n+}(aq)]}$$

2. **Simplification:** By convention, the concentration (activity) of a pure solid, $[M(s)]$, is taken as unity (1). Therefore:

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

This matches the expression in **Option (A)**.
3. **Logarithmic Identity:** Using the property of logarithms where $-\ln(\frac{1}{x}) = \ln(x)$, we can rewrite the equation:

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

This matches the expression in **Option (B)**.
Conclusion: Since both expressions (A) and (B) are mathematically identical and represent the Nernst equation correctly for the given reduction reaction, the correct answer is **(C)**.

Answer: (C)

Q9.

Solution

Concept: Electrochemical cells are classified into two main categories 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).

Solution: To identify the secondary cell, let's look at the given options:
1. **(A) Dry cell:** A primary cell commonly used in flashlights and transistors. The reaction involves the oxidation of Zinc and reduction of Manganese dioxide. It cannot be recharged. 2. **(B) Mercury cell:** A primary cell used in low-current devices like hearing aids and watches. It provides a constant voltage but is not rechargeable. 3. **(C) Lead storage battery:** This is a **secondary cell** used in automobiles and inverters. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as the cathode, with 38% sulphuric acid as the electrolyte. The chemical reactions are reversible upon recharging. 4. **(D) Fuel cell:** These are galvanic cells designed to convert the energy of combustion of fuels (like hydrogen, methane, methanol) directly into electrical energy. They are distinct from storage cells as they require a continuous supply of reactants.
Conclusion: The Lead storage battery is a classic example of a secondary cell.

$\boxed{\textbf{Answer: (C)}}$

Q10.

Solution

Concept: Kohlrausch's Law of Independent Migration of Ions states that the limiting molar conductivity (Λ_m°) of an electrolyte can be represented as the sum of the individual contributions of its constituent anions and cations. For an electrolyte A_xB_y:

$$\Lambda_m^\circ(A_xB_y) = x\lambda_A^\circ + y\lambda_B^\circ$$

This law is particularly useful for calculating the Λ_m° of **weak electrolytes** (like acetic acid) using the values of strong electrolytes.

Solution: To find the limiting molar conductivity of acetic acid (CH_3COOH), we need to combine the ions CH_3COO^- and H^+. We can achieve this by algebraically combining strong electrolytes that contain these ions:

1. **Target Equation:**

$$\Lambda_m^\circ(CH_3COOH) = \lambda_{CH_3COO^-}^\circ + \lambda_{H^+}^\circ$$

2. **Using Strong Electrolytes:**

- $\Lambda_m^\circ(CH_3COONa) = \lambda_{CH_3COO^-}^\circ + \lambda_{Na^+}^\circ$
- $\Lambda_m^\circ(HCl) = \lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ$
- $\Lambda_m^\circ(NaCl) = \lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$

3. **Algebraic Combination:** By adding the first two and subtracting the third, the unwanted ions (Na^+ and Cl^-) cancel out:

$$[\lambda_{CH_3COO^-}^\circ + \lambda_{Na^+}^\circ] + [\lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ] - [\lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ] = \lambda_{CH_3COO^-}^\circ + \lambda_{H^+}^\circ$$

4. **Final Expression:**

$$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) - \Lambda_m^\circ(NaCl)$$

Conclusion: This corresponds to the expression in option (A).

Answer: (A)

Q11.

Solution

Concept: The **Rate Law** is an expression that relates the rate of a chemical reaction to the molar concentration of the reactants, each raised to a power representing the order of the reaction with respect to that reactant. For the reaction $A + B \to C$, the general rate law is:

$$\text{Rate} = k[A]^x[B]^y$$

Where:

- x is the order with respect to A.
- y is the order with respect to B.

Solution: We determine x and y based on the experimental data provided:
1. **Order with respect to A (x):** The problem states that doubling the concentration of A ($[A] \to 2[A]$) results in the rate quadrupling ($\text{Rate} \to 4 \times \text{Rate}$).

$$(2)^x = 4 \implies (2)^x = 2^2 \implies x = 2$$

Thus, the reaction is **second order** with respect to A.
2. **Order with respect to B (y):** The problem states that doubling the concentration of B ($[B] \to 2[B]$) has **no effect** on the rate ($\text{Rate} \to 1 \times \text{Rate}$).

$$(2)^y = 1 \implies (2)^y = 2^0 \implies y = 0$$

Thus, the reaction is **zero order** with respect to B.
3. **Deriving the Rate Law:** Substituting $x = 2$ and $y = 0$ into the general rate law:

$$\text{Rate} = k[A]^2[B]^0$$

Since any value raised to the power of zero is 1 ($[B]^0 = 1$):

$$\text{Rate} = k[A]^2$$

Conclusion: The rate depends only on the square of the concentration of A. This matches option (B).

$\boxed{\textbf{Answer: (B)}}$

Q12.

Solution

Concept: The units of the **rate constant** (k) for a chemical reaction depend on the overall order of the reaction. For a general reaction of order n, the rate law is:

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

The unit of the rate is always concentration divided by time, which is $mol\,L^{-1}\,s^{-1}$.
Solution: To find the units for a **zero-order reaction** ($n = 0$): 1. **The Rate Law:**

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

Since any value raised to the power of 0 is 1:

$$\text{Rate} = k$$

2. **Equating Units:** Because the rate constant k is equal to the rate itself in a zero-order reaction, its units must be the same as the units of the rate.

$$\text{Units of } k = \text{Units of Rate} = \frac{\text{Concentration}}{\text{Time}}$$

$$\text{Units of } k = mol\,L^{-1}\,s^{-1}$$

[Image of zero order reaction rate vs concentration graph]
Analysis of other options:

- **(A)** s^{-1}**:** Units for a **first-order** reaction ($n = 1$).
- **(C)** $L\,mol^{-1}\,s^{-1}$**:** Units for a **second-order** reaction ($n = 2$).
- **(D)** $L^2\,mol^{-2}\,s^{-1}$**:** Units for a **third-order** reaction ($n = 3$).

General Formula: The units of k for an n^{th} order reaction can be calculated using:

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

For zero order ($n = 0$): $(mol\,L^{-1})^{1-0}\,s^{-1} = mol\,L^{-1}\,s^{-1}$.

Answer: (B)

Q13.

Solution

Concept: The **half-life** ($t_{1/2}$) of a reaction is the time required for the concentration of a reactant to decrease to half of its initial value. For a **first-order reaction**, the half-life is independent of the initial concentration and is related to the rate constant (k) by a specific formula.

Formula: The relation between half-life and the rate constant for a first-order reaction is:

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

Solution: 1. **Identify Given Values:**

- $t_{1/2} = 69.3$ seconds

2. **Rearrange the Formula to solve for k:**

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

3. **Substitute the values:**

$$k = \frac{0.693}{69.3}$$

$$k = \frac{69.3 \times 10^{-2}}{69.3}$$

$$k = 0.01\, s^{-1}$$

Analysis of options:

- **(A)** 0.01 s^{-1}**:** Correct. This matches our calculated value.
- **(B), (C), (D):** Incorrect due to decimal placement errors.

Conclusion: The rate constant for the reaction is 0.01 s^{-1}.

Answer: (A)

Q14.

Solution

Concept: The **activation energy** (E_a) is the minimum amount of energy required by reactant molecules to undergo a chemical reaction. The relationship between the rate constant (k), temperature (T), and activation energy is given by the **Arrhenius Equation**:

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

Where:

- k is the rate constant.
- A is the Arrhenius factor (frequency factor).
- R is the gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$).
- T is the absolute temperature (in Kelvin).

Solution: To calculate E_a experimentally, we observe how the rate constant changes as the temperature changes. Taking the natural logarithm of the Arrhenius equation for two different temperatures (T_1 and T_2) with corresponding rate constants (k_1 and k_2), we get:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

1. **Experimental Method:** By measuring the rate constant at **two different temperatures**, we can solve for the single unknown variable, E_a. 2. **Graphical Method:** Alternatively, one can plot $\log k$ vs $1/T$. The slope of the resulting straight line is equal to $-E_a/2.303R$.
Analysis of options:

- **(A):** Incorrect. A single rate constant at one temperature cannot provide E_a unless the frequency factor (A) is already known.
- **(B):** Correct. This provides enough data to use the logarithmic form of the Arrhenius equation.
- **(C):** Incorrect. While collisions relate to the frequency factor, they do not directly determine E_a.
- **(D):** Incorrect. A catalyst **lowers** the activation energy, but using one doesn't help you *determine* the original activation energy of the reaction.

Conclusion: Activation energy is determined by comparing rate constants at different temperatures.

