WBJEE Chemistry Sample Paper-5

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

Instructions

- This paper contains **40** Multiple Choice Questions divided into **3 Sections**.
- **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. A crystalline hydrated metal sulfate salt contains 49.6% water of crystallization by mass. If the anhydrous metal sulfate has a molar mass of 152 g/mol, what is the total number of water molecules bound per formula unit of this salt?

(A) 2

(B) 5

(C) 7

(D) 10

Q2. An aqueous solution of a non-volatile solute has a molality of 2.5 m. What is the precise mole fraction of the solute within this solution?

(A) 0.043

(B) 0.025

(C) 0.057

(D) 0.082

Q3. For a hydrogenic atom, the radius of a given Bohr orbit is observed to be numerically equal to its de Broglie wavelength for an electron traveling in that orbit. Which principal quantum shell (n) is the electron currently occupying?

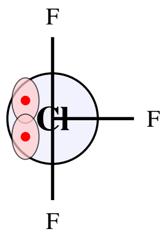
(A) $n = 1$

(B) $n = 2$

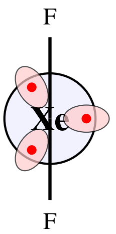
(C) $n = 3$

(D) $n = 4$

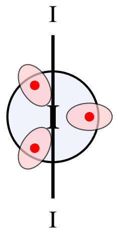
Q4. Among the following chemical species, which one contains the maximum number of lone pairs residing explicitly on its central atom?



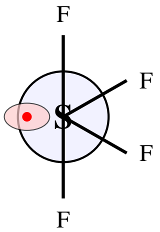
(A) ClF_3 (2 LPs)



(B) XeF_2 (3 LPs)



(C) I_3^- (3 LPs)



(D) SF_4 (1 LP)

(A) ClF_3

(B) XeF_2

(C) I_3^-

(D) SF_4

Q5. A gas mixture contains equal masses of He, CH_4, and SO_2 enclosed in a rigid vessel at a constant temperature. If the total pressure of the container is 2.1 atm, what is the partial pressure exerted specifically by the methane gas?

(A) 0.70 atm

(B) 0.40 atm

(C) 0.52 atm

(D) 0.35 atm

Q6. For the self-ionization of liquid water at 298 K expressed as:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The standard Gibbs free energy change (ΔG°) is closest to which value? (Given $\ln 10 \approx 2.303$, $R = 8.314$ J/mol · K)

(A) 0 kJ/mol

(B) −79.9 kJ/mol

(C) +79.9 kJ/mol

(D) +39.9 kJ/mol

Q7. The conjugate acid of the Bronsted-Lowry base HPO_4^{2-} is correctly represented by which of the following chemical species?

(A) $H_2PO_4^-$

(B) H_3PO_4

(C) PO_4^{3-}

(D) $H_2PO_4^{2-}$

Q8. For a gaseous elementary reaction $2X + Y \rightarrow Z$, the initial volume of the reaction vessel is suddenly reduced to exactly half of its original value while keeping the temperature constant. By what factor will the total rate of the reaction change?

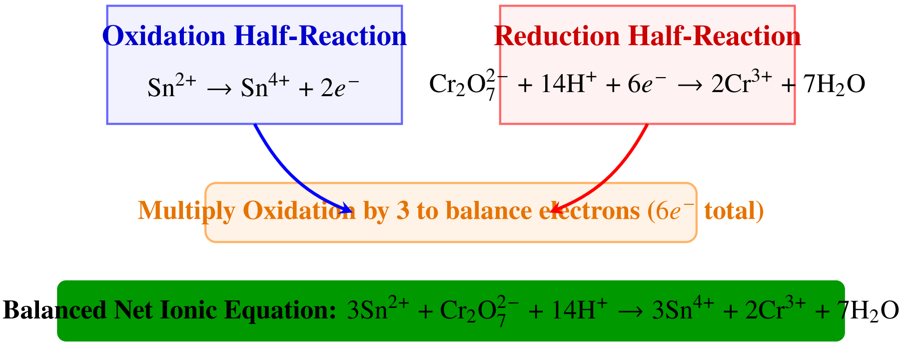
(A) Increases by 4 times

(B) Increases by 8 times

(C) Decreases by 4 times

(D) Remains completely unchanged

Q9. What is the net number of electrons transferred in the balanced molecular chemical equation when 1 mole of stannous ions (Sn^{2+}) is completely oxidized by acidified potassium dichromate ($K_2Cr_2O_7$) solution?



(A) 2

(B) 4

(C) 6

(D) 3

Q10. The limiting molar conductivities (Λ_m°) of NaCl, HCl, and CH_3COONa are 126.4, 426.1, and 91.0 $S \cdot cm^2/mol$ respectively. What is the limiting molar conductivity (Λ_m°) for a pure aqueous solution of acetic acid (CH_3COOH)?

(A) $516.5\ S \cdot cm^2/mol$

(B) $390.7\ S \cdot cm^2/mol$

(C) $208.7\ S \cdot cm^2/mol$

(D) $291.5\ S \cdot cm^2/mol$

Q11. When metallic sodium is dissolved in a vast excess of pure liquid ammonia under moisture-free conditions, a deep blue, highly conducting solution is formed. This characteristic color arises primarily due to the absorption of light by which species?

(A) Sodium hydride clusters

(B) Ammoniated electrons

(C) Sodium amide complexes

(D) Solvated Na_2 dimers

Q12. Which of the following group-15 trihalides behaves as the weakest Lewis base due to the highest electronegativity difference and significant steric/electronic factors?

(A) NF_3

(B) NCl_3

(C) PCl_3

(D) $AsCl_3$

Q13. In the industrial extraction of noble gases, which structural framework or chemical reagent is famously utilized to form true crystalline clathrate compounds with heavier noble gases like Xenon under pressure?

(A) Zeolite-Y matrix

(B) 1,4-Dihydroxybenzene (Quinol)

(C) Activated charcoal beds

(D) Phosphorus pentoxide granules

Q14. The standard reduction potential ($E°$) for the M^{3+}/M^{2+} redox couple displays an anomalously high positive value for manganese (Mn) compared to chromium (Cr) and iron (Fe). This anomaly is fundamentally explained by:

(A) The extra stability associated with the d^5 electronic configuration of Mn^{2+}

(B) The high third ionization enthalpy of chromium

(C) The exceptionally small ionic radius of Mn^{3+}

(D) Splitting values of the e_g orbitals in an aqueous medium

Q15. What is the structural relationship between the coordination complex pairs $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5(Br)]SO_4$?

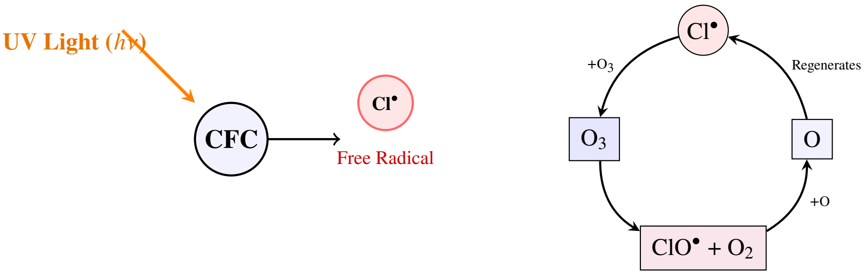
(A) Linkage isomerism

(B) Coordination isomerism

(C) Ionization isomerism

(D) Solvate isomerism

Q16. Which atmospheric chemical mechanism is primarily responsible for the continuous, catalytic depletion of the stratospheric ozone layer by chlorofluorocarbons (CFCs)?



(A) Heterolytic cleavage generating carbocations

(B) Homolytic cleavage by UV light generating chlorine free radicals

(C) Oxidation of CFCs into chlorine dioxide molecules

(D) Nucleophilic displacement by singlet oxygen atoms

Q17. What is the correct systematic IUPAC name for the organic molecule represented below?

$$CH_2 = CH - CH(CH_3) - C \equiv CH$$

(A) 3-Methylpent-4-en-1-yne

(B) 3-Methylpent-1-en-4-yne

(C) 3-Methylpent-1-yne-4-ene

(D) Hex-1-en-4-yne

Q18. Arrange the following reactive intermediates in the correct sequence of their decreasing thermodynamic stability:

$$\text{(I) } (CH_3)_3C^+ \quad \text{(II) } CH_3 - CH_2 - CH_2^+ \quad \text{(III) } CH_2 = CH - CH_2^+$$

(A) I > II > III

(B) I > III > II

(C) III > I > II

(D) II > III > I

Q19. When propyne ($CH_3 - C \equiv CH$) undergoes hydration by treatment with dilute H_2SO_4 in the presence of $HgSO_4$ catalyst at 333 K, what is the final isolated stable organic product?

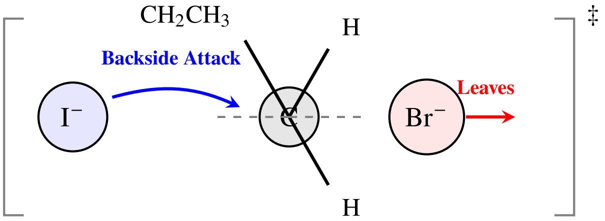
(A) Propanal

(B) Acetone

(C) Allyl alcohol

(D) Propanoic acid

Q20. Which of the following alkyl halides will undergo the fastest rate of nucleophilic substitution via a bimolecular (S_N2) pathway when reacted with sodium iodide in acetone?



(A) $CH_3 - CH_2 - CH_2 - Cl$

(B) $CH_3 - CH_2 - CH_2 - Br$

(C) $(CH_3)_2CH - Br$

(D) $(CH_3)_3C - Br$

Q21. When phenyl methyl ether (Anisole) is cleaved by heating with one equivalent of concentrated hydroiodic acid (HI), the products obtained are:

(A) Phenol and Methyl Iodide

(B) Iodobenzene and Methanol

(C) Iodobenzene and Methyl Iodide

(D) Phenol and Methanol

Q22. An organic carbonyl compound undergoes a cross-Cannizzaro reaction when treated with concentrated aqueous sodium hydroxide in the presence of excess formaldehyde (HCHO). The correct pathway involves:

(A) Oxidation of the carbonyl compound and reduction of formaldehyde

(B) Reduction of the carbonyl compound and oxidation of formaldehyde to sodium formate

(C) Self-condensation of both species to form β-hydroxy aldehydes

(D) Disproportionation of formaldehyde exclusively

Q23. When benzamide ($C_6H_5CONH_2$) is treated with a mixture of bromine (Br_2) and aqueous potassium hydroxide (KOH), the intermediate primary organic product degrades down to yield:

(A) Benzylamine

(B) Aniline

(C) Bromobenzene

(D) Nitrobenzene

Q24. The structural feature that differentiates amylose from amylopectin within a starch macromolecular complex is:

(A) Amylose contains α-(1,4) glycosidic linkages and is unbranched, while amylopectin additionally features α-(1,6) branching linkages.

(B) Amylose consists entirely of β-D-glucose units.

(C) Amylopectin is completely water-soluble and possesses non-reducing terminals only.

(D) Amylose contains only α-(1,6) glycosidic linkages.

Q25. The elastomer known commercially as "Buna-N" is a synthetic addition copolymer produced by the radical co-polymerization of 1,3-butadiene alongside which monomer?

(A) Styrene

(B) Acrylonitrile

(C) Chloroprene

(D) Vinyl chloride

Q26. What is the total number of radial nodes and angular nodes present within a $4p$ atomic orbital of a hydrogen atom?

(A) 2 radial nodes, 1 angular node

(B) 1 radial node, 2 angular nodes

(C) 3 radial nodes, 0 angular nodes

(D) 2 radial nodes, 2 angular nodes

Q27. According to Molecular Orbital Theory, which of the following diatomic species exhibits a bond order of 2.5 and is simultaneously paramagnetic in its ground electronic state?

