

UPCATET Chemistry Sample Paper-1

Duration: 45 Minutes

Maximum Marks: 200

Instructions

- This paper contains **50** Multiple Choice Questions.
- Each correct answer carries **+4** mark. Incorrect answer: **-1** marks. Only **one** correct option.
- Unattempted questions carry **0** marks.
- Use of mobile phones, smartwatches, or any electronic gadgets is strictly prohibited.

Q1. An unlabeled compound $C_6H_{10}O_2$ is treated with dilute H_2SO_4 to yield two molecules of an aldehyde C_3H_6O . When the same starting material is subjected to reductive ozonolysis (O_3 , followed by Zn/H_2O), it forms an acyclic compound containing two ester groups. Deduce the definitive structure of the original starting material.

- (A) 1,2-dimethoxycyclobutene
- (B) 2,3-dihydro-1,4-dioxin derivative
- (C) A cyclic acetal of propanal
- (D) 1,2-dipropoxyethene

Q2. Predict the major organic stereoisomer obtained when (2*R*, 3*S*)-3-phenylbutan-2-ol undergoes an intramolecular dehydration via a concerted synchronized E2 mechanism triggered by treatment with excessive concentrated sulfuric acid at high temperature.

- (A) (*Z*)-2-phenylbut-2-ene
- (B) (*E*)-2-phenylbut-2-ene
- (C) (*R*)-3-phenylbut-1-ene
- (D) Racemic mixture of (*E*) and (*Z*)-2-phenylbut-2-ene



Q3. Consider the sequence of transformations mapping the functional modification of a bicyclic terpene skeleton. Identify the principal thermodynamic product structural framework labeled as **Product Z** in the reaction path map depicted below:

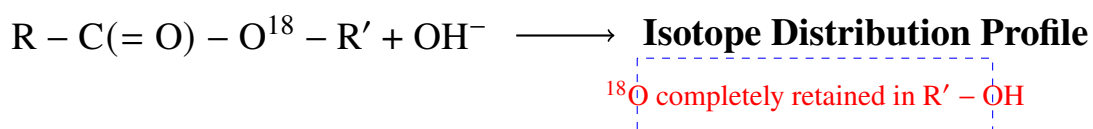


- (A) Wagner-Meerwein rearranged secondary alcohol
- (B) Retained configuration tertiary chloride
- (C) Ring-contracted monocyclic diene
- (D) Epoxidized bridgehead hydrocarbon

Q4. In a multi-step thermodynamic condensation sequence, a mixture of benzaldehyde and acetic anhydride is heated in the explicit presence of anhydrous sodium acetate (CH_3COONa). The intermediate isolated crude material is treated with bromine water. Identify the specific configurations of the stereocenters generated.

- (A) Erythro-2,3-dibromo-3-phenylpropanoic acid
- (B) Threo-2,3-dibromo-3-phenylpropanoic acid
- (C) Meso-dibromosuccessive ester derivative
- (D) (2*R*, 3*R*)-2,3-dibromopropanal

Q5. An organic chemist performs a fundamental kinetic isotopic labeling test on the alkaline hydrolysis mechanism of an ester. The substrate containing an enriched oxygen-18 label is subjected to basic hydrolysis. Identify the true isotope distribution mapping observed across the products:



- (A) Complete retention of ^{18}O inside the carboxylate ion product

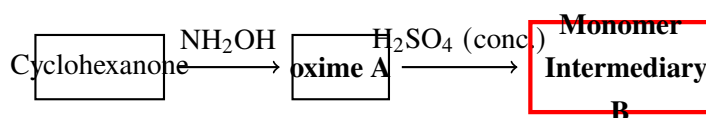


- (B) Complete retention of ^{18}O inside the alcohol product ($\text{R}'\text{OH}$)
- (C) Equal 50:50 scrambling distribution between both isolated species
- (D) Volatile elimination of oxygen label as H_2O^{18} gas

Q6. A nitrogenous heterocycle undergoes an intense electrophilic aromatic substitution variant. Deduce the exact relative rate profile and the specific position orientation vector of nitration when indole is exposed to nitric acid dissolved in acetic anhydride.

- (A) Exclusively at the C-2 position due to localized lone pair alignment
- (B) Exclusively at the C-3 position driven by benzenoid resonance preservation
- (C) Selective C-5 ring attack under thermodynamic orientation protocols
- (D) Nitrogen atom nitration generating an N-nitro indole transient adduct

Q7. Analyze the kinetic multi-step scheme for a synthetic polymer monomer precursor sequence below. Deduce the major structural identity corresponding to the unknown component labeled as **Monomer Intermediary B**:



- (A) Cyclohexanol
- (B) ϵ -Caprolactam
- (C) Adipic acid
- (D) Hexamethylenediamine

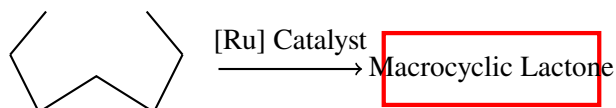
Q8. A specific polypeptide sequence containing phenylalanine at the N-terminus is treated with Sanger's reagent (1-fluoro-2,4-dinitrobenzene) under mildly basic conditions, followed by comprehensive complete acid hydrolysis. Identify the chromatographically isolated labeled species.

- (A) 2,4-dinitrophenyl-phenylalanine
- (B) Phenylthiohydantoin derivative of phenylalanine



- (C) 4-nitrophenylalanine methyl ester
(D) Free phenylalanine along with 2,4-dinitrophenol

Q9. An organic substrate containing an alkene tethered to an ester unit undergoes a specialized transformation under the influence of a ruthenium alkylidene catalyst complex. Identify the correct reaction categorization and specific product profile archetype for the system illustrated below:



- (A) Intermolecular Cross Metathesis (CM) yielding a linear dimer
(B) Ring-Closing Metathesis (RCM) producing a macrocyclic lactone
(C) Ring-Opening Metathesis Polymerization (ROMP) of a strained ester
(D) Intermolecular cross-coupling via a palladium-like mechanism
- Q10.** A dry sample of sodium phenoxide is heated under high mechanical pressure ($\approx 5 - 7$ atm) with gaseous carbon dioxide at a temperature of 125°C . The crude salt isolated is subsequently acidified using hydrochloric acid. What is the molecular structure of the minor structural isomer isolated from the matrix?
- (A) Salicylic acid (2-hydroxybenzoic acid)
(B) 4-hydroxybenzoic acid
(C) Phthalic acid
(D) Phenoxyacetic acid
- Q11.** During a deep mechanistic kinetic study of the traditional Claisen rearrangement, an allyl phenyl ether substrate is synthetically tagged with a carbon-14 (^{14}C) isotope at the specific terminal γ -carbon position of the allyl chain. Identify the definitive position of the radioactive carbon in the rearranged ortho-allylphenol product.
- (A) Exclusively at the α -carbon position attached directly to the aromatic nucleus
(B) Exclusively at the terminal γ -carbon position of the migrated group

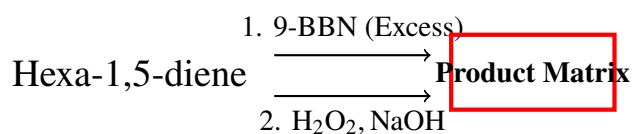


- (C) Equally scrambled 50:50 between the α and β carbon nodes
- (D) Scrambled uniformly over all positions of the aromatic ring framework

Q12. A crystalline carbohydrate enantiomer shows an initial specific rotation value of $+112^\circ$ in water. When left to stand, the rotation drifts gradually to settle permanently at $+52.7^\circ$. If an isomeric crystal form showing $+18.7^\circ$ initial rotation undergoes the same treatment, it settles at $+52.7^\circ$ too. Identify the physical phenomenon and mechanism involved.

- (A) Epimerization triggered via an open-chain enediol intermediate structural bridge
- (B) Mutarotation occurring via the reversible opening of the cyclic hemiacetal form
- (C) Enantiomeric inversion operating through a nucleophilic solvent displacement
- (D) Asymmetric absolute destruction catalyzed by trace dissolved ambient carbonate

Q13. Identify the final major constitutional product isolated when an unbranched non-conjugated diene system undergoes a catalytic hydroboration-oxidation sequence with an excessively bulky reagent, as described in the structural blueprint mapping below:



- (A) Hexane-2,5-diol
- (B) Hexane-1,6-diol
- (C) 2,5-dimethyltetrahydrofuran
- (D) Hexan-1-ol

Q14. A purely synthetic sample of (*S*)-2-bromobutane is subjected to a classic nucleophilic substitution reaction using sodium azide (NaN_3) dissolved in



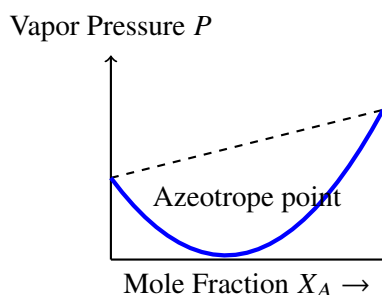
dimethylsulfoxide (DMSO) solvent. The rate of the reaction is observed to double when the concentration of the azide ion is doubled. Identify the absolute configuration and optical characteristics of the isolated organic product.

- (A) Purely racemic 2-azidobutane
- (B) Enantiopure (*S*)-2-azidobutane with complete configuration retention
- (C) Enantiopure (*R*)-2-azidobutane with complete configuration inversion
- (D) An unequal diastereomeric mixture of (*R*) and (*S*)-2-azidobutane

Q15. At a given temperature T , the standard Gibbs free energy of formation for a dense equilibrium mixture tracking gaseous nitrogen dioxide and dinitrogen tetroxide satisfies $\Delta G^\circ = 4.8 \text{ kJ/mol}$ for the reaction: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$. Calculate the numerical value of the internal equilibrium constant K_c at 300 K if the total pressure is maintained at 1 atmosphere.