Answer: (B)

Q15.

Solution

Concept: A **pseudo-first-order reaction** is a chemical reaction that is actually of a higher order (usually second order) but behaves as a first-order reaction under specific experimental conditions. This typically occurs when the concentration of one of the reactants is so high that it remains effectively constant throughout the course of the reaction.

Solution: Consider a second-order reaction involving two reactants, A and B:

$$\text{Rate} = k[A][B]$$

If reactant **B is present in a large excess** (e.g., as a solvent like water), its concentration $[B]$ change is negligible during the reaction ($[B] \approx [B]_0$).

1. **Mathematical Derivation:** We can combine the constant concentration of B with the rate constant k:

$$\text{Rate} = (k[B])[A]$$

Let $k' = k[B]$. The rate law becomes:

$$\text{Rate} = k'[A]$$

Now, the reaction follows **first-order kinetics** with respect to reactant A.

2. **Common Examples:**

- **Acid-catalyzed hydrolysis of ethyl acetate:** Water is present in such large excess that its concentration does not change significantly.
- **Inversion of cane sugar:** Hydrolysis of sucrose in an aqueous solution.

Analysis of options:

- **(A):** Correct. This is the fundamental condition required to simplify the rate law to first order.
- **(B):** Incorrect. If concentrations are equal, it remains a second-order reaction.
- **(C):** Incorrect. It is molecularly a higher-order reaction behaving as first order.
- **(D):** Incorrect. Like all chemical reactions, the rate constant k (and thus k') is temperature-dependent according to the Arrhenius equation.

Conclusion: A pseudo-first-order reaction occurs when one reactant's concentration is in large excess.

$\boxed{\textbf{Answer: (A)}}$

Q16.

Solution

Concept: An ion is **paramagnetic** if it contains one or more **unpaired electrons** in its electronic configuration. These unpaired electrons are attracted by a magnetic field. Conversely, if all electrons are paired, the ion is **diamagnetic**.

Solution: To determine the magnetic nature, we must write the electronic configurations of the given ions (Atomic numbers: $Sc = 21, Cr = 24, Cu = 29, Zn = 30$):

(a) **(A)** Sc^{3+}**:**

- Neutral $Sc : [Ar]3d^1 4s^2$
- $Sc^{3+} : [Ar]3d^0 4s^0$ (No unpaired electrons $\implies$ **Diamagnetic**)

(b) **(B)** Cu^+**:**

- Neutral $Cu : [Ar]3d^{10} 4s^1$
- $Cu^+ : [Ar]3d^{10} 4s^0$ (All d-electrons are paired $\implies$ **Diamagnetic**)

(c) **(C)** Zn^{2+}**:**

- Neutral $Zn : [Ar]3d^{10} 4s^2$
- $Zn^{2+} : [Ar]3d^{10} 4s^0$ (All d-electrons are paired $\implies$ **Diamagnetic**)

(d) **(D)** Cr^{3+}**:**

- Neutral $Cr : [Ar]3d^5 4s^1$
- $Cr^{3+} : [Ar]3d^3 4s^0$

Analysis: In Cr^{3+}, there are **three unpaired electrons** in the $3d$ subshell (t_{2g}^3 configuration in crystal field theory). This makes the ion strongly **paramagnetic**.

Conclusion: Only Cr^{3+} possesses unpaired electrons among the given options.

$\boxed{\textbf{Answer: (D)}}$

Q17.

Solution

Concept: Lanthanoid contraction refers to the steady decrease in the atomic and ionic radii of the lanthanoid elements ($Z = 58$ to 71) with increasing atomic number. This occurs because of the **poor shielding effect** of the $4f$ electrons. As the nuclear charge increases, the $4f$ electrons fail to effectively shield the outer electrons from the nucleus, causing the entire electron cloud to be pulled inward.

Solution: A significant consequence of lanthanoid contraction is its effect on the elements of the second ($4d$) and third ($5d$) transition series that follow the lanthanoids.

1. **Comparison of Radii:** Normally, atomic radius increases down a group (from $4d$ to $5d$) due to the addition of a new principal energy level. However, for elements following the lanthanoids, the expected increase in size is almost exactly cancelled out by the lanthanoid contraction.

2. **Specific Case (Group 4):**

- **Zirconium (Zr):** Belongs to the $4d$ series (Period 5).
- **Hafnium (Hf):** Belongs to the $5d$ series (Period 6).

Because the 14 lanthanoid elements ($58Ce$ to $71Lu$) sit between La and Hf, the contraction that occurs across them makes the atomic radius of **Hafnium** ($159\,pm$) almost identical to that of **Zirconium** ($160\,pm$).

Analysis of options:

- **(A) Zr and Y:** Y is in the same period as Zr, but they belong to different groups; their sizes are different.
- **(B) Zr and Nb:** These are adjacent elements in the same period; Nb is slightly smaller than Zr.
- **(C) Zr and Hf:** Correct. This is the classic textbook example of chemical twins due to lanthanoid contraction.
- **(D) Zr and Zn:** Zn is in the $3d$ series and is significantly smaller than Zr.

Conclusion: Due to lanthanoid contraction, Zr and Hf have nearly identical physical and chemical properties because of their similar sizes.

Answer: (C)

Q18.

Solution

Concept: The oxidation states of transition elements are determined by the involvement of both $(n-1)d$ and ns electrons in bond formation. Because the energy levels of these orbitals are very close, transition metals exhibit a wide variety of oxidation states.

Solution: 1. **The 3d Series:** In the first transition series ($3d$), the highest oxidation state is **+7**, shown by Manganese (Mn) in compounds like $KMnO_4$. This corresponds to the loss/sharing of all seven valence electrons ($3d^5 4s^2$). 2. **The 4d and 5d Series:** As we move to heavier transition elements, the stability of higher oxidation states increases.

- **Ruthenium** (Ru) in the $4d$ series and **Osmium** (Os) in the $5d$ series exhibit an oxidation state of **+8**.
- Common examples include Osmium tetroxide (OsO_4) and Ruthenium tetroxide (RuO_4).

Analysis of options:

- **(A) +7:** This is the highest for the $3d$ series (Manganese), but not for the transition elements as a whole.
- **(B) +8:** Correct. This is the maximum oxidation state observed in the transition block (specifically in Group 8 elements like Os and Ru).
- **(C) +6:** Common for Chromium (Cr) and Molybdenum (Mo), but not the absolute highest.
- **(D) +5:** Common for Vanadium (V), but not the absolute highest.

Conclusion: While +7 is famous for Manganese, the heavy metals Osmium and Ruthenium push the limit to +8.

Answer: (B)

Q19.

Solution

Concept: Potassium dichromate ($K_2Cr_2O_7$) is a powerful **oxidizing agent**, especially in acidic media. When it reacts with concentrated hydrochloric acid (HCl), it undergoes a redox reaction. The HCl acts as both an acid and a **reducing agent**.

Solution: 1. **The Reaction:** In this reaction, the dichromate ion ($Cr_2O_7^{2-}$) contains Chromium in the +6 oxidation state. It oxidizes the chloride ions (Cl^-) from the HCl to elemental chlorine gas (Cl_2), while the Chromium itself is reduced to the +3 oxidation state (forming $CrCl_3$).

2. **The Balanced Chemical Equation:**

$$K_2Cr_2O_7 + 14HCl\,(\text{conc.}) \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$

Analysis of options:

- **(A)** O_2**:** Oxygen is not evolved in this reaction; the oxidizing power is spent on the chloride ions.
- **(B)** Cl_2**:** Correct. Greenish-yellow chlorine gas is evolved as the Cl^- ions lose electrons.
- **(C)** CrO_2Cl_2**:** This is **Chromyl Chloride**. This reddish-brown vapor is formed when $K_2Cr_2O_7$ reacts with a **solid metal chloride** (like $NaCl$) and concentrated H_2SO_4 (the Chromyl Chloride Test). It is not the primary gas evolved when reacting directly with conc. HCl in this context.
- **(D)** HCl**:** HCl is a reactant, not the evolved product.

Conclusion: The reaction produces chlorine gas due to the oxidation of the chloride ions by the dichromate.

Answer: (B)

Q20.

Solution

Concept: To name a coordination compound according to **IUPAC nomenclature**, specific rules must be followed:

(a) Name the cation first, followed by the anion.

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

(c) Use numerical prefixes (di, tri, tetra, hexa, etc.) to indicate the number of ligands.

(d) If the complex ion is an anion, the metal's name ends in the suffix **"-ate"**.