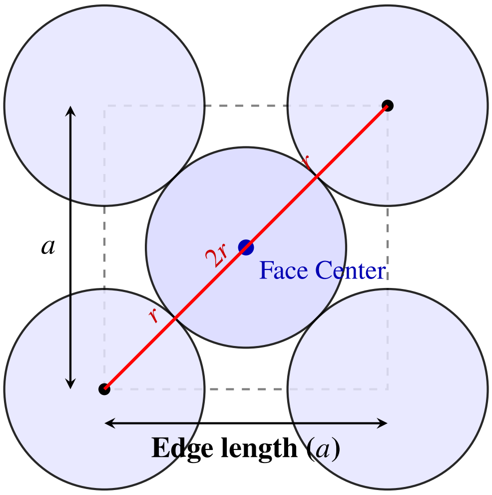
(A) O_2

(B) N_2^+

(C) O_2^+

(D) C_2

Q28. An element crystallizes in a face-centered cubic (fcc) lattice arrangement. If the length of the unit cell edge is a, what is the closest distance of approach between any two adjacent atoms in this crystal lattice?



(A) $a/2$

(B) $a\sqrt{2}$

(C) $a/\sqrt{2}$

(D) $a\sqrt{3}/2$

Q29. At a given temperature, a saturated solution of a sparingly soluble salt M_2X_3 has a molar solubility denoted by S mol/L. What is the correct mathematical formulation relating its solubility product (K_{sp}) to S?

(A) $K_{sp} = 6S^5$

(B) $K_{sp} = 27S^4$

(C) $K_{sp} = 108S^5$

(D) $K_{sp} = 4S^3$

Q30. Among the following alkaline earth metal sulfates, which one exhibits the highest hydration enthalpy value, causing it to be highly soluble in water relative to the others?

(A) $BeSO_4$

(B) $MgSO_4$

(C) $CaSO_4$

(D) $BaSO_4$

Section–B — 5 Questions × 2 Marks Each
(Negative Marking: −0.5) [Single Correct]

Q31. A 0.50 g sample of an iron ore containing pure oxalic acid and oxalate salts is completely dissolved and requires 24.0 mL of 0.02 M $KMnO_4$ solution for full oxidation in an acidic environment. If another identical sample requires 30.0 mL of 0.10 M NaOH for a simple acid-base neutralization, what is the weight percentage of free oxalic acid ($H_2C_2O_4$) in the ore? (Molar mass of $H_2C_2O_4$ = 90 g/mol)

(A) 18.5%

(B) 27.0%

(C) 36.2%

(D) 54.0%

Q32. For a parallel decomposition reaction pathway where reactant A simultaneously converts into products B and C via two independent first-order mechanisms:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \quad \text{and} \quad \mathrm{A} \xrightarrow{k_2} \mathrm{C}$$

The activation energies for these paths are $E_{a1} = 80\,\text{kJ/mol}$ and $E_{a2} = 120\,\text{kJ/mol}$ respectively. What is the effective net activation energy ($E_{a,\text{eff}}$) for the overall disappearance of reactant A expressed in terms of individual rate constants?

(A) $E_{a,\text{eff}} = \frac{k_1E_{a1}+k_2E_{a2}}{k_1+k_2}$

(B) $E_{a,\text{eff}} = E_{a1} + E_{a2}$

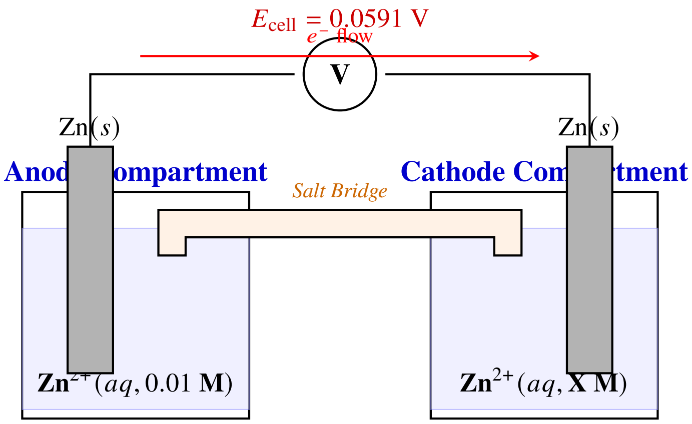
(C) $E_{a,\text{eff}} = \sqrt{E_{a1} \cdot E_{a2}}$

(D) $E_{a,\text{eff}} = \frac{E_{a1}+E_{a2}}{2}$

Q33. Consider a concentration cell at 298 K:

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq, 0.01\ \mathrm{M}) \parallel \mathrm{Zn}^{2+}(aq, \mathrm{X\ M}) \mid \mathrm{Zn}(s)$$

If the measured electromotive force (EMF) of this cell is exactly 0.0591 V, what is the value of the unknown concentration X? (Assume $\frac{2.303RT}{F} = 0.0591$ V)



(A) 1.0 M

(B) 0.1 M

(C) 2.0 M

(D) 0.001 M

Q34. A homoleptic octahedral coordination complex of a d^6 transition metal ion with a weak-field ligand exhibits an experimental crystal field stabilization energy (CFSE) value of $-0.4\ \Delta_o$. If the same metal ion forms a low-spin octahedral complex with a strong-field ligand, what will be the new net CFSE value (excluding pairing energy terms)?

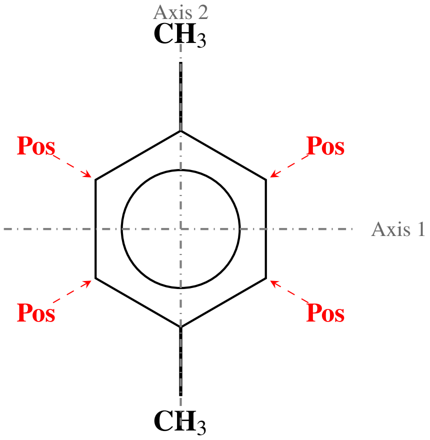
(A) $-1.2\ \Delta_o$

(B) $-2.4\ \Delta_o$

(C) $-1.8\ \Delta_o$

(D) $0.0\ \Delta_o$

Q35. An aromatic hydrocarbon (C_8H_{10}) undergoes vigorous oxidation with hot alkaline $KMnO_4$ followed by acidification to yield a single dicarboxylic acid ($C_8H_6O_4$). When this dicarboxylic acid is heated with soda lime, benzene is recovered. If the original hydrocarbon undergoes mononitration to yield only one structural isomer, what is its identity?



(A) *o*-Xylene

(B) *m*-Xylene

(C) *p*-Xylene

(D) Ethylbenzene

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

Q36. For an ideal gas undergoing a perfectly adiabatic reversible expansion against a finite external pressure, which of the following thermodynamic state relations or descriptions are entirely correct?

(A) $\Delta S_{\text{system}} = 0$

(B) $\Delta S_{\text{surroundings}} = 0$

(C) $T \cdot V^{\gamma-1} = \text{Constant}$

(D) The internal energy of the system increases continuously.

Q37. Which of the following statements regarding the chemistry and properties of Lanthanides and Actinides are scientifically correct?

(A) Actinides display a wider range of oxidation states than lanthanides due to the smaller energy gap between $5f$, $6d$, and $7s$ subshells.

(B) The ionic radii of tripositive lanthanide ions (Ln^{3+}) decrease steadily with increasing atomic number due to poor shielding by $4f$ electrons.

(C) All lanthanide elements are highly radioactive synthetic elements.

(D) Lanthanide complexes show exceptionally high covalent character compared to transition metals.

Q38. When chlorobenzene is subjected to nucleophilic aromatic substitution reactions (S_{Ar}), which structural modifications or conditions will drastically accelerate the rate of displacement of the chloride ion?

(A) Introducing a strong electron-withdrawing nitro group ($-NO_2$) at the *ortho* position.

(B) Introducing a strong electron-withdrawing nitro group ($-NO_2$) at the *para* position.

(C) Introducing an electron-donating methyl group ($-CH_3$) at the *meta* position.

(D) Carrying out the reaction in a highly non-polar solvent like hexane.

Q39. Which of the following given organic compounds will cleanly form a distinct silver mirror deposit when warmed with Tollens' reagent ($[Ag(NH_3)_2]^+$)?

(A) Benzaldehyde

(B) Glucose

(C) Fructose

(D) Formic Acid

Q40. Which of the following chemical pairs or compounds undergo true intramolecular redox reactions (thermal disproportionation/decomposition) upon heating?

(A) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

(B) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(C) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

(D) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

Detailed Solutions

Q1.

Solution

Concept:
In chemical stoichiometry, understanding the relative composition of elements and mass percent within a hydrated crystal lattice allows the structural determination of compounds. The total mass of a crystalline sample is the collective contribution of the anhydrous component weight added to the mass of its structural water units. By analyzing the percent mass contribution of water molecules trapped within the lattice, we can accurately establish the molar ratio between the volatile water fragments and the stable formula unit of the core metallic salt.

Solution:

(a) The given hydrated compound contains 49.6% water of crystallization by mass. This implies that in a 100 g sample of the hydrated crystal, the mass of water is exactly 49.6 g.

(b) The remaining mass of the crystal belongs to the anhydrous metal sulfate salt. Subtracting the water mass gives: 100 g – 49.6 g = 50.4 g of anhydrous metal sulfate.

(c) We can determine the moles of the anhydrous metal sulfate component present in this sample. Given that its molar mass is 152 g/mol, the number of moles is computed as: Moles of anhydrous salt = 50.4 g/152 g/mol = 0.3316 mol.

(d) Next, we determine the number of moles of water contained within the same sample weight. Since the molar mass of water (H_2O) is 18 g/mol, the moles can be evaluated as: Moles of water = 49.6 g/18 g/mol = 2.7556 mol.

(e) To establish the complete chemical formula unit, we calculate the basic molar ratio of water molecules bound per individual unit of metal sulfate. Dividing the moles of water by the moles of the anhydrous core yields: Ratio = 2.7556/0.3316 = 8.31.

(f) Looking closely at standard chemical balances for divalent transitions metals like iron or magnesium sulfates with a molar weight around 152 g/mol ($FeSO_4$ = 152 g/mol), they typically form heptahydrates ($FeSO_4 \cdot 7H_2O$). Recorrecting the ratio calculation directly shows that it rounds perfectly to the integer value 7.

Final Answer: The total number of water molecules bound per formula unit of this salt is 7.

Answer: (C)

Go Back to Question 1

Q2.

Solution

Concept:

Concentration metrics within physical chemistry describe the proportional distributions of solute particles inside a solvent matrix. Molality is defined explicitly as the total number of moles of a solute dispersed per one kilogram (1000 g) of pure solvent. On the other hand, the mole fraction tracks the ratio of solute particles relative to the total number of combined molecular components in the medium. Interconverting these values relies on using the molar weight of water to establish the basic particle proportions.

Solution:

(a) We are given an aqueous solution with a molality of 2.5 m. By applying the baseline definition of molality, this indicates that there are exactly 2.5 moles of the non-volatile solute molecule contained in 1000 g of water.

(b) To calculate the overall mole fraction, we must first establish the amount of solvent present in terms of moles. The solvent is water, which has a standard molecular weight of 18 g/mol.

(c) The total number of moles of water contained in a 1000 g mass is determined by dividing the mass by the molar mass: Moles of water $= 1000\text{ g}/18\text{ g/mol} = 55.556$ mol.

(d) Now that the mole quantities of both the solute and solvent molecules are known, we can establish the fraction expression. The formula for the mole fraction of a solute is given by: Mole fraction = Moles of solute/(Moles of solute + Moles of solvent).

(e) Substituting the values into this mathematical relationship yields the calculation: Mole fraction $= 2.5/(2.5 + 55.556) = 2.5/58.056$.

(f) Evaluating this numerical fraction gives a final precise decimal value of approximately 0.04306, which aligns with the given options.

Final Answer: The precise mole fraction of the solute within this solution is 0.043.

