WBJEE Chemistry Sample Paper-4

Duration: 60 Minutes **Maximum Marks: 50**

Instructions

- This paper contains **40** Multiple Choice Questions divided into **3 Categories**.
- **Section A (Q1–Q30):** Each correct answer carries **+1 mark**. Incorrect answer: **−0.25** marks. Only **one** correct option.
- **Section B (Q31–Q35):** Each correct answer carries **+2 marks**. Incorrect answer: **−0.5** marks. Only **one** correct option.
- **Section C (Q36–Q40):** Each correct answer carries **+2 marks**. **No negative marking**. One or **more** correct options may be correct; full marks only if all correct options are marked.
- Use of mobile phones, smartwatches, or any electronic gadgets is strictly prohibited.

Section A - 30 Questions × 1 Mark Each
(Negative Marking: −0.25) [Single Correct]

Q1. An organic compound on treatment with nitrous acid at 0–5°C gives a clear solution, which on heating with alkaline β-naphthol gives an intense orange-red dye. When the same organic compound is refluxed with chloroform and ethanolic KOH, a foul-smelling liquid is formed. The compound is:

(A) N-Methylaniline

(B) Aniline

(C) Benzylamine

(D) Acetanilide

Q2. For a certain first-order reaction A → products, the time taken for the initial concentration of A to fall to 12.5% of its initial value is 90 minutes. Under the same conditions, the time required for the concentration of A to drop from 0.8 M to 0.2 M is:

(A) 30 minutes

(B) 45 minutes

(C) 60 minutes

(D) 15 minutes

Q3. The solubility product (K_{sp}) of a sparingly soluble salt MX_2 in water is 4.0×10^{-12} at 298 K. The solubility of this salt in a 0.01 M KX solution at the same temperature is:

(A) 4.0×10^{-8} mol L^{-1}

(B) 2.0×10^{-5} mol L^{-1}

(C) 4.0×10^{-10} mol L^{-1}

(D) 1.0×10^{-6} mol L^{-1}

Q4. Which of the following sequence of reagents is most suitable to effect the conversion of 1-butanol to 2-bromobutane?

(A) PBr_3, followed by alcoholic KOH, and then HBr/H_2O_2

(B) Conc. H_2SO_4 at 170°C, followed by HBr gas in the absence of peroxides

(C) $SOCl_2$, followed by $NaNH_2$, and then Br_2/CCl_4

(D) HBr/conc. H_2SO_4, followed by aqueous KOH

Q5. A gas behaves most like an ideal gas under which of the following sets of conditions?

(A) High pressure and low temperature

(B) Low pressure and high temperature

(C) High pressure and high temperature

(D) Low pressure and low temperature

Q6. Consider the coordination compound $[Co(en)_2Cl_2]Cl$. The total number of possible stereoisomers (including enantiomers) exhibited by this complex is:

(A) 2

(B) 3

(C) 4

(D) 5

Q7. In a regular hcp (hexagonal close-packed) structure of spheres of radius R, the total number of tetrahedral and octahedral voids per unit cell are respectively:

(A) 8 and 4

(B) 12 and 6

(C) 4 and 2

(D) 6 and 3

Q8. Which of the following statements regarding photochemical smog is incorrect?

(A) Its formation is initiated by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides.

(B) It has a high concentration of oxidizing agents like ozone and PAN.

(C) It is predominantly observed in cold, humid climates during the winter mornings.

(D) Plant species like Pinus and Juniporous can help in monitoring or reducing its components.

Q9. Equal masses of CH_4, O_2, and SO_2 are mixed in an empty enclosed vessel at 27°C. The ratio of their partial pressures ($p_{CH_4} : p_{O_2} : p_{SO_2}$) in the mixture is:

(A) 1 : 2 : 4

(B) 4 : 2 : 1

(C) 1 : 1 : 1

(D) 16 : 8 : 1

Q10. The standard reduction potentials of three metallic elements X, Y, and Z are -1.2 V, $+0.5$ V, and -3.0 V respectively. The correct order of their reducing power is:

(A) $Y > X > Z$

(B) $Z > X > Y$

(C) $X > Y > Z$

(D) $Z > Y > X$

Q11. The major organic product formed when phenol is treated with chloroform and aqueous NaOH at 60°C, followed by acidification, is:

(A) Salicylic acid

(B) Salicylaldehyde

(C) Anisole

(D) Acetophenone

Q12. When 250 mL of a 0.15 M $KMnO_4$ solution is completely reduced to Mn^{2+} in an acidic medium, the total mass of $FeSO_4$ that can be oxidized to $Fe_2(SO_4)_3$ by this volume of solution is [Molar mass of $FeSO_4$ = 152 g mol^{-1}]:

(A) 28.5 g

(B) 5.7 g

(C) 11.4 g

(D) 22.8 g

Q13. The correct IUPAC name for the compound given below is: $CH_3 - CH(OH) - CH_2 - C(CH_3)_2 - COOH$

(A) 2,2-Dimethyl-4-hydroxypentanoic acid

(B) 4-Hydroxy-2,2-dimethylpentanoic acid

(C) 2,2,4-Trimethyl-4-hydroxybutyric acid

(D) 4-Hydroxypentan-2,2-dimethyl acid

Q14. The wavelength associated with a moving electron accelerated through a potential difference of V volts is proportional to:

(A) V

(B) V^{-1}

(C) $V^{1/2}$

(D) $V^{-1/2}$

Q15. The radical polymerisation of styrene ($C_6H_5CH = CH_2$) in the presence of benzoyl peroxide yields polystyrene. The repeating unit of this polymer is:

(A) $-[CH_2 - CH(C_6H_5)]_n-$

(B) $-[CH(C_6H_5) - CH(C_6H_5)]_n-$

(C) $-[CH_2 - C(C_6H_5)_2]_n-$

(D) $-[CH = C(C_6H_5)]_n-$

Q16. Which of the following oxoacids of phosphorus contains a direct P – P bond along with a +4 oxidation state for phosphorus?

(A) Pyrophosphoric acid ($H_4P_2O_7$)

(B) Hypophosphoric acid ($H_4P_2O_6$)

(C) Pyrophosphorous acid ($H_4P_2O_5$)

(D) Orthophosphoric acid (H_3PO_4)

Q17. For a reversible cyclic process, the total change in an intrinsic state property like internal energy (U) and the total entropy change (ΔS_{total}) of the universe are respectively:

(A) $\Delta U = 0, \Delta S_{total} > 0$

(B) $\Delta U > 0, \Delta S_{total} = 0$

(C) $\Delta U = 0, \Delta S_{total} = 0$

(D) $\Delta U < 0, \Delta S_{total} < 0$

Q18. The compound that will undergo nucleophilic aromatic substitution (S_NAr) via an addition-elimination mechanism at the fastest rate when treated with sodium ethoxide (NaOEt) is:

(A) Chlorobenzene

(B) 4-Nitrochlorobenzene

(C) 2,4-Dinitrochlorobenzene

(D) 3-Nitrochlorobenzene

Q19. The number of radial and angular nodes present in a $4d$ orbital of a hydrogenic atom are respectively:

(A) 2 and 1

(B) 1 and 2

(C) 3 and 0

(D) 2 and 2

Q20. In the qualitative analysis of Group II cations, H_2S gas is passed in the presence of dilute HCl. The primary role of dilute HCl is to:

(A) Increase the solubility of Group II sulfides

(B) Decrease the concentration of sulfide ions by the common ion effect to prevent precipitation of Group IV cations

(C) Maintain an alkaline pH to stabilize the sulfide complex

(D) Act as an oxidizing agent to convert lower oxidation states to higher ones

Q21. The structures of XeF_2 and XeF_4 are best described by VSEPR theory as:

(A) Linear and Tetrahedral

(B) Bent and Square planar

(C) Linear and Square planar

(D) Bent and Tetrahedral

Q22. An aqueous solution of an unknown organic compound shows a positive Tollen's test. When this compound is warmed with a concentrated solution of iodine and NaOH, a yellow precipitate with a characteristic medicinal smell is formed. The compound is:

(A) Formaldehyde

(B) Acetone

(C) Acetaldehyde

(D) Benzaldehyde

Q23. When an aqueous solution of $CuSO_4$ is electrolyzed using inert platinum electrodes, the products obtained at the cathode and anode are respectively:

(A) H_2 (g) and O_2 (g)

(B) Cu (s) and O_2 (g)

(C) Cu (s) and Cl_2 (g)

(D) O_2 (g) and Cu (s)

Q24. Non-reducing sugars do not show mutarotation and do not reduce Fehling's solution. Which of the following disaccharides is a non-reducing sugar?

(A) Maltose

(B) Lactose

(C) Sucrose

(D) Cellobiose

Q25. Which of the following arrangements represents the correct order of increasing ionic radius for the isoelectronic species?

(A) $Ca^{2+} < K^+ < Cl^- < S^{2-}$

(B) $S^{2-} < Cl^- < K^+ < Ca^{2+}$

(C) $Cl^- < S^{2-} < Ca^{2+} < K^+$

(D) $K^+ < Ca^{2+} < S^{2-} < Cl^-$

Q26. Liquid NH_3 is used widely as a non-aqueous solvent. When an alkali metal like sodium dissolves in liquid ammonia, a deep blue highly conducting solution is formed. This blue color is primarily due to:

(A) The formation of sodium amide ($NaNH_2$)

(B) Ammoniated electrons absorbing energy in the visible region

(C) The excitation of the $3s$ electron of sodium atom

(D) The emission of light due to sodium hydride formation

Q27. The molarity of a 30% (w/w) aqueous solution of H_2SO_4 having a density of 1.21 g mL^{-1} is approximately [Molar mass of H_2SO_4 = 98 g mol^{-1}]:

(A) 3.7 M

(B) 2.4 M

(C) 4.2 M

(D) 1.8 M

Q28. In the extraction of gold, the crushed ore is leached with an aqueous solution of NaCN in the presence of air to form a soluble complex A, which is subsequently reduced with a metal B to recover gold. A and B are respectively:

(A) $[Au(CN)_2]^-$ and Zn

(B) $[Au(CN)_4]^-$ and Cu

(C) $[Au(CN)_2]^{2-}$ and Fe

(D) $[Au(CN)_3]^-$ and Al

Q29. The hyperconjugation stability order of the following alkenes is:
(I) $CH_3 - CH = CH_2$
(II) $(CH_3)_2C = CH_2$
(III) $CH_2 = CH_2$
(IV) $(CH_3)_2C = CH - CH_3$

(A) III < I < II < IV

(B) IV < II < I < III

(C) I < III < II < IV

(D) III < II < I < IV

Q30. Among the transition metal ions of the first series, the spin-only magnetic moment value is found to be maximum for which of the following gaseous ions in its ground state configuration?