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

Solution: Let's analyze $K_3[Fe(CN)_6]$ step-by-step:
1. **Identify the ions:** The compound dissociates into $3K^+$ (cations) and $[Fe(CN)_6]^{3-}$ (anionic complex). 2. **Determine the Oxidation State of Fe (x):**

$$3(+1) + x + 6(-1) = 0$$

$$3 + x - 6 = 0$$

$$x - 3 = 0 \implies x = +3$$

The oxidation state of Iron is **III**. 3. **Name the Cation:** Potassium (numerical prefixes like 'tri' are not used for the counter-ion). 4. **Name the Complex Anion:**

- Six cyanide ligands: **hexacyano** (or hexacyanido).
- Central metal in an anion: Iron becomes **ferrate**.
- Full anion name: **hexacyanoferrate(III)**.

Analysis of options:

- **(A):** This is the common (trivial) name, not the IUPAC name.
- **(B):** Incorrect oxidation state (II instead of III).
- **(C):** Correct. Follows all IUPAC rules perfectly.
- **(D):** Incorrect. "Tri-potassium" and "iron" (instead of ferrate) violate IUPAC rules for this structure.

Conclusion: The correct IUPAC name is Potassium hexacyanoferrate(III).

Answer: (C)

Q21.

Solution

Concept: **Linkage isomerism** occurs in coordination compounds containing **ambidentate ligands**. An ambidentate ligand is a ligand that has two or more different donor atoms and can coordinate to the central metal atom through either of them.

Common Ambidentate Ligands:

- **Nitrito-N ($-NO_2$):** Coordinates via Nitrogen.
- **Nitrito-O ($-ONO$):** Coordinates via Oxygen.
- **Thiocyanato ($-SCN$):** Coordinates via Sulfur.
- **Isothiocyanato ($-NCS$):** Coordinates via Nitrogen.

2+ showing different bonding modes]

Solution: We examine the ligands in each complex to find an ambidentate one:

(a) **(A)** $[Co(NH_3)_5(NO_2)]Cl_2$**:** This complex contains the **nitro** (NO_2^-) group. Since NO_2^- is ambidentate, it can bind as $M - NO_2$ (nitro) or $M - ONO$ (nitrito). Therefore, it exhibits linkage isomerism.

(b) **(B)** $[Co(NH_3)_5Cl]SO_4$**:** This exhibits **ionization isomerism** (the Cl^- and SO_4^{2-} can swap places), but NH_3, Cl^-, and SO_4^{2-} are not ambidentate.

(c) **(C)** $[Pt(NH_3)_2Cl_2]$**:** This exhibits **geometrical isomerism** (cis and trans forms), but lacks ambidentate ligands.

(d) **(D)** $[Fe(H_2O)_6]Cl_3$**:** This is a simple coordination compound with no isomerism of the linkage type.

Conclusion: Only the complex with the NO_2 ligand can form a linkage isomer.

Answer: (A)

Q22.

Solution

Concept: The **Spectrochemical Series** is an experimentally determined series in which ligands are arranged in the increasing order of their **crystal field splitting energy** (Δ).

Solution: According to Crystal Field Theory (CFT), ligands produce different degrees of splitting of the d-orbitals.

- **Weak Field Ligands:** These produce small d-orbital splitting (low Δ_o). Halides and oxygen-donor ligands generally fall into this category.
- **Strong Field Ligands:** These produce large d-orbital splitting (high Δ_o). Carbon and nitrogen-donor ligands generally fall into this category.

The Sequence: The partial order of the spectrochemical series is:

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

Analysis of options: Comparing the ligands Cl^-, F^-, OH^-, and CN^-:

- Cl^- (Chloride) is a very weak field ligand.
- F^- (Fluoride) is stronger than Cl^-.
- OH^- (Hydroxide) is stronger than F^-.
- CN^- (Cyanide) is one of the strongest field ligands.

The correct increasing order of field strength is:

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

Conclusion: This sequence matches **Option (A)**.

$\boxed{\textbf{Answer: (A)}}$

Q23.

Solution

Concept: The hybridization and geometry of coordination compounds can be determined using **Valence Bond Theory (VBT)**. The process involves identifying the oxidation state of the metal, its electronic configuration, and the nature of the ligands (strong field vs. weak field).

Solution: To find the hybridization of $[Ni(CO)_4]$ (Nickel tetracarbonyl), follow these steps:

1. **Oxidation State of Nickel (Ni):** Carbon monoxide (CO) is a neutral ligand.

$$x + 4(0) = 0 \implies x = 0$$

The oxidation state of Nickel in this complex is **0**.

2. **Electronic Configuration:**

- Atomic number of $Ni = 28$.
- Ground state $Ni : [Ar]3d^8 4s^2$.

3. **Effect of Ligand:** CO is a very **strong field ligand**. According to the spectrochemical series, strong field ligands cause the pairing of electrons. In this case, the two electrons from the $4s$ orbital are pushed into the $3d$ orbitals to pair up with the existing 8 electrons.

- Rearranged configuration: $[Ar]3d^{10} 4s^0$.

4. **Hybridization:** With the $3d$ subshell completely filled ($3d^{10}$), the four pairs of electrons from the four CO ligands must occupy the next available empty orbitals: one $4s$ and three $4p$ orbitals.

- Hybridization = sp^3

5. **Geometry:** An sp^3 hybridization always corresponds to a **tetrahedral** geometry. Since there are no unpaired electrons, the complex is also **diamagnetic**.

Analysis of options:

- **(A)** sp^3**, tetrahedral:** Correct.
- **(B)** dsp^2**, square planar:** Incorrect. This occurs in Ni^{2+} complexes with strong field ligands (like $[Ni(CN)_4]^{2-}$).
- **(C) & (D):** Incorrect. These are for coordination number 6, whereas here the coordination number is 4.

Conclusion: The complex $[Ni(CO)_4]$ has sp^3 hybridization and a tetrahedral shape.

$\boxed{\textbf{Answer: (A)}}$

Q24.

Solution

Concept: The **spin-only magnetic moment** (μ_s) of a coordination compound is determined by the number of unpaired electrons (n) present in the central metal ion. It is calculated using the formula:

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

where BM stands for Bohr Magneton.

Solution: To find the magnetic moment of $[MnBr_4]^{2-}$, we follow these steps:

1. **Determine the Oxidation State of Mn (x):** Bromide (Br^-) is a unidentate anionic ligand with a charge of -1.

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

$$x - 4 = -2 \implies x = +2$$

The central metal ion is Mn^{2+}.

2. **Electronic Configuration:**

- Atomic number of $Mn = 25$.
- Ground state $Mn : [Ar]3d^5 4s^2$.
- Mn^{2+} ion : $[Ar]3d^5 4s^0$.

3. **Nature of Ligand and Pairing:** Br^- is a **weak field ligand** (low in the spectrochemical series). In a tetrahedral complex like $[MnBr_4]^{2-}$, weak field ligands do not cause pairing of electrons. Therefore, the five electrons in the $3d$ orbital remain unpaired.

$$\text{Number of unpaired electrons } (n) = 5$$

Solution

4. **Calculate Magnetic Moment:** Substitute $n = 5$ into the formula:

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

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

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

$$\mu_s \approx 5.916 \text{ or } 5.92 \text{ BM}$$

Analysis of options:

- **(A) 5.92 BM:** Matches our calculation ($n = 5$).
- **(B) 4.90 BM:** Corresponds to $n = 4$.
- **(C) 3.87 BM:** Corresponds to $n = 3$.
- **(D) 1.73 BM:** Corresponds to $n = 1$.

Conclusion: The presence of five unpaired electrons in the Mn^{2+} ion results in a magnetic moment of 5.92 BM.

Answer: (A)

Q25.

Solution

Concept: Certain coordination compounds of transition metals exhibit significant biological activity. Platinum-based complexes, in particular, are widely used in chemotherapy to inhibit the division of cancer cells by binding to their DNA.
[Image of chemical structure of cisplatin]
Solution: 1. **(B) Cis-platin:** This is the correct answer. The IUPAC name is **cis-diamminedichloroplatinum(II)**, with the formula $cis-[Pt(NH_3)_2Cl_2]$.

- In the **cis** isomer, the two ammonia (NH_3) ligands are adjacent to each other, as are the two chloride (Cl^-) ligands.
- It works by entering cancer cells and forming cross-links with DNA, which prevents the cell from replicating and eventually leads to programmed cell death (apoptosis).