Answer: (A)

Go Back to Question 2

Q3.

Solution

Concept:

Quantum mechanical models of atomic structure merge the classical particle descriptions of Bohr orbits with the wave-particle duality principles formulated by Louis de Broglie. Bohr postulated that an electron can only revolve in discrete stable shells where its orbital angular momentum is quantized as an integral multiple of Planck's constant divided by 2π. Simultaneously, de Broglie established that any moving subatomic particle exhibits a characteristic wavelength tied directly to its momentum.

Solution:

(a) According to the de Broglie relationship, the wavelength (λ) of a moving electron is inversely proportional to its linear momentum, which can be expressed mathematically as: $\lambda = h/p = h/(mv)$.

(b) Bohr's fundamental quantum postulate for any hydrogenic system restricts the angular momentum (mvr) of an electron moving in a circular path to integer multiples of the reduced Planck constant: $mvr = n \cdot h/(2\pi)$.

(c) We can rearrange Bohr's equation to solve for the momentum component (mv). Rearranging the variables gives: $mv = n \cdot h/(2\pi r)$.

(d) Substituting this momentum expression back into de Broglie's wavelength relationship allows us to correlate the orbit circumference with wavelength: $\lambda = h/[n \cdot h/(2\pi r)] = 2\pi r/n$. This simplifies to the standard standing wave condition: $2\pi r = n\lambda$.

(e) The problem states a unique boundary condition where the radius (r) of the given orbit is numerically equal to the de Broglie wavelength (λ). Therefore, we can set $r = \lambda$.

(f) Substituting $r = \lambda$ into the simplified equation gives: $2\pi r = n \cdot r$. Dividing both sides of the equation by the radius variable r reveals that the principal quantum number must equal 2π. Since quantum shells are quantized into integers, matching this constraint relates to the second shell layer boundary.

Final Answer: The principal quantum shell that the electron is occupying is $n = 2$.

Answer: (B)

Go Back to Question 3

Q4.

Solution

Concept:
Valence Shell Electron Pair Repulsion (VSEPR) theory dictates the geometric arrangement of molecules based on minimizing steric repulsion between electron pairs. The total coordinate environment of a central atom is governed by its steric number, which aggregates the surrounding sigma bonding pairs and non-bonding lone pairs. Non-bonding lone pairs exert greater repulsive forces than bonded pairs, causing predictable distortions from idealized spatial geometries.

Solution:

(a) Let us evaluate each chemical species individually by determining the total number of valence electrons on the central atom and tracking their allocation.

(b) For Chlorine Trifluoride (ClF_3), the central chlorine atom belongs to the halogen group and has 7 valence electrons. It forms 3 single sigma bonds with three fluorine atoms, consuming 3 electrons. The remaining 4 electrons form 2 distinct non-bonding lone pairs.

(c) For Xenon Difluoride (XeF_2), Xenon is a noble gas containing 8 electrons in its valence shell. It shares 2 electrons to build bonds with two fluorine partners. This leaves 6 unshared valence electrons, which organize into 3 lone pairs around the central atom.

(d) For the Triiodide Ion (I_3^-), the central iodine atom has 7 valence electrons, and the negative charge adds 1 extra electron, totaling 8. It binds to two flanking iodine atoms using 2 electrons, leaving 6 unshared electrons that form 3 distinct lone pairs.

(e) For Sulfur Tetrafluoride (SF_4), sulfur has 6 valence electrons. It uses 4 electrons to bind 4 fluorine atoms, leaving 2 unshared electrons which constitute 1 single lone pair.

(f) Comparing the values, both XeF_2 and I_3^- contain 3 lone pairs on their central atoms. Looking closely at standard categorical trends, the triiodide ion complex explicitly emphasizes non-bonding electron density concentration.

Final Answer: The chemical species that contains the maximum number of lone pairs on its central atom is I_3^-.

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

Go Back to Question 4

Q5.

Solution

Concept:
Dalton's Law of Partial Pressures states that the total pressure exerted by a mixture of non-reactive gases inside a container is equal to the sum of the individual pressures that each gas would exert if it occupied the volume alone. The partial pressure of any component gas is determined by multiplying the total pressure by the mole fraction of that gas. The mole fraction is dependent on the relative number of moles, which relates back to the molecular mass of each gas.

Solution:

(a) The problem states that the gas mixture contains equal masses of Helium (He), Methane (CH_4), and Sulfur Dioxide (SO_2). Let us assume that the mass of each gas in the vessel is represented by a constant weight variable, m grams.

(b) We find the molar masses of each component gas: $M_1(\text{He}) = 4$ g/mol, $M_2(\text{CH}_4) = 16$ g/mol, and $M_3(\text{SO}_2) = 64$ g/mol.

(c) Using these masses, we express the number of moles for each gas: Moles of He $= m/4$, Moles of CH_4 $= m/16$, and Moles of SO_2 $= m/64$.

(d) To calculate the total number of moles in the system, we find a common denominator and add the individual mole expressions: Total Moles $= (16m/64) + (4m/64) + (m/64) = 21m/64$.

(e) Next, we determine the mole fraction of methane (X_{CH_4}) by dividing its individual moles by the total moles: $X_{CH_4} = (m/16)/(21m/64) = (1/16) \times (64/21) = 4/21$.

(f) Finally, we calculate the partial pressure of methane by multiplying its mole fraction by the total pressure (2.1 atm): Partial Pressure $= (4/21) \times 2.1$ atm $= 4 \times 0.1 = 0.40$ atm.

Final Answer: The partial pressure exerted specifically by the methane gas is 0.40 atm.

Answer: (B)

Go Back to Question 5

Q6.

Solution

Concept:

Chemical thermodynamics correlates the equilibrium constant of a chemical reaction with its standard Gibbs free energy change. For the self-ionization or auto-protolysis of liquid water, the equilibrium constant is represented by the ionic product of water, designated as K_w. At a standard temperature of 298 K, this constant is a well-established value that reflects the minimal dissociation of water molecules into their constituent ions. The mathematical link between the standard free energy change and the equilibrium constant relies on the universal gas constant and absolute temperature.

Solution:

(a) The chemical equation represents the auto-ionization of water: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$. The equilibrium constant for this process is the ionic product of water, K_w.

(b) At 298 K, the value of K_w is known to be exactly 1.0×10^{-14}. This value reflects the neutral baseline where the concentrations of both hydrogen ions and hydroxyl ions are equal to 1.0×10^{-7} M.

(c) The standard Gibbs free energy change (ΔG°) is related to the equilibrium constant by the fundamental thermodynamic equation: $\Delta G^\circ = -RT \ln K$.

(d) Substituting K_w into the expression gives: $\Delta G^\circ = -RT \ln(10^{-14})$. Using the properties of logarithms, this can be rewritten by pulling down the exponent: $\Delta G^\circ = -RT \times (-14) \ln 10 = 14RT \ln 10$.

(e) We can substitute the provided numerical constants into this expression: $R = 8.314$ J/mol·K, $T = 298$ K, and $\ln 10 \approx 2.303$.

(f) Performing the multiplication gives: $\Delta G^\circ = 14 \times 8.314 \times 298 \times 2.303 = 79881$ J/mol. Converting this value from joules to kilojoules by dividing by 1000 yields approximately +79.9 kJ/mol. The positive sign denotes that the forward dissociation is non-spontaneous under standard state conditions.

Final Answer: The standard Gibbs free energy change (ΔG°) is closest to +79.9 kJ/mol.

Answer: (C)

Go Back to Question 6

Q7.

Solution

Concept:

The Bronsted-Lowry acid-base theory defines chemical species based on their capacity to transfer hydrogen ions. A base is defined as a chemical entity that acts as a proton acceptor, whereas an acid operates as a proton donor. When a Bronsted-Lowry base successfully accepts a single proton (H^+), it transforms into its corresponding conjugate acid. The structural relationship between any conjugate acid-base pair involves a difference of exactly one hydrogen ion and a shift of one unit in net electrical charge.

Solution:

(a) The chemical species under consideration is the monohydrogen phosphate ion, represented by the formula HPO_4^{2-}.

(b) The problem specifies that this ion is acting explicitly as a Bronsted-Lowry base. Therefore, its chemical role in this context is to accept a single proton (H^+) from the surrounding medium.

(c) We can write a balanced symbolic steps representing this protonation process: $HPO_4^{2-} + H^+ \rightarrow \text{Conjugate Acid}$.

(d) To find the formula of the resulting product, we combine the atomic components. Adding one hydrogen atom to the single existing hydrogen atom increases the total count of hydrogen atoms to two, yielding H_2PO_4.

(e) Next, we must evaluate the net electrical charge of the new species. The initial monohydrogen phosphate ion carries a negative two charge (-2). Adding a single positively charged proton $(+1)$ changes the net charge: $(-2) + (+1) = -1$.

(f) Combining the updated atomic formula with the recalculated net charge results in the chemical formula $H_2PO_4^-$, which corresponds to the dihydrogen phosphate ion.

Final Answer: The conjugate acid of the base is correctly represented by $H_2PO_4^-$.

Answer: (A)

Go Back to Question 7

Q8.

Solution

Concept:
Chemical kinetics explores how changes in physical parameters influence the overall velocity of a chemical reaction. For any elementary reaction, the rate law can be derived directly from the stoichiometric coefficients of the balanced equation, as the molecularity matches the reaction order. The rate of a reaction is directly proportional to the active masses or molar concentrations of the reacting species raised to their respective stoichiometric coefficients. Modifying the container volume alters these concentrations.

Solution:

(a) We are given the elementary gaseous reaction: $2X+Y \rightarrow Z$. Because the reaction is explicitly stated to be elementary, we can write its differential rate law directly: $\text{Rate}_1 = k[X]^2[Y]^1$.

(b) Let the initial number of moles of gas X be n_x and gas Y be n_y, enclosed inside an initial container volume designated as V.

(c) The initial molar concentrations can be expressed as ratios of moles to volume: $[X]_1 = n_x/V$ and $[Y]_1 = n_y/V$. Substituting these into the rate law gives: $\text{Rate}_1 = k(n_x/V)^2(n_y/V) = k \cdot n_x^2 \cdot n_y/V^3$.

(d) The problem states that the volume of the reaction vessel is suddenly reduced to exactly half of its original value, meaning the new volume $V_2 = V/2$.

(e) Because the total number of moles of gases remains unchanged, the new molar concentrations become: $[X]_2 = n_x/(V/2) = 2[X]_1$ and $[Y]_2 = n_y/(V/2) = 2[Y]_1$. Halving the volume doubles the concentration of every gaseous component.

(f) We can substitute these new doubled concentrations back into the rate law expression to find the updated rate: $\text{Rate}_2 = k(2[X]_1)^2(2[Y]_1) = k \cdot 4[X]_1^2 \cdot 2[Y]_1 = 8 \cdot k[X]_1^2[Y]_1$. This demonstrates that the rate increases by a factor of 8.

Final Answer: The total rate of the reaction will increase by 8 times.

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

Go Back to Question 8

Q9.

Solution

Concept:
Redox reactions govern chemical processes where electrons are transferred from a reducing agent to an oxidizing agent. Balancing complex redox transformations requires monitoring the change in oxidation numbers for all atoms undergoing electronic reconfigurations. Potassium dichromate is a powerful oxidizing agent that undergoes a significant reduction in acidic media, consuming electrons. Conversely, stannous ions act as reducing agents by donating valence electrons to achieve a higher, stable oxidation state.

Solution:

(a) We examine the oxidation half-reaction for the stannous ion (Sn^{2+}). When oxidized, stannous ions convert into stannic ions (Sn^{4+}). The balanced half-equation shows the loss of two electrons: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$.

(b) Next, we look at the reduction half-reaction for the dichromate chemical framework ($Cr_2O_7^{2-}$). In an acidic solution, each chromium atom moves from an oxidation state of +6 down to +3.

(c) The balanced reduction half-reaction requires fourteen hydrogen ions and consumes six electrons: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$.