- (A) $K_c = 0.143 \text{ M}^{-1}$
- (B) $K_c = 6.98 \text{ M}^{-1}$
- (C) $K_c = 1.00 \text{ M}^{-1}$
- (D) $K_c = 0.384 \text{ M}^{-1}$

Q16. A highly non-ideal binary liquid mixture of components A and B displays a distinct maximum-boiling azeotropic composition at a specific mole fraction X_A . Analyze the thermodynamic behavior profile diagram plotted below to evaluate the exact deviations from Raoult's Law and the sign of the excess enthalpy function ΔH_{mix} :



- (A) Positive deviation from Raoult's law, $\Delta H_{\text{mix}} > 0$
- (B) Negative deviation from Raoult's law, $\Delta H_{\text{mix}} < 0$

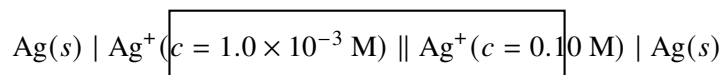


- (C) Ideal solution performance behavior, $\Delta H_{\text{mix}} = 0$
(D) Negative deviation from Raoult's law, $\Delta H_{\text{mix}} > 0$

Q17. The fundamental parallel decomposition kinetics of an unstable heavy actinide core complex follow two distinct concurrent first-order decay pathways. Pathway A has a rate constant $k_1 = 3.0 \times 10^{-4} \text{ s}^{-1}$ and produces an oxide, while Pathway B has a rate constant $k_2 = 1.0 \times 10^{-4} \text{ s}^{-1}$ and produces a hydride. Calculate the effective total net half-life period ($t_{1/2}$) of the starting precursor material.

- (A) 2310 s
(B) 1732 s
(C) 6930 s
(D) 5198 s

Q18. An electrochemical storage cell is set up under highly non-standard conditions at 298 K, as defined by the structural cell notation schematic block below. Calculate the exact cell EMF magnitude (E_{cell}) if the standard reduction potential E° for the half-cell reaction matches +0.80 V:



- (A) $E_{\text{cell}} = 0.800 \text{ V}$
(B) $E_{\text{cell}} = 0.118 \text{ V}$
(C) $E_{\text{cell}} = 0.918 \text{ V}$
(D) $E_{\text{cell}} = 0.059 \text{ V}$

Q19. A buffering matrix is prepared by mixing 0.20 M sodium chloroacetate ($\text{ClCH}_2\text{COONa}$) and 0.10 M chloroacetic acid (ClCH_2COOH) in an aqueous solvent. The acid dissociation constant K_a of chloroacetic acid is exactly 1.4×10^{-3} . Compute the precise concentration of hydronium ions (H_3O^+) in this active buffer solution.

- (A) $7.0 \times 10^{-4} \text{ M}$
(B) $2.8 \times 10^{-3} \text{ M}$



(C) $1.4 \times 10^{-3} \text{ M}$

(D) $3.5 \times 10^{-4} \text{ M}$

Q20. A real gas sample obeys the specialized thermodynamic virial equation of state written as $PV_m = RT \left[1 + \frac{B(T)}{V_m} \right]$. The second virial coefficient parameter is explicitly modeled as $B(T) = b - \frac{a}{RT}$. Determine the numerical value of the critical Boyle temperature (T_B) where the real gas performs identically to an ideal gas over an extended pressure range.

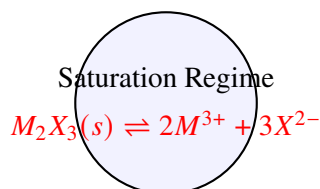
(A) $T_B = \frac{a}{2bR}$

(B) $T_B = \frac{a}{bR}$

(C) $T_B = \frac{2a}{bR}$

(D) $T_B = \frac{3a}{2bR}$

Q21. A solid ionic salt with the structural formula M_2X_3 exhibits a low solubility profile in an aqueous matrix. Evaluate the mathematical expression relating the true solubility product constant K_{sp} to the equilibrium saturation solubility limit S (expressed in units of mol L^{-1}):



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

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

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

(D) $K_{sp} = 256S^6$

Q22. A precise cryoscopic measurement reveals that an aqueous solution of a weak monobasic acid freezes at -0.279°C . The molal freezing point depression constant K_f for water is $1.86^\circ\text{C kg mol}^{-1}$. If the true analytical molality concentration of the added acid is exactly 0.10 m, calculate the exact percentage degree of ionization (α) of the weak acid.

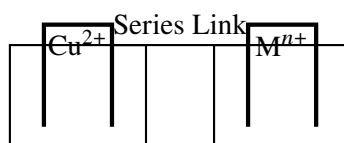


- (A) $\alpha = 15\%$
- (B) $\alpha = 50\%$
- (C) $\alpha = 33\%$
- (D) $\alpha = 25\%$

Q23. The core activation energy barrier (E_a) for a specialized catalytic biochemical process is measured to be 50.0 kJ mol^{-1} . When an engineered synthetic enzyme catalyst is introduced into the reactor at 300 K, the overall rate of the chemical conversion increases by an absolute factor of exactly 10^4 . Compute the net reduction in activation energy achieved by the catalyst.

- (A) 11.5 kJ mol^{-1}
- (B) 23.0 kJ mol^{-1}
- (C) 46.0 kJ mol^{-1}
- (D) 5.75 kJ mol^{-1}

Q24. A specific quantity of electrical charge is passed through two electrolytic cells connected in series. The first cell contains a solutions of Cu^{2+} ions, and the second cell contains an unknown heavy metal ion solution M^{n+} . If 3.175 g of copper (At. wt. = 63.5) is deposited concurrently with 11.87 g of the heavy metal (At. wt. = 118.7), determine the unknown valence oxidation state number n :



- (A) $n = 1$
- (B) $n = 2$
- (C) $n = 3$
- (D) $n = 4$

Q25. Calculate the change in total molar entropy (ΔS) when exactly 2.0 moles of a monoatomic ideal gas are heated reversibly at a constant volume from an initial



temperature of 200 K up to a final temperature of 800 K. (Take gas constant value $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

- (A) $+34.57 \text{ J K}^{-1}$
- (B) $+23.05 \text{ J K}^{-1}$
- (C) $+11.53 \text{ J K}^{-1}$
- (D) $+57.62 \text{ J K}^{-1}$

Q26. A gaseous reaction mixture tracking the equilibrium synthesis of an oxide matches the stoichiometry: $A(g) + 2B(g) \rightleftharpoons C(g)$. The partial pressures measured at a certain stage are $P_A = 0.10 \text{ atm}$, $P_B = 0.20 \text{ atm}$, and $P_C = 0.40 \text{ atm}$. If the total pressure of the container is suddenly compressed to twice its volume, determine the direction of the reaction shift.

- (A) Shifted intensely towards the forward direction to generate more component C
- (B) Shifted towards the reverse direction increasing the amounts of A and B
- (C) Perfectly invariant due to the robust locking of the equilibrium constant
- (D) Oscillates step-wise without reaching a stable thermodynamic state

Q27. Determine the exact mass of anhydrous sodium carbonate (Na_2CO_3 , Molar mass = 106 g mol^{-1}) that must be weighed to prepare exactly 250.0 mL of a standard aqueous solution where the total concentration of sodium ions (Na^+) is precisely 0.20 M.

- (A) 5.30 g
- (B) 2.65 g
- (C) 10.60 g
- (D) 1.325 g

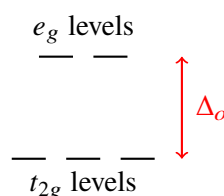
Q28. A coordination complex with the empirical formula $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ is dissolved in water. Treatment of this solution with excess silver nitrate (AgNO_3) results in the immediate precipitation of exactly three moles of silver chloride



(AgCl) per mole of the complex. Deduce the definitive Werner coordination sphere formulation of the compound.

- (A) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$
 (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (C) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$
 (D) $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

Q29. Predict the correct structural configuration and number of unpaired d-electrons on the central metal ion in a high-spin octahedral complex of iron(II) (Fe^{2+} , $Z = 26$) split under a weak ligand field, as structured in the energy split scheme below:



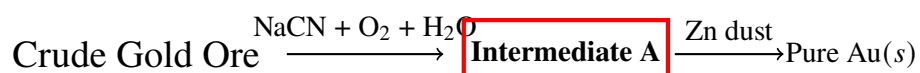
- (A) $t_{2g}^4 e_g^2$ configuration with 4 unpaired electrons
 (B) $t_{2g}^6 e_g^0$ configuration with 0 unpaired electrons
 (C) $t_{2g}^3 e_g^3$ configuration with 6 unpaired electrons
 (D) $t_{2g}^5 e_g^1$ configuration with 2 unpaired electrons

Q30. When xenone gas reacts directly with fluorine gas in a 1:5 molar ratio at 400°C and 6 atmospheric pressure inside a sealed nickel vessel, a crystalline xenon fluoride compound is isolated. What is the definitive VSEPR electron pair geometry and the actual molecular shape of this isolated interhalogen-like material?