2. **(C) Trans-platin:** The **trans** isomer, $trans-[Pt(NH_3)_2Cl_2]$, where similar ligands are opposite to each other, is **not** effective as an anti-cancer agent. It is more easily deactivated by the body and does not form the same specific DNA cross-links as the cis form.
3. **(D) Zeise's salt:** This is an organometallic compound with the formula $K[PtCl_3(\eta^2-C_2H_4)]\cdot H_2O$. While it was the first organometallic compound discovered, it is not used in cancer therapy.
Conclusion: Cis-platin is one of the most effective and commonly used anti-cancer drugs in medicine.

Answer: (B)

Q26.

Solution

Concept: The reaction of alkyl halides with aqueous KOH is a **Nucleophilic Substitution** (S_N) reaction. Depending on the structure of the alkyl halide, it can follow either the S_N1 (unimolecular) or S_N2 (bimolecular) mechanism.

Solution: In this case, we are comparing different classes of alkyl chlorides:

- **(A)** CH_3Cl**:** Methyl chloride (primary-like)
- **(B)** CH_3CH_2Cl**:** Ethyl chloride (1° alkyl halide)
- **(C)** $(CH_3)_2CHCl$**:** Isopropyl chloride (2° alkyl halide)
- **(D)** $(CH_3)_3CCl$**:** tert-Butyl chloride (3° alkyl halide)

1. **Mechanism Preference:** Aqueous KOH provides the OH^- nucleophile. For **tertiary** (3°) alkyl halides like $(CH_3)_3CCl$, the reaction proceeds via the S_N1 **mechanism** because the resulting carbocation is highly stabilized by inductive effects and hyperconjugation.

2. **Rate of Reaction:** The rate of an S_N1 reaction is determined by the stability of the carbocation formed.

- $(CH_3)_3CCl$ forms a 3° **carbocation** (most stable).
- $(CH_3)_2CHCl$ forms a 2° **carbocation**.
- CH_3CH_2Cl forms a 1° **carbocation** (least stable).

3. **Comparison:** While CH_3Cl would be fastest in an S_N2 reaction due to lack of steric hindrance, **tertiary alkyl halides** (3°) generally react much faster in aqueous/polar protic conditions because the S_N1 pathway is extremely efficient for them. In most competitive examinations, $(CH_3)_3CCl$ is identified as the most reactive in aqueous KOH due to this shift in mechanism and the high stability of the tert-butyl cation.

Conclusion: Tertiary butyl chloride reacts fastest because it forms the most stable intermediate.

Answer: (D)

Q27.

Solution

Concept: The **Finkelstein reaction** is a classic organic reaction used for the synthesis of alkyl iodides. It is an S_N2 (Substitution Nucleophilic Bimolecular) reaction where an alkyl chloride or alkyl bromide is converted into an alkyl iodide through an exchange of halogen atoms.

Solution: The reaction is carried out using specific reagents and conditions to drive the equilibrium forward:

1. **Reagents:** The typical reagent used is **Sodium Iodide** (NaI) dissolved in **dry acetone**. 2. **Mechanism:**

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

(Where $X = Cl, Br$) 3. **Driving Force (Le Chatelier's Principle):** Acetone is used because NaI is soluble in it, but the resulting $NaCl$ or $NaBr$ are **insoluble** in acetone and precipitate out. The precipitation of the byproduct shifts the equilibrium to the right, ensuring a high yield of the alkyl iodide ($R - I$).

Analysis of options:

- **(A)** NaI **in dry acetone:** Correct. This defines the Finkelstein reaction.
- **(B)** AgF **in water:** This is a reagent used in the **Swarts reaction** to prepare alkyl fluorides.
- **(C)** Cl_2 **in** UV **light:** This is used for the **free radical halogenation** of alkanes.
- **(D)** PCl_5**:** This is used to convert alcohols into alkyl chlorides.

Conclusion: The Finkelstein reaction specifically refers to the exchange of halogens using NaI in dry acetone.

$\boxed{\textbf{Answer: (A)}}$

Q28.

Solution

Concept: The **S_N2 (Substitution Nucleophilic Bimolecular)** mechanism is a one-step process where the nucleophile attacks the reactive center at the same time the leaving group departs. This simultaneous "push-pull" action has a very specific spatial requirement.

Solution: 1. **Back-side Attack:** In an S_N2 reaction, the nucleophile attacks the carbon atom from the side directly opposite to the leaving group. This is because the leaving group is electron-rich and repels the incoming nucleophile from the front. 2. **Transition State:** As the nucleophile approaches, the three other groups attached to the carbon atom "flip" to the other side, much like an umbrella blowing inside out in a strong wind. 3. **Stereochemical Result:** This process leads to a complete **Walden Inversion**. If the starting material is a single enantiomer (chiral), the product will also be a single stereoisomer, but its spatial arrangement (configuration) will be the opposite of the starting material.

Analysis of options:

- **(A) Mixture of diastereomers:** Incorrect. This usually happens when there are multiple chiral centers and only some change.
- **(B) Racemic mixture:** Incorrect. Racemization (50% inversion, 50% retention) is characteristic of the **S_N1** mechanism due to the planar carbocation intermediate.
- **(C) Single stereoisomer with inverted configuration:** Correct. This is the hallmark of the S_N2 mechanism.
- **(D) Single stereoisomer with retained configuration:** Incorrect. Retention is rare and usually involves specialized mechanisms like S_Ni.

Conclusion: S_N2 reactions at a chiral center always proceed with 100% inversion of configuration.

Answer: (C)

Q29.

Solution

Concept: The **Wurtz-Fittig reaction** is a variation of the Wurtz reaction. While the Wurtz reaction involves two alkyl halides, and the Fittig reaction involves two aryl halides, the **Wurtz-Fittig reaction** involves a mixture of an **alkyl halide** and an **aryl halide** reacting with sodium metal in the presence of dry ether.

Solution: 1. **Reaction Mechanism:** The reaction typically involves the formation of an organometallic intermediate. Sodium reacts with the halides to couple the alkyl group (R) and the aryl group (Ar).

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

2. **Example:** The reaction of Bromobenzene (an aryl halide) with Methyl bromide (an alkyl halide) in the presence of sodium and dry ether yields **Toluene** (an alkylarene).

$$C_6H_5Br + CH_3Br + 2Na \xrightarrow{\text{dry ether}} C_6H_5 - CH_3 + 2NaBr$$

Analysis of options:

- **(A) Alkanes:** Prepared via the **Wurtz reaction** (two alkyl halides).
- **(B) Alkenes:** Usually prepared via dehydrohalogenation or dehydration, not this coupling method.
- **(C) Alkylarenes:** Correct. This reaction specifically attaches an alkyl chain to a benzene ring (aromatic ring).
- **(D) Aryl halides:** These are the *reactants* used in the process, not the products.

Conclusion: The Wurtz-Fittig reaction is a primary method for synthesizing alkyl-substituted aromatic compounds (alkylarenes).

Answer: (C)

Q30.

Solution

Concept: The **Lucas reagent** is used in organic chemistry to distinguish between primary (1°), secondary (2°), and tertiary (3°) alcohols. It works by converting alcohols into their corresponding alkyl chlorides, which are insoluble in the reagent and cause the solution to become cloudy (turbid).

Solution: 1. **Composition:** Lucas reagent consists of a solution of **concentrated Hydrochloric acid** (HCl) and **anhydrous Zinc chloride** ($ZnCl_2$).

- $ZnCl_2$ acts as a Lewis acid catalyst, helping to break the $C - OH$ bond.

2. **Reaction Mechanism:**

$$R - OH + HCl \xrightarrow{\text{anhyd. } ZnCl_2} R - Cl + H_2O$$

3. **Observation of the Test:**

- **Tertiary alcohols** (3°)**:** React **immediately**, producing turbidity at room temperature.
- **Secondary alcohols** (2°)**:** React within **5 minutes** to produce turbidity.
- **Primary alcohols** (1°)**:** Do **not** produce turbidity at room temperature (may react upon heating).

Analysis of options:

- **(A)** HCl + **anhyd.** $ZnCl_2$**:** Correct. This is the standard definition of the Lucas reagent.
- **(B)** HCl + **Hydrated** $ZnCl_2$**:** Incorrect. The $ZnCl_2$ must be anhydrous to act effectively as a catalyst in this substitution.
- **(C)** $HNO_3 + H_2SO_4$**:** Incorrect. This is a **nitrating mixture** used for the nitration of aromatic compounds.
- **(D)** $Pd + BaSO_4$**:** Incorrect. This is part of the **Lindlar's catalyst** or **Rosenmund reduction** catalyst.

Conclusion: Lucas reagent is a mixture of concentrated HCl and anhydrous $ZnCl_2$.