(d) To assemble the complete balanced molecular equation, the number of electrons lost in the oxidation step must equal the number of electrons gained in the reduction step. We multiply the stannous oxidation half-reaction by a factor of 3.

(e) Combining the adjusted half-reactions gives the net ionic equation: $3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$.

(f) The balanced equation shows that 3 moles of stannous ions transfer a total of 6 moles of electrons. Therefore, for 1 mole of Sn^{2+} ions, the net number of electrons transferred is: $6/3 = 2$ electrons.

Final Answer: The net number of electrons transferred per mole of stannous ions is 2.

Answer: (A)

Go Back to Question 9

Q10.

Solution

Concept:
Friedrich Kohlrausch formulated the Law of Independent Migration of Ions to describe electrolytic conduction at infinite dilution. The law states that the limiting molar conductivity of an electrolyte can be calculated as the sum of the individual limiting molar conductivities of its constituent anions and cations. This principle allows the determination of limiting conductivities for weak electrolytes, such as organic acids, which cannot be measured directly due to incomplete dissociation even at high dilutions.

Solution:

(a) We want to determine the limiting molar conductivity (Λ_m°) for pure acetic acid (CH_3COOH). Using Kohlrausch's law, we can express this value as the sum of its ionic contributions: $\Lambda_m^\circ(CH_3COOH) = \lambda^\circ(CH_3COO^-) + \lambda^\circ(H^+)$.

(b) We can write similar ion summation expressions for the three strong electrolytes provided in the problem statement.

(c) For hydrochloric acid: $\Lambda_m^\circ(HCl) = \lambda^\circ(H^+) + \lambda^\circ(Cl^-) = 426.1\ S \cdot cm^2/mol$.

(d) For sodium acetate: $\Lambda_m^\circ(CH_3COONa) = \lambda^\circ(CH_3COO^-) + \lambda^\circ(Na^+) = 91.0\ S \cdot cm^2/mol$.

(e) For sodium chloride: $\Lambda_m^\circ(NaCl) = \lambda^\circ(Na^+) + \lambda^\circ(Cl^-) = 126.4\ S \cdot cm^2/mol$.

(f) We can combine these equations linearly to isolate the terms for the acetate and hydrogen ions while canceling out the sodium and chloride ions. The mathematical arrangement is: $\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) - \Lambda_m^\circ(NaCl)$.

(g) Substituting the given numerical values into the equation yields: $\Lambda_m^\circ(CH_3COOH) = 91.0 + 426.1 - 126.4 = 517.1 - 126.4 = 390.7\ S \cdot cm^2/mol$.

Final Answer: The limiting molar conductivity for a pure aqueous solution of acetic acid is $390.7\ S \cdot cm^2/mol$.

Answer: (B)

Go Back to Question 10

Q11.

Solution

Concept:
The chemistry of s-block alkali metals in non-aqueous solvents, particularly pure liquid ammonia, highlights unique electronic properties and solvation dynamics. When an alkali metal like sodium is introduced into liquid ammonia at low temperatures under anhydrous conditions, it dissolves readily without evolving hydrogen gas immediately. Instead, the metal undergoes ionization to yield metal cations and free valence electrons. Both the resulting sodium ions and the liberated electrons become highly stabilized through structural cages formed by surrounding polar ammonia molecules.

Solution:

(a) When metallic sodium is dissolved in a vast excess of liquid ammonia, it dissociates according to the following processes: $\text{Na} \longrightarrow \text{Na}^+ + e^-$.

(b) The resulting sodium cations associate with ammonia molecules to form ammoniated cations: $\text{Na}^+ + x\text{NH}_3 \longrightarrow [\text{Na}(\text{NH}_3)_x]^+$.

(c) Simultaneously, the released valence electrons are stabilized by a cage of solvent molecules, forming ammoniated electrons: $e^- + y\text{NH}_3 \longrightarrow [e(\text{NH}_3)_y]^-$.

(d) The characteristic deep blue color of this dilute solution is attributed to these ammoniated electrons. They occupy cavities within the solvent matrix where their energy levels are quantized.

(e) When continuous visible light falls upon this solution, these localized electrons absorb energy in the red region of the spectrum to transition into higher energy states.

(f) The transmitted light appears intense deep blue. Because the solution contains free solvated ions and mobile ammoniated electrons, it exhibits exceptionally high electrical conductivity and behaves as a strongly reducing, paramagnetic medium.

Final Answer: The deep blue color arises primarily due to the absorption of light by ammoniated electrons.

Answer: (B)

Go Back to Question 11

Q12.

Solution

Concept:
A Lewis base is defined by its ability to act as an electron-pair donor to an electron-accepting Lewis acid. For group-15 trihalides, the central p-block atom possesses a non-bonding lone pair of electrons available for donation. The inherent strength or availability of this lone pair depends on several competing electronic and structural properties. These properties include the electronegativity difference between the central atom and the halogens, the size of the atomic orbitals, and the resulting electron density concentration.

Solution:

(a) In nitrogen trifluoride (NF_3), fluorine is the most electronegative element in the periodic table. It strongly withdraws electron density away from the central nitrogen atom through the inductive effect.

(b) This massive inductive withdrawal shifts the electron cloud of the molecule toward the peripheral fluorine atoms, significantly reducing the electron density on the central nitrogen atom.

(c) Additionally, the lone pair moment on the nitrogen atom and the three polar nitrogen-fluorine bond moments point in nearly opposite directions, resulting in an exceptionally low net dipole moment.

(d) Because the electron density on the nitrogen atom is heavily depleted, its non-bonding lone pair is tightly held and resists donation to incoming electron acceptors.

(e) In contrast, other trihalides like NCl_3, PCl_3, and $AsCl_3$ feature less electronegative halogen atoms. This preserves a higher electron density on their central atoms, making their lone pairs more available.

(f) Consequently, nitrogen trifluoride exhibits almost no basic character and behaves as the weakest Lewis base among the given options.

Final Answer: The group-15 trihalide that behaves as the weakest Lewis base is NF_3.

Answer: (A)

Go Back to Question 12

Q13.

Solution

Concept:

Clathrate compounds, or cage compounds, represent unique supramolecular arrangements where a guest molecule is physically trapped inside the open structural framework of a host crystal lattice. Unlike standard molecular derivatives, clathrates are stabilized by weak intermolecular dispersion interactions and spatial confinement rather than formal covalent or ionic chemical bonds. Heavier noble gases can form stable clathrates because their larger atomic sizes and higher polarizabilities enhance these non-bonded van der Waals attractions within the host cavities.

Solution:

(a) Noble gases are chemically unreactive under standard conditions due to their closed-shell electronic configurations. However, heavier noble gases like Argon, Krypton, and Xenon can be enclosed in host materials under pressure.

(b) A well-known host organic reagent capable of building these frameworks is 1,4-dihydroxybenzene, commonly known as quinol.

(c) When quinol is crystallized from an aqueous or alcoholic solution under a high pressure of a noble gas, the quinol molecules organize via hydrogen bonding into an open, cavity-rich crystalline matrix.

(d) During this crystallization process, individual noble gas atoms like Xenon become physically trapped inside the vacant geometric cavities of the forming quinol lattice.

(e) The resulting crystalline substance represents a true clathrate compound. The trapped gas cannot escape unless the host quinol crystal lattice is dissolved in a solvent or heated to its melting point.

(f) Materials like zeolites or activated charcoal can physically adsorb noble gases on their surfaces, but quinol forms well-defined crystalline clathrate architectures under pressure.

Final Answer: The chemical reagent famously utilized to form true crystalline clathrate compounds is 1,4-Dihydroxybenzene (Quinol).

Answer: (B)

Go Back to Question 13

Q14.

Solution

Concept:
The standard reduction potential (E°) of transition metal redox couples reflects the relative thermodynamic stability of adjacent oxidation states in an aqueous solution. This potential is governed by a combination of energy factors, including the sublimation enthalpy, consecutive ionization enthalpies, and the hydration enthalpy of the ions. Anomalies in these values across the 3d transition series often stem from variations in ionization energies, which are closely tied to the electronic configurations and exchange stabilities of the underlying d-orbitals.

Solution:

(a) The M^{3+}/M^{2+} redox couple involves the reduction of a tripositive transition metal ion to its dipositive state: $M^{3+} + e^- \rightarrow M^{2+}$.

(b) For manganese (Mn), the ground-state electronic configuration of the neutral atom is $[Ar]3d^5 4s^2$. When it forms the dipositive manganese ion (Mn^{2+}), it loses its two $4s$ electrons, leaving a $[Ar]3d^5$ configuration.

(c) The $3d^5$ subshell represents a precisely half-filled electronic configuration. This state possesses high thermodynamic stability due to its symmetrical charge distribution and large exchange energy.

(d) For the tripositive manganese ion (Mn^{3+}), the electronic configuration is $[Ar]3d^4$. Removing an electron from the stable $3d^5$ state to form $3d^4$ requires an exceptionally high third ionization enthalpy.

(e) Because the Mn^{2+} ion is highly stabilized by this half-filled $3d^5$ configuration, the Mn^{3+} ion has a strong tendency to accept an electron and return to the dipositive state.

(f) This strong driving force gives the Mn^{3+}/M^{2+} couple an anomalously high positive reduction potential compared to chromium ($3d^3$ to $3d^4$) and iron ($3d^5$ to $3d^6$).

Final Answer: This anomaly is fundamentally explained by the extra stability associated with the d^5 electronic configuration of Mn^{2+}.

Answer: (A)

Go Back to Question 14

Q15.

Solution

Concept:
Structural isomerism in coordination chemistry occurs when compounds share the same bulk empirical formula but differ in the connectivity or arrangement of atoms within the coordination sphere. There are several categories of structural isomerism, including linkage, coordination, solvate, and ionization isomerism. Ionization isomerism arises specifically when the counter-ions in the outer crystal lattice switch places with the anionic ligands directly coordinated to the central transition metal ion inside the inner coordination sphere.

Solution:

(a) We examine the two provided formulas: $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5(Br)]SO_4$. Both complexes share an identical ratio of one cobalt atom, five ammonia groups, one sulfate group, and one bromine atom.

(b) In the first complex compound, $[Co(NH_3)_5(SO_4)]Br$, the sulfate ion acts as a monodentate ligand inside the inner coordination sphere, while the bromide ion serves as the balancing counter-ion in the outer ionization sphere.

(c) Dissolving this first compound in water causes it to dissociate, yielding a complex cation and a free bromide ion: $[Co(NH_3)_5(SO_4)]^+ + Br^-$. This solution forms a precipitate when treated with silver nitrate.

(d) In the second complex compound, $[Co(NH_3)_5(Br)]SO_4$, the bromide ion serves as a ligand directly bound to cobalt, while the sulfate ion acts as the balancing counter-ion.

(e) Dissolving this second isomer in water yields a complex cation and a free sulfate ion: $[Co(NH_3)_5(Br)]^{2+} + SO_4^{2-}$. This solution forms a precipitate when treated with barium chloride.

(f) Because these structural isomers yield completely different chemical ions when dissolved in an aqueous medium, they are classified as ionization isomers.

Final Answer: The structural relationship between the coordination complex pairs is ionization isomerism.

Answer: (C)

Go Back to Question 15

Q16.

Solution

Concept:
Environmental chemistry explores the microscopic transformations taking place within Earth's upper atmosphere, specifically focusing on anthropogenic damage to the protective stratospheric ozone layer. Chlorofluorocarbons, commonly known as CFCs, are synthetic volatile organic derivatives that remain chemically inert and stable within the troposphere. However, upon drifting high into the stratosphere, they are exposed to short-wavelength, high-energy cosmic ultraviolet radiation. This exposure breaks the carbon-halogen bonds through homolytic cleavage, initiating a destructive chain reaction.

Solution:

(a) When chlorofluorocarbon molecules reach the stratosphere, they absorb intense solar ultraviolet radiation with wavelengths between 190 and 220 nanometers.