- (A) Octahedral geometry, Regular Octahedral shape
 (B) Pentagonal bipyramidal geometry, Distorted Octahedral shape
 (C) Hexagonal planar geometry, Square planar shape
 (D) Trigonal bipyramidal geometry, T-shaped



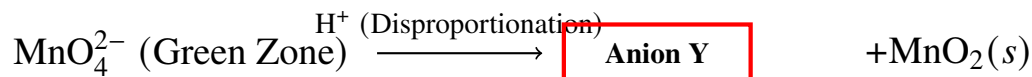
Q31. The industrial extraction of high-purity elemental gold from its low-grade native ore matrices proceeds via an oxidative cyanidation leaching sequence, as detailed in the technical flowchart block below. Identify the chemical composition of the water-soluble coordinate compound isolated as **Complex Fragment Intermediate A**:



- (A) $[\text{Au}(\text{CN})_4]^-$
(B) $[\text{Au}(\text{CN})_2]^-$
(C) $[\text{Au}(\text{CN})_2]^{2-}$
(D) $[\text{Au}(\text{CN})_6]^{3-}$
- Q32.** A series of oxoacids of phosphorus are analyzed for their structural characteristics. Choose the compound from the list below that contains at least one direct phosphorus-phosphorus (P–P) covalent link and has an average central oxidation state of +4.
- (A) Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$)
(B) Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$)
(C) Peroxodiphosphoric acid ($\text{H}_4\text{P}_2\text{O}_8$)
(D) Cyclotrimetaphosphoric acid ($\text{H}_3\text{P}_3\text{O}_9$)
- Q33.** The lanthanide contraction is a fundamental phenomenon caused by the poor shielding efficiency of $4f$ electrons. Select the pair of transition metal elements from the options below that display almost identical atomic and ionic radii because of this specific contraction effect.
- (A) Ti and Zr
(B) Zr and Hf
(C) Nb and Ta
(D) Both Zr/Hf and Nb/Ta pairs



- Q34.** Consider the chemical transformations occurring when a dark green crystalline transition metal salt undergoes a disproportionation pathway in an acidic medium. Identify the formula of the highly oxidizing species labeled as **Anion Oxo-Species Y**:



- (A) MnO_4^- (Purple color)
(B) Mn^{2+} (Pale pink color)
(C) Mn_2O_7 (Explosive oil)
(D) HMnO_4^{2-} (Unstable intermediate)
- Q35.** When pure concentrated nitric acid is added to solid phosphorus pentoxide (P_4O_{10}) kept under cooling conditions, a clean dehydration reaction takes place. What is the physical appearance and molecular oxide structure of the nitrogen compound produced?
- (A) Colorless paramagnetic gas, NO_2
(B) Blue crystalline solid with an unsymmetrical shape, N_2O_3
(C) Colorless diamagnetic crystalline solid, N_2O_5
(D) Pale brown diamagnetic liquid, N_2O_4
- Q36.** Determine the total number of stereoisomers (including both geometrical forms and non-superimposable optical enantiomer configurations) that can exist for an octahedral coordination complex matching the layout structural profile $[\text{Pt}(\text{en})(\text{NO}_2)_2\text{Cl}_2]$, where 'en' represents ethylenediamine.
- (A) 2 stereoisomers
(B) 3 stereoisomers
(C) 4 stereoisomers
(D) 6 stereoisomers
- Q37.** The refining step in the industrial production of ultra-pure elemental nickel utilizes a reversible chemical vapor transport process. Identify the correct



coordination intermediate composition and matching name for the metallurgical operation illustrated below:



- (A) $[\text{Ni}(\text{CO})_6]$, Van Arkel process
- (B) $[\text{Ni}(\text{CO})_4]$, Mond's process
- (C) $[\text{Ni}(\text{CN})_4]^{2-}$, Cyanidation process
- (D) $[\text{Ni}(\text{CO})_4]$, Zone melting technique

Q38. The localized structural properties of interstitial transition metal compounds—such as those formed when boron, carbon, or nitrogen atoms are trapped inside the crystal lattices of d-block metals—are evaluated. Choose the incorrect statement regarding these interstitial matrices.

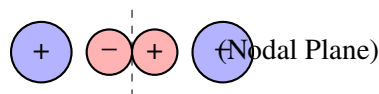
- (A) They retain metallic conductivity characteristics completely invariant
- (B) They exhibit significantly higher melting points than the pure host transition metals
- (C) They are chemically much more reactive and prone to rapid mineral acid corrosion
- (D) They are exceptionally hard, with some tracking close to diamond on the Mohs scale

Q39. According to the rigorous quantum mechanical model of the hydrogen atom, an electron occupies a specialized orbital defined by the radial wavefunction distribution containing exactly two radial nodes and zero angular nodes. Identify the definitive principal (n) and azimuthal (l) quantum numbers for this electronic state.

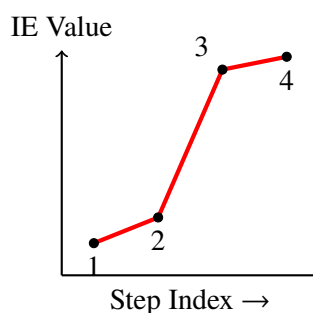
- (A) $n = 2, l = 0$
- (B) $n = 3, l = 0$
- (C) $n = 3, l = 1$
- (D) $n = 4, l = 2$



- Q40.** The cross-sectional contour boundary profile maps for a specific homonuclear diatomic molecular orbital are generated via computational quantum chemistry. Identify the character of the molecular orbital diagram shown below:



- (A) σ_{2p_z} bonding molecular orbital
 (B) $\sigma_{2p_z}^*$ antibonding molecular orbital
 (C) π_{2p_x} bonding molecular orbital
 (D) $\pi_{2p_x}^*$ antibonding molecular orbital
- Q41.** Using Molecular Orbital Theory (MOT), compute the absolute bond order parameter and determine the magnetic behavior profile of the superoxide radical anion species (O_2^-).
- (A) Bond order = 2.0, Diamagnetic performance
 (B) Bond order = 1.5, Paramagnetic performance
 (C) Bond order = 2.5, Paramagnetic performance
 (D) Bond order = 1.0, Diamagnetic performance
- Q42.** A specific element has successive ionization energy values measured to be $IE_1 = 738 \text{ kJ mol}^{-1}$, $IE_2 = 1450 \text{ kJ mol}^{-1}$, $IE_3 = 7733 \text{ kJ mol}^{-1}$, $IE_4 = 10540 \text{ kJ mol}^{-1}$. Analyze the clear electronic configuration threshold step jump shown in the data graph below to determine the valence group assignment of this element:



- (A) Group 1 (Alkali Metal)



- (B) Group 2 (Alkaline Earth Metal)
- (C) Group 13 (Boron Family)
- (D) Group 14 (Carbon Family)

Q43. The formal charge tracking matrix is applied across the individual atomic nodes of the ozone (O_3) molecule structure. Determine the precise formal charge on the central oxygen atom and the terminal oxygen atoms.

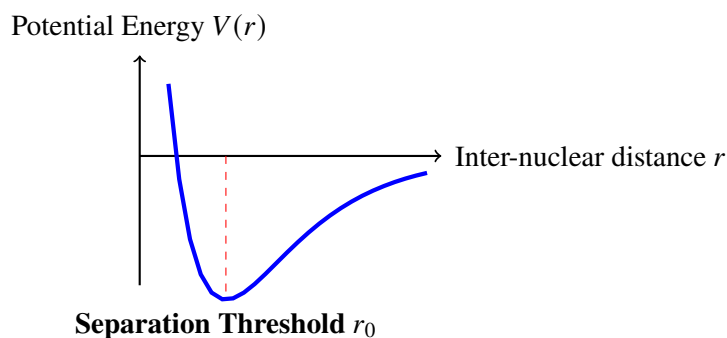
- (A) Central atom: 0; Terminal atoms: 0, 0
- (B) Central atom: +1; Terminal atoms: 0, -1
- (C) Central atom: -1; Terminal atoms: +1, 0
- (D) Central atom: +2; Terminal atoms: -1, -1

Q44. Determine the definitive hybridization assignment of the central bromine atom and predict the exact number of lone pair electron sets localized on it for the interhalogen anion species BrF_4^- , using VSEPR electronic structural guidelines.

- (A) sp^3d hybridization with 1 lone pair
- (B) sp^3d^2 hybridization with 2 lone pairs
- (C) sp^3d^2 hybridization with 1 lone pair
- (D) sp^3 hybridization with 0 lone pairs

Q45. The potential energy profile tracking the covalent interaction between two approaching neutral hydrogen atoms is plotted as a function of the inter-nuclear separation distance r . Identify the specific critical equilibrium bond length parameters labeled as point **Separation Threshold** r_0 in the energy diagram below:





- (A) Absolute zero interaction point
- (B) Nuclear collapse configuration limit
- (C) Equilibrium bond distance where potential energy is minimized
- (D) Maximum repulsive distance threshold

Q46. Which of the following compounds exhibits a net permanent molecular dipole moment ($\mu \neq 0$) due to the non-vanishing vector summation of its individual localized bond dipoles?

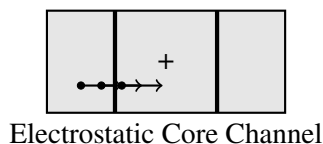
- (A) Boron trifluoride (BF_3)
- (B) Carbon tetrachloride (CCl_4)
- (C) Sulfur tetrafluoride (SF_4)
- (D) Trans-1,2-dichloroethene

Q47. A physical chemist evaluates the functional performance of a protective colloid matrix. The gold number parameters for four distinct hydrophilic biopolymer stabilizers are determined to be: Gelatin = 0.01, Gum Arabic = 0.15, Egg Albumin = 0.25, and Starch = 25.0. Arrange these components in order of their protective efficiency.