Answer: (A)

Q31.

Solution

Concept: The acidity of phenols is determined by the stability of the resulting **phenoxide ion** (ArO^-). Any factor that stabilizes the negative charge on the oxygen atom will increase the acidity.

- **Electron Withdrawing Groups (EWG):** Groups like $-NO_2$ withdraw electron density via **inductive effect** ($-I$) and **resonance effect** ($-R$), stabilizing the phenoxide ion and increasing acidity.
- **Position Matters:** Resonance effects are only effective at the **ortho** and **para** positions.

Solution: Let's compare the given compounds:
1. **(A) Phenol:** No electron-withdrawing groups; least acidic in this group. 2. **(C) m-Nitrophenol:** The $-NO_2$ group at the meta position only exerts a $-I$ **effect**. It is more acidic than phenol but less than the others. 3. **(B) o-Nitrophenol:** The $-NO_2$ group exerts both $-I$ and $-R$ effects. However, **intramolecular hydrogen bonding** occurs between the $-OH$ group and the $-NO_2$ group, which makes it slightly harder to release the proton (H^+). 4. **(D) p-Nitrophenol:** The $-NO_2$ group at the para position exerts both $-I$ and $-R$ effects. Unlike the ortho isomer, there is **no intramolecular hydrogen bonding** to hinder proton release. In fact, it forms **intermolecular hydrogen bonds**, which don't affect the acidity of the single molecule as much as the internal bond does in the ortho case.
Acidity Order: p-Nitrophenol > o-Nitrophenol > m-Nitrophenol > Phenol
Analysis of options:

- **(D) p-Nitrophenol:** Correct. It has the strongest combined electron-withdrawing effect without the interference of intramolecular hydrogen bonding.

Conclusion: Para-nitrophenol is the most acidic because the nitro group effectively stabilizes the phenoxide ion via resonance from the para position.

Answer: (D)

Q32.

Solution

Concept: The **Reimer-Tiemann reaction** is a classic organic chemical reaction used for the ortho-formylation of phenols. It involves the treatment of phenol with chloroform in the presence of a strong base to introduce a formyl ($-CHO$) group onto the aromatic ring.

Solution: 1. **Reaction Conditions:** Phenol reacts with **chloroform** ($CHCl_3$) and aqueous **sodium hydroxide** ($NaOH$). 2. **The Intermediate:** The reaction proceeds through the generation of a highly reactive electrophile, **dichlorocarbene** ($: CCl_2$), formed by the alpha-elimination of HCl from chloroform. 3. **The Product:** The electrophile attacks the phenoxide ion primarily at the **ortho** position. After subsequent hydrolysis of the intermediate, the final product obtained is **Salicylaldehyde** (2-hydroxybenzaldehyde).

$$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow o - C_6H_4(OH)CHO + 3NaCl + 2H_2O$$

[Image of chemical structure of Salicylaldehyde]

Analysis of options:

- **(A) Salicylaldehyde:** Correct. This is the main product when chloroform is used.
- **(B) Salicylic acid:** Incorrect. This product is formed if **carbon tetrachloride** (CCl_4) is used instead of chloroform.
- **(C) Benzaldehyde:** Incorrect. Benzaldehyde lacks the hydroxyl ($-OH$) group essential to the starting material (phenol).
- **(D) Benzoic acid:** Incorrect. This is not the product of the formylation pathway.

Conclusion: The standard Reimer-Tiemann reaction specifically yields salicylaldehyde as the major product.

Answer: (A)

Q33.

Solution

Concept: The synthesis of **Aspirin** (Acetylsalicylic acid) is an **acetylation** reaction. In this process, the phenolic hydroxyl group ($-OH$) of salicylic acid is converted into an ester group ($-OCOCH_3$) by reacting it with an acetylating agent in the presence of an acid catalyst.

Solution: 1. **The Reaction:** Salicylic acid (2-hydroxybenzoic acid) reacts with **acetic anhydride** [$(CH_3CO)_2O$] or acetyl chloride (CH_3COCl). 2. **Mechanism:** The oxygen atom of the phenolic $-OH$ group attacks the carbonyl carbon of the acetic anhydride, leading to the removal of an acetic acid molecule as a byproduct. 3. **The Balanced Chemical Equation:**

$$C_6H_4(OH)COOH + (CH_3CO)_2O \xrightarrow{H^+} C_6H_4(OCOCH_3)COOH + CH_3COOH$$

The product $C_6H_4(OCOCH_3)COOH$ is **Acetylsalicylic acid**, commonly known as **Aspirin**.

Analysis of options:

- **(A)** CH_3OH **(Methanol):** Reacting salicylic acid with methanol yields **Methyl salicylate** (Oil of Wintergreen), which is an ester of the carboxylic acid group, not the hydroxyl group.
- **(B)** $(CH_3CO)_2O$ **(Acetic anhydride):** Correct. This is the standard reagent used for the acetylation of the phenolic group to produce Aspirin.
- **(C)** CH_3Cl **(Methyl chloride):** This would lead to ether formation (methylation) rather than acetylation.
- **(D)** CH_3CHO **(Acetaldehyde):** This does not result in the formation of an acetyl ester.

Conclusion: Acetic anhydride is the reagent required to convert salicylic acid into aspirin via acetylation.

$\boxed{\textbf{Answer: (B)}}$

Q34.

Solution

Concept: The reaction of phenol with zinc dust is a classic example of a **reduction reaction**. In this process, the phenolic hydroxyl group ($-OH$) is removed and replaced by a hydrogen atom, effectively deoxygenating the aromatic ring.

Solution: 1. **The Reaction:** When phenol (C_6H_5OH) vapors are passed over heated **Zinc dust**, the zinc acts as a reducing agent. 2. **Mechanism:** The zinc atom reacts with the oxygen of the hydroxyl group to form **Zinc oxide** (ZnO). This leaves the phenyl radical to combine with the remaining hydrogen atom. 3. **The Balanced Chemical Equation:**

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

The organic product formed is **Benzene**.

Analysis of options:

- **(A) Benzene:** Correct. This is the standard product of the distillation of phenol with zinc.
- **(B) Toluene:** Incorrect. Toluene ($C_6H_5CH_3$) requires the addition of a methyl group, which is not provided by zinc.
- **(C) Benzaldehyde:** Incorrect. This is an oxidation product of toluene or a reduction product of benzoyl chloride, not a direct product of phenol and zinc.
- **(D) Benzoic acid:** Incorrect. This is an oxidized form of the aromatic side chain.

Conclusion: Distillation with zinc dust is a common laboratory method to convert phenol back into its parent hydrocarbon, benzene.

Answer: (A)

Q35.

Solution

Concept: **Aldol condensation** is a characteristic reaction of aldehydes and ketones that possess at least one **α-hydrogen atom** (a hydrogen atom attached to the carbon atom immediately adjacent to the carbonyl group). In the presence of a dilute alkali (like $NaOH$), these compounds undergo self-condensation to form β-hydroxy aldehydes (aldols) or β-hydroxy ketones (ketols).

Solution: To determine which compound will **not** undergo Aldol condensation, we must check for the presence of α-hydrogens:

1. **(A)** CH_3CHO **(Acetaldehyde):** The carbonyl carbon is attached to a methyl group ($-CH_3$). It has **three α-hydrogens**. It undergoes Aldol condensation. 2. **(B)** CH_3COCH_3 **(Acetone):** The carbonyl carbon is attached to two methyl groups. It has **six α-hydrogens**. It undergoes Aldol condensation. 3. **(C)** C_6H_5CHO **(Benzaldehyde):** The carbonyl group is attached directly to the benzene ring. The carbon atom of the benzene ring attached to the $-CHO$ group has no hydrogen atoms (it is bonded to three other carbons in the ring). Thus, it has **zero α-hydrogens**.

- Because it lacks α-hydrogens, Benzaldehyde **cannot** undergo self-Aldol condensation. Instead, it undergoes the **Cannizzaro reaction**.

4. **(D)** CH_3CH_2CHO **(Propanal):** The α-carbon is the $-CH_2-$ group. It has **two α-hydrogens**. It undergoes Aldol condensation.

Analysis of options:

- **(C)** C_6H_5CHO**:** This is the only compound in the list that lacks the structural requirement (the α-H) for the Aldol reaction.

Conclusion: Benzaldehyde does not give Aldol condensation; it typically requires a partner with α-hydrogens to participate in a "Cross-Aldol" reaction, but cannot react with itself in this manner.

$\boxed{\textbf{Answer: (C)}}$

Q36.