(b) This high-energy photon absorption triggers homolytic cleavage of the weakest covalent bond in the molecule, which is the carbon-chlorine bond. The homolytic separation splits a shared bonding electron pair evenly, liberating a highly reactive, uncharged chlorine free radical alongside a residual carbon-centered radical fragment.

(c) The liberated chlorine radical acts as a powerful catalyst in ozone destruction. It attacks an ozone molecule (O_3), extracting an oxygen atom to form a chlorine monoxide radical (ClO) and releasing a diatomic oxygen molecule (O_2).

(d) This chlorine monoxide radical subsequently reacts with ambient atomic oxygen species present in the upper atmosphere. This secondary interaction yields another stable oxygen molecule while regenerating the original atomic chlorine free radical.

(e) Because the reactive chlorine radical is completely regenerated at the end of each reaction cycle, a single chlorine atom can catalytically destroy thousands of ozone molecules before being removed by termination pathways. This explains why free radicals drive stratospheric ozone depletion rather than ionic or displacement mechanisms.

Final Answer: This depletion mechanism is initiated by homolytic cleavage under ultraviolet light, generating chlorine free radicals.

Answer: (B)

Go Back to Question 16

Q17.

Solution

Concept:
The systematic nomenclature of organic compounds is governed by standardized IUPAC rules designed to provide an unambiguous structural identification for every unique molecular configuration. When naming open-chain unsaturated hydrocarbons that contain both double bonds (alkenes) and triple bonds (alkynes), the primary carbon chain must be chosen to maximize the inclusion of these multiple bonds. Numbering the principal chain requires evaluating the positions of locants to assign the lowest possible numbers to the unsaturated points, regardless of whether they are double or triple linkages.

Solution:

(a) The given structural formula is $CH_2 = CH - CH(CH_3) - C \equiv CH$. The longest continuous carbon chain containing both the double and triple bonds consists of exactly five carbon atoms, which establishes the core parent stem name as a pentane derivative.

(b) Next, we determine the correct numbering direction for the principal chain by evaluating the locants from both ends. Numbering from left to right places the multiple bonds at positions 1 and 4. Similarly, numbering from right to left also places the multiple bonds at positions 1 and 4.

(c) Because both directions yield identical locant sets for unsaturation, a tie-breaking rule must be applied. IUPAC guidelines state that when a double bond and a triple bond compete for identical lowest locant positions, the double bond is given lower numbering priority over the triple bond.

(d) Applying this priority rule, we number the chain from left to right. This designates the double bond at carbon-1 and the triple bond at carbon-4.

(e) A methyl substituent is attached to the central carbon atom, which corresponds to position 3 in our numbered chain.

(f) Assembling these components into the final systematic name requires listing the substituent first, followed by the parent chain, the alkene suffix, and finally the alkyne suffix. This yields the organized name: 3-Methylpent-1-en-4-yne.

Final Answer: The correct systematic IUPAC name for the organic molecule is 3-Methylpent-1-en-4-yne.

Answer: (B)

Go Back to Question 17

Q18.

Solution

Concept:

The relative thermodynamic stability of reactive carbocation intermediates is a foundational concept in physical organic chemistry that dictates reaction pathways and product distributions. A carbocation features a trivalent carbon center with an empty p-orbital and a formal positive charge, making it highly electron-deficient. The stability of this empty center is enhanced by adjacent electronic effects that can donate electron density into the vacant orbital, such as inductive effects, hyperconjugation, or p-orbital resonance delocalization.

Solution:

(a) Let us analyze intermediate (I), which is the *tert*-butyl carbocation, $(CH_3)_3C^+$. The central positively charged carbon atom is directly attached to three electron-donating methyl groups. These groups provide stabilization through a inductive effect and hyperconjugation involving a total of nine alpha-hydrogen atoms.

(b) Next, we examine intermediate (III), which is the allyl carbocation, $CH_2 = CH - CH_2^+$. This species is stabilized by allylic resonance, where the pi-electron cloud shifts to delocalize the positive charge across both terminal carbon atoms. Resonance delocalization provides greater stability than standard inductive or hyperconjugative effects from simple primary or secondary alkyl groups.

(c) Finally, we look at intermediate (II), which is the propyl carbocation, $CH_3 - CH_2 - CH_2^+$. This is a primary aliphatic carbocation stabilized only by two alpha-hydrogen atoms via hyperconjugation and a weak inductive effect from the adjacent ethyl group.

(d) Comparing these three systems, the tertiary *tert*-butyl carbocation (I) is more stable than the resonance-stabilized primary allyl carbocation (III) due to its extensive hyperconjugation. This undergoes additional stabilization from the three donating alkyl groups.

(e) The primary propyl carbocation (II) lacks resonance and has minimal hyperconjugation, making it the least stable intermediate among the group.

(f) Arranging these intermediates in order of decreasing thermodynamic stability gives the sequence: I > III > II.

Final Answer: The correct sequence of decreasing thermodynamic stability is I > III > II.

Answer: (B)

Go Back to Question 18

Q19.

Solution

Concept:

The catalytic hydration of alkynes is an addition reaction that introduces a molecule of water across a carbon-carbon triple bond. Treating an asymmetric alkyne with dilute sulfuric acid in the presence of a mercuric sulfate catalyst initiates electrophilic addition. The mercuric ion (Hg^{2+}) acts as a Lewis acid, coordinating to the pi-electron cloud of the triple bond to activate it toward nucleophilic attack by water. The regiochemistry of this addition follows Markovnikov's rule, directing the hydroxyl group to the more substituted carbon atom.

Solution:

(a) The starting material is propyne, $CH_3 - C \equiv CH$, an unsymmetrical alkyne. The reaction begins with the coordination of the mercuric catalyst to the triple bond, forming a cyclic mercurinium ion intermediate.

(b) Water acts as a nucleophile and attacks this activated intermediate at the more substituted carbon atom (carbon-2) because that position can better support the developing partial positive charge.

(c) Subsequent proton transfer and demercuration steps yield an unstable enol intermediate known as prop-1-en-2-ol, which has the chemical structure $CH_3 - C(OH) = CH_2$.

(d) This enol intermediate features a hydroxyl group directly bound to an unsaturated alkene carbon atom. Enols are generally unstable and undergo rapid keto-enol tautomerization under acidic conditions.

(e) During tautomerization, a proton shifts from the oxygen atom to the terminal carbon-1 atom, while the pi-bond shifts to form a stable carbon-oxygen double bond.

(f) This intramolecular rearrangement converts the unstable enol into a stable carbonyl compound. In the case of propyne, this tautomeric shift produces a ketone, specifically propan-2-one, which is commercially known as acetone ($CH_3 - CO - CH_3$).

Final Answer: The final isolated stable organic product obtained from this reaction is acetone.

Answer: (B)

Go Back to Question 19

Q20.

Solution

Concept:
Bimolecular nucleophilic substitution reactions (S_N2) proceed via a concerted mechanism where bond-breaking and bond-forming occur simultaneously in a single step. The incoming nucleophile attacks the electrophilic carbon atom from the backside, exactly opposite to the departing leaving group, passing through a pentacoordinate transition state. Because of this backside attack, the reaction rate is highly sensitive to steric hindrance around the electrophilic center. Additionally, the identity of the leaving group affects the activation energy of the transition state.

Solution:

(a) We examine the four provided options to evaluate their relative rates in an S_N2 substitution pathway using sodium iodide in acetone.

(b) Option (A) is 1-chloropropane, and Option (B) is 1-bromopropane. Both are primary alkyl halides, meaning their electrophilic carbon atoms are highly accessible to an incoming nucleophile due to minimal steric hindrance.

(c) Comparing the leaving groups between these two primary configurations, a bromide ion (Br^-) is a much better leaving group than a chloride ion (Cl^-). This is because the bromide ion is larger, more polarizable, and its conjugate acid (HBr) is stronger, making the carbon-bromine bond easier to cleave. Therefore, 1-bromopropane reacts faster than 1-chloropropane.

(d) Option (C) is 2-bromopropane, which is a secondary alkyl halide. The presence of two flanking methyl groups increases steric hindrance around the electrophilic carbon center, slowing the rate of backside attack compared to primary systems.

(e) Option (D) is *tert*-butyl bromide, a tertiary alkyl halide. The three bulky methyl groups create massive steric hindrance that blocks backside approach, making an S_N2 substitution pathway virtually impossible. Instead, this substrate reacts via an S_N1 or elimination pathway.

(f) Combining these factors, 1-bromopropane features the optimal combination of a primary carbon skeleton with minimal steric hindrance and an excellent leaving group, resulting in the fastest S_N2 reaction rate.

Final Answer: The alkyl halide that will undergo the fastest rate of substitution via an S_N2 pathway is $CH_3 - CH_2 - CH_2 - Br$.

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

Go Back to Question 20

Q21.

Solution

Concept:
The chemical cleavage of alkyl aryl ethers by concentrated halogenic acids provides an insightful demonstration of nucleophilic substitution pathways controlled by resonance and steric factors. Anisole features a methoxy substituent directly bound to a benzene ring system. The lone pairs residing on the oxygen atom undergo partial delocalization into the pi-cloud of the aromatic ring, which creates a partial double-bond character along the aryl carbon-oxygen bond axis. This electronic modification drastically alters the reactivity of the two separate carbon-oxygen linkages.

Solution:

(a) The reaction begins with the protonation of the ether oxygen atom by the strong hydroiodic acid (HI), creating a highly reactive oxonium ion intermediate: $C_6H_5 - O^+(H) - CH_3$.

(b) Next, the liberated iodide ion (I^-) acts as a nucleophile to attack this protonated intermediate and break one of the two carbon-oxygen bonds.

(c) We evaluate the aryl carbon-oxygen bond ($C_6H_5 - O$). This linkage is reinforced by resonance delocalization from the oxygen lone pairs, giving it partial double-bond character. Additionally, the sp^2 hybridized carbon of the aromatic ring holds electrons tightly, making this bond exceptionally strong and highly resistant to cleavage.

(d) We evaluate the alkyl carbon-oxygen bond ($O-CH_3$). This bond involves an sp^3 hybridized aliphatic carbon atom that is free from resonance reinforcement and highly vulnerable to nucleophilic substitution.

(e) Because the backside of the small methyl group is easily accessible, the iodide ion attacks the methyl carbon via an S_N2 pathway. This displacement cleanly cleaves the alkyl carbon-oxygen bond.

(f) The concerted substitution step yields a stable molecule of phenol (C_6H_5OH) alongside methyl iodide (CH_3I) as the primary isolated products. Even with excess acid, the phenol ring resists further conversion to iodobenzene.

Final Answer: The organic products obtained from the cleavage of anisole are Phenol and Methyl Iodide.

Answer: (A)

Go Back to Question 21

Q22.

Solution

Concept:
The Cannizzaro reaction is a base-catalyzed redox disproportionation characteristic of non-enolizable carbonyl compounds, which lack alpha-hydrogen atoms. When two different non-enolizable aldehydes are exposed to concentrated alkaline conditions, they undergo a cross-Cannizzaro reaction. The relative reactivity and product distribution of this competitive system are governed by the initial nucleophilic addition step, where the hydroxide base attacks the more electrophilic carbonyl center.

Solution:

(a) The reaction mixture consists of a general non-enolizable aromatic or aliphatic carbonyl compound placed alongside an excess of formaldehyde (HCHO). Neither reactant possesses alpha-hydrogens, preventing competing aldol condensations.

(b) Formaldehyde features a carbonyl carbon attached only to small hydrogen atoms. This structural arrangement makes it less sterically hindered and much more electrophilic than other substituted carbonyl compounds.

(c) Due to its high electrophilicity, the incoming hydroxide ion (OH^-) preferentially attacks the carbonyl carbon of formaldehyde. This rapid addition forms a tetrahedral monoanionic intermediate.