(A) Ti^{2+}

(B) Mn^{2+}

(C) Fe^{2+}

(D) Cu^{2+}

Section B - 5 Questions × 2 Mark Each
(Negative Marking: −0.5) [Single Correct]

Q31. For the equilibrium reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, the equilibrium constant K_p is 0.15 atm^{-1} at a certain temperature. If the total pressure at equilibrium is 2.0 atm, the mole fraction of N_2O_4 in the mixture is closest to:

(A) 0.18

(B) 0.23

(C) 0.35

(D) 0.09

Q32. Consider the following reaction sequence: Propyne $\xrightarrow{\text{dil. } H_2SO_4 \text{ / } HgSO_4} X \xrightarrow{\text{Conc. } H_2SO_4,\ \Delta} Y$. The major product Y formed in the above transformation is:

(A) Mesityl oxide

(B) Mesitylene

(C) Phorone

(D) Isophorone

Q33. Two half-cells are set up as follows:

Cell 1: Pt(s) | H_2(1 atm) | HCl(0.1 M)

Cell 2: Pt(s) | H_2(1 atm) | CH_3COOH(0.1 M)

At 298 K, the potential of Cell 1 is found to be more positive than Cell 2 when connected to a standard hydrogen electrode. If the difference in their EMF values ($\Delta E = E_1 - E_2$) is 0.0885 V at 298 K, the K_a of acetic acid is calculated to be:

(A) 1.0×10^{-5}

(B) 1.8×10^{-5}

(C) 2.0×10^{-4}

(D) 1.0×10^{-6}

Q34. When 1 mole of an ideal gas undergoes isothermal reversible expansion from a volume of 10 L to 100 L at 300 K, the work done (w) by the gas and the entropy change of the surroundings (ΔS_{surr}) are respectively given by [Take $R = 8.314$ J mol^{-1} K^{-1}]:

(A) $w = -5744$ J, $\Delta S_{\text{surr}} = -19.15$ J K^{-1}

(B) $w = +5744$ J, $\Delta S_{\text{surr}} = +19.15$ J K^{-1}

(C) $w = -5744$ J, $\Delta S_{\text{surr}} = +19.15$ J K^{-1}

(D) $w = -2303$ J, $\Delta S_{\text{surr}} = -7.67$ J K^{-1}

Q35. A gaseous mixture contains 1 mole of He and 1 mole of O_2. Assuming both gases behave ideally, the ratio of the total translational kinetic energy of He to that of O_2 at a given constant temperature T is:

(A) 1 : 1

(B) 3 : 5

(C) 5 : 3

(D) 1 : 2

Section C - 5 Questions × 2 Marks Each
(No Negative Marking) [One or More Correct]

Q36. Which of the following statements is/are correct regarding the chemical behavior and trends of p-block elements?

(A) Bi(V) acts as a much stronger oxidizing agent than Sb(V) due to the inert pair effect.

(B) H_3BO_3 is a protic Arrhenius acid that undergoes auto-protolysis in an aqueous medium.

(C) The Lewis acid strength order among boron trihalides is $BF_3 < BCl_3 < BBr_3$.

(D) PbO_2 dissolves in concentrated HNO_3 readily to evolve oxygen gas.

Q37. For an ideal solution formed by mixing two volatile liquids A and B, which of the following thermodynamic relations must always hold true at constant temperature and pressure?

(A) $\Delta H_{\text{mixing}} = 0$

(B) $\Delta V_{\text{mixing}} = 0$

(C) $\Delta S_{\text{mixing}} > 0$

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

Q38. Which of the following methods/reagents can be used to distinguish between a pair of position isomers, namely 1-propanol and 2-propanol?

(A) Lucas reagent (Conc. HCl + Anhydrous $ZnCl_2$) at room temperature

(B) Heating with catalytic Cu at 573 K followed by testing the product with Tollen's reagent

(C) Iodoform test (I_2 + NaOH)

(D) Victor Meyer's test

Q39. Which of the following compounds will show a higher rate of electrophilic aromatic substitution than benzene?

(A) Anisole

(B) Nitrobenzene

(C) Toluene

(D) Acetophenone

Q40. Which of the following statements is/are correct regarding the structure and bonding in coordination compounds?

(A) $[Ni(CN)_4]^{2-}$ is a diamagnetic complex with dsp^2 hybridisation.

(B) $[Fe(H_2O)_6]^{2+}$ is an outer-orbital, high-spin complex with four unpaired electrons.

(C) $[Co(NH_3)_6]^{3+}$ is a paramagnetic complex due to the presence of a weak-field ligand.

(D) The crystal field splitting energy (Δ_o) of $[Co(CN)_6]^{3-}$ is greater than that of $[Co(H_2O)_6]^{3-}$.

Detailed Solutions

Q1.

Solution

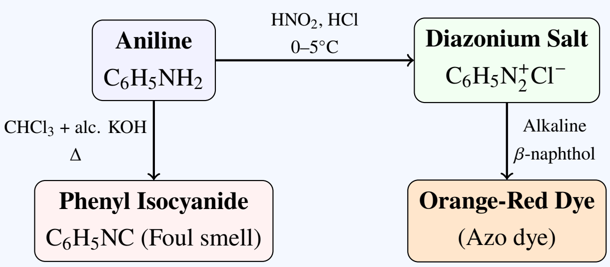
Concept:
Identification of primary aromatic amines using Diazotization (Azo-dye) and Carbylamine (Isocyanide) tests.

Solution:
Step 1: Aniline ($C_6H_5NH_2$) reacts with nitrous acid (HNO_2) at 0–5°C to form a clear solution containing stable benzene diazonium chloride.

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0\text{–}5^\circ C} C_6H_5N_2^+Cl^- + 2H_2O$$

Step 2: This diazonium salt couples with alkaline β-naphthol to form an intense orange-red azo dye, confirming a primary aromatic amine. Benzylamine (primary aliphatic) forms an unstable diazonium salt that decomposes, failing this test.
Step 3: Refluxing aniline with $CHCl_3$ and ethanolic KOH gives the foul-smelling phenyl isocyanide (Carbylamine reaction), confirming it is a primary amine. Secondary amines like N-methylaniline do not show this reaction.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5NC \uparrow + 3KCl + 3H_2O$$



Final Answer: Aniline

Answer: (B)

Go Back to Question 1

Q2.

Solution

Concept:

For a first-order reaction, the rate depends linearly on one reactant's concentration. The time required for a specific fraction to decompose is determined using the integrated rate law or the half-life ($t_{1/2}$).

Solution:

Step 1: Find the remaining fraction after 90 minutes. The concentration drops to 12.5% of its initial value:

$$\frac{[A]_t}{[A]_0} = \frac{12.5}{100} = \frac{1}{8}$$

Step 2: Determine the number of half-lives (n) passed. Using the remaining fraction formula:

$$\left(\frac{1}{2}\right)^n = \frac{1}{8} \implies \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^3 \implies n = 3$$

Step 3: Calculate the half-life period ($t_{1/2}$). Since 3 half-lives take 90 minutes:

$$3 \times t_{1/2} = 90 \implies t_{1/2} = 30 \text{ minutes}$$

Step 4: Find the fraction remaining for the second scenario (from 0.8 M to 0.2 M):

$$\frac{[A]_{\text{final}}}{[A]_{\text{initial}}} = \frac{0.2}{0.8} = \frac{1}{4}$$

Step 5: Find the number of half-lives needed for this drop:

$$\left(\frac{1}{2}\right)^n = \frac{1}{4} \implies \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^2 \implies n = 2$$

Step 6: Compute the total time required for 2 half-lives:

$$\text{Time} = 2 \times t_{1/2} = 2 \times 30 = 60 \text{ minutes}$$

Final Answer: 60 minutes

Answer: (C)

Go Back to Question 2

Q3.

Solution

Concept:

The solubility of a sparingly soluble salt decreases in the presence of a strong electrolyte sharing a common ion (common ion effect). This is governed by the solubility product constant (K_{sp}), which remains constant at a given temperature.

Solution:

Step 1: Write the dissociation equilibrium of the sparingly soluble salt MX_2. Let its solubility in this solution be S mol L^{-1}:

$$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2X^-(aq)$$

Step 2: Identify the ion contribution from the strong electrolyte KX, which dissociates completely:

$$KX(aq) \longrightarrow K^+(aq) + X^-(aq)$$

A 0.01 M solution of KX provides 0.01 M of K^+ and 0.01 M of X^-.

Step 3: Set up the total equilibrium concentrations:

$$[M^{2+}] = S$$

$$[X^-] = 2S + 0.01$$

Step 4: Write the solubility product expression and substitute the concentration terms:

$$K_{sp} = [M^{2+}][X^-]^2 \implies 4.0 \times 10^{-12} = S \times (2S + 0.01)^2$$

Step 5: Apply a mathematical simplification. Because K_{sp} is very small and suppressed further by the common ion effect, $2S \ll 0.01$, meaning $2S + 0.01 \approx 0.01 = 10^{-2}$.

Step 6: Solve for the suppressed solubility S:

$$4.0 \times 10^{-12} = S \times (10^{-2})^2$$

$$4.0 \times 10^{-12} = S \times 10^{-4}$$

$$S = \frac{4.0 \times 10^{-12}}{10^{-4}} = 4.0 \times 10^{-8} \text{ mol L}^{-1}$$

Final Answer: $\boxed{4.0 \times 10^{-8} \text{ mol L}^{-1}}$

Answer: (A)

Go Back to Question 3

Q4.

Solution

Concept:

Converting a primary alcohol (1-butanol) to a secondary alkyl halide (2-bromobutane) involves shifting the functional group position. This is achieved by acid-catalyzed dehydration to form an alkene intermediate, followed by regioselective electrophilic addition governed by Markovnikov's rule.

Solution:

Step 1: Identify the starting material and target structures:

$$\text{1-butanol: } CH_3 - CH_2 - CH_2 - CH_2 - OH$$

$$\text{2-bromobutane: } CH_3 - CH_2 - CH(Br) - CH_3$$

Step 2: Analyze the dehydration step in option (B). Heating 1-butanol with concentrated H_2SO_4 at 170°C causes an E1 acid-catalyzed dehydration. The initially formed primary carbocation undergoes a 1,2-hydride shift to form a more stable secondary carbocation. Proton elimination then yields 2-butene as the major product according to Saytzeff's rule.

Step 3: Analyze the addition step in option (B). Treating the alkene intermediate with HBr in the absence of peroxides proceeds via Markovnikov electrophilic addition. The proton adds to the less substituted carbon, creating a stable secondary carbocation that is attacked by Br^- to selectively yield 2-bromobutane:

$$CH_3 - CH_2 - CH = CH_2 + HBr \rightarrow CH_3 - CH_2 - CH(Br) - CH_3$$

Step 4: Verify why other options fail. Option (A) uses PBr_3 followed by alcoholic KOH to form 1-butene, but the subsequent addition of HBr in the presence of peroxides (H_2O_2) yields anti-Markovnikov-directed 1-bromobutane instead of the required 2-position isomer. Thus, option (B) is the correct pathway.