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 a primary alcohol, while another molecule is oxidized to a carboxylic acid salt.

Solution: To undergo the Cannizzaro reaction, a carbonyl compound must meet specific criteria: 1. **Absence of α-hydrogens:** If α-hydrogens were present, the aldehyde would undergo **Aldol condensation** instead, as the base would deprotonate the α-carbon to form an enolate. 2. **Type of Compound:** The reaction is specific to **aldehydes**. Ketones generally do not undergo this reaction under standard conditions. 3. **Examples:**

- **Formaldehyde ($HCHO$):** No α-carbon, hence no α-hydrogen.
- **Benzaldehyde (C_6H_5CHO):** The α-carbon is part of the benzene ring and has no attached hydrogen.
- **Trimethylacetaldehyde ($(CH_3)_3CCHO$):** The α-carbon is quaternary and has no hydrogens.

Analysis of options:

- **(A) Aldehydes with α-hydrogen:** These undergo Aldol condensation.
- **(B) Aldehydes without α-hydrogen:** Correct. This is the fundamental requirement for the Cannizzaro reaction.
- **(C) Ketones with α-hydrogen:** These undergo Aldol condensation.
- **(D) Only aromatic aldehydes:** Incorrect. While many aromatic aldehydes (like Benzaldehyde) give this reaction, aliphatic aldehydes without α-hydrogens (like Formaldehyde) also give it.

Conclusion: The Cannizzaro reaction is the "alternative" pathway for aldehydes that cannot form enolates due to the lack of α-hydrogens.

Answer: (B)

Q37.

Solution

Concept: The reactivity of carbonyl compounds ($> C = O$) towards **nucleophilic addition** depends on two main factors:

(a) **Electronic Factor:** Groups that increase the electron density on the carbonyl carbon (via $+I$ or $+R$ effects) decrease its electrophilicity, making it less reactive toward nucleophiles.

(b) **Steric Factor:** Bulky groups around the carbonyl carbon hinder the approach of the nucleophile, decreasing reactivity.

Solution: Let's analyze the three compounds:
1. CH_3CHO **(Acetaldehyde):** It has one methyl group which exerts a small $+I$ (inductive) effect. Steric hindrance is low because there is only one relatively small alkyl group and one hydrogen atom. It is the **most reactive** in this set.
2. $PhCHO$ **(Benzaldehyde):** The carbonyl group is attached to a benzene ring. While the phenyl group is bulky, the primary reason for decreased reactivity is the **resonance effect** ($+R$). The electron density from the benzene ring is delocalized into the carbonyl carbon, significantly reducing its positive charge and electrophilicity.

$$C_6H_5 - CHO \longleftrightarrow \text{Resonance stabilization of carbonyl carbon}$$

3. CH_3COCH_3 **(Acetone):** This is a ketone. It has **two** methyl groups providing a stronger combined $+I$ effect than a single methyl group. More importantly, it has significant **steric hindrance** from both sides, making the nucleophilic attack difficult. Ketones are generally less reactive than aldehydes.
Reactivity Comparison:

- Aldehydes are more reactive than ketones: $CH_3CHO > CH_3COCH_3$.
- Aliphatic aldehydes are more reactive than aromatic aldehydes: $CH_3CHO > PhCHO$.
- Between $PhCHO$ and CH_3COCH_3, the resonance stabilization in $PhCHO$ makes it slightly more reactive than a hindered ketone like acetone in most standard nucleophilic additions, but the general order for these specific competitive exams follows: **Aliphatic Aldehyde > Aromatic Aldehyde > Ketone**.

Analysis of options:

- **(A)** $CH_3CHO > PhCHO > CH_3COCH_3$**:** Correct. This follows the standard hierarchy where the aliphatic aldehyde is fastest, followed by the aromatic aldehyde, with the sterically hindered ketone being the slowest.

Conclusion: Acetaldehyde is the most reactive due to minimal steric hindrance and resonance, while Acetone is the least reactive due to steric crowding and inductive effects.

Answer: (A)

Q38.

Solution

Concept: **Tollens' reagent** is a mild oxidizing agent used primarily to distinguish between aldehydes and ketones. While aldehydes are easily oxidized to carboxylic acids by this reagent, ketones (except α-hydroxy ketones) generally do not react. This test is famously known as the **Silver Mirror Test**.

Solution: 1. **Composition:** Tollens' reagent is a coordination compound solution containing the **diamminesilver(I)** complex, represented as $[Ag(NH_3)_2]^+$. 2. **Preparation:** It is prepared by adding a dilute ammonia solution (NH_4OH) to a silver nitrate ($AgNO_3$) solution until the initial brown precipitate of silver oxide (Ag_2O) just redissolves.

- Therefore, it is chemically defined as **ammoniacal silver nitrate**.

3. **The Reaction:** When an aldehyde is heated with Tollens' reagent in an alkaline medium, the silver ions (Ag^+) are reduced to metallic silver (Ag), which deposits on the inner wall of the test tube, creating a mirror effect.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2Ag \downarrow + 4NH_3 + 2H_2O$$

Analysis of options:

- **(A) Alkaline $KMnO_4$:** This is known as **Baeyer's reagent**, used to test for unsaturation (double or triple bonds).
- **(B) Ammoniacal silver nitrate:** Correct. This is the definition of Tollens' reagent.
- **(C) Ammoniacal cuprous chloride:** This is used to detect terminal alkynes (forms a red precipitate).
- **(D) $I_2/NaOH$:** This is the reagent used for the **Iodoform test** to detect methyl ketones or alcohols.

Conclusion: Tollens' reagent is specifically the ammoniacal solution of silver nitrate.

Answer: (B)

Q39.

Solution

Concept: The boiling point of an organic compound is primarily determined by the strength of the **intermolecular forces** holding its molecules together. Carboxylic acids exhibit much higher boiling points than aldehydes, ketones, or even alcohols of similar molecular masses.

Solution: The exceptionally high boiling points of carboxylic acids are due to two main related factors:

1. **Extensive Hydrogen Bonding:** The carboxylic acid group ($-COOH$) contains both a polar carbonyl group ($C = O$) and a polar hydroxyl group ($-OH$). This allows for very strong intermolecular hydrogen bonding between the oxygen of one molecule and the hydrogen of the hydroxyl group of another.

2. **Formation of Dimers:** In the liquid phase and even in the vapor phase, carboxylic acid molecules exist as **cyclic dimers**. In a dimer, two molecules are held together by two separate hydrogen bonds. This effectively doubles the size of the unit that needs to be vaporized, requiring significantly more thermal energy to break these bonds and reach the boiling point.

3. **Comparison with Aldehydes:** Aldehydes ($-CHO$) are polar, but they do not have a hydrogen atom directly bonded to an oxygen. Therefore, they only experience **dipole-dipole interactions**, which are much weaker than the hydrogen bonding and dimerization found in carboxylic acids.

Analysis of options:

- **(A) Hydrogen bonding:** True, but incomplete.
- **(B) Formation of dimers:** True, but this is a result of the hydrogen bonding.
- **(C) More polar nature:** While true, polarity alone doesn't account for the massive difference without considering the specific hydrogen bonding.
- **(D) Both A and B:** Correct. Both the existence of hydrogen bonds and the resulting stable dimeric structure are responsible for the high boiling points.

Conclusion: Carboxylic acids have higher boiling points because they associate through hydrogen bonding to form stable dimers.

Answer: (D)

Q40.

Solution

Concept: The acidity of carboxylic acids is primarily influenced by the **Inductive Effect ($-I$ effect)** of substituents attached to the α-carbon.

- **Electron-Withdrawing Groups (EWG):** Groups like chlorine ($-Cl$) withdraw electron density away from the carboxylate group, which stabilizes the resulting conjugate base ($RCOO^-$) by delocalizing the negative charge.
- **Cumulative Effect:** The more electron-withdrawing groups present on the α-carbon, the greater the stabilization of the conjugate base and the higher the acidity.

Solution: We compare the given acids based on the number of chlorine atoms (electronegative atoms) attached to the methyl group:
1. **(A)** CH_3COOH **(Acetic acid):** The methyl group is an electron-donating group ($+I$ effect), which destabilizes the conjugate base. It is the **weakest** acid in this series. 2. **(B)** $ClCH_2COOH$ **(Chloroacetic acid):** One chlorine atom exerts a $-I$ effect, increasing acidity relative to acetic acid. 3. **(C)** $Cl_2CHCOOH$ **(Dichloroacetic acid):** Two chlorine atoms exert a much stronger combined $-I$ effect, further increasing the acidity. 4. **(D)** Cl_3CCOOH **(Trichloroacetic acid):** Three chlorine atoms exert the **maximum $-I$ effect**. This strongly pulls electron density away from the $O-H$ bond, making it very easy to release the proton (H^+) and making the resulting Cl_3CCOO^- ion very stable.
Acidity Order: $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$
Analysis of options:

- **(D)** Cl_3CCOOH**:** Correct. It has the highest number of electronegative substituents, making it the strongest acid among the choices.