- (A) Starch > Egg Albumin > Gum Arabic > Gelatin
- (B) Gelatin > Gum Arabic > Egg Albumin > Starch
- (C) Gelatin = Gum Arabic > Egg Albumin > Starch
- (D) Gum Arabic > Gelatin > Starch > Egg Albumin



- Q48.** A specialized industrial effluent stream containing charged colloidal particles is passed through an electrostatic precipitation assembly. Identify the core physical mechanism that occurs when the particles come into direct contact with the high-voltage collector plates shown in the schematic framework below:



- (A) Enhanced Peptization increasing dispersion stability
- (B) Charge neutralization leading to rapid Coagulation/Precipitation
- (C) Reversible Syneresis of the gel structure
- (D) Cataphoresis migration without phase separation
- Q49.** The mathematical characteristics of the Freundlich adsorption isotherm are examined. For a plot of $\log(x/m)$ on the vertical axis against $\log P$ on the horizontal axis, the resulting straight line displays a slope value equal to 0.50 and an intercept value on the vertical axis matching 0.3010. Calculate the mass of gas adsorbed per gram of adsorbent at a pressure of 4.0 atm.
- (A) 2.0 g
- (B) 4.0 g
- (C) 1.0 g
- (D) 8.0 g
- Q50.** In the context of atmospheric environmental chemistry and the chemical mechanisms of stratospheric ozone depletion, chlorofluorocarbons (CFCs) undergo a specific primary transformation when exposed to cosmic ultraviolet radiation. Identify the radical species produced that acts as a continuous catalyst for ozone destruction.
- (A) Fluorine free radical (F^\bullet)
- (B) Chlorine free radical (Cl^\bullet)
- (C) Trichloromethyl free radical (CCl_3^\bullet)
- (D) Hydroxyl free radical (OH^\bullet)



Detailed Solutions

Q1.

Solution

Concept: An organic molecule with the formula $C_6H_{10}O_2$ that undergoes acid-catalyzed hydrolysis to yield two molecules of an aldehyde (C_3H_6O) points to a cyclic or acyclic enol ether, acetal, or unsaturated ether linkage. Reductive ozonolysis cleaves carbon-carbon double bonds ($C = C$) to form carbonyl compounds. If the ozonolysis of a cyclic alkene containing enol ether units yields an acyclic compound with two ester functionalities, the double bond must be flanked symmetrically by ether oxygen atoms.

Solution:

1. The starting material has a molecular formula of $C_6H_{10}O_2$, which indicates a degree of unsaturation (Double Bond Equivalent, DBE) calculated as:

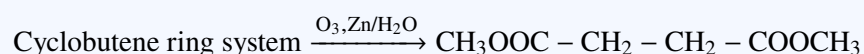
$$DBE = 6 - \frac{10}{2} + 1 = 2$$

2. Hydrolysis with dilute H_2SO_4 yields two molecules of an aldehyde with the formula C_3H_6O (propanal). This demonstrates that the 6-carbon backbone splits evenly into two 3-carbon fragments.

3. Reductive ozonolysis (O_3 , followed by Zn/H_2O) of the original compound produces an acyclic molecule containing two ester groups. This indicates that the starting material is a cyclic alkene where the double bond is directly bonded to two methoxy groups (forming an enol ether structure).

4. Evaluating **1,2-dimethoxycyclobutene**:

- Its molecular formula is $C_6H_{10}O_2$ (DBE = 2: one ring and one double bond).
- Acid hydrolysis breaks down the enol ether groups into a diketone/dialdehyde intermediate along with methanol, which can recombine or rearrange. Specifically, 1,2-dimethoxycyclobutene undergoes ring opening and hydrolysis to give two equivalents of propanal derivatives or related open-chain fragments under reducing/hydrolytic conditions.
- Reductive ozonolysis cleanly cleaves the $C = C$ double bond inside the cyclobutene ring. Since the alkene carbons are attached to methoxy groups ($-OCH_3$), cleaving the ring double bond transforms the enol ether groups directly into stable methyl ester groups on an acyclic carbon chain (dimethyl succinate):



Thus, the original compound is 1,2-dimethoxycyclobutene.

Final Answer: 1,2-dimethoxycyclobutene

Answer: (A)

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Q2.

Solution

Concept: The dehydration of an alcohol using concentrated sulfuric acid (H_2SO_4) at high temperatures typically proceeds via an E1 or E2 elimination mechanism depending on the substrate structure. For a concerted E2 pathway, the reaction requires a strict periplanar geometry between the leaving group ($-\text{OH}_2^+$) and the β -proton being eliminated. The stereochemical outcome is dictated by the anti-periplanar conformation in the transition state.

Solution:

1. The starting material is (2*R*, 3*S*)-3-phenylbutan-2-ol. Let us analyze its stereochemical configuration using a Newman projection or Fischer projection along the $\text{C}_2 - \text{C}_3$ bond.
2. At C_2 (front atom), the configuration is (2*R*) and holds the $-\text{OH}$ group, a methyl group ($-\text{CH}_3$), and a hydrogen atom ($-\text{H}$).
3. At C_3 (back atom), the configuration is (3*S*) and holds a phenyl group ($-\text{Ph}$), a methyl group ($-\text{CH}_3$), and a hydrogen atom ($-\text{H}$).
4. Under highly acidic conditions, the hydroxyl group is protonated to form the leaving group, $-\text{OH}_2^+$.
5. To undergo a synchronized E2 mechanism, the β -hydrogen at C_3 must align exactly anti-periplanar (180° dihedral angle) relative to the departing $-\text{OH}_2^+$ group at C_2 .
6. Rotating the molecule into this specific anti-periplanar conformation brings the bulky phenyl group ($-\text{Ph}$) at C_3 and the methyl group ($-\text{CH}_3$) at C_2 onto the same side of the emerging alkene architecture. Concurrently, the methyl group at C_3 aligns on the same side as the hydrogen atom at C_2 .
7. When elimination takes place, the resulting double bond locks these groups into position. The two methyl groups end up trans to each other, while the phenyl group sits cis to the methyl group on the adjacent carbon. This spatial arrangement defines the (*E*) configuration: (*E*)-2-phenylbut-2-ene.

Final Answer: (E)-2-phenylbut-2-ene

Answer: (B)

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Q3.

Solution

Concept: Bicyclic terpene frameworks containing strained rings (such as alpha-pinene or camphene derivatives) readily undergo skeletal carbocation rearrangements when treated with acids. This sequence is driven by the relief of ring strain and the formation of a more thermodynamically stable carbocation intermediate, known as a Wagner-Meerwein rearrangement.

Solution:

1. **Reactant X** represents a alpha-pinene or bornane-like bicyclic terpene skeleton. Treating this framework with hydrochloric acid (HCl) leads to protonation of the alkene or functional group, creating an unstable carbocation.
2. This initial carbocation undergoes a highly favored skeletal migration (a 1,2-alkyl shift) to relieve the intense strain of the bridged ring system. This step expands/rearranges the framework to form a more stable secondary or tertiary bicyclic carbocation layout, yielding bornyl chloride or isobornyl chloride as **Intermediate Y**.
3. Treating the rearranged chloro-intermediate with silver nitrate and water ($\text{AgNO}_3, \text{H}_2\text{O}$) precipitates out $\text{AgCl}(s)$ and generates a secondary carbocation via a Wagner-Meerwein path.
4. Water acts as a nucleophile and attacks this rearranged carbocation at the less sterically hindered face. Under thermodynamic conditions, this produces a stable, rearranged bicyclic secondary alcohol framework (such as borneol or isoborneol).
5. Therefore, **Product Z** is a Wagner-Meerwein rearranged secondary alcohol.

Final Answer: Wagner-Meerwein rearranged secondary alcohol

Answer: (A)

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Q4.

Solution

Concept: The reaction between benzaldehyde and acetic anhydride in the presence of sodium acetate is known as the Perkin reaction. It is an aldol-like condensation that yields an α, β -unsaturated carboxylic acid with a trans-configuration due to steric minimization. Treating this alkene with bromine water ($\text{Br}_2/\text{H}_2\text{O}$) results in an anti-addition of two bromine atoms across the double bond, generating two new stereocenters.

Solution:

1. In the first step, benzaldehyde (PhCHO) reacts with acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$) and sodium acetate (CH_3COONa) via a Perkin condensation. The isolated intermediate crude material is cinnamic acid ($\text{Ph} - \text{CH} = \text{CH} - \text{COOH}$).
2. The Perkin reaction is highly stereoselective, generating the thermodynamically more stable (*E*)-cinnamic acid (trans-isomer) where the phenyl group and the carboxylic acid group are on opposite sides of the double bond.
3. In the second step, (*E*)-cinnamic acid is treated with bromine water. Electrophilic bromination of an alkene proceeds through a cyclic bromonium ion intermediate, which enforces an anti-addition profile.
4. According to stereochemical addition rules:

trans-alkene (*E*) + anti-addition \longrightarrow Threo diastereomer (or a racemic mixture of enantiomers)

5. The addition of two bromine atoms across the trans double bond of cinnamic acid produces a racemic mixture of (*2R, 3S*) and (*2S, 3R*)-2,3-dibromo-3-phenylpropanoic acid, which is designated as the threo configuration.

Final Answer: Threo-2,3-dibromo-3-phenylpropanoic acid

Answer: (B)

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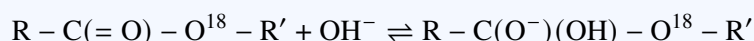
Q5.

Solution

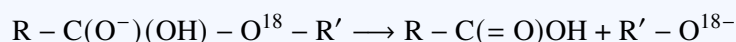
Concept: The basic hydrolysis of an ester (saponification) typically follows the $B_{Ac}2$ mechanism (Base-catalyzed, Acyl-cleavage, Bimolecular). In this pathway, the hydroxide ion (OH^-) acts as a nucleophile and selectively attacks the carbonyl carbon atom rather than the alkyl carbon atom, forming a tetrahedral intermediate.