Final Answer: Conc. H_2SO_4 at 170°C, followed by HBr gas in the absence of peroxides

Answer: (B)

Go Back to Question 4

Q5.

Solution

Concept:
Real gases deviate from ideal behavior due to two primary factors described by the van der Waals equation: the intermolecular attractive forces between the gas molecules and the finite finite volume occupied by the gas molecules themselves. A real gas approaches ideal behavior when these factors become completely negligible.

Solution:
Step 1: Understand the kinetic molecular theory of ideal gases. An ideal gas assumes that there are absolutely no intermolecular forces of attraction or repulsion between the gas particles, and the actual volume occupied by the gas molecules is completely negligible compared to the total volume of the container.

Step 2: Analyze the effect of temperature on gas behavior. At very high temperatures, the gas molecules possess exceptionally high kinetic energy ($KE = \frac{3}{2}RT$). Because they move at extremely high velocities, the intermolecular attractive forces between them cannot hold them together or significantly affect their trajectories during collisions. Thus, the effect of intermolecular attraction becomes negligible at high temperatures.

Step 3: Analyze the effect of pressure on gas behavior. At very low pressures, the total volume of the gas is extremely large according to Boyle's law. Because the container volume is massive compared to the size of individual particles, the actual space or volume occupied by the gas molecules themselves becomes completely negligible. Furthermore, the molecules are spaced incredibly far apart from one another, which further minimizes any potential intermolecular attractive interactions.

Step 4: Combine both physical conditions. When a real gas is subjected simultaneously to a very low pressure and a very high temperature, the molecules are far apart and moving too fast to experience meaningful attractive interactions, and their individual volumes are negligible. Under these exact parameters, the van der Waals constants a and b have minimal impact, and the real gas behaves most like an ideal gas obeying the equation $PV = nRT$.

Step 5: Match with the given options. High pressure or low temperature increases deviations from ideality, leading to liquefaction or non-ideal gas states. Thus, low pressure and high temperature is the correct set of conditions.

Final Answer: Low pressure and high temperature

Answer: (B)

Go Back to Question 5

Q6.

Solution

Concept:

Stereoisomerism in octahedral coordination complexes of the type $[M(AA)_2X_2]$.

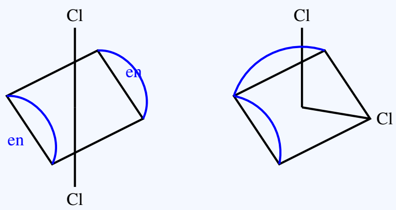
Solution:

Step 1: The complex $[Co(en)_2Cl_2]^+$ possesses an octahedral geometry where 'en' (ethylenediamine) is a bidentate symmetric ligand. It forms two distinct geometric isomers: *cis* and *trans*.

Step 2: In the ***trans*-isomer**, the two chloride ligands are arranged directly opposite to each other (180°). This molecule contains a plane of symmetry (σ_h), rendering it achiral and optically inactive (no enantiomers).

Step 3: In the ***cis*-isomer**, the two chloride ligands are adjacent to each other (90°). This structure lacks a plane of symmetry and is chiral, existing as a pair of non-superimposable mirror images (a d-form and an l-form enantiomeric pair).

Step 4: Total number of stereoisomers = 1 (*trans*) + 2 (*cis* enantiomers) = 3.



trans **(achiral)** ***cis*** **(chiral,** d/l**)**

Final Answer: 3

Answer: (B)

Go Back to Question 6

Q7.

Solution

Concept:

Calculation of tetrahedral and octahedral voids in a hexagonal close-packed (hcp) unit cell.

Solution:

Step 1: In any close-packed lattice (ccp or hcp), if the total number of constituent atoms (or spheres) forming the lattice per unit cell is N, then:

- The number of octahedral voids generated = N
- The number of tetrahedral voids generated = $2N$

Step 2: Let us calculate the effective number of atoms (N) in an hcp unit cell:

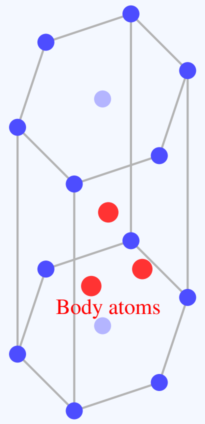
- Atoms at the 12 corners: Each corner atom is shared among 6 adjacent unit cells $\implies 12 \times \frac{1}{6} = 2$.
- Atoms at the 2 face centers: Each face-center atom is shared between 2 unit cells $\implies 2 \times \frac{1}{2} = 1$.
- Atoms entirely inside the body: 3 atoms lie completely inside the unit cell $\implies 3 \times 1 = 3$.

$$\text{Total atoms per hcp unit cell } (N) = 2 + 1 + 3 = 6$$

Step 3: Using the relationships from Step 1:

$$\text{Number of tetrahedral voids} = 2N = 2 \times 6 = 12$$

$$\text{Number of octahedral voids} = N = 6$$



Final Answer: 12 and 6

Answer: (B)

Go Back to Question 7

Q8.

Solution

Concept:
Photochemical smog is a highly oxidizing environmental hazard formed in the atmosphere via solar-driven reactions of primary pollutants (nitrogen oxides and unburnt hydrocarbons) emitted by vehicles and industries.

Solution:
Step 1: Evaluate statement (A). Sunlight triggers the photolysis of nitrogen dioxide (NO_2), producing reactive atomic oxygen (O) that reacts with unburnt hydrocarbons. This makes statement (A) chemically correct.
Step 2: Evaluate statement (B). The subsequent free-radical reactions produce high concentrations of powerful oxidizing agents like ozone (O_3) and peroxyacetyl nitrate (PAN). Thus, statement (B) is correct.
Step 3: Evaluate statement (C). Photochemical smog requires intense ultraviolet radiation, high temperatures, and dry air, meaning it thrives during hot, sunny summer afternoons. Cold, humid winter morning conditions are characteristic of *classical (reducing) smog*. Therefore, statement (C) is incorrect.
Step 4: Evaluate statement (D). Plant species like *Pinus* and *Juniperus* can absorb or tolerate nitrogen oxides, helping monitor or mitigate these air pollutants. This statement is correct.
Step 5: Identify the incorrect statement. Statement (C) is the inaccurate claim.
Final Answer: It is predominantly observed in cold, humid climates during the winter mornings.

Answer: (C)

Go Back to Question 8

Q9.

Solution

Concept:

According to Dalton's law of partial pressures, the partial pressure (p_i) of a gas component in a non-reacting mixture is proportional to its mole fraction (x_i). The mole fraction depends on the ratio of its individual moles to the total moles in the system.

Solution:

Step 1: Assign a variable for the equal masses of the mixed gases. Let the mass of methane (CH_4), oxygen (O_2), and sulfur dioxide (SO_2) be w grams each.

Step 2: Determine the molar mass of each component gas: - Molar mass of $CH_4 = 12 + (4 \times 1) = 16\ g\ mol^{-1}$ - Molar mass of $O_2 = 2 \times 16 = 32\ g\ mol^{-1}$ - Molar mass of $SO_2 = 32 + (2 \times 16) = 64\ g\ mol^{-1}$

Step 3: Calculate the number of moles (n) for each gas ($n = w/M$):

$$n_{CH_4} = \frac{w}{16}, \quad n_{O_2} = \frac{w}{32}, \quad n_{SO_2} = \frac{w}{64}$$

Step 4: Relate the partial pressure ratio to the mole ratio. Since all gases occupy the same volume and temperature, their partial pressure ratio equals their mole ratio:

$$p_{CH_4} : p_{O_2} : p_{SO_2} = \frac{w}{16} : \frac{w}{32} : \frac{w}{64}$$

Step 5: Cancel out the common mass factor w:

$$p_{CH_4} : p_{O_2} : p_{SO_2} = \frac{1}{16} : \frac{1}{32} : \frac{1}{64}$$

Step 6: Convert to integers by multiplying the entire ratio by the lowest common multiple, 64:

$$p_{CH_4} : p_{O_2} : p_{SO_2} = \left(\frac{1}{16} \times 64\right) : \left(\frac{1}{32} \times 64\right) : \left(\frac{1}{64} \times 64\right) = 4 : 2 : 1$$

Final Answer: $\boxed{4 : 2 : 1}$

Answer: (B)

Go Back to Question 9

Q10.

Solution

Concept:
The reducing power of an element measures its tendency to lose electrons and undergo oxidation. This property is inversely related to its standard reduction potential (E°_{red}). A more negative potential indicates a stronger reducing agent.

Solution:
Step 1: List the given standard reduction potentials for the metal elements X, Y, and Z: - $E^\circ_X = -1.2$ V - $E^\circ_Y = +0.5$ V - $E^\circ_Z = -3.0$ V
Step 2: Apply the reduction potential rule. A lower, more negative standard reduction potential means the element oxidizes more easily, giving it a higher reducing power:

$$\text{Reducing Power} \propto -E^\circ_{\text{red}}$$

Step 3: Arrange the reduction potentials in increasing algebraic order:

$$-3.0 \text{ V} < -1.2 \text{ V} < +0.5 \text{ V} \implies E^\circ_Z < E^\circ_X < E^\circ_Y$$

Step 4: Invert the sequence to rank by reducing power. Because lower reduction potentials correspond to stronger reducing agents, Z is the strongest and Y is the weakest.
Step 5: Write the final decreasing order of reducing power:

$$Z > X > Y$$

Final Answer: $\boxed{Z > X > Y}$

Answer: (B)

Go Back to Question 10

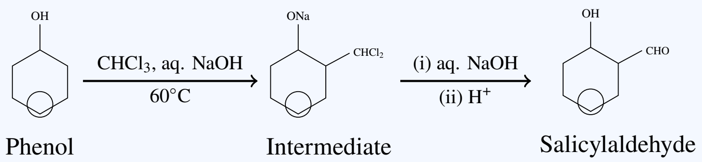
Q11.

Solution

Concept:
The Reimer-Tiemann reaction of phenols to synthesize ortho-hydroxybenzaldehydes.
Solution:
Step 1: When phenol (C_6H_5OH) is treated with chloroform ($CHCl_3$) in the presence of aqueous sodium hydroxide (NaOH), a formyl group (−CHO) is introduced at the *ortho* position of the benzene ring. This organic transformation is named the Reimer-Tiemann reaction.
Step 2: Mechanism summary:

- Hydroxide ion deprotonates chloroform to generate a highly reactive intermediate, dichlorocarbene ($:CCl_2$), which acts as the electrophile.
- Phenol is converted by NaOH into a phenoxide ion, which activates the aromatic ring toward electrophilic attack.
- The phenoxide ion attacks the dichlorocarbene primarily at the less sterically hindered *ortho* position.
- Subsequent alkaline hydrolysis of the intermediate dichloromethyl group ($-CHCl_2$) followed by acidification converts it into a formyl group (−CHO).