Conclusion: Trichloroacetic acid is the strongest because the cumulative inductive effect of three chlorine atoms significantly stabilizes the conjugate base.

Answer: (D)

Q41.

Solution

Concept: The basicity of amines is determined by the availability of the lone pair of electrons on the nitrogen atom. In the **gaseous phase**, factors like solvation (hydration) and steric hindrance do not play a significant role. Therefore, the basicity is purely governed by the **Inductive Effect** ($+I$ **effect)** of the alkyl groups.

Solution: 1. **Inductive Effect** ($+I$)**:** Alkyl groups ($-R$) are electron-releasing in nature. They push electron density toward the nitrogen atom, making the lone pair more available for donation to an acid (proton). 2. **Comparison:**

- **Tertiary Amines** ($3°$)**:** Have three alkyl groups (R_3N) providing the maximum $+I$ effect. This results in the highest electron density on nitrogen.
- **Secondary Amines** ($2°$)**:** Have two alkyl groups (R_2NH).
- **Primary Amines** ($1°$)**:** Have only one alkyl group (RNH_2).
- **Ammonia** (NH_3)**:** Has no alkyl groups to increase electron density via induction.

3. **Gaseous Phase Order:** Since there are no solvent molecules to stabilize the cations through hydrogen bonding, the more alkyl groups attached, the more stable the resulting ammonium ion becomes due to charge dispersal by the $+I$ effect.

$$\text{Order: } 3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine} > NH_3$$

Note: This order changes in the **aqueous phase** (e.g., $2^\circ > 3^\circ > 1^\circ$ for methyl amines) because of the combined effects of induction, solvation, and steric hindrance. However, for the **gaseous phase**, the rule is straightforward.

Analysis of options:

- **(A)** $3^\circ > 2^\circ > 1^\circ > NH_3$**:** Correct. It perfectly follows the trend of the inductive effect.

Conclusion: In the absence of solvent effects, tertiary amines are the most basic due to the cumulative electron-donating effect of three alkyl groups.

Answer: (A)

Q42.

Solution

Concept: The **Gabriel phthalimide synthesis** is a specific and highly efficient chemical reaction used to synthesize **pure primary amines**. It avoids the common problem of over-alkylation (mixture of 1°, 2°, and 3° amines) typically seen in the Hoffman ammonolysis of alkyl halides.

Solution: The reaction proceeds through the following steps: 1. **Salt Formation:** Phthalimide is treated with ethanolic KOH to form **potassium phthalimide**. 2. **Alkylation:** The potassium salt reacts with an **alkyl halide ($R - X$)** via an S_N2 mechanism to form N-alkylphthalimide. 3. **Hydrolysis:** Basic hydrolysis (using $NaOH$) or hydrazinolysis (using NH_2NH_2) of N-alkylphthalimide yields the **primary aliphatic amine** ($R - NH_2$) and phthalic acid/phthalazine-1,4-dione.

Limitations: * **Aromatic Amines:** This method **cannot** be used to prepare **primary aromatic amines** (like aniline). This is because aryl halides ($Ar - X$) do not undergo the nucleophilic substitution (S_N2) required for the second step of the synthesis.

Analysis of options:

- **(A) Primary aliphatic amines:** Correct. The reaction is specifically designed for these.
- **(B) Primary aromatic amines:** Incorrect. Aryl halides are unreactive towards the phthalimide anion.
- **(C) Secondary amines:** Incorrect. The stoichiometry and mechanism are restricted to 1° amines.
- **(D) Tertiary amines:** Incorrect.

Conclusion: Gabriel phthalimide synthesis is the preferred method for making pure primary aliphatic amines.

$\boxed{\textbf{Answer: (A)}}$

Q43.

Solution

Concept: The **Hinsberg Test** is a classic analytical method used to distinguish between primary (1°), secondary (2°), and tertiary (3°) amines. The test relies on the reaction of the amine with the **Hinsberg reagent** to form sulfonamides with differing solubilities in alkali.

Solution: 1. **Identity:** The Hinsberg reagent is **Benzene sulphonyl chloride** ($C_6H_5SO_2Cl$).
2. **Reaction with Amines:**

- **Primary Amines (1°):** React to form an N-alkylbenzene sulfonamide. This product contains an acidic hydrogen attached to nitrogen, making it **soluble in alkali** ($NaOH$).
- **Secondary Amines (2°):** React to form an N,N-dialkylbenzene sulfonamide. Since there is no acidic hydrogen on the nitrogen, the product is **insoluble in alkali**.
- **Tertiary Amines (3°):** Do **not react** with benzene sulphonyl chloride under standard conditions (they remain insoluble in the reagent but dissolve in acid).

Analysis of options:

- **(A) Benzene sulphonyl chloride:** Correct. This is the active sulfonylating agent used in the test.
- **(B) Benzene sulphonic acid:** Incorrect. This is the hydrated, non-reactive form ($C_6H_5SO_3H$).
- **(C) Benzamide:** Incorrect. This is an amide ($C_6H_5CONH_2$), not a reagent for amine testing.
- **(D) Chlorobenzene:** Incorrect. This is a simple aryl halide.

Conclusion: Benzene sulphonyl chloride is the Hinsberg reagent used to separate and identify classes of amines.

Answer: (A)

Q44.

Solution

Concept: The reaction of a primary aromatic amine with nitrous acid (HNO_2) at low temperatures is known as **Diazotization**. Since nitrous acid is unstable, it is prepared *in situ* (within the reaction mixture) by reacting **sodium nitrite ($NaNO_2$)** with an excess of a strong mineral acid like **hydrochloric acid (HCl)**.

Solution: 1. **The Reaction:** When Aniline ($C_6H_5NH_2$) is treated with $NaNO_2$ and HCl at a cold temperature (typically **0°C to 5°C**), it undergoes diazotization. 2. **Mechanism:** The nitrous acid reacts with the primary amine group to form the highly reactive and versatile **diazonium cation**. 3. **The Product:** The resulting compound is **Benzene diazonium chloride** ($C_6H_5N_2^+Cl^-$). * **Stability:** This salt is relatively stable in cold aqueous solution due to resonance stabilization from the benzene ring, but it decomposes rapidly if the temperature rises above 5°C. 4. **The Balanced Chemical Equation:**

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

Analysis of options:

- **(A) Benzene:** Incorrect. This is formed by reducing the diazonium salt with H_3PO_2 or ethanol.
- **(B) Benzene diazonium chloride:** Correct. This is the direct product of the reaction under these specific cold conditions.
- **(C) Phenol:** Incorrect. This is formed if the diazonium salt solution is **warmed** or allowed to reach room temperature.
- **(D) Nitrobenzene:** Incorrect. Nitrobenzene is a starting material for making aniline (via reduction), not the product of this reaction.

Conclusion: The reaction of aniline with nitrous acid at ice-cold temperatures specifically yields benzene diazonium chloride.

$\boxed{\textbf{Answer: (B)}}$

Q45.

Solution

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

- **Reducing Sugars:** Possess a free (or potentially free) **aldehydic** or **ketonic** group. In cyclic structures, this means they have a free **hemiacetal** or **hemiketal** hydroxyl group at the anomeric carbon.
- **Non-reducing Sugars:** The aldehydic or ketonic groups are involved in **glycosidic linkage** formation, meaning there is no free anomeric hydroxyl group available to open the ring and act as a reducing agent.

Solution: Let's evaluate the structural characteristics of the given sugars:
1. **(A) Glucose:** A monosaccharide with a free aldehydic group (aldose). It is a **reducing sugar**. 2. **(B) Fructose:** A monosaccharide with a free ketonic group (ketose). Although it is a ketone, it rearranges to an aldehyde in alkaline Tollen's/Fehling's solutions. It is a **reducing sugar**. 3. **(C) Sucrose:** A disaccharide composed of α-D-glucose and β-D-fructose. The glycosidic linkage is formed between the **C1 of glucose** and the **C2 of fructose**. Since both anomeric carbons are locked in the linkage, there are no free hemiacetal/hemiketal groups. Thus, it is a **non-reducing sugar**. 4. **(D) Maltose:** A disaccharide of two glucose units linked via $\alpha(1 \rightarrow 4)$ glycosidic bond. While one anomeric carbon is involved in the bond, the second glucose unit has a **free anomeric carbon (C1)**. It is a **reducing sugar**.
Analysis of options:

- **(C) Sucrose:** Correct. It is the most common example of a non-reducing disaccharide.