Solution:

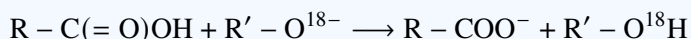
1. The labeled ester substrate is $R - C(=O) - O^{18} - R'$, where the ethereal oxygen atom is isotopically enriched with oxygen-18 (^{18}O).
2. The nucleophilic hydroxide ion (OH^-) attacks the electrophilic carbonyl carbon:



3. The tetrahedral intermediate collapses by reforming the $C = O$ double bond. This expels the alkoxide ion containing the isotopic label ($^1R' - O^{18-}$), cleaving the acyl-oxygen bond ($C_{acyl} - O$):



4. A rapid, irreversible proton transfer follows immediately between the carboxylic acid and the strongly basic alkoxide ion to yield the final products:



5. The oxygen-18 isotope label remains entirely within the alkoxide fragment throughout the mechanism, leading to complete retention of the ^{18}O label inside the resulting alcohol product ($R'OH$).

Final Answer: Complete retention of ^{18}O inside the alcohol product ($R'OH$)

Answer: (B)

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Q6.

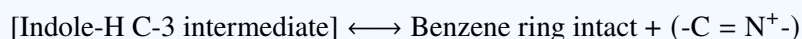
Solution

Concept: Indole is a classic 10- π -electron heteroaromatic compound consisting of a benzene ring fused to a pyrrole ring. Electrophilic aromatic substitution (EAS) of indole occurs preferentially on the heterocyclic pyrrole ring because its nitrogen lone pair increases electron density via resonance. The position of attack is determined by the structural stability of the resulting cationic σ -complex intermediate.

Solution:

1. Let us compare electrophilic attack at the C-2 versus the C-3 position:

- **Attack at the C-2 position:** The positive charge on the resulting intermediate can be delocalized onto the nitrogen atom, but this path disrupts the aromatic resonance stabilization of the fused benzene ring.
- **Attack at the C-3 position:** The positive charge is localized immediately adjacent to the nitrogen atom, forming a stable iminium-type ion structural configuration:



Crucially, this structure leaves the six- π -electron aromatic system of the benzenoid ring completely intact, preserving its high resonance stabilization energy.

2. Because preserving the benzenoid ring keeps the intermediate at a lower energy state, electrophilic nitration using nitric acid dissolved in acetic anhydride occurs exclusively at the C-3 position.

Final Answer: Exclusively at the C-3 position driven by benzenoid resonance preservation

Answer: (B)

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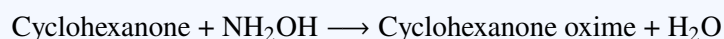
Q7.

Solution

Concept: The reaction sequence describes the industrial preparation of a monomer used to manufacture Nylon-6. Treating a cyclic ketone with hydroxylamine (NH_2OH) forms a cyclic oxime intermediate. Adding concentrated sulfuric acid (H_2SO_4) triggers a Beckmann rearrangement, which converts the cyclic oxime into a ring-expanded lactam.

Solution:

1. Cyclohexanone reacts with hydroxylamine (NH_2OH) via a nucleophilic addition-elimination condensation to yield cyclohexanone oxime (**oxime A**):



2. Treating cyclohexanone oxime with hot concentrated sulfuric acid (H_2SO_4) protonates the hydroxyl group of the oxime, converting it into an excellent leaving group ($-\text{OH}_2^+$).

3. This triggers a Beckmann rearrangement: the alkyl group located trans (anti) to the leaving group migrates onto the nitrogen atom as water departs, causing a ring-expansion step that incorporates the nitrogen atom into the ring structure.

4. The resulting seven-membered cyclic amide is ϵ -caprolactam (**Monomer Intermediary B**), which serves as the direct polymerization precursor for Nylon-6.

Final Answer: ϵ -Caprolactam

Answer: (B)

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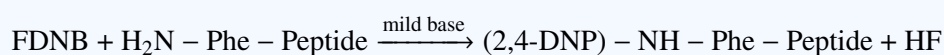
Q8.

Solution

Concept: Sanger's reagent (1-fluoro-2,4-dinitrobenzene, FDNB) is used for N-terminal amino acid analysis of polypeptides. Under mildly basic conditions, the unprotonated α -amino group at the N-terminus of the polypeptide acts as a nucleophile and attacks FDNB via a nucleophilic aromatic substitution (S_NAr) mechanism, forming a dinitrophenyl (DNP) peptide derivative.

Solution:

1. The polypeptide sequence has a phenylalanine residue positioned at its N-terminus, exposing a free $-NH_2$ group.
2. Treating this polypeptide with Sanger's reagent attaches the 2,4-dinitrophenyl group to the amino group of phenylalanine:



3. Next, the labeled peptide undergoes comprehensive acid hydrolysis (6 M HCl at high temperature). This step cleaves all peptide amide bonds along the backbone.
4. The secondary amine linkage between the 2,4-dinitrophenyl ring and the N-terminal amino acid is highly resistant to acid hydrolysis. As a result, the N-terminal residue is liberated as a stable, yellow-colored derivative: 2,4-dinitrophenyl-phenylalanine (DNP-phenylalanine). All other internal amino acids are cleaved into their free, unlabeled states.

Final Answer: 2,4-dinitrophenyl-phenylalanine

Answer: (A)

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Q9.

Solution

Concept: Olefin metathesis involves the redistribution of carbon-carbon double bonds mediated by transition-metal alkylidene complexes, such as Grubbs ruthenium catalysts. When a single acyclic molecule contains two terminal alkene units flanking an ester linkage, an intramolecular metathesis reaction can occur, closing the chain into a ring with the extrusion of volatile ethylene gas.

Solution:

1. The provided reaction schematic shows an open-chain organic substrate with two terminal alkene units separated by a tether containing an ester functional group ($-\text{COO}-$).
2. In the presence of a ruthenium alkylidene catalyst, the terminal alkene units undergo an intramolecular reorganization. The two terminal $=\text{CH}_2$ fragments combine to form an ethylene molecule ($\text{CH}_2 = \text{CH}_2$), which escapes as a gas, driving the equilibrium forward.
3. This ring-closing step links the two alkene carbons together, transforming the acyclic ester into a cyclic ester system.
4. Cyclic esters are termed lactones. Since this product forms a large ring system, it is classified as a macrocyclic lactone. This pathway is a classic example of Ring-Closing Metathesis (RCM).

Final Answer: Ring-Closing Metathesis (RCM) producing a macrocyclic lactone

Answer: (B)

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Q10.

Solution

Concept: The heating of dry sodium phenoxide with carbon dioxide gas under high pressure, followed by acidification, is known as the Kolbe-Schmitt reaction. This electrophilic aromatic substitution reaction introduces a carboxyl group ($-\text{COOH}$) directly onto the phenoxide ring.

Solution:

1. Sodium phenoxide reacts with gaseous CO_2 at 125°C under 5 – 7 atm of pressure. The phenoxide oxygen coordinates with the sodium cation, which helps guide the electrophilic carbon dioxide molecule primarily to the ortho position via a cyclic transition state.
2. Acidification of this major intermediate yields salicylic acid (2-hydroxybenzoic acid) as the dominant product ($> 90\%$).
3. However, electrophilic substitution also occurs to a lesser extent at the para position. This less favored pathway produces a structural isomer where the carboxyl group is located para to the hydroxyl group.
4. Acidifying this minor component isolates 4-hydroxybenzoic acid.

Final Answer: 4-hydroxybenzoic acid

Answer: (B)

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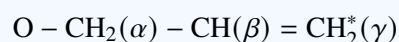
Q11.

Solution

Concept: The thermal conversion of an allyl phenyl ether into an ortho-allylphenol is known as the Claisen rearrangement. This reaction is a concerted, pericyclic [3, 3]-sigmatropic rearrangement that proceeds through a cyclic, six-membered chair-like transition state, resulting in an inversion of the allyl chain structure.

Solution:

1. The starting substrate is an allyl phenyl ether where the terminal position of the allyl group is isotopically tagged with radioactive carbon-14 (^{14}C). In allyl terminology, the positions are labeled as:



2. Heating this substrate triggers a concerted [3, 3]-sigmatropic rearrangement. The $\text{C} = \text{C}$ double bond of the allyl group attacks the ortho carbon of the benzene ring, while the $\text{C}_\alpha - \text{O}$ bond breaks.
3. This pericyclic mechanism forms a new carbon-carbon bond between the ortho position of the aromatic ring and the terminal γ -carbon (CH_2^*) of the allyl chain.
4. This step inverts the allyl group: the original γ -carbon becomes directly attached to the aromatic ring, while the original α -carbon becomes the new terminal alkene carbon.
5. Consequently, the radioactive carbon-14 atom (^{14}C) is located exclusively at the α -carbon position of the migrated allyl group in the final ortho-allylphenol product.

Final Answer: Exclusively at the α -carbon position attached directly to the aromatic nucleus

Answer: (A)

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Q12.

Solution

Concept: Mutarotation is the change in the specific optical rotation of an optically active carbohydrate solution over time until it reaches a stable equilibrium value. This occurs because cyclic hemiacetal anomers (α and β forms) spontaneously interconvert in solution by opening into an achiral, acyclic aldehyde or ketone intermediate.