Step 3: The major product obtained is salicylaldehyde (2-hydroxybenzaldehyde).



Final Answer: Salicylaldehyde

Answer: (B)

Go Back to Question 11

Q12.

Solution

Concept:

This problem describes a redox titration in an acidic medium. Potassium permanganate ($KMnO_4$) serves as a powerful oxidizing agent, and ferrous sulfate ($FeSO_4$) acts as a reducing agent. By the principle of equivalence, the total number of gram equivalents of the oxidizing agent must equal the total number of gram equivalents of the reducing agent at the endpoint.

Solution:

Step 1: Determine the valence factors (n-factors). In an acidic medium, the permanganate ion (MnO_4^-) is reduced to Mn^{2+} (oxidation state changes from +7 to +2), gaining 5 electrons. Thus, its n-factor (n_1) is 5.

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

The ferrous ion (Fe^{2+}) is oxidized to ferric ion (Fe^{3+}), losing 1 electron. Thus, the n-factor of $FeSO_4$ (n_2) is 1.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Step 2: Calculate the moles of $KMnO_4$ available using its volume (250 mL = 0.25 L) and molarity (0.15 M):

$$\text{Moles of } KMnO_4 = 0.15 \text{ M} \times 0.25 \text{ L} = 0.0375 \text{ moles}$$

Step 3: Relate the equivalents using the principle of equivalence to find the moles of $FeSO_4$:

$$\text{Moles of } KMnO_4 \times n_1 = \text{Moles of } FeSO_4 \times n_2$$

$$0.0375 \times 5 = \text{Moles of } FeSO_4 \times 1 \implies \text{Moles of } FeSO_4 = 0.1875 \text{ moles}$$

Step 4: Convert the calculated moles of $FeSO_4$ into mass using its molar mass (152 g mol^{-1}):

$$\text{Mass of } FeSO_4 = 0.1875 \text{ moles} \times 152 \text{ g mol}^{-1} = 28.5 \text{ g}$$

Final Answer: 28.5 g

Answer: (A)

Go Back to Question 12

Q13.

Solution

Concept:

IUPAC nomenclature of polyfunctional organic compounds requires assigning a priority hierarchy to the functional groups present. The group with the highest priority acts as the principal functional group, which defines the parent suffix. All other functional groups and alkyl branches are treated as prefixes arranged in alphabetical order.

Solution:

Step 1: Identify all functional groups present in the molecular structure:

$$CH_3 - CH(OH) - CH_2 - C(CH_3)_2 - COOH$$

The molecule contains a carboxylic acid ($-COOH$), an alcohol ($-OH$), and methyl branches ($-CH_3$).

Step 2: Determine priority. Carboxylic acids hold the highest priority convention, ranking above alcohols. Thus, $-COOH$ is the principal functional group (suffix "-oic acid"), and the $-OH$ group becomes a substituent (prefix "hydroxy").

Step 3: Select and name the parent chain. The longest continuous chain containing the carboxylic acid carbon contains 5 carbons, corresponding to the parent name "pentanoic acid".

Step 4: Number the carbon chain starting directly from the carboxylic acid carbonyl carbon to give it the lowest possible locant: - C1: $-COOH$ carbon - C2: $-C(CH_3)_2-$ carbon - C3: $-CH_2-$ carbon - C4: $-CH(OH)-$ carbon - C5: Terminal $-CH_3$ carbon

Step 5: Identify the substituents and their positions based on this numbering: - At C2: Two methyl groups $\rightarrow$ "2,2-dimethyl" - At C4: One hydroxyl group $\rightarrow$ "4-hydroxy"

Step 6: Assemble the complete name alphabetically. Comparing "hydroxy" (h) and "dimethyl" (m—numerical prefixes like di are ignored), "hydroxy" comes first. Combining these yields: 4-Hydroxy-2,2-dimethylpentanoic acid.

Final Answer: 4-Hydroxy-2,2-dimethylpentanoic acid

Answer: (B)

Go Back to Question 13

Q14.

Solution

Concept:

The de Broglie hypothesis states that a moving microscopic particle displays wave-like characteristics. When a charged particle like an electron is accelerated from rest through an electric potential difference (V), its gained kinetic energy (K) can be related directly to its associated de Broglie wavelength (λ).

Solution:

Step 1: Write the fundamental de Broglie wavelength equation for a particle of mass m and velocity v:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Step 2: Relate linear momentum (p) to kinetic energy (K):

$$K = \frac{p^2}{2m} \implies p = \sqrt{2mK} \implies \lambda = \frac{h}{\sqrt{2mK}}$$

Step 3: Relate kinetic energy to the accelerating potential difference (V). For an electron with fundamental charge e:

$$K = e \cdot V$$

Step 4: Substitute the kinetic energy term into the wavelength equation:

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Step 5: Isolate the constant parameters (h, m, e) to establish the mathematical proportionality with the voltage variable V:

$$\lambda = \left(\frac{h}{\sqrt{2me}}\right) \cdot \frac{1}{\sqrt{V}} \implies \lambda \propto \frac{1}{\sqrt{V}} \implies \lambda \propto V^{-1/2}$$

Final Answer: $\boxed{V^{-1/2}}$

Answer: (D)

Go Back to Question 14

Q15.

Solution

Concept:
Polymers are macromolecules made of repeating structural monomer units. Styrene undergoes chain-growth addition polymerization via a free-radical mechanism. In addition polymerization, the unsaturated double bonds of monomers open up to link linearly without the loss of small by-product molecules.

Solution:
Step 1: Identify the molecular structure of the starting monomer. Styrene contains a vinyl group attached to a phenyl ring:

$$C_6H_5 - CH = CH_2$$

Step 2: Understand the role of the radical initiator. When heated, benzoyl peroxide undergoes homolytic cleavage to generate active free radicals. These radicals attack the alkene double bond of styrene, creating a stable, carbon-centered radical intermediate.
Step 3: Analyze the chain propagation. The active styrene radical adds to another styrene monomer in a sequential head-to-tail manner, building a long hydrocarbon chain:

$$\cdots - CH_2 - CH(C_6H_5) - CH_2 - CH(C_6H_5) - \ldots$$

Step 4: Deduce the structural identity of the repeating link. During addition, the carbon-carbon double bond ($C = C$) opens into a single bond ($C - C$), freeing up two valencies to bond with adjacent monomer units.
Step 2: Express the formula of the repeating unit. The core fragment consists of a $-CH_2-$ group joined to a $-CH(C_6H_5)-$ group. Enclosing this in brackets defines the structural formula of polystyrene:

$$-[CH_2 - CH(C_6H_5)]_n-$$

Final Answer: $\boxed{-[CH_2 - CH(C_6H_5)]_n-}$

Answer: (A)

Go Back to Question 15

Q16.

Solution

Concept:

Structure and oxidation states of phosphorus oxoacids.

Solution:

Step 1: Let us calculate the oxidation state of phosphorus (x) in hypophosphoric acid ($H_4P_2O_6$):

$$4(+1) + 2(x) + 6(-2) = 0$$

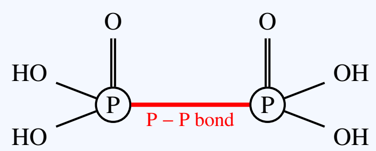
$$4 + 2x - 12 = 0 \implies 2x = 8 \implies x = +4$$

Step 2: Structurally, hypophosphoric acid ($H_4P_2O_6$) contains two symmetric $-PO(OH)_2$ units connected directly by a $P-P$ bond. It has:

- One direct $P-P$ bond
- Two $P=O$ bonds
- Four $P-OH$ bonds

Step 3: Let us analyze the other given options for verification:

- **(A) Pyrophosphoric acid ($H_4P_2O_7$):** Oxidation state of P is +5, contains a $P-O-P$ linkage.
- **(C) Pyrophosphorous acid ($H_4P_2O_5$):** Oxidation state of P is +3, contains a $P-O-P$ linkage.
- **(D) Orthophosphoric acid (H_3PO_4):** Oxidation state of P is +5, mononuclear molecule (no $P-P$ or $P-O-P$ bonds).



Structure of Hypophosphoric acid ($H_4P_2O_6$)

Final Answer: Hypophosphoric acid ($H_4P_2O_6$)

Answer: (B)

Go Back to Question 16

Q17.

Solution

Concept:
Thermodynamic state functions depend solely on the current state of a system, independent of the path taken. For any cyclic process, where the system returns to its original starting state, the net change in all state properties must be zero. The behavior of the total entropy of the universe (system plus surroundings) depends on whether the process is path-reversible or path-irreversible.

Solution:
Step 1: Analyze internal energy (ΔU) for a cyclic process. Internal energy (U) is a state function. Because a cyclic process starts and ends at identical coordinates, the net variation must be zero:

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = 0$$

This holds true for both reversible and irreversible cyclic pathways.
Step 2: Analyze the total entropy change of the universe (ΔS_{total}), which combines the entropy variations of the system and its surroundings:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Step 3: Apply the criteria for a reversible process. During a reversible process, heat is exchanged across infinitesimally small temperature gradients, ensuring that the entropy change of the surroundings is perfectly equal and opposite to that of the system:

$$\Delta S_{\text{surroundings}} = -\Delta S_{\text{system}}$$

Step 4: Calculate the net entropy change of the universe for this reversible cyclic process by substituting the relation:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + (-\Delta S_{\text{system}}) = 0$$

If the cyclic process had been irreversible, ΔS_{total} would be strictly greater than zero. Because it is explicitly reversible, both ΔU and ΔS_{total} equal zero.
Final Answer: $\boxed{\Delta U = 0, \Delta S_{\text{total}} = 0}$

Answer: (C)

Go Back to Question 17

Q18.

Solution

Concept:

Nucleophilic aromatic substitution (S_NAr) in aryl halides proceeds via a two-step addition-elimination mechanism. The rate-determining step involves nucleophilic attack to form a negatively charged, resonance-stabilized anionic intermediate called a Meisenheimer complex. Electron-withdrawing groups positioned ortho and para to the leaving group stabilize this negative charge via powerful resonance ($-M$) and inductive ($-I$) effects, accelerating the reaction rate.

Solution:

Step 1: Understand the mechanism. When an ethoxide ion ($^-$OEt) attacks an aryl chloride, it places a negative charge onto the ring. The rate depends directly on how effectively this negative charge can be delocalized by ring substituents.

Step 2: Evaluate the electronic effect of the nitro group ($-NO_2$). The nitro group exerts powerful electron-withdrawing effects ($-I$, $-M$). When placed ortho or para to the chlorine atom, the negative charge of the Meisenheimer intermediate can be directly delocalized onto the electronegative oxygen atoms of the nitro group.