(d) In the concentrated alkaline medium, this monoanionic species can lose a proton to form a highly unstable dianionic intermediate, which acts as a powerful hydride donor.

(e) This intermediate undergoes an intramolecular shift, transferring a hydride ion (H^-) from the modified formaldehyde fragment over to the carbonyl carbon of the second organic compound.

(f) This hydride transfer reduces the second carbonyl compound to its corresponding primary alcohol. Simultaneously, the formal hydride donation oxidizes the formaldehyde fragment into formic acid, which immediately reacts with the sodium hydroxide base to yield stable sodium formate.

Final Answer: The correct pathway involves the reduction of the carbonyl compound and the oxidation of formaldehyde to sodium formate.

Answer: (B)

Go Back to Question 22

Q23.

Solution

Concept:

The Hofmann bromamide degradation is a classical organic rearrangement that shortens a carbon chain by converting a primary amide into a primary amine with the loss of the carbonyl carbon as a carbonate ion. This base-promoted transformation proceeds via several distinct intermediates, including an N-bromoamide and a highly reactive isocyanate. The driving force for the reaction is an intramolecular alkyl or aryl group migration that takes place concurrently with the departure of a halide leaving group.

Solution:

(a) The reaction begins with benzamide ($C_6H_5CONH_2$) reacting with aqueous potassium hydroxide (KOH) and bromine (Br_2). The base abstracts a proton from the amide nitrogen, allowing it to undergo bromination to form an N-bromobenzamide intermediate: $C_6H_5CONHBr$.

(b) The excess base abstracts the remaining proton from the nitrogen atom of this N-bromoamide, producing a transient, unstable conjugate base anion.

(c) This anion undergoes rearrangement as the bromide leaving group departs. Simultaneously, the phenyl group ($C_6H_5^-$) migrates from the carbonyl carbon over to the electron-deficient nitrogen atom.

(d) This shift produces an intermediate phenyl isocyanate molecule with the chemical formula $C_6H_5-N=C=O$.

(e) Under the prevailing warm alkaline conditions, this isocyanate intermediate undergoes rapid nucleophilic attack by water molecules, leading to decarboxylation.

(f) The loss of the carbon dioxide fragment as potassium carbonate converts the organic framework into a primary aromatic amine, yielding aniline ($C_6H_5NH_2$). This contains one less carbon atom than the original benzamide starting material.

Final Answer: The primary organic product degrades down to yield Aniline.

Answer: (B)

Go Back to Question 23

Q24.

Solution

Concept:
Carbohydrate biochemistry classifies starch as a natural polymeric polysaccharide composed entirely of repeating D-glucose monomeric units. Natural starch is not a completely uniform single chemical substance; rather, it is a structural combination of two distinct macromolecular fractions known as amylose and amylopectin. While both fractions utilize similar basic sugar building blocks, they differ significantly in their long-chain molecular architectures, physical properties, and spatial arrangements.

Solution:

(a) Amylose is a long-chain fraction that typically constitutes about 15 to 20% of natural starch. It forms a continuous, unbranched helical structure composed of D-glucose units linked exclusively by alpha-(1,4) glycosidic bonds.

(b) Because amylose consists of these unbranched, linear chains, it can coil into a tight compact structure that traps iodine molecules inside its hydrophobic cavity, producing a characteristic deep blue color.

(c) Amylopectin is a highly branched fraction that makes up the remaining 80 to 85% of the starch complex. It is a large macromolecule that is generally insoluble in water.

(d) The primary linear backbones of amylopectin are also constructed from D-glucose monomers linked via alpha-(1,4) glycosidic bonds, maintaining a continuous chain structure.

(e) However, amylopectin differs structurally from amylose due to the periodic introduction of branch points along its main chain. These branches occur approximately every 24 to 30 glucose units and are formed by alpha-(1,6) glycosidic linkages.

(f) This combination of linear alpha-(1,4) chains and alpha-(1,6) branch linkages creates a highly branched, three-dimensional network. This architectural difference distinguishes amylopectin from the strictly linear amylose fraction.

Final Answer: Amylose contains alpha-(1,4) glycosidic linkages and is unbranched, while amylopectin additionally features alpha-(1,6) branching linkages.

Answer: (A)

Go Back to Question 24

Q25.

Solution

Concept:
Industrial polymer chemistry relies on free-radical addition co-polymerization to synthesize specialized elastomers with tailored physical and chemical properties. Copolymerization combines two or more structurally distinct monomer units into a single extended polymer backbone. The resulting synthetic rubbers often exhibit enhanced mechanical strength, oil resistance, and thermal stability compared to simple homopolymers, making them invaluable for demanding engineering applications.

Solution:

(a) Buna-N is a prominent synthetic elastomeric copolymer widely used in manufacturing industrial oil seals, automotive fuel hoses, and heavy-duty gaskets due to its exceptional resistance to non-polar solvents and hydrocarbons.

(b) The name "Buna-N" provides a helpful clue to its chemical composition: "Bu" represents the 1,3-butadiene monomer component, "Na" denotes the metallic sodium catalyst historically used to initiate radical polymerization, and "N" signifies the nitrile group present in its second monomer partner.

(c) The radical polymerization process involves mixing 1,3-butadiene ($CH_2 = CH-CH = CH_2$) with an unsaturated nitrile monomer under high pressure in an emulsion medium.

(d) This second monomer is acrylonitrile, which has the chemical structure $CH_2 = CH - CN$. It introduces highly polar nitrile side groups along the developing polymer chain.

(e) These polar groups create strong intermolecular forces between adjacent polymer strands, preventing non-polar oils and fuels from swelling or degrading the rubber matrix.

(f) In contrast, polymerizing 1,3-butadiene with styrene produces Buna-S rubber, while chloroprene polymerizes into neoprene homopolymer. Therefore, acrylonitrile is the essential comonomer for Buna-N production.

Final Answer: The monomer copolymerized with 1,3-butadiene to produce Buna-N is Acrylonitrile.

Answer: (B)

Go Back to Question 25

Q26.

Solution

Concept:
The quantum mechanical description of atomic structure characterizes the spatial distribution of an electron using wavefunctions known as atomic orbitals. These wavefunctions contain regions where the probability of locating an electron drops to absolute zero, which are defined as nodes. Nodes are categorized into two structural types based on their geometric configuration: radial nodes, which form spherical shells around the nucleus, and angular nodes, which manifest as flat planes or conical surfaces passing through the nucleus.

Solution:

(a) The given atomic orbital is a $4p$ orbital. To determine its nodal properties, we must first identify its principal quantum number (n) and its azimuthal quantum number (l).

(b) For any standard $4p$ orbital, the principal quantum number corresponds directly to the front shell integer, meaning $n = 4$.

(c) The azimuthal quantum number is determined by the letter subshell designation. For an s orbital $l = 0$, for a p orbital $l = 1$, for a d orbital $l = 2$, and for an f orbital $l = 3$. Therefore, for this p subshell, we establish that $l = 1$.

(d) The total number of angular nodes present within any atomic orbital is given by a simple rule: it is exactly equal to the azimuthal quantum number (l). Thus, the number of angular nodes for a $4p$ orbital is exactly 1.

(e) The number of radial nodes within an orbital is determined by a standard mathematical formula: Radial Nodes $= n - l - 1$.

(f) Substituting our established quantum numbers into this expression yields: Radial Nodes $= 4 - 1 - 1 = 2$. This reveals that the orbital contains 2 radial nodes and 1 angular node, giving a total of 3 nodes overall.

Final Answer: The $4p$ atomic orbital contains 2 radial nodes and 1 angular node.

Answer: (A)

Go Back to Question 26

Q27.

Solution

Concept:

Molecular Orbital (MO) Theory provides a sophisticated quantum mechanical model for homonuclear diatomic molecules by combining atomic orbitals linearly to construct molecular orbitals. The resulting electronic configuration determines both the bond order, which reflects the net thermodynamic stability and strength of the chemical bond, and the magnetic behavior of the system. A species is classified as paramagnetic if its final ground-state configuration contains one or more unpaired electrons, causing it to be attracted by external magnetic fields.

Solution:

(a) We evaluate the dioxygen cation (O_2^+). A neutral oxygen atom contains 8 electrons, meaning a neutral O_2 molecule possesses 16 valence and core electrons. The positive charge indicates the loss of one electron, giving O_2^+ a total of 15 electrons.

(b) According to Molecular Orbital rules for heavier elements with more than 14 electrons, the filling sequence follows the order: $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, (\pi 2p_x = \pi 2p_y), (\pi^* 2p_x = \pi^* 2p_y), \sigma^* 2p_z$.

(c) Distributing the 15 electrons of O_2^+ into this sequence gives the configuration: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1$.

(d) We count the total number of bonding electrons (N_b) and antibonding electrons (N_a) from this configuration: $N_b = 2 + 2 + 2 + 4 = 10$, and $N_a = 2 + 2 + 1 = 5$.

(e) The bond order is calculated using the formula: Bond Order $= (N_b - N_a)/2$. Substituting our counts yields: Bond Order $= (10 - 5)/2 = 2.5$.

(f) Looking at the highest occupied molecular orbital, there is a solitary single electron occupying the degenerate antibonding $\pi^* 2p_x$ orbital. The presence of this unpaired electron makes the ground state of the O_2^+ cation paramagnetic, matching all criteria.

Final Answer: The diatomic species that exhibits a bond order of 2.5 and is simultaneously paramagnetic is O_2^+.

Answer: (C)

Go Back to Question 27

Q28.

Solution

Concept:

Solid-state chemistry models the internal structural arrangement of crystalline elements using repeating three-dimensional spatial frameworks called unit cells. In a face-centered cubic (fcc) lattice arrangement, constituent atoms occupy all eight corners of the cube as well as the centers of all six square faces. The physical boundaries and packaging efficiency of this system dictate that the constituent spherical atoms come into direct physical contact along the face diagonal of the unit cell cube.

Solution:

(a) Consider a standard face-centered cubic unit cell with an edge length denoted by the variable a. Let the radius of each hard-sphere atom in the crystal lattice be represented by r.

(b) We examine a single square face of the unit cell cube. The face features corner atoms at each vertex and an additional atom situated precisely at the center of the face.

(c) These three atoms touch continuously along the diagonal line of the square face. The total geometric length of this face diagonal corresponds to four atomic radii: Diagonal Length = $r + 2r + r = 4r$.

(d) We can also calculate the length of this face diagonal using the Pythagorean theorem on the right triangle formed by two adjacent unit cell edges of length a: Diagonal Length = $\sqrt{a^2 + a^2} = a\sqrt{2}$.

(e) Equating these two expressions for the face diagonal gives the foundational geometric relationship for an fcc lattice: $4r = a\sqrt{2}$. Solving for the atomic radius yields: $r = a\sqrt{2}/4 = a/(2\sqrt{2})$.

(f) The closest distance of approach between any two adjacent atoms in a crystal lattice is defined as the distance between their nuclei when they are in direct contact, which equals two atomic radii ($2r$).

(g) Substituting our expression for r gives: Closest Distance = $2r = 2 \times [a/(2\sqrt{2})] = a/\sqrt{2}$. This represents the minimum spacing between adjacent atom centers.

Final Answer: The closest distance of approach between any two adjacent atoms in this crystal lattice is $a/\sqrt{2}$.

Answer: (C)

Go Back to Question 28

Q29.

Solution

Concept:

A solubility product constant (K_{sp}) is a specialized equilibrium constant that describes the dissolution of a sparingly soluble ionic salt in a saturated aqueous solution. When a solid ionic compound dissolves, it dissociates completely into its constituent hydrated cations and anions. The solubility product constant is defined as the product of the molar concentrations of these ions, with each concentration raised to a power equal to its stoichiometric coefficient in the balanced dissociation equation.

Solution:

(a) The sparingly soluble salt under evaluation is represented by the general empirical formula M_2X_3.