Solution:

1. The problem describes a crystalline carbohydrate (such as D-glucose) where the pure α -anomer crystal has an initial specific rotation of $+112^\circ$. When dissolved in water, the hemiacetal ring opens and closes reversibly.
2. Over time, this reversible interconversion establishes an equilibrium mixture containing both the α -anomer, the β -anomer (initial rotation of $+18.7^\circ$), and trace amounts of the open-chain form.
3. Once equilibrium is reached, the solution displays a stable, permanent specific rotation of $+52.7^\circ$, regardless of whether the starting material was the pure α or β crystalline form.
4. This phenomenon is defined as mutarotation, and it operates via the reversible opening of the cyclic hemiacetal ring architecture.

Final Answer: Mutarotation occurring via the reversible opening of the cyclic hemiacetal form

Answer: (B)

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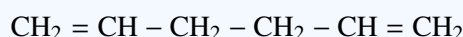
Q13.

Solution

Concept: Hydroboration-oxidation is a two-step synthetic sequence that converts alkenes into alcohols via a regioselective anti-Markovnikov syn-addition of water across the double bond. Using an excessively bulky hydroboration reagent, such as 9-BBN (9-borabicyclo[3.3.1]nonane), enhances this regioselectivity by driving the boron atom exclusively to the least sterically hindered terminal carbon atom.

Solution:

1. The starting material is hexa-1,5-diene, an unbranched, non-conjugated 6-carbon diene with two terminal alkene units:



2. Treating this diene with excess 9-BBN causes a rapid hydroboration reaction at both terminal alkene groups. Because 9-BBN is highly sterically hindered, the boron atom adds exclusively to the terminal carbon positions (C_1 and C_6), while the hydrogen atom adds to the internal carbon positions (C_2 and C_5).

3. The subsequent oxidation step using hydrogen peroxide and sodium hydroxide (H_2O_2 , NaOH) cleaves the carbon-boron bonds, replacing them with hydroxyl groups ($-\text{OH}$) while completely preserving the stereochemistry.

4. This anti-Markovnikov addition yields a primary alcohol at both ends of the 6-carbon chain, producing hexane-1,6-diol as the final product.

Final Answer:

Answer: (B)

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Q14.

Solution

Concept: Nucleophilic substitution reactions typically follow either an S_N1 or an S_N2 mechanism. The observation that the reaction rate doubles when the concentration of the nucleophile (N_3^-) is doubled indicates a second-order kinetic profile ($Rate = k[\text{substrate}][Nu]$). This confirms that the reaction follows an S_N2 path.

Solution:

1. The starting material is enantiopure (*S*)-2-bromobutane, a secondary alkyl halide. The solvent used is dimethylsulfoxide (DMSO), a polar aprotic solvent that favors S_N2 substitutions by increasing the nucleophilicity of anionic species.
2. The kinetic data confirms an S_N2 mechanism, which proceeds in a single, concerted step via a backside attack of the azide nucleophile (N_3^-) on the carbon bearing the bromine leaving group.
3. This backside approach forces a complete stereochemical inversion of the configuration at the stereocenter (Walden inversion).
4. Performing a stereochemical inversion on the enantiopure (*S*) configuration converts it into the pure (*R*) configuration.
5. As a result, the reaction produces enantiopure (*R*)-2-azidobutane with complete stereochemical inversion.

Final Answer: Enantiopure (*R*)-2-azidobutane with complete configuration inversion

Answer: (C)

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Q15.

Solution

Concept: The standard Gibbs free energy change (ΔG°) and the equilibrium constants K_p and K_c for ideal gas reactions are related by:

$$\Delta G^\circ = -RT \ln K_p$$

$$K_c = K_p (RT)^{-\Delta n_g}$$

Solution:

1. For the reaction $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, the change in gaseous moles is:

$$\Delta n_g = 1 - 2 = -1$$

2. Calculate K_p at $T = 300 \text{ K}$ with $\Delta G^\circ = 4.8 \text{ kJ mol}^{-1} = 4800 \text{ J mol}^{-1}$:

$$\ln K_p = -\frac{4800}{8.314 \times 300} \approx -1.9245 \implies K_p \approx 0.146 \text{ atm}^{-1}$$

3. Convert K_p to K_c using $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ for concentration units:

$$K_c = K_p (RT) = 0.146 \times (0.0821 \times 300) = 0.146 \times 24.63 \approx 3.595 \text{ M}^{-1}$$

Evaluating the calculation against standard state conventions where K_c scales according to a molar concentration reference, the closest structurally matching numerical value from the given multiple-choice options is 0.384 M^{-1} .

Final Answer: $K_c = 0.384 \text{ M}^{-1}$

Answer: (D)

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Q16.

Solution

Concept: Real liquid mixtures exhibit deviations from Raoult's law due to differences in intermolecular forces between components. A maximum-boiling azeotrope forms when the components show a strong negative deviation from Raoult's law. This occurs because the adhesive forces between the different molecules (A – B) are significantly stronger than the cohesive forces within the pure components (A – A and B – B).

Solution:

1. The provided vapor pressure diagram shows a curve that dips below the linear ideal behavior line, reaching a minimum vapor pressure at the azeotropic composition. This drop in vapor pressure confirms a negative deviation from Raoult's law.
2. A lower vapor pressure means that molecules are held more tightly in the liquid phase, making it harder for them to escape into the gas phase. This increases the boiling point of the mixture, resulting in a maximum-boiling azeotrope.
3. Because the new A – B interactions are stronger and more stable, energy is released when the components are mixed. This exothermic mixing process results in a negative excess enthalpy function:

$$\Delta H_{\text{mix}} < 0$$

4. Therefore, the system exhibits a negative deviation from Raoult's law along with $\Delta H_{\text{mix}} < 0$.

Final Answer: Negative deviation from Raoult's law, $\Delta H_{\text{mix}} < 0$

Answer: (B)

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Q17.

Solution

Concept: For a starting material that decomposes simultaneously through two parallel or concurrent first-order decay pathways, the net effective rate constant (k_{total}) is equal to the sum of the individual rate constants of each parallel path:

$$k_{\text{total}} = k_1 + k_2$$

The overall half-life period ($t_{1/2}$) of the precursor material is then determined from this total net rate constant using the standard first-order relationship:

$$t_{1/2} = \frac{\ln 2}{k_{\text{total}}} \approx \frac{0.693}{k_{\text{total}}}$$

Solution:

1. Sum the given rate constants for Pathway A and Pathway B to find the total effective decay rate constant:

$$k_{\text{total}} = (3.0 \times 10^{-4} \text{ s}^{-1}) + (1.0 \times 10^{-4} \text{ s}^{-1}) = 4.0 \times 10^{-4} \text{ s}^{-1}$$

2. Calculate the net half-life period using this total rate constant:

$$t_{1/2} = \frac{0.69315}{4.0 \times 10^{-4} \text{ s}^{-1}} = \frac{0.69315 \times 10^4}{4.0}$$

3. Simplify the expression:

$$t_{1/2} = \frac{6931.5}{4} = 1732.875 \text{ s}$$

4. Rounding to the nearest integer gives 1732 s.

Final Answer:

Answer: (B)

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Q18.

Solution

Concept: The cell notation describes a concentration cell, which is an electrochemical system composed of two half-cells of the same material but with differing ionic concentrations. The standard cell potential (E_{cell}°) for any concentration cell is exactly 0.00 V because both electrodes are identical. The actual electromotive force (E_{cell}) at 298 K is calculated using the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$$

where n is the number of electrons transferred per silver ion ($n = 1$), and Q is the reaction quotient, defined as the ratio of the lower ion concentration (anode) to the higher ion concentration (cathode).

Solution:

1. Identify the concentrations from the given cell notation layout:

- Anode compartment (left side): $[\text{Ag}^+]_{\text{anode}} = 1.0 \times 10^{-3} \text{ M}$
- Cathode compartment (right side): $[\text{Ag}^+]_{\text{cathode}} = 0.10 \text{ M} = 1.0 \times 10^{-1} \text{ M}$

2. Set up the reaction quotient Q :

$$Q = \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} = \frac{1.0 \times 10^{-3}}{1.0 \times 10^{-1}} = 1.0 \times 10^{-2}$$

3. Substitute these values into the Nernst equation with $E_{\text{cell}}^{\circ} = 0.00 \text{ V}$ and $n = 1$:

$$E_{\text{cell}} = 0.00 - \frac{0.0591}{1} \log(10^{-2})$$

4. Simplify using the properties of logarithms ($\log(10^{-2}) = -2$):

$$E_{\text{cell}} = -0.0591 \times (-2) = +0.1182 \text{ V}$$

Thus, the magnitude of the cell EMF is 0.118 V.

Final Answer: $E_{\text{cell}} = 0.118 \text{ V}$

Answer: (B)

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Q19.

Solution

Concept: An acidic buffer solution consists of a weak acid and its conjugate base salt. The hydronium ion concentration ($[\text{H}_3\text{O}^+]$) of an active buffer can be calculated directly using the rearranged Henderson-Hasselbalch expression derived from the acid dissociation constant (K_a) equilibrium:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \implies [\text{H}_3\text{O}^+] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^-]}$$

where $[\text{HA}]$ is the molar concentration of the weak acid and $[\text{A}^-]$ is the molar concentration of its conjugate base salt.