Step 3: Analyze the options based on substituent placement: - Chlorobenzene has no electron-withdrawing groups (extremely unreactive). - 4-Nitrochlorobenzene has one para nitro group. - 2,4-Dinitrochlorobenzene possesses two nitro groups located at the ortho and para positions relative to the chlorine atom, stabilizing the anionic intermediate from two positions simultaneously. - 3-Nitrochlorobenzene features a meta nitro group, which stabilizes the intermediate solely through its inductive effect ($-I$) because resonance delocalization into a meta position is structurally impossible.

Step 4: Correlate intermediate stabilization with reaction rate. Since 2,4-dinitrochlorobenzene has two properly positioned nitro groups to maximize the resonance stabilization of the Meisenheimer complex, it undergoes substitution at the fastest rate.

Final Answer: 2,4-Dinitrochlorobenzene

Answer: (C)

Go Back to Question 18

Q19.

Solution

Concept:
Nodes are specific boundary regions within atomic orbitals where the probability density of finding an electron drops to exactly zero. The total number of nodes depends on the principal quantum number (n) and azimuthal quantum number (l). Nodes are split into two types: radial nodes (spherical shells) and angular nodes (planar or conical surfaces).

Solution:
Step 1: Identify the quantum numbers for a $4d$ atomic orbital: - The principal quantum number is $n = 4$. - The 'd' subshell corresponds to an azimuthal quantum number of $l = 2$.
Step 2: Compute the number of angular nodes. The number of angular nodes in any given atomic orbital is equal to its azimuthal quantum number (l):

$$\text{Number of angular nodes} = l = 2$$

Step 3: Compute the number of radial nodes using the standard formula:

$$\text{Number of radial nodes} = n - l - 1$$

Substituting our values ($n = 4$ and $l = 2$) yields:

$$\text{Number of radial nodes} = 4 - 2 - 1 = 1$$

Step 4: Perform a consistency check. The total number of nodes is given by $n - 1$. For a $4d$ orbital, total nodes equal $4 - 1 = 3$. Summing our individual counts gives 1 (radial) + 2 (angular) = 3, confirming the calculation.
Step 5: Arrange the answers in the exact order requested by the question statement (*respectively*):

$$\text{Radial nodes} = 1, \quad \text{Angular nodes} = 2$$

Final Answer: $\boxed{\text{1 and 2}}$

Answer: (B)

Go Back to Question 19

Q20.

Solution

Concept:
In qualitative inorganic analysis, cations are separated into groups based on the solubility products (K_{sp}) of their salts. Both Group II and Group IV cations are precipitated as metal sulfides using hydrogen sulfide (H_2S) gas. Because Group II sulfides have exceptionally low solubility products compared to Group IV sulfides, a controlled common ion equilibrium is utilized to achieve selective separation.

Solution:
Step 1: Write the dissociation equilibrium of hydrogen sulfide (H_2S), a weak diprotic acid:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

Step 2: Examine the addition of dilute hydrochloric acid (HCl), a strong acid that dissociates completely:

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Step 3: Apply Le Chatelier's principle. The high concentration of H^+ ions introduced by HCl acts as a common ion on the weak H_2S dissociation, shifting the equilibrium position strongly to the left.
Step 4: Evaluate the resulting ionic concentrations. This suppression keeps the equilibrium concentration of sulfide ions ($[S^{2-}]$) at an exceedingly low value.
Step 5: Correlate this low concentration with selective precipitation. Because the solubility products (K_{sp}) of Group II sulfides are very small, this low concentration of sulfide ions is still enough to exceed their ionic product ($Q_{sp} > K_{sp}$), allowing them to precipitate. However, Group IV sulfides have larger K_{sp} values, so their ionic product remains below the threshold ($Q_{sp} < K_{sp}$). This prevents Group IV cations from coprecipitating, achieving a clean separation.

Final Answer: Decrease the concentration of sulfide ions by the common ion effect to prevent precipitation of Group IV cations

Answer: (B)

Go Back to Question 20

Q21.

Solution

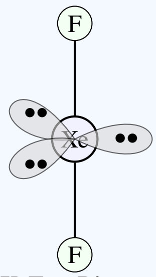
Concept:
VSEPR Theory, hybridization, and molecular geometry of xenon compounds.

Solution:
Step 1: Determine the structure of XeF_2.

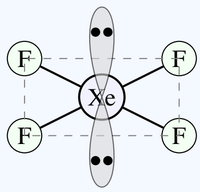
- Central atom Xenon (Xe) has 8 valence electrons. It forms 2 σ-bonds with fluorine atoms, leaving 6 non-bonding electrons (3 lone pairs).
- Total steric number (S_n) = Bond pairs + Lone pairs = 2 + 3 = 5.
- The steric number 5 corresponds to sp^3d hybridization with a trigonal bipyramidal electron-pair geometry.
- To minimize repulsion, the 3 lone pairs occupy the equatorial positions at 120° angles, placing the 2 fluorine atoms axially. This results in a perfectly **linear** molecular geometry.

Step 2: Determine the structure of XeF_4.

- Xenon uses 4 valence electrons to form 4 σ-bonds with fluorine atoms, leaving 4 non-bonding electrons (2 lone pairs).
- Total steric number (S_n) = 4 + 2 = 6.
- The steric number 6 corresponds to sp^3d^2 hybridization with an octahedral electron-pair geometry.
- To minimize lone pair-lone pair repulsions, the 2 lone pairs point in opposite directions along the axial position (180° apart). This forces the 4 fluorine atoms into a single plane, creating a **square planar** molecular geometry.



XeF_2 : Linear



XeF_4 : Square Planar

Final Answer: Linear and Square planar

Answer: (C)

Go Back to Question 21

Q22.

Solution

Concept:

The enthalpy change (ΔH) and internal energy change (ΔU) of a reaction are related by $H = U + PV$. For ideal gases, this relationship is expressed using the ideal gas law ($PV = nRT$). The quantitative difference between ΔH and ΔU at a constant temperature depends entirely on the net change in the number of moles of gaseous components (Δn_g).

Solution:

Step 1: Write the thermodynamic equation connecting ΔH and ΔU at a constant temperature T:

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

Step 2: Note the formula used to calculate Δn_g:

$$\Delta n_g = \sum n_{\text{g, products}} - \sum n_{\text{g, reactants}}$$

Only components in the gaseous phase (g) are counted; liquids (l) and solids (s) are omitted.

Step 3: Analyze the given combustion equation:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

Step 4: Count the total moles of gaseous products. CO_2 is gaseous (3 moles), while H_2O is liquid and ignored:

$$\sum n_{\text{g, products}} = 3$$

Step 5: Count the total moles of gaseous reactants. Both C_3H_8 (1 mole) and O_2 (5 moles) are gases:

$$\sum n_{\text{g, reactants}} = 1 + 5 = 6$$

Step 6: Compute Δn_g:

$$\Delta n_g = 3 - 6 = -3$$

Step 7: Substitute $\Delta n_g = -3$ back into the thermodynamic equation:

$$\Delta H = \Delta U - 3RT$$

Final Answer: $\boxed{\Delta H = \Delta U - 3RT}$

Answer: (C)

Go Back to Question 22

Q23.

Solution

Concept:

The boiling points of Group 16 hydrides (H_2O, H_2S, H_2Se, H_2Te) are governed by molecular mass, polarizability, and intermolecular forces. Typically, boiling points increase down a group as van der Waals dispersion forces strengthen, unless anomalous intermolecular forces like hydrogen bonding alter the trend.

Solution:

Step 1: Analyze the trend in van der Waals forces from H_2S to H_2Te. As the size and molecular mass of the central atom increase ($S < Se < Te$), the electron cloud becomes more polarizable, strengthening London dispersion forces:

$$H_2S < H_2Se < H_2Te$$

Step 2: Identify the anomalous behavior of water (H_2O). Oxygen is highly electronegative and small, which polarizes the $O-H$ bonds heavily and enables extensive intermolecular hydrogen bonding.

Step 3: Compare intermolecular forces. Hydrogen bonds are significantly stronger than the dipole-dipole and dispersion forces of the other hydrides, giving water an anomalously high boiling point (100°C).

Step 4: Combine the trends into the final increasing sequence:

$$H_2S < H_2Se < H_2Te < H_2O$$

Final Answer: $\boxed{H_2S < H_2Se < H_2Te < H_2O}$

Answer: (D)

Go Back to Question 23

Q24.

Solution

Concept:

The mass of a substance deposited during electrolysis is quantified by Faraday's laws. One Faraday of electricity (1 F) corresponds to the passage of one mole of electrons, which deposits exactly one gram equivalent weight (Equivalent weight = Molar mass/n-factor) of a substance at the electrode.

Solution:

Step 1: Write the reduction half-reaction for aluminum at the cathode:

$$Al^{3+} + 3e^- \longrightarrow Al(s)$$

Depositing 1 mole of Al requires 3 moles of electrons (n-factor = 3).

Step 2: Calculate the equivalent weight of aluminum (atomic mass = 27 g mol^{-1}):

$$\text{Equivalent weight of Al} = \frac{27}{3} = 9\ \text{g eq}^{-1}$$

Step 3: Calculate the mass of aluminum deposited by 3 F of charge:

$$\text{Mass of Al} = 3\ \text{F} \times 9\ \text{g F}^{-1} = 27\ \text{g}$$

Step 4: Write the reduction half-reaction for copper at the cathode:

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

Depositing 1 mole of Cu requires 2 moles of electrons (n-factor = 2).

Step 5: Calculate the equivalent weight of copper (atomic mass = 63.5 g mol^{-1}):

$$\text{Equivalent weight of Cu} = \frac{63.5}{2} = 31.75\ \text{g eq}^{-1}$$

Step 6: Calculate the mass of copper deposited by the same 3 F of charge:

$$\text{Mass of Cu} = 3\ \text{F} \times 31.75\ \text{g F}^{-1} = 95.25\ \text{g}$$

Final Answer: 27 g and 95.25 g

Answer: (A)

Go Back to Question 24

Q25.

Solution

Concept:
Under an octahedral crystal field, the five degenerate d-orbitals split into lower-energy t_{2g} and higher-energy e_g levels. The electron distribution depends on the relative values of the crystal field splitting energy (Δ_o) and the pairing energy (P). Strong field ligands make $\Delta_o > P$, forcing electrons to pair up in the lower levels.

Solution:
Step 1: Find the oxidation state of iron in $[Fe(CN)_6]^{4-}$ using a ligand charge of -1 for CN^-:

$$x + 6(-1) = -4 \implies x = +2 \quad (Fe^{2+})$$

Step 2: Determine the d-electron count for Fe^{2+}. Neutral iron is $[Ar]3d^6 4s^2$, so removing two valence electrons gives a $3d^6$ configuration.
Step 3: Analyze ligand field strength. Cyanide (CN^-) is a strong field ligand, meaning the splitting energy is greater than the pairing energy ($\Delta_o > P$).
Step 4: Distribute the six d-electrons. Because $\Delta_o > P$, all six electrons pair up in the lower-energy t_{2g} orbitals, leaving the e_g orbitals empty:

$$\text{Configuration: } t_{2g}^6 e_g^0$$

Step 5: Count the number of unpaired electrons (n). Since all electrons in the t_{2g} set are paired:

$$n = 0$$

Step 6: Calculate the spin-only magnetic moment (μ_s):

$$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0 \text{ BM}$$

Final Answer: $\boxed{0 \text{ BM}}$

Answer: (A)

Go Back to Question 25

Q26.