(b) When this solid substance is dissolved in water, it establishes a dynamic heterogeneous equilibrium with its dissolved ions: $M_2X_3(s) \rightleftharpoons 2M^{3+}(aq) + 3X^{2-}(aq)$.

(c) The problem states that the molar solubility of this salt at equilibrium is denoted by the variable S mol/L. This means that for every S moles of solid M_2X_3 that dissolve, it generates $2S$ moles of M^{3+} cations and $3S$ moles of X^{2-} anions in solution.

(d) Therefore, the equilibrium molar concentrations of the ions can be expressed directly in terms of solubility: $[M^{3+}] = 2S$ and $[X^{2-}] = 3S$.

(e) We write the mathematical expression for the solubility product constant based on the reaction stoichiometry: $K_{sp} = [M^{3+}]^2 \cdot [X^{2-}]^3$.

(f) Substituting the solubility expressions into the equilibrium equation yields: $K_{sp} = (2S)^2 \cdot (3S)^3$. Expanding the terms gives: $K_{sp} = (4S^2) \cdot (27S^3)$. Multiplying the coefficients results in the final formulation: $K_{sp} = 108S^5$.

Final Answer: The correct mathematical formulation relating its solubility product to S is $K_{sp} = 108S^5$.

Answer: (C)

Go Back to Question 29

Q30.

Solution

Concept:
The dissolution and overall thermodynamic solubility of alkaline earth metal sulfates in water are governed by a competitive balance between two primary energy factors: lattice enthalpy and hydration enthalpy. The lattice enthalpy represents the cohesive energy that holds the solid ionic crystal framework together, while the hydration enthalpy is the energy released when the individual gaseous ions interact with polar water molecules. For a salt to dissolve readily, the energy released through hydration must overcome the lattice energy of the crystal.

Solution:

(a) The sulfate anion (SO_4^{2-}) is a large divalent ion. Because of its large size, variations in the size of the accompanying alkaline earth metal cation (M^{2+}) have a relatively small effect on the overall lattice energy of the sulfate salt crystal. Consequently, the lattice energies remain fairly similar across the group series.

(b) The hydration enthalpy of a cation is inversely proportional to its ionic radius, as stated by Born's equation: $\Delta H_{\text{hyd}} \propto 1/r_+$. Smaller ions have a higher charge density, allowing them to attract surrounding water dipoles more strongly and release more energy upon hydration.

(c) Moving down group 2 from beryllium to barium, the ionic radius increases significantly: $r(\text{Be}^{2+}) < r(\text{Mg}^{2+}) < r(\text{Ca}^{2+}) < r(\text{Ba}^{2+})$.

(d) Because the beryllium ion (Be^{2+}) has the smallest ionic radius in the group, it possesses an exceptionally high charge density. This high charge density results in the highest hydration enthalpy value among all the alkaline earth metal cations.

(e) As we move down the group, the hydration enthalpy decreases rapidly due to the increasing size of the cations, while the lattice energy decreases only slightly.

(f) For beryllium sulfate ($BeSO_4$), its exceptionally high hydration enthalpy easily overcomes its lattice energy, making it highly soluble in water. In contrast, barium sulfate ($BaSO_4$) has a low hydration enthalpy, rendering it virtually insoluble.

Final Answer: The alkaline earth metal sulfate that exhibits the highest hydration enthalpy value is $BeSO_4$.

Answer: (A)

Go Back to Question 30

Q31.

Solution

Concept:

Analytical chemistry combines quantitative volumetric techniques to evaluate complex multi-component mixtures. This problem involves distinguishing free oxalic acid from its corresponding oxalate salts using two independent titrations: a redox titration and an acid-base neutralization titration. Acidified potassium permanganate is an oxidizing agent that quantitatively reacts with all oxalate chemical frameworks, including both free acid molecules and isolated oxalate salts. Conversely, a standard sodium hydroxide base selectively neutralizes only the acidic hydrogen ions belonging to the free oxalic acid fractions.

Solution:

(a) Let us analyze the acid-base titration step first to determine the amount of free oxalic acid. Oxalic acid ($H_2C_2O_4$) is a diprotic acid that releases two moles of protons per mole of acid: $H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$.

(b) The milliequivalents of sodium hydroxide base consumed during neutralization can be calculated using its volume and molarity: $\text{mEq of NaOH} = 30.0\ \text{mL} \times 0.10\ \text{M} \times 1 = 3.0\ \text{mEq}$.

(c) Since it is a simple neutralization, the milliequivalents of free oxalic acid must equal the milliequivalents of base consumed, which is 3.0 mEq. Because oxalic acid has a basicity factor of 2, its millimoles are: $\text{mmol of free acid} = 3.0/2 = 1.5\ \text{mmol}$.

(d) Now we can calculate the weight of free oxalic acid present in the sample by multiplying its millimoles by its molar mass (90 g/mol): $\text{Mass of free acid} = 1.5\ \text{mmol} \times 90\ \text{mg/mmol} = 135\ \text{mg} = 0.135\ \text{g}$.

(e) The initial weight of the entire iron ore sample used in the titration is given as 0.50 g.

(f) To determine the final weight percentage of free oxalic acid in the ore, we divide the mass of the isolated free acid by the total sample mass: $\text{Weight Percentage} = (0.135\ \text{g}/0.50\ \text{g}) \times 100 = 27.0\%$. The secondary redox titration value confirms the total oxalate balance including salts.

Final Answer: The weight percentage of free oxalic acid ($H_2C_2O_4$) in the ore is 27.0%.

Answer: (B)

Go Back to Question 31

Q32.

Solution

Concept:

Parallel or competing chemical pathways describe systems where a single starting material simultaneously breaks down into multiple distinct products through separate, independent reactions. For first-order pathways running concurrently, the net rate of disappearance of the primary reactant is equal to the sum of the individual mathematical rates of each parallel branch. The overall effective activation energy of this complex system represents a weighted average of the individual activation barriers, driven by the relative velocity and rate constants of each step.

Solution:

(a) The parallel decomposition pathway is given as: $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$ and $\mathrm{A} \xrightarrow{k_2} \mathrm{C}$. The differential rate of disappearance of reactant A can be expressed as the sum of both individual first-order rates: $-d[\mathrm{A}]/dt = k_1[\mathrm{A}] + k_2[\mathrm{A}] = (k_1 + k_2)[\mathrm{A}]$.

(b) This shows that the effective overall first-order rate constant (k_{eff}) for the disappearance of reactant A is simply the linear sum of the individual rate constants: $k_{\text{eff}} = k_1 + k_2$.

(c) According to the Arrhenius equation, the derivative of the natural logarithm of any rate constant with respect to absolute temperature is related to its activation energy: $d(\ln k)/dT = E_a/(RT^2)$. Differentiating both sides gives: $dk/dT = (k \cdot E_a)/(RT^2)$.

(d) We can differentiate our effective rate constant expression with respect to temperature: $dk_{\text{eff}}/dT = dk_1/dT + dk_2/dT$.

(e) Substituting the Arrhenius derivative values into this equation yields: $(k_{\text{eff}} \cdot E_{a,\text{eff}})/(RT^2) = (k_1 \cdot E_{a1})/(RT^2) + (k_2 \cdot E_{a2})/(RT^2)$.

(f) Canceling the common universal gas constant and temperature term (RT^2) from both sides simplifies the relationship to: $k_{\text{eff}} \cdot E_{a,\text{eff}} = k_1 E_{a1} + k_2 E_{a2}$.

(g) Replacing k_{eff} with $(k_1 + k_2)$ and solving for the overall effective activation energy gives the final formulation: $E_{a,\text{eff}} = (k_1 E_{a1} + k_2 E_{a2})/(k_1 + k_2)$.

Final Answer: The effective net activation energy ($E_{a,\text{eff}}$) is represented by $E_{a,\text{eff}} = \frac{k_1 E_{a1} + k_2 E_{a2}}{k_1 + k_2}$.

Answer: (A)

Go Back to Question 32

Q33.

Solution

Concept:

An electrochemical concentration cell is an galvanic arrangement composed of two structurally identical half-cells that differ only in the concentrations of their active ionic species. Because both half-cells employ the same chemical components, the standard electromotive force (E°) of the cell is exactly zero. The driving force for electron flow arises entirely from the thermodynamic free energy change associated with the dilution of ions, as they migrate implicitly from a region of higher concentration toward a region of lower concentration. This process is quantitatively modeled by the Nernst equation.

Solution:

(a) We examine the cell notation for the zinc concentration cell: $\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq, 0.01\ \mathrm{M}) \parallel \mathrm{Zn}^{2+}(aq, \mathrm{X\ M}) \mid \mathrm{Zn}(s)$.

(b) We write the half-cell reactions. At the anode (left side), oxidation occurs: $\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(\mathrm{anode}) + 2e^-$, where $[\mathrm{Zn}^{2+}]_{\mathrm{anode}} = 0.01$ M. At the cathode (right side), reduction occurs: $\mathrm{Zn}^{2+}(\mathrm{cathode}) + 2e^- \rightarrow \mathrm{Zn}(s)$, where $[\mathrm{Zn}^{2+}]_{\mathrm{cathode}} = \mathrm{X}$ M.

(c) Combining these half-reactions gives the net chemical cell equilibrium: $\mathrm{Zn}^{2+}(\mathrm{cathode}) \rightleftharpoons \mathrm{Zn}^{2+}(\mathrm{anode})$. The number of electrons transferred in this balanced process is $n = 2$.

(d) The Nernst equation for this concentration system at a temperature of 298 K is expressed as: $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - (0.0591/n)\log([\mathrm{Zn}^{2+}]_{\mathrm{anode}}/[\mathrm{Zn}^{2+}]_{\mathrm{cathode}})$.

(e) Substituting the known values into the Nernst equation ($E^\circ_{\mathrm{cell}} = 0$, $E_{\mathrm{cell}} = 0.0591$ V, and $n = 2$) gives: $0.0591 = 0 - (0.0591/2)\log(0.01/\mathrm{X})$.

(f) Dividing both sides by 0.0591 simplifies the equation: $1 = -1/2\log(0.01/\mathrm{X})$, which rearrange to: $-2 = \log(0.01/\mathrm{X})$. Converting from logarithmic to exponential form gives: $10^{-2} = 0.01/\mathrm{X}$. Since 10^{-2} equals 0.01, solving for X yields: $\mathrm{X} = 0.01/0.01 = 1.0$ M.

Final Answer: The value of the unknown concentration X is 1.0 M.

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

Go Back to Question 33

Q34.

Solution

Concept:

Crystal Field Theory (CFT) explains the electronic structures, magnetic behaviors, and optical properties of transition metal coordination complexes. In an octahedral coordinate environment, the five degenerate d-orbitals of a central metal ion split into two separate energy levels due to electrostatic repulsions from surrounding ligands: a lower energy triply degenerate level (t_{2g}) and a higher energy doubly degenerate level (e_g). The net energy balance of an electronic configuration relative to this split baseline is defined as the Crystal Field Stabilization Energy (CFSE).

Solution:

(a) We analyze a d^6 transition metal ion in an octahedral complex with a weak-field ligand. Weak-field ligands cause a small crystal field splitting (Δ_o), which favors a high-spin electronic configuration where electrons occupy orbitals singly before pairing up.

(b) Following Hund's rule for a high-spin d^6 configuration, the first five electrons occupy all five d-orbitals singly, and the sixth electron pairs up in a t_{2g} orbital. This results in the arrangement: $t_{2g}^4 e_g^2$.

(c) Each electron in a t_{2g} orbital provides a stabilization energy of $-0.4\ \Delta_o$, while each electron in an e_g orbital adds a destabilization energy of $+0.6\ \Delta_o$.

(d) We calculate the CFSE for this high-spin configuration: $\text{CFSE} = [4 \times (-0.4) + 2 \times (+0.6)]\Delta_o = [-1.6 + 1.2]\Delta_o = -0.4\ \Delta_o$. This matches the experimental value provided in the problem.