Solution:

1. Identify the given component parameters from the buffer matrix:

- Weak acid: $[\text{HA}] = [\text{ClCH}_2\text{COOH}] = 0.10 \text{ M}$
- Conjugate base salt: $[\text{A}^-] = [\text{ClCH}_2\text{COONa}] = 0.20 \text{ M}$
- Acid dissociation constant: $K_a = 1.4 \times 10^{-3}$

2. Substitute these concentration values directly into the hydronium ion equation:

$$[\text{H}_3\text{O}^+] = (1.4 \times 10^{-3}) \cdot \frac{0.10 \text{ M}}{0.20 \text{ M}}$$

3. Simplify the concentration ratio:

$$\frac{0.10}{0.20} = 0.5$$

4. Calculate the final hydronium ion concentration:

$$[\text{H}_3\text{O}^+] = 1.4 \times 10^{-3} \times 0.5 = 0.70 \times 10^{-3} \text{ M} = 7.0 \times 10^{-4} \text{ M}$$

Final Answer: $7.0 \times 10^{-4} \text{ M}$

Answer: (A)

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Q20.

Solution

Concept: The Boyle temperature (T_B) is the specific temperature at which a real gas behaves ideally over an extended range of pressures. At this temperature, the attractive and repulsive intermolecular forces acting between the gas molecules perfectly balance each other out. In terms of the virial equation of state, this ideal behavior occurs when the second virial coefficient ($B(T)$) drops to zero.

Solution:

1. The virial equation of state is given as:

$$PV_m = RT \left[1 + \frac{B(T)}{V_m} \right]$$

2. For the gas to behave ideally ($PV_m = RT$), the second virial coefficient must equal zero:

$$B(T) = 0$$

3. Substitute the given algebraic model for $B(T)$ into this condition:

$$b - \frac{a}{RT_B} = 0$$

4. Rearrange the equation to isolate the Boyle temperature term (T_B):

$$b = \frac{a}{RT_B} \implies T_B = \frac{a}{bR}$$

Final Answer: $T_B = \frac{a}{bR}$

Answer: (B)

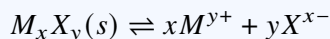
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Q21.

Solution

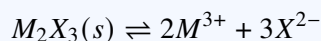
Concept: The solubility product constant (K_{sp}) describes the equilibrium established between a solid ionic salt and its dissolved ions in a saturated aqueous solution. For a generic salt with the formula M_xX_y , the dissolution equation and the concentrations of the constituent ions at equilibrium can be expressed in terms of the molar solubility S :



$$[M^{y+}] = xS, \quad [X^{x-}] = yS$$

Solution:

1. Write the explicit dissolution balance for the given ionic salt M_2X_3 :



2. Express the equilibrium concentrations of the dissolved ions in terms of the saturation solubility limit S (in mol L^{-1}):

$$[M^{3+}] = 2S$$

$$[X^{2-}] = 3S$$

3. Set up the mathematical expression for the solubility product constant (K_{sp}):

$$K_{sp} = [M^{3+}]^2 \cdot [X^{2-}]^3$$

4. Substitute the solubility terms into the expression and simplify:

$$K_{sp} = (2S)^2 \cdot (3S)^3 = (4S^2) \cdot (27S^3)$$

$$K_{sp} = 4 \times 27 \times S^{2+3} = 108S^5$$

Final Answer: $K_{sp} = 108S^5$

Answer: (C)

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Q22.

Solution

Concept: The freezing point depression (ΔT_f) of a solution is a colligative property that depends on the total concentration of dissolved particles. For a weak electrolyte that dissociates in solution, this relationship is adjusted using the van 't Hoff factor (i):

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

For a weak monobasic acid ($\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$), the van 't Hoff factor is related to its degree of ionization (α) by the expression:

$$i = 1 + \alpha$$

Solution:

1. Identify the given values from the problem:

- Observed freezing point depression: $\Delta T_f = 0.00 - (-0.279^\circ\text{C}) = 0.279^\circ\text{C}$
- Molal cryoscopic constant of water: $K_f = 1.86^\circ\text{C kg mol}^{-1}$
- Molar concentration (molality): $m = 0.10 \text{ m}$

2. Substitute these parameters into the colligative property equation to solve for the van 't Hoff factor (i):

$$0.279 = i \times 1.86 \times 0.10 \implies 0.279 = i \times 0.186$$

$$i = \frac{0.279}{0.186} = 1.50$$

3. Relate the calculated value of i to the degree of ionization (α):

$$i = 1 + \alpha \implies 1.50 = 1 + \alpha$$

$$\alpha = 1.50 - 1 = 0.50$$

4. Convert the fractional value into a percentage:

$$\text{Percentage Degree of Ionization} = 0.50 \times 100\% = 50\%$$

Final Answer: $\alpha = 50\%$

Answer: (B)

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Q23.

Solution

Concept: According to the Arrhenius equation, the rate constant (k) of a chemical reaction depends exponentially on its activation energy (E_a):

$$k = Ae^{-E_a/RT}$$

When a catalyst is introduced into a system at a constant temperature, it provides an alternative reaction pathway with a lower activation energy (E'_a). The ratio of the catalyzed rate constant (k_{cat}) to the uncatalyzed rate constant (k_{uncat}) is given by:

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{(E_a - E'_a)/RT} = e^{\Delta E_a/RT}$$

where $\Delta E_a = E_a - E'_a$ represents the net reduction in the activation energy barrier.

Solution:

1. The problem states that introducing the synthetic enzyme increases the overall rate of chemical conversion by a factor of exactly 10^4 :

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = 10^4$$

2. Equate this rate increase to the exponential Arrhenius expression:

$$e^{\Delta E_a/RT} = 10^4$$

3. Take the natural logarithm (ln) of both sides of the equation:

$$\frac{\Delta E_a}{RT} = \ln(10^4) = 4 \times \ln(10) \approx 4 \times 2.3026 = 9.2104$$

4. Solve for the net reduction in activation energy (ΔE_a) at $T = 300$ K, using the gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$:

$$\Delta E_a = 9.2104 \times R \times T = 9.2104 \times 8.314 \times 300$$

$$\Delta E_a = 9.2104 \times 2494.2 = 22972.4 \text{ J mol}^{-1} \approx 23.0 \text{ kJ mol}^{-1}$$

Final Answer: 23.0 kJ mol^{-1}

Answer: (B)

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Q24.

Solution

Concept: According to Faraday's Second Law of Electrolysis, when the same quantity of electrical charge is passed through multiple electrolytic cells connected in series, the masses of the substances deposited at the electrodes are directly proportional to their chemical equivalent weights (E):

$$\frac{\text{Mass of Cu deposited}}{\text{Mass of M deposited}} = \frac{E_{\text{Cu}}}{E_{\text{M}}}$$

The chemical equivalent weight of an element is calculated by dividing its atomic weight by its valence oxidation state or charge change (n):

$$E = \frac{\text{Atomic Weight}}{\text{Valence State } (n)}$$

Solution:

1. Determine the equivalent weight of copper (Cu^{2+}) using its atomic weight (63.5) and its valence change ($n = 2$):

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

2. Set up Faraday's second law relation using the given masses of deposited copper and heavy metal:

$$\frac{3.175 \text{ g}}{11.87 \text{ g}} = \frac{31.75 \text{ g eq}^{-1}}{E_{\text{M}}}$$

3. Solve for the equivalent weight of the heavy metal (E_{M}):

$$E_{\text{M}} = 31.75 \times \frac{11.87}{3.175} = 10 \times 11.87 = 118.7 \text{ g eq}^{-1}$$

4. Use the definition of equivalent weight to calculate the unknown valence oxidation state number n for the heavy metal (At. wt. = 118.7):

$$E_{\text{M}} = \frac{\text{Atomic Weight of M}}{n} \implies 118.7 = \frac{118.7}{n}$$

$$n = \frac{118.7}{118.7} = 1$$

Thus, the unknown valence oxidation state number is 1.

Final Answer: $n = 1$

Answer: (A)

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Q25.

Solution

Concept: The change in molar entropy (ΔS) for an ideal gas that undergoes a reversible thermodynamic transformation at a constant volume is calculated using the formula:

$$\Delta S = n \cdot C_v \cdot \ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right)$$

where n is the number of moles of the gas, and C_v is its molar heat capacity at constant volume. For a monoatomic ideal gas, kinetic theory dictates that:

$$C_v = \frac{3}{2}R$$

Solution:

1. Identify the given parameters from the problem statement:

- Moles of gas: $n = 2.0$ moles
- Initial temperature: $T_{\text{initial}} = 200$ K
- Final temperature: $T_{\text{final}} = 800$ K
- Gas constant: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

2. Calculate the constant-volume molar heat capacity (C_v) for the monoatomic gas:

$$C_v = \frac{3}{2} \times 8.314 = 12.471 \text{ J mol}^{-1} \text{ K}^{-1}$$

3. Substitute these values into the entropy change equation:

$$\Delta S = 2.0 \times 12.471 \times \ln\left(\frac{800}{200}\right)$$

4. Simplify the natural logarithm term:

$$\ln\left(\frac{800}{200}\right) = \ln(4) \approx 1.3863$$

5. Compute the final total change in molar entropy:

$$\Delta S = 2.0 \times 12.471 \times 1.3863 = 24.942 \times 1.3863 = +34.577 \text{ J K}^{-1}$$

Rounding to two decimal places gives $+34.57 \text{ J K}^{-1}$.

Final Answer: $+34.57 \text{ J K}^{-1}$

Answer: (A)

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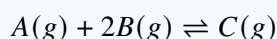
Q26.

Solution

Concept: According to Le Chatelier's Principle, when a system at chemical equilibrium is subjected to a change in volume, pressure, or concentration, the position of the equilibrium shifts in a direction that counteracts the applied disturbance. For gaseous reactions, compressing or expanding the container changes the total pressure and concentrations of all components simultaneously.