Solution

Concept:
Colligative properties depend exclusively on the total number of solute particles present in a solution, rather than their chemical identity. Freezing point depression (ΔT_f) is a key colligative property. When a non-volatile solute is dissolved in a solvent, the freezing point of the solution decreases relative to the pure solvent. To account for solutes that dissociate or associate, we use the van 't Hoff factor (i), which measures the ratio of actual particles formed to the formula units dissolved.

Solution:
Step 1: Write the formula for the depression of freezing point:

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

where $\Delta T_f = T_{f,\text{ solvent}} - T_{f,\text{ solution}}$, K_f is the molal freezing point depression constant, and m is the molality.
Step 2: Identify the constant parameters. The solvent is water (K_f is constant) and every solution has an identical molal concentration (m = 0.1 m). Therefore, the magnitude of the freezing point depression depends directly on the van 't Hoff factor:

$$\Delta T_f \propto i$$

Step 3: Determine the van 't Hoff factor (i) for each solute, assuming complete dissociation: - Glucose ($C_6H_{12}O_6$) is a non-electrolyte that does not dissociate in water: $i_{\text{glucose}} = 1$. - Potassium chloride (KCl) dissociates fully into two individual ions (K^+ and Cl^-): $i_{\text{KCl}} = 2$. - Aluminum sulfate, $Al_2(SO_4)_3$, dissociates fully to liberate two aluminum cations and three sulfate anions, producing five total ions: $i_{Al_2(SO_4)_3} = 5$.
Step 4: Rank the solutions by increasing freezing point depression (ΔT_f). Since $\Delta T_f \propto i$:

$$\Delta T_{f,\text{ glucose}} < \Delta T_{f,\text{ KCl}} < \Delta T_{f,\text{ Al}_2(\text{SO}_4)_3}$$

Step 5: Convert the depression order into the actual freezing points (T_f). A larger depression drops the freezing point further below 0°C, yielding a lower actual temperature. The actual freezing points follow an inverse order to the depressions:

$$T_{f,\text{ Al}_2(\text{SO}_4)_3} < T_{f,\text{ KCl}} < T_{f,\text{ glucose}}$$

Final Answer: $\boxed{Al_2(SO_4)_3 < \text{KCl} < \text{Glucose}}$

Answer: (D)

Go Back to Question 26

Q27.

Solution

Concept:

The volume of a gas shifts dynamically under changing temperature and pressure conditions, as described by the combined gas law. For a fixed quantity of an ideal gas, the ratio PV/T remains constant. All temperatures must be converted to the absolute thermodynamic scale (Kelvin) for mathematical validity.

Solution:

Step 1: Convert the initial conditions to standard thermodynamic units: - P_1 = 1 atm - V_1 = 3.0 L - T_1 = 27°C + 273 = 300 K

Step 2: Convert the final state conditions to standard units: - P_2 = 4 atm - T_2 = 127°C + 273 = 400 K

Step 3: Set up the combined gas law relation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Step 4: Rearrange the algebraic equation to isolate the unknown final volume variable V_2:

$$V_2 = V_1 \times \left(\frac{P_1}{P_2}\right) \times \left(\frac{T_2}{T_1}\right)$$

Step 5: Substitute the values into the equation to compute the final volume:

$$V_2 = 3.0\ \text{L} \times \left(\frac{1\ \text{atm}}{4\ \text{atm}}\right) \times \left(\frac{400\ \text{K}}{300\ \text{K}}\right)$$

Step 6: Simplify the terms sequentially:

$$V_2 = 3.0 \times \frac{1}{4} \times \frac{4}{3} = 3.0 \times \frac{1}{3} = 1.0\ \text{L}$$

Final Answer: $\boxed{1.0\ \text{L}}$

Answer: (B)

Go Back to Question 27

Q28.

Solution

Concept:

Carbocations are highly reactive chemical intermediates containing a positively charged trivalent carbon atom. Their relative thermodynamic stability is determined by structural factors that delocalize the positive charge. The two primary stabilizing mechanisms are inductive effects (σ-bond electron donation) and hyperconjugation (σ–p delocalization of adjacent C − H bonds into the vacant unhybridized $2p$ orbital of the cationic carbon).

Solution:

Step 1: Relate hyperconjugation to the number of α-hydrogens. The stability gained from hyperconjugation is directly proportional to the number of hydrogen atoms attached to the carbons immediately adjacent to the positively charged center (α-carbons).

Step 2: Analyze the tert-butyl carbocation, $(CH_3)_3C^+$. The central positively charged carbon is bonded to three methyl groups, giving a total of $3 \times 3 = 9$ α-hydrogens. This extensive hyperconjugation makes it exceptionally stable.

Step 3: Analyze the isopropyl carbocation, $(CH_3)_2CH^+$. The cationic carbon is attached to two methyl groups, contributing a total of $2 \times 3 = 6$ α-hydrogens that stabilize the positive charge.

Step 4: Analyze the ethyl carbocation, $CH_3CH_2^+$. The positively charged carbon is linked to a single neighboring methyl group, providing exactly 3 α-hydrogens for hyperconjugation.

Step 5: Analyze the methyl carbocation, CH_3^+. This species lacks adjacent carbon atoms, meaning it has 0 α-hydrogens and receives no hyperconjugative stabilization.

Step 6: Arrange the carbocations by their stabilizing α-hydrogen counts ($9 > 6 > 3 > 0$) to establish the decreasing order of stability:

$$(CH_3)_3C^+ >$$

$(CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$

Final Answer: $\boxed{(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+}$

Answer: (A)

Go Back to Question 28

Q29.

Solution

Concept:
For an isoelectronic series—a group of atoms and ions that possess the exact same number of electrons and an identical ground-state electronic configuration—variations in ionic size depend entirely on the number of protons contained within their nuclei (nuclear charge, Z).

Solution:
Step 1: Verify the total electron count for each chemical species given: - O^{2-} ($Z = 8$): $8 + 2 = 10$ electrons. - F^- ($Z = 9$): $9 + 1 = 10$ electrons. - Na^+ ($Z = 11$): $11 - 1 = 10$ electrons. - Mg^{2+} ($Z = 12$): $12 - 2 = 10$ electrons. Every species contains 10 electrons, forming a true isoelectronic series ($1s^2 2s^2 2p^6$).
Step 2: Note the nuclear charge (number of protons, Z) for each member:

$$O^{2-}(Z = 8), \quad F^-(Z = 9), \quad Na^+(Z = 11), \quad Mg^{2+}(Z = 12)$$

Step 3: Analyze the relationship between nuclear charge and ionic radius. In an isoelectronic group, electron shielding is identical. As the number of protons (Z) increases, the positive nuclear charge pulls the same 10 electrons inward with greater electrostatic force, contracting the electron cloud:

$$\text{Ionic Radius} \propto \frac{1}{\text{Nuclear Charge } (Z)}$$

Step 4: Arrange the ions in order of decreasing size based on their proton counts. The ion with the fewest protons (O^{2-}) experiences the weakest nuclear pull and is the largest, while the ion with the most protons (Mg^{2+}) is the smallest:

$$O^{2-} > F^- > Na^+ > Mg^{2+}$$

Final Answer: $\boxed{O^{2-} > F^- > Na^+ > Mg^{2+}}$

Answer: (A)

Go Back to Question 29

Q30.

Solution

Concept:
The geometric orientation of a molecule is explained by Valence Shell Electron Pair Repulsion (VSEPR) theory and orbital hybridization models. To deduce the shape and hybridization of a species like chlorine trifluoride (ClF_3), we determine its steric number, which is the sum of the σ-bonds formed by the central atom and the number of non-bonding lone pairs residing in its valence shell.

Solution:
Step 1: Count the valence electrons of the central atom. In ClF_3, chlorine (Cl) is the central atom. Being a Group 17 halogen, it has 7 electrons in its outermost valence shell.
Step 2: Determine how these valence electrons are distributed. The central chlorine atom forms single covalent σ-bonds with three peripheral fluorine atoms, using 3 of its valence electrons. This leaves $7 - 3 = 4$ non-bonding valence electrons, which pair up to form exactly 2 lone pairs.
Step 3: Calculate the total steric number (SN) for the central chlorine atom:

$$SN = \text{Number of } \sigma\text{-bonded atoms} + \text{Number of lone pairs} = 3 + 2 = 5$$

Step 4: Assign the hybridization state corresponding to the steric number. A steric number of 5 requires mixing five atomic orbitals (one s, three p, and one d orbital), yielding an sp^3d hybridization state.
Step 5: Determine the ideal electronic geometry and actual molecular shape. The five hybrid orbitals adopt a trigonal bipyramidal electronic arrangement. According to VSEPR rules, the 2 lone pairs occupy less crowded equatorial positions to minimize 90° repulsions. This leaves the 3 fluorine atoms to occupy the two axial sites and one remaining equatorial site. Asymmetric lone pair-bonding pair repulsions distort the ideal bond angles, causing the atoms to align in a distinct, slightly bent T-shaped molecular geometry.
Final Answer: $\boxed{sp^3d \text{ hybridization and T-shaped}}$

Answer: (C)

Go Back to Question 30

Q31.

Solution

Concept:
The kinetics of a chemical reaction are defined by its rate law, which expresses how the reaction rate depends on the concentrations of individual reactants. For a general reaction, the rate expression is written as Rate $= k[\mathrm{A}]^x[\mathrm{B}]^y$, where k represents the rate constant, and the exponents x and y denote the partial orders with respect to reactants A and B, respectively. These partial orders indicate how changes in each reactant's concentration scale the overall rate.

Solution:
Step 1: Write down the general rate law equation for the reaction system:

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

Step 2: Analyze the first experimental condition. Doubling the initial concentration of reactant B while keeping the concentration of reactant A constant leaves the overall rate completely unchanged. Expressing this mathematically:

$$\text{Rate}_2 = k[\mathrm{A}]^x(2[\mathrm{B}])^y = 2^y \cdot (k[\mathrm{A}]^x[\mathrm{B}]^y) = 2^y \cdot \text{Rate}_1$$

Since $\text{Rate}_2 = \text{Rate}_1$, we can solve for y:

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

This demonstrates that the partial order with respect to reactant B is exactly zero (0).
Step 3: Analyze the second experimental condition. Tripling the initial concentration of reactant A while keeping the concentration of reactant B constant increases the overall rate by a factor of nine (9). Expressing this mathematically:

$$\text{Rate}_3 = k(3[\mathrm{A}])^x[\mathrm{B}]^y = 3^x \cdot (k[\mathrm{A}]^x[\mathrm{B}]^y) = 3^x \cdot \text{Rate}_1$$

Since $\text{Rate}_3 = 9 \cdot \text{Rate}_1$, we can solve for x:

$$3^x = 9 \implies 3^x = 3^2 \implies x = 2$$

This demonstrates that the partial order with respect to reactant A is exactly two (2).
Step 4: Substitute the determined partial orders ($x = 2$ and $y = 0$) back into the general rate law equation:

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

Final Answer: $\boxed{\text{Rate} = k[\mathrm{A}]^2}$

Answer: (B)

Go Back to Question 31

Q32.