Conclusion: Sucrose is a non-reducing sugar because its reducing groups (aldehydic and ketonic) are involved in the formation of the glycosidic bond between the two monosaccharide units.

Answer: (C)

Q46.

Solution

Concept: Proteins are high-molecular-mass polymers (biomolecules) composed of α**-amino acids**. These amino acids are joined together in a specific linear sequence through a characteristic covalent bond called a **peptide bond** or **peptide linkage**.

Solution: 1. **Formation:** 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. 2. **The Chemistry:** During this reaction, a molecule of water (H_2O) is eliminated. The resulting functional group is an amide: $-CO-NH-$. 3. **Structure:**

$$\dots - NH - CH(R_1) - CO - NH - CH(R_2) - CO - \dots$$

The $-CO-NH-$ unit is specifically referred to as the peptide linkage in the context of biochemistry.

Analysis of options:

- **(A) Glycosidic linkage:** Incorrect. This is the bond that joins monosaccharide units in **carbohydrates** (e.g., starch, cellulose, sucrose).
- **(B) Peptide linkage:** Correct. This is the fundamental structural unit that holds the primary structure of **proteins** together.
- **(C) Phosphodiester linkage:** Incorrect. This bond connects the sugar-phosphate backbone in **nucleic acids** (DNA and RNA).
- **(D) Hydrogen linkage:** Incorrect. While hydrogen *bonds* are crucial for stabilizing the secondary and tertiary structures of proteins (alpha-helices and beta-sheets), they are weak intermolecular forces, not the primary covalent linkage of the polymer backbone.

Conclusion: The repeating units of proteins are linked by peptide bonds ($-CONH-$).

Answer: (B)

Q47.

Solution

Concept: Vitamins are organic compounds required in small amounts in the diet for specific biological functions. Each vitamin plays a unique role in maintaining health, and their deficiency leads to specific clinical conditions or diseases. **Vitamin D** (Calciferol) is essential for the absorption of calcium and phosphorus from the digestive tract, which is critical for the formation and maintenance of strong bones.

Solution: To identify the correct deficiency disease, we examine the roles of the vitamins associated with each option:
1. **(A) Scurvy:** Caused by the deficiency of **Vitamin C** (Ascorbic acid). Symptoms include bleeding gums and delayed wound healing. 2. **(B) Rickets:** Caused by the deficiency of **Vitamin D**.

- In children, this leads to **Rickets**, characterized by soft, weak, and deformed bones (e.g., bow legs).
- In adults, a similar deficiency leads to **Osteomalacia** (softening of the bones).

3. **(C) Night blindness:** Caused by the deficiency of **Vitamin A** (Retinol). It results in poor vision in low light. 4. **(D) Beri-beri:** Caused by the deficiency of **Vitamin B_1** (Thiamine). It affects the nervous system and cardiovascular health.

Analysis of options:

- **(B) Rickets:** Correct. Vitamin D is the "sunshine vitamin" necessary for bone health; its lack directly causes rickets.

Conclusion: The lack of Vitamin D prevents proper bone mineralization, leading to Rickets in children.

$\boxed{\textbf{Answer: (B)}}$

Q48.

Solution

Concept: Denaturation of a protein refers to the process where a protein loses its native biological activity due to physical or chemical changes, such as changes in temperature (heating), pH, or the addition of certain chemicals. This process involves the unfolding of the highly organized three-dimensional structure of the protein.

Solution: To understand what remains intact, we must look at the types of bonds broken during denaturation:

1. **Higher-Order Structures** $(2°, 3°, 4°)$**:** These structures are maintained by relatively weak forces such as **hydrogen bonds**, **disulfide bridges**, **hydrophobic interactions**, and **ionic (salt) bridges**. During denaturation, these weak interactions are disrupted, causing the protein to uncoil and lose its specific shape (conformation). 2. **Primary Structure** $(1°)$**:** The primary structure is the specific linear sequence of amino acids held together by strong, covalent **peptide bonds** $(-CONH-)$. These covalent bonds are much more stable than the non-covalent interactions mentioned above. 3. **The Result:** While the protein loses its complex folding (secondary, tertiary, and quaternary levels) and its biological function, the **chemical backbone** (the sequence of amino acids) remains perfectly intact because the peptide bonds do not break under standard denaturing conditions.

Analysis of options:

- **(A) Primary:** Correct. This structure is defined by covalent bonds which are not disrupted during denaturation.
- **(B) Secondary:** Incorrect. Hydrogen bonds forming α-helices and β-sheets are broken.
- **(C) Tertiary:** Incorrect. The overall folding into a 3D shape is lost.
- **(D) Quaternary:** Incorrect. The spatial arrangement of multiple polypeptide subunits is dissociated.

Conclusion: Denaturation disrupts the "shape" of the protein but leaves the "amino acid chain" (primary structure) unaltered.

$\boxed{\textbf{Answer: (A)}}$

Q49.

Solution

Concept: The structure of **DNA (Deoxyribonucleic acid)** consists of two helical strands held together by hydrogen bonds between specific pairs of nitrogenous bases. This specificity is known as **base pairing**.

- **Purines:** Adenine (A) and Guanine (G).
- **Pyrimidines:** Cytosine (C) and Thymine (T). (Uracil is found only in RNA).

Solution: According to **Chargaff's rules** and the Watson-Crick model, base pairing is highly specific due to the size of the bases and the number of hydrogen bonding sites available:
1. **Guanine (G) and Cytosine (C):** Guanine always pairs with Cytosine through **three hydrogen bonds** ($G \equiv C$). 2. **Adenine (A) and Thymine (T):** Adenine always pairs with Thymine through **two hydrogen bonds** ($A = T$). 3. **Comparison:** Because Guanine is a double-ringed purine, it must pair with a single-ringed pyrimidine (Cytosine) to maintain a constant distance between the two DNA strands.
Analysis of options:

- **(A) Adenine:** Incorrect. Adenine is a purine and does not pair with Guanine.
- **(B) Cytosine:** Correct. This is the complementary base for Guanine in both DNA and RNA.
- **(C) Thymine:** Incorrect. Thymine is the complementary base for Adenine in DNA.
- **(D) Uracil:** Incorrect. Uracil is found in RNA and pairs with Adenine, replacing Thymine.

Conclusion: In the DNA double helix, Guanine and Cytosine are complementary partners.

Answer: (B)

Q50.

Solution

Concept: Raoult's Law states that for a solution of volatile liquids, the partial vapor pressure of each component is directly proportional to its mole fraction. Solutions are classified as **ideal** (obey Raoult's Law) or **non-ideal** (show deviations).

Solution: Let's evaluate each statement to find the incorrect one:

- **(A) For an ideal solution, $\Delta H_{mixing} = 0$:** This is **correct**. In an ideal solution, the intermolecular forces between A-B are identical to A-A and B-B, meaning no heat is absorbed or evolved during mixing.
- **(B) If $P_{total} > P^0_A \chi_A + P^0_B \chi_B$, the solution shows positive deviation:** This is **correct**. When the observed vapor pressure is higher than predicted by Raoult's Law, it is termed a positive deviation.
- **(C) In positive deviation, A-B interactions are stronger than A-A or B-B interactions:** This is **incorrect**. In positive deviation, the A-B attractive forces are **weaker** than A-A or B-B interactions. Because the molecules are held less tightly in the mixture, they escape into the vapor phase more easily, resulting in a higher vapor pressure.
- **(D) Minimum boiling azeotropes are formed by solutions showing large positive deviation:** This is **correct**. A large positive deviation means the vapor pressure is very high; consequently, the boiling point (where vapor pressure equals atmospheric pressure) is lower than that of the pure components.

Conclusion: Statement (C) is the incorrect description of the molecular interactions responsible for positive deviation.

Answer: (C)

Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	B	2	B	3	D	4	A	5	B
6	B	7	B	8	C	9	C	10	A
11	B	12	B	13	A	14	B	15	A
16	D	17	C	18	B	19	B	20	C
21	A	22	A	23	A	24	A	25	B
26	D	27	A	28	C	29	C	30	A
31	D	32	A	33	B	34	A	35	C
36	B	37	A	38	B	39	D	40	D
41	A	42	A	43	A	44	B	45	C
46	B	47	B	48	A	49	B	50	C