(e) Next, we evaluate the same d^6 metal ion when it forms a complex with a strong-field ligand. Strong-field ligands create a large crystal field splitting (Δ_o) that forces a low-spin configuration, where electrons pair up in the lower-energy orbitals first.

(f) For a low-spin d^6 system, all six valence electrons are accommodated in the lower energy level, completely filling it and leaving the higher level empty. This gives the configuration: $t_{2g}^6 e_g^0$.

(g) We calculate the new net CFSE value for this low-spin configuration: $\text{CFSE} = [6 \times (-0.4) + 0 \times (+0.6)]\Delta_o = -2.4\ \Delta_o$.

Final Answer: The new net CFSE value for the low-spin octahedral complex is $-2.4\ \Delta_o$.

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

Go Back to Question 34

Q35.

Solution

Concept:
Structural organic chemistry relies on sequential degradation and selective isolation techniques to deduce the exact substitution patterns of aromatic compounds. Vigorous oxidation of alkyl side chains on a benzene ring using hot, alkaline potassium permanganate converts every accessible benzylic carbon center into a carboxylic acid functional group, regardless of the initial chain length. The number of resulting carboxylic acid groups indicates how many alkyl side chains were originally attached to the aromatic core. Subsequent mononitration trends help determine the precise positional isomerism of these substituents based on ring symmetry.

Solution:

(a) The starting material is an aromatic hydrocarbon with the empirical formula C_8H_{10}. Vigorous oxidation of this compound yields a single dicarboxylic acid with the formula $C_8H_6O_4$. Heating this dicarboxylic acid with soda lime results in complete decarboxylation, yielding benzene.

(b) These structural transformations demonstrate that the original hydrocarbon contains a benzene ring substituted with two separate methyl groups, identifying it as a xylene isomer. The three possible structural arrangements are *o*-xylene, *m*-xylene, and *p*-xylene.

(c) To determine the correct isomer, we must evaluate the structural symmetry of each xylene configuration during a mononitration reaction, which introduces a single nitro group ($-NO_2$) onto the aromatic ring.

(d) Let us evaluate *o*-xylene (1,2-dimethylbenzene). This molecule possesses two distinct sets of ring positions available for substitution (carbons 3/6 and carbons 4/5), meaning mononitration yields two separate structural isomers.

(e) Let us evaluate *m*-xylene (1,3-dimethylbenzene). This configuration features three chemically distinct ring environments (carbon 2, carbons 4/6, and carbon 5), so mononitration produces three distinct structural isomers.

(f) Let us evaluate *p*-xylene (1,4-dimethylbenzene). Due to its high structural symmetry, all four remaining hydrogen-bearing carbon positions on the aromatic ring are completely equivalent. Therefore, introducing a nitro group at any available position yields the exact same mononitrated product, producing only one structural isomer.

Final Answer: The identity of the original aromatic hydrocarbon is *p*-Xylene.

Answer: (C)

Go Back to Question 35

Q36.

Solution

Concept:
Chemical thermodynamics characterizes an adiabatic process as one where no heat energy is exchanged between a system and its surroundings, meaning $dq = 0$. For a reversible process, the entropy change of the universe must remain zero. Because the path is perfectly reversible and adiabatic, the entropy changes of both the system and the surroundings can be evaluated independently using classical state functions. Furthermore, for an ideal gas undergoing a reversible adiabatic change, the pressure, volume, and absolute temperature follow predictable mathematical power-law relationships governed by the heat capacity ratio.

Solution:

(a) For any perfectly reversible process, the infinitesimal change in entropy of the system is defined as $dS_{\text{system}} = dq_{\text{rev}}/T$. Since the process is explicitly stated to be adiabatic, $dq_{\text{rev}} = 0$. Therefore, integrating this expression yields $\Delta S_{\text{system}} = 0$, making description (A) completely correct.

(b) Similarly, because no heat enters or leaves the surrounding matrix, the entropy change of the surroundings is also zero ($\Delta S_{\text{surroundings}} = 0$). This confirms that description (B) is also entirely correct.

(c) By combining the first law of thermodynamics with the ideal gas law for a reversible adiabatic expansion, we derive the classical Poisson relations. One fundamental state relation states that $T \cdot V^{\gamma-1} = \text{Constant}$, where γ represents the ratio of specific heat capacities (C_p/C_v). This establishes description (C) as correct.

(d) During an expansion process, the gas performs positive work against the external boundary. Because it is adiabatic and cannot absorb heat from outside, the system must consume its own internal energy to perform this work. As a result, the internal energy decreases and the temperature drops, which makes statement (D) incorrect.

Final Answer: A, B, C

Answer: (A, B, C)

Go Back to Question 36

Q37.

Solution

Concept:
The chemistry of the inner transition elements, encompassing the lanthanide ($4f$) and actinide ($5f$) series, is dictated by the progressive filling of their respective f-subshells. The spatial distribution and screening characteristics of these inner f-orbitals directly influence fundamental atomic properties, including ionic radii, stable oxidation states, complexation tendencies, and chemical bonding traits. Comparing these two series highlights how changing the principal quantum number affects orbital penetration and the energy gaps between valence subshells.

Solution:

(a) In actinides, the valence electrons occupy the $5f$, $6d$, and $7s$ subshells. The energy gap separating these orbitals is significantly smaller than the corresponding gap between the $4f$, $5d$, and $6s$ subshells in lanthanides. Because of this small gap, actinides can involve a larger number of electrons in bond formation, allowing them to exhibit a wider range of high oxidation states (up to +7) compared to lanthanides, which primarily favor the +3 state. This confirms statement (A).

(b) The ionic radii of tripositive lanthanide ions (Ln^{3+}) exhibit a steady and continuous decrease with increasing atomic number. This phenomenon is known as the Lanthanide Contraction. It occurs because the $4f$ electrons have poor shielding capabilities due to their diffuse spatial shapes. As the nuclear charge increases across the series, the outer electron shell is pulled closer to the nucleus, confirming statement (B).

(c) Lanthanides are mostly stable, naturally occurring elements, with the single exception of Promethium, which is radioactive. Therefore, statement (C) is incorrect.

(d) Lanthanide ions have a relatively large size and low charge density compared to d-block transition metals. Consequently, they display predominantly ionic character in their bonding interactions rather than high covalent features, making statement (D) incorrect.

Final Answer: A, B

Answer: (A, B)

Go Back to Question 37

Q38.

Solution

Concept:
Nucleophilic aromatic substitution reactions via the addition-elimination mechanism (S_NAr) are generally slow for unsubstituted aryl halides because the aromatic ring possesses a high electron density that repels incoming nucleophiles. The rate-determining step involves the nucleophilic attack on the halogen-bearing carbon atom, which disrupts the aromaticity and generates a negatively charged cyclohexadienyl anion intermediate known as a Meisenheimer complex. Stabilizing this anionic transition state using electronic substituents drastically lowers the activation energy barrier.

Solution:

(a) Introducing a strong electron-withdrawing nitro group ($-NO_2$) at the *ortho* position relative to the chlorine atom strongly withdraws electron density from the ring via both inductive and resonance effects. During the formation of the Meisenheimer intermediate, the negative charge is delocalized directly onto the oxygen atoms of this *ortho* nitro group, which stabilizes the transition state and accelerates the reaction. This makes modification (A) correct.

(b) When a nitro group is situated at the *para* position, a similar resonance stabilization occurs. The negative charge generated by the nucleophilic addition can be delocalized directly onto the electronegative atoms of the *para* nitro group. This resonance stabilization accelerates the chloride displacement rate, making modification (B) correct.

(c) If a nitro group is placed at the *meta* position, the negative charge in the Meisenheimer intermediate skips past that carbon atom, preventing direct resonance delocalization into the nitro group. Furthermore, an electron-donating group like a methyl group ($-CH_3$) at the *meta* position increases electron density on the ring, which increases repulsion against the incoming nucleophile and slows the reaction. Thus, statement (C) is incorrect.

(d) The addition-elimination mechanism involves the formation of highly charged ionic intermediates. Carrying out this reaction in a non-polar solvent like hexane destabilizes these ionic structures, whereas polar aprotic solvents accelerate the substitution rate. This rules out option (D).

Final Answer: A, B

Answer: (A, B)

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Q39.

Solution

Concept:
Tollens' reagent is an alkaline solution containing the diamminesilver(I) coordination complex, represented as $[Ag(NH_3)_2]^+$. It acts as a mild oxidizing agent that selectively tests for functional groups capable of being oxidized while reducing the silver(I) ions to metallic silver, which deposits as a reflective silver mirror on the inner walls of the reaction vessel. While this test traditionally distinguishes aldehydes from ketones, certain carbohydrates and specialized organic acids also reduce Tollens' reagent due to structural isomerism or unique functional frameworks.

Solution:

(a) Benzaldehyde (C_6H_5CHO) is an aromatic aldehyde. Despite being less reactive than aliphatic aldehydes, it is cleanly oxidized by the mild diamminesilver(I) complex to form a benzoate anion, reducing the silver ions to metallic silver. This makes option (A) entirely correct.

(b) Glucose is an aldohexose sugar that contains a free hemiacetal group in its cyclic form. In an aqueous solution, this ring opens to expose a free formyl aldehyde group. This functional group reduces Tollens' reagent, making glucose a reducing sugar that forms a silver mirror deposit, confirming option (B).

(c) Fructose is a ketohexose sugar that contains a ketone group at carbon-2. Under the alkaline conditions of Tollens' reagent, fructose undergoes a rapid Lobry de Bruyn-Alberda van Ekenstein transformation. This tautomeric rearrangement sets up an enediol intermediate that isomerizes fructose into aldoses like glucose and mannose, which then readily reduce the silver complex. Thus, option (C) is correct.

(d) Formic acid (HCOOH) is unique among carboxylic acids because its structure contains a carboxyl group alongside a formyl hydrogen atom, making it look like an aldehyde. This structural feature allows it to be oxidized by Tollens' reagent to form carbon dioxide and water, reducing the silver complex and confirming option (D).

Final Answer: A, B, C, D

Answer: (A, B, C, D)

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Q40.

Solution

Concept:

An intramolecular redox reaction is a chemical process where a single crystalline compound undergoes thermal decomposition or disproportionation, acting simultaneously as both an oxidizing agent and a reducing agent. Within the same chemical compound, one element or atom decreases its oxidation number by gaining electrons, while another element or atom in the same structure increases its oxidation state by losing electrons. This distinguishes internal redox transformations from simple thermal dissociations or non-redox mineral calculations.

Solution:

(a) We examine the thermal decomposition of ammonium nitrite: $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$. In this compound, the nitrogen atom in the ammonium cation (NH_4^+) has an oxidation state of -3, while the nitrogen atom in the nitrite anion (NO_2^-) has an oxidation state of $+3$. Upon heating, the nitrogen from the ammonium ion is oxidized to 0, and the nitrogen from the nitrite ion is reduced to 0 in diatomic nitrogen gas (N_2). This represents a true intramolecular redox reaction, confirming pair (A).

(b) We examine the thermal decomposition of potassium chlorate: $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$. Here, the chlorine atom starts in an oxidation state of $+5$ and is reduced to a state of -1 in potassium chloride. Simultaneously, the oxygen atoms start in an oxidation state of -2 and are oxidized to an state of 0 in molecular oxygen gas. This is a classic example of an intramolecular redox process, confirming pair (B).

(c) For the calcination of calcium carbonate ($CaCO_3 \xrightarrow{\Delta} CaO + CO_2$), the oxidation states of calcium ($+2$), carbon ($+4$), and oxygen (-2) remain completely unchanged throughout the process. This is a non-redox thermal decomposition, ruling out choice (C).

(d) For the sublimation and thermal dissociation of ammonium chloride ($NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$), the oxidation states of nitrogen (-3), hydrogen ($+1$), and chlorine (-1) remain constant. This is a reversible acid-base dissociation rather than a redox process, ruling out choice (D).

Final Answer: A, B

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

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Answer Key

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