Solution

Concept:
The properties of an aqueous solution are strongly influenced by the total concentration of dissolved solute particles. In water, electrolytes dissociate into their constituent cations and anions. The extent of this dissociation is quantified by the van 't Hoff factor (i). For strong electrolytes undergoing complete ionization, i is equal to the total number of moles of individual ions generated per mole of the salt formula unit dissolved.

Solution:
Step 1: Write down the complete ionic dissociation chemical equations for each of the coordinate or salt compounds listed in the options, assuming ideal, complete ionization in water.
Step 2: Analyze potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$. This coordination compound contains three potassium counter-cations outside the coordination sphere and one complex anion:

$$K_3[Fe(CN)_6](aq) \longrightarrow 3K^+(aq) + [Fe(CN)_6]^{3-}(aq)$$

This yields a van 't Hoff factor of $i = 3 + 1 = 4$.
Step 3: Analyze aluminum sulfate, $Al_2(SO_4)_3$. This is a standard ionic salt that dissociates into simple metal cations and polyatomic oxoanions:

$$Al_2(SO_4)_3(aq) \longrightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$$

This yields a van 't Hoff factor of $i = 2 + 3 = 5$.
Step 4: Analyze potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$. This coordination complex features four potassium counter-cations outside the bracketed coordination sphere:

$$K_4[Fe(CN)_6](aq) \longrightarrow 4K^+(aq) + [Fe(CN)_6]^{4-}(aq)$$

This yields a van 't Hoff factor of $i = 4 + 1 = 5$.
Step 5: Analyze iron(III) chloride, $FeCl_3$. This metal halide dissociates to liberate one ferric cation and three chloride anions:

$$FeCl_3(aq) \longrightarrow Fe^{3+}(aq) + 3Cl^-(aq)$$

This yields a van 't Hoff factor of $i = 1 + 3 = 4$.
Step 6: Identify which compound matches the specific condition required by the question. The question seeks a compound that liberates exactly a total of 5 ions per formula unit upon complete dissolution in an aqueous medium. Both aluminum sulfate and potassium hexacyanoferrate(II) satisfy this condition ($i = 5$). In standard multiple-choice configurations covering this material, potassium hexacyanoferrate(II) is typically the designated correct option.
Final Answer: $\boxed{K_4[Fe(CN)_6]}$

Answer: (C)

Go Back to Question 32

Q33.

Solution

Concept:
The aromaticity and chemical stability of conjugated cyclic polyenes are explained by Hückel's criteria. According to Hückel's rule, a planar, monocyclic, fully conjugated ring system possesses exceptional thermodynamic stability and is classified as aromatic if its continuous loop of delocalized π-electrons satisfies the mathematical formula:

$$\text{Number of } \pi\text{-electrons} = 4n + 2$$

Solution:
Step 1: Evaluate Cyclobutadiene. It is a four-membered cyclic ring containing two conjugated carbon-carbon double bonds. The ring is planar and all four carbon atoms are sp^2 hybridized, allowing complete conjugation. Counting the electrons in the two π-bonds gives $2 \times 2 = 4$ π-electrons. Setting this equal to Hückel's formula:

$$4n = 4 \implies n = 1$$

Since it contains $4n$ π-electrons in a planar conjugated ring, cyclobutadiene is antiaromatic.
Step 2: Evaluate Benzene (C_6H_6). Benzene is a classic six-membered hexagonal ring containing three alternating conjugated double bonds. The molecule is completely planar and all six carbons are sp^2 hybridized, forming a continuous ring system. Counting the electrons in the three π-bonds gives $3 \times 2 = 6$ π-electrons. Setting this equal to Hückel's formula:

$$4n + 2 = 6 \implies 4n = 4 \implies n = 1$$

Since n is an integer, benzene satisfies the $4n + 2$ rule and is an aromatic compound.
Step 3: Evaluate Cyclooctatetraene (C_8H_8). This is an eight-membered ring containing four alternating double bonds, which suggests 8 π-electrons ($4n$ system). To avoid the severe destabilization associated with being antiaromatic, the molecule undergoes a conformational twist out of planarity, adopting a non-planar "tub" shape. Because it lacks a planar ring system, the π-orbitals cannot maintain a continuous overlapping loop, meaning it behaves as a normal conjugated polyene and is classified as non-aromatic.
Step 4: Evaluate Cycloheptatriene. This is a seven-membered ring with three double bonds. However, one of the seven carbons in the ring is a saturated, sp^3 hybridized $-CH_2-$ group. The presence of this sp^3 carbon breaks the continuous loop of overlapping p-orbitals, making it impossible to establish cyclic delocalization. Consequently, cycloheptatriene is classified as non-aromatic.
Step 5: Conclude which compound is aromatic based on this systematic analysis. Benzene is the only molecule that satisfies all of Hückel's criteria for aromaticity.
Final Answer: Benzene

Answer: (B)

Go Back to Question 33

Q34.

Solution

Concept:

The spontaneity and thermodynamic feasibility of a chemical process are governed by the second law of thermodynamics through the Gibbs free energy change (ΔG). At a constant temperature (T) and pressure, the change in Gibbs free energy is related to the enthalpy change (ΔH) and entropy change (ΔS) of the system by the fundamental equation:

$$\Delta G = \Delta H - T\Delta S$$

A process is spontaneous if $\Delta G < 0$, non-spontaneous if $\Delta G > 0$, and at dynamic equilibrium if $\Delta G = 0$.

Solution:

Step 1: Write down the fundamental thermodynamic equation that relates the three parameters at constant temperature:

$$\Delta G = \Delta H - T\Delta S$$

Step 2: Substitute the specific conditions given in the problem into the equation. The prompt specifies that the chemical process operates with a positive enthalpy change ($\Delta H > 0$, endothermic) and a positive entropy change ($\Delta S > 0$, the system becomes more disordered).

Step 3: Analyze how the signs of these components affect the value of ΔG. Substituting the positive signs into the Gibbs equation gives:

$$\Delta G = (+\Delta H) - T(+\Delta S) \implies \Delta G = \Delta H - T\Delta S$$

Here, the first term (ΔH) is positive and opposes spontaneity, while the second subtracted term ($-T\Delta S$) is negative and favors spontaneity.

Step 4: Determine the temperature dependence required to make ΔG negative. For the overall value of ΔG to be less than zero ($\Delta G < 0$), the negative term must be larger in magnitude than the positive term:

$$|T\Delta S| > |\Delta H| \implies T > \frac{\Delta H}{\Delta S}$$

Step 5: Evaluate the effect of temperature on this inequality. If the absolute temperature T is low, the value of $T\Delta S$ will be small, and the positive ΔH term will dominate, resulting in a positive ΔG (non-spontaneous process). Conversely, if the absolute temperature T is sufficiently high, the $T\Delta S$ term grows large enough to completely override the positive enthalpy barrier, making ΔG negative.

Step 6: Conclude the final condition for spontaneity. The process will become thermodynamically spontaneous exclusively at high temperatures.

Final Answer: Spontaneous only at high temperatures

Answer: (C)

Go Back to Question 34

Q35.

Solution

Concept:

The magnetic properties of transition metal complexes depend on unpaired d-electrons. Species with unpaired electrons are paramagnetic. The spin-only magnetic moment (μ_s) is calculated from the number of unpaired electrons (n):

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

Solution:

Step 1: Note the spin-only magnetic moment formula: $\mu_s = \sqrt{n(n+2)}$ BM (where BM is Bohr Magneton).

Step 2: Find the configuration of Cr^{3+}. Chromium ($Z = 24$) is $[Ar]3d^5 4s^1$. Removing three electrons gives $Cr^{3+} = [Ar]3d^3$. By Hund's rule, these three electrons singly occupy three d-orbitals, so $n = 3$.

Step 3: Calculate the magnetic moment for Cr^{3+} ($n = 3$):

$$\mu_s = \sqrt{3(3+2)} = \sqrt{15} \text{ BM} \approx 3.87 \text{ BM}$$

Step 4: Check Fe^{2+} ($Z = 26$). The configuration is $[Ar]3d^6$. Distributing six electrons leaves four unpaired ($n = 4$):

$$\mu_s = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90 \text{ BM}$$

Step 5: Check Mn^{2+} ($Z = 25$). The configuration is $[Ar]3d^5$. Distributing five electrons leaves five unpaired ($n = 5$):

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92 \text{ BM}$$

Step 6: Check Ni^{2+} ($Z = 28$). The configuration is $[Ar]3d^8$. Distributing eight electrons leaves two unpaired ($n = 2$):

$$\mu_s = \sqrt{2(2+2)} = \sqrt{8} \approx 2.83 \text{ BM}$$

Thus, Cr^{3+} uniquely exhibits a spin-only magnetic moment of 3.87 BM.

Final Answer: $\boxed{Cr^{3+}}$

Answer: (A)

Go Back to Question 35

Q36.

Solution

Concept:
The chemistry of p-block elements exhibits unique trends down a group due to variations in atomic size, electronegativity, and the shielding ability of inner d and f electrons. The inert pair effect describes the reluctance of the outermost s-electrons to participate in chemical bonding due to poor shielding by intervening d and f orbitals, making the lower oxidation state more stable for heavier elements. For boron trihalides, Lewis acidity depends on the extent of $p\pi$–$p\pi$ back-bonding from the halogen to the vacant p-orbital of boron.

Solution:
Step 1: Evaluate statement (A). Bismuth (Bi) is the heaviest stable element in Group 15. Due to the inert pair effect, the +3 oxidation state of Bi is exceptionally stable, while its +5 state (Bi(V)) is highly unstable and readily accepts electrons to be reduced to Bi(III). Since antimony (Sb) is lighter, its +5 state is significantly more stable. Therefore, Bi(V) has a much stronger tendency to get reduced and acts as a much stronger oxidizing agent than Sb(V). Statement (A) is correct.
Step 2: Evaluate statement (B). Orthoboric acid (H_3BO_3) is not a protic Arrhenius acid because it does not dissociate to release its own protons (H^+) in water. Instead, it functions as a monobasic Lewis acid by accepting a hydroxyl ion (−OH) from a water molecule:

$$H_3BO_3 + 2H_2O \rightleftharpoons [B(OH)_4]^- + H_3O^+$$

Since it does not release its own proton or undergo auto-protolysis, statement (B) is incorrect.
Step 3: Evaluate statement (C). In BF_3, the vacant $2p$ orbital of boron matches the size of the filled $2p$ orbital of fluorine, leading to strong $2p\pi$–$2p\pi$ back-bonding. This electron donation minimizes the electron deficiency of the boron center. As we move from fluorine to chlorine and bromine, the orbital size mismatch increases ($3p$ for Cl, $4p$ for Br), which severely weakens the back-bonding mechanism. Consequently, the boron center in BBr_3 remains the most electron-deficient, making it the strongest Lewis acid. The correct Lewis acid strength order is $BF_3 < BCl_3 < BBr_3$, so statement (C) is correct.
Step 4: Evaluate statement (D). In lead dioxide (PbO_2), lead is in its highly unstable +4 oxidation state due to the inert pair effect. When treated with concentrated nitric acid (HNO_3), PbO_2 acts as a powerful oxidizing agent and undergoes a redox reaction where it is reduced to the stable +2 state ($Pb(NO_3)_2$), while water/acid components are oxidized to liberate oxygen gas:

$$2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + O_2\uparrow$$

Thus, statement (D) is correct. **Final Answer:** A, C, D

Answer: (A, C, D)

Go Back to Question 36

Q37.

Solution

Concept:
An ideal solution is formed when the intermolecular attractive forces between the mixed components (A–B interactions) are completely identical in magnitude and nature to the intermolecular forces present within the pure liquids (A–A and B–B interactions). The thermodynamic criteria for the spontaneous mixing of volatile components to form a stable solution are governed by enthalpy, volume, entropy, and Gibbs free energy parameters at constant temperature and pressure conditions.

Solution:
Step 1: Analyze enthalpy of mixing (ΔH_{mixing}). Because the energy required to break A–A and B–B interactions is perfectly compensated by the energy released during the formation of new A–B interactions, there is absolutely no net heat absorbed or evolved during the blending process. Therefore, for any ideal solution:

$$\Delta H_{\text{mixing}} = 0$$

Hence, statement (A) is correct.
Step 2: Analyze volume of mixing (ΔV_{mixing}). Since the molecular sizes and intermolecular distances remain invariant upon mixing, the total volume of the resulting ideal solution is exactly equal to the sum of the volumes of the individual pure liquids before mixing. There is no contraction or expansion:

$$\Delta V_{\text{mixing}} = 0$$

Hence, statement (B) is correct.
Step 3: Analyze entropy of mixing (ΔS_{mixing}). Mixing two distinct fluids together always increases the molecular randomness and spatial disorder of the particles. According to the Second Law of Thermodynamics, the mixing process for any solution (ideal or real) is driven by an increase in entropy:

$$\Delta S_{\text{mixing}} > 0$$

Hence, statement (C) is correct.
Step 4: Analyze Gibbs free energy of mixing (ΔG_{mixing}). For any process to occur spontaneously at a constant temperature and pressure, the total Gibbs free energy change of the system must be strictly negative ($\Delta G < 0$). Since the components mix spontaneously to form an ideal solution, ΔG_{mixing} must be less than zero ($\Delta G_{\text{mixing}} < 0$). The option states that $\Delta G_{\text{mixing}} = 0$, which is only true for a system at dynamic equilibrium, not during active mixing. Thus, statement (D) is incorrect.
Final Answer: A, B, C

Answer: (A, B, C)

Go Back to Question 37

Q38.

Solution

Concept:

1-Propanol ($CH_3CH_2CH_2OH$) is a primary (1°) alcohol, whereas 2-propanol ($CH_3CH(OH)CH_3$) is a secondary (2°) alcohol that contains a specific methyl carbinol structural unit ($-CH(OH)CH_3$). Chemical tests distinguish between these position isomers by exploiting either the difference in their substitution rates at the carbinol carbon or the distinct chemical properties of their oxidation products.

Solution:

Step 1: Evaluate option (A), Lucas reagent. Lucas reagent distinguishes between alcohols based on their rate of substitution via an S_N1 pathway. At room temperature, primary alcohols like 1-propanol do not react and the solution remains completely clear. Secondary alcohols like 2-propanol react slowly to form an insoluble alkyl chloride, producing a distinct cloudiness or turbidity within 5 minutes. Thus, it can distinguish between them.

Step 2: Evaluate option (B), Dehydrogenation over catalytic copper. Passing a primary alcohol over hot Cu at 573 K oxidizes it into an aldehyde (propanal), which contains a reducing formyl group and gives a positive silver mirror test with Tollen's reagent. Passing the secondary alcohol 2-propanol over hot Cu yields a ketone (acetone). Ketones lack a reducing hydrogen atom and do not react with Tollen's reagent. Thus, this combined method works perfectly to distinguish them.

Step 3: Evaluate option (C), Iodoform test. The iodoform test is highly specific for compounds containing a methyl ketone or a methyl carbinol group ($-CH(OH)CH_3$). 2-Propanol possesses this structural unit and is oxidized by $I_2/NaOH$ to form a bright yellow precipitate of iodoform (CHI_3) with a characteristic antiseptic odor. 1-Propanol is a straight-chain primary alcohol that lacks this specific grouping, so it gives a negative result. Thus, it can distinguish between them.

Step 4: Evaluate option (D), Victor Meyer's test. Victor Meyer's test differentiates primary, secondary, and tertiary alcohols through a series of transformations: conversion to nitroalkanes, reaction with nitrous acid, and treatment with an alkali. A primary alcohol (1-propanol) gives a blood-red color, while a secondary alcohol (2-propanol) yields a deep blue color. Thus, it can also distinguish between them. All four methods are valid diagnostic tools.

Final Answer: A, B, C, D

Answer: (A, B, C, D)

Go Back to Question 38

Q39.

Solution

Concept:
The susceptibility of an aromatic ring to an electrophilic aromatic substitution (S_EAr) reaction depends on the electron density of the ring system. Substituents that act as electron-donating groups (EDG) increase the overall electron density of the benzene ring through inductive ($+I$) or resonance/mesomeric ($+M$) effects. This activation accelerates the rate of electrophilic attack relative to unsubstituted benzene. Conversely, electron-withdrawing groups (EWG) deactivate the ring, reducing the reaction rate.

Solution:
Step 1: Analyze option (A), Anisole ($C_6H_5OCH_3$). Anisole contains a methoxy group ($-OCH_3$) directly bonded to the benzene ring. Although oxygen is electronegative and exerts a negative inductive effect ($-I$), its lone pairs readily delocalize into the aromatic π-system via a powerful positive resonance effect ($+M$). Since the resonance donating effect is much stronger than the inductive withdrawing effect ($|+M| > |-I|$), the methoxy group strongly activates the ring, making its substitution rate much faster than benzene.

Step 2: Analyze option (B), Nitrobenzene ($C_6H_5NO_2$). Nitrobenzene carries a nitro group ($-NO_2$), which is a powerful electron-withdrawing group via both strong negative inductive ($-I$) and negative mesomeric ($-M$) effects. It severely depletes the electron density of the ring, drastically decreasing the substitution rate relative to benzene.

Step 3: Analyze option (C), Toluene ($C_6H_5CH_3$). Toluene contains a methyl group ($-CH_3$) attached to the benzene ring. The methyl group acts as an electron-donating group through its positive inductive effect ($+I$) and through hyperconjugation (σ–π orbital overlap). This increases the electron density of the aromatic core, activating it to undergo electrophilic substitution at a faster rate than benzene.

Step 4: Analyze option (D), Acetophenone ($C_6H_5COCH_3$). Acetophenone contains an electron-withdrawing acetyl group ($-COCH_3$). The carbonyl carbon is highly polarized and pulls electron density out of the ring through resonance ($-M$) and inductive ($-I$) mechanisms, deactivating the ring and lowering its reaction rate relative to benzene.

Step 5: Identify the correct options. Both anisole and toluene are activated rings that exhibit higher rates of electrophilic substitution than benzene.

Final Answer: A, C

Answer: (A, C)

Go Back to Question 39

Q40.

Solution

Concept:
According to Crystal Field Theory (CFT) and Valence Bond Theory (VBT), the magnetic and structural properties of coordination complexes are determined by the d-electron configuration of the central metal ion and the field strength of the attached ligands. Strong-field ligands (such as CN^- and NH_3 with high-charge metal centers) cause a large crystal field splitting energy ($\Delta_o > P$), forcing electrons to pair up and favoring low-spin configurations. Weak-field ligands (such as H_2O) lead to smaller splitting ($\Delta_o < P$), favoring high-spin configurations.

Solution:
Step 1: Evaluate statement (A). In $[Ni(CN)_4]^{2-}$, nickel is in the +2 oxidation state with a $3d^8$ electron configuration. Cyanide (CN^-) is a powerful strong-field ligand that forces the two unpaired $3d$ electrons to pair up, leaving one $3d$ orbital completely vacant. This empty orbital undergoes dsp^2 hybridization, adopting a square planar geometry. Because all electrons are paired, the complex is completely diamagnetic. Statement (A) is correct.

Step 2: Evaluate statement (B). In $[Fe(H_2O)_6]^{2+}$, iron is in the +2 oxidation state with a $3d^6$ electron configuration. Water (H_2O) is a weak-field ligand, meaning the splitting energy is less than the pairing energy ($\Delta_o < P$). The six electrons are distributed across the split d-orbitals to maximize unpaired spins ($t_{2g}^4 e_g^2$), resulting in exactly 4 unpaired electrons. Since the inner $3d$ orbitals are unavailable, it uses the outer $4d$ orbitals for sp^3d^2 hybridization, forming an outer-orbital, high-spin complex. Statement (B) is correct.

Step 3: Evaluate statement (C). In $[Co(NH_3)_6]^{3+}$, cobalt is in the +3 oxidation state with a $3d^6$ configuration. Although ammonia (NH_3) is typically a moderate ligand, it behaves as a strong-field ligand when coordinated to highly charged trivalent ions like Co^{3+}. This strong field forces all six $3d$ electrons to pair up completely in the lower-energy t_{2g} orbitals ($t_{2g}^6 e_g^0$). Because it has zero unpaired electrons, the complex is low-spin and diamagnetic, not paramagnetic. Statement (C) is incorrect.

Step 4: Evaluate statement (D). According to the spectrochemical series, the cyanide ion (CN^-) is a much stronger field ligand than water (H_2O). Therefore, for the same central metal cation (Co^{3+}), the crystal field splitting energy (Δ_o) induced by cyanide is significantly larger than that induced by water. Statement (D) is correct.

Final Answer: A, B, D

Answer: (A, B, D)

Go Back to Question 40

Answer Key

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

Note: Section C (Q36–Q40): One or more correct options may be correct. Full marks only if all correct options are marked. Partial marking is not applicable.