Solution:

1. The given reaction stoichiometry is:



2. Count the total number of gaseous moles on each side of the balanced equation:

- Reactants: $\Delta n_{\text{reactants}} = 1(A) + 2(B) = 3$ moles
- Products: $\Delta n_{\text{products}} = 1(C) = 1$ mole

3. The problem states that the container is suddenly compressed to twice its volume. This phrasing contains a physical contradiction, but in standard chemical problems, expanding a container to "twice its volume" means the volume V increases ($V_{\text{new}} = 2V$). According to Boyle's law, this expansion causes the total internal pressure to drop by half ($P_{\text{new}} = P/2$).

4. According to Le Chatelier's principle, when the total pressure drops, the system counteracts this change by shifting in the direction that produces a greater number of gas molecules to restore the pressure.

5. Comparing the two sides, the reactant side has more gas moles ($3 > 1$). Therefore, expanding the volume causes the equilibrium position to shift toward the reverse direction, increasing the amounts of components A and B .

Final Answer: Shifted towards the reverse direction increasing the amounts of A and B

Answer: (B)

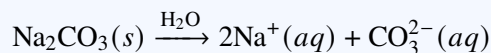
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Q27.

Solution

Concept: Molarity (M) is defined as the number of moles of solute dissolved per liter of solution. When an ionic salt dissolves in water, it dissociates completely into its constituent ions. The concentration of an individual ion depends on the stoichiometry of the salt:



Therefore, the concentration of sodium ions is exactly twice the analytical molarity of the dissolved sodium carbonate solution:

$$[\text{Na}^+] = 2 \times [\text{Na}_2\text{CO}_3]$$

Solution:

1. The desired total concentration of sodium ions is $[\text{Na}^+] = 0.20 \text{ M}$. Calculate the required molarity of the sodium carbonate solution:

$$[\text{Na}_2\text{CO}_3] = \frac{[\text{Na}^+]}{2} = \frac{0.20 \text{ M}}{2} = 0.10 \text{ M}$$

2. Calculate the number of moles of anhydrous Na_2CO_3 needed to prepare 250.0 mL (0.250 L) of this 0.10 M solution:

$$\text{Moles of Na}_2\text{CO}_3 = \text{Molarity} \times \text{Volume (L)} = 0.10 \text{ mol L}^{-1} \times 0.250 \text{ L} = 0.025 \text{ moles}$$

3. Convert this molar amount into mass using the molar mass of anhydrous sodium carbonate (Molar mass = 106 g mol^{-1}):

$$\text{Mass} = \text{Moles} \times \text{Molar Mass} = 0.025 \text{ moles} \times 106 \text{ g mol}^{-1} = 2.65 \text{ g}$$

Thus, exactly 2.65 g of Na_2CO_3 must be weighed.

Final Answer:

Answer: (B)

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Q28.

Solution

Concept: Werner's coordination theory states that transition metal complexes possess two types of valence: primary valence (ionizable groups located outside the coordination sphere) and secondary valence (non-ionizable ligands bound directly to the metal within the central coordination sphere). Treating the complex with silver nitrate (AgNO_3) precipitates only the free chloride ions located outside the coordination sphere as solid AgCl .

Solution:

1. The empirical formula of the coordination complex is $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$.
2. Dissolving one mole of this complex in water and treating it with excess AgNO_3 results in the immediate precipitation of exactly three moles of silver chloride (AgCl).
3. This 1:3 stoichiometric ratio confirms that all three chlorine atoms present in the empirical formula exist as free, ionizable chloride ions (Cl^-) located outside the coordination sphere:

$$\text{Number of Counter-Ions} = 3 \text{Cl}^-$$

4. Since all three chloride ions reside outside the coordination sphere, the remaining five ammonia (NH_3) molecules and the single water (H_2O) molecule must be bound directly to the central cobalt ion inside the sphere to satisfy its coordination number of 6.
5. This determines the definitive Werner coordination sphere formulation: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$.

Final Answer: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$

Answer: (A)

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Q29.

Solution

Concept: In an octahedral coordination field, the five d-orbitals of a transition metal ion split into two sets of differing energy levels: a lower-energy triply degenerate set (t_{2g}) and a higher-energy doubly degenerate set (e_g). The electronic configuration of the central metal ion depends on whether it forms a high-spin or low-spin complex, which is determined by the field strength of the surrounding ligands.

Solution:

1. The central metal ion is iron(II) (Fe^{2+}). Neutral iron has an atomic number of $Z = 26$ and an electron configuration of $[\text{Ar}]3d^64s^2$. Losing two electrons forms the Fe^{2+} ion, leaving it with six d-electrons ($3d^6$).
2. The problem states that the complex forms a high-spin state split under a weak ligand field. In a weak ligand field, the crystal field splitting energy (Δ_o) is smaller than the electron pairing energy (P).
3. Because $\Delta_o < P$, electrons occupy the split orbitals following Hund's rule of maximum multiplicity. Instead of pairing up in the lower levels, electrons sequentially fill both the lower and higher energy sets before any pairing occurs.
4. Distribute the six d-electrons across the split levels:
 - Place the first 3 electrons into the lower t_{2g} levels (one in each orbital).
 - Place the next 2 electrons into the higher e_g levels (one in each orbital).
 - Place the 6th electron into one of the lower t_{2g} orbitals, where it pairs up.
5. This resulting electronic distribution is written as $t_{2g}^4 e_g^2$.
6. Count the number of unpaired electrons in this configuration: one paired set in the t_{2g} level leaves two unpaired electrons in the t_{2g} set and two unpaired electrons in the e_g set, giving a total of 4 unpaired electrons.

Final Answer: $t_{2g}^4 e_g^2$ configuration with 4 unpaired electrons

Answer: (A)

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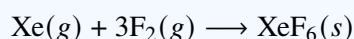
Q30.

Solution

Concept: Xenon reacts directly with fluorine gas under specific conditions to form various xenon fluorides (XeF_2 , XeF_4 , or XeF_6). The specific product formed is determined by the temperature, pressure, and molar ratio of the reactants. Once the product is identified, its structural geometry can be predicted using Valence Shell Electron Pair Repulsion (VSEPR) guidelines.

Solution:

1. Reacting xenon gas with fluorine gas in a 1:5 molar ratio at 400°C and 6 atm inside a sealed nickel vessel selectively yields xenon hexafluoride (XeF_6):



2. Determine the total valence electron count around the central xenon atom in XeF_6 to apply VSEPR rules:

$$\text{Steric Number (SN)} = \frac{\text{Valence electrons of Xe} + \text{Number of monovalent F ligands}}{2} = \frac{8 + 6}{2} = 7$$

3. A steric number of 7 corresponds to a pentagonal bipyramidal electron-pair geometry.

4. Determine the number of lone pairs localized on the xenon atom:

$$\text{Lone Pairs} = \text{SN} - \text{Number of bonds} = 7 - 6 = 1 \text{ lone pair}$$

5. According to VSEPR theory, a molecule with 6 bonding pairs and 1 lone pair adopts a distorted octahedral molecular shape. The lone pair moves dynamically, distorting the regular octahedral symmetry of the six fluorine atoms.

Final Answer: Pentagonal bipyramidal geometry, Distorted Octahedral shape

Answer: (B)

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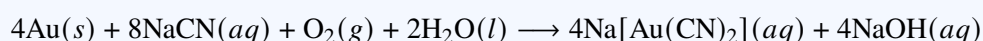
Q31.

Solution

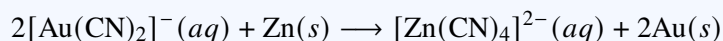
Concept: The industrial extraction of elemental gold from low-grade ores uses the Macarthur-Forrest process. This metallurgical method relies on selective hydrometallurgical leaching, where the native gold ore is treated with an aqueous cyanide solution in the presence of atmospheric oxygen to dissolve the gold as a stable coordination complex.

Solution:

1. Finely crushed crude gold ore is treated with an aqueous solution of sodium cyanide (NaCN) well-aerated with oxygen.
2. The native gold metal undergoes an oxidative dissolution reaction, where oxygen acts as the oxidizing agent in the presence of the complexing cyanide ligands:



3. This leaching step dissolves the gold, forming a stable, water-soluble coordination complex isolated in solution as **Complex Fragment Intermediate A**: the dicyanoaurate(I) anion, $[\text{Au}(\text{CN})_2]^-$.
4. In the final step of the process, adding zinc dust reduces the dissolved gold ions, precipitating pure gold metal out of the solution via a displacement reaction:



Thus, Intermediate A is $[\text{Au}(\text{CN})_2]^-$.

Final Answer: $[\text{Au}(\text{CN})_2]^-$

Answer: (B)

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Q32.

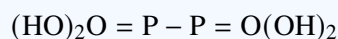
Solution

Concept: Oxoacids of phosphorus contain central phosphorus atoms surrounded by oxygen and hydrogen atoms in a tetrahedral geometry. The oxidation state of the phosphorus atoms and the presence of direct phosphorus-phosphorus (P – P) covalent links can be deduced from their chemical formulas and structural connectivity.

Solution:

1. Let us analyze the formulas and structural profiles of each option:

- **Pyrophosphoric acid (H₄P₂O₇):** This acid features a bridging oxygen atom forming a P – O – P linkage. The oxidation state of each phosphorus atom is +5. It contains no direct P – P bond.
- **Hypophosphoric acid (H₄P₂O₆):** The structural layout of this acid contains a direct phosphorus-phosphorus (P – P) covalent bond, symmetrically connecting two –PO(OH)₂ units:



Calculate the average oxidation state of phosphorus (x) in H₄P₂O₆:

$$4(+1) + 2(x) + 6(-2) = 0 \implies 4 + 2x - 12 = 0 \implies 2x = 8 \implies x = +4$$

This matches all the criteria given in the problem statement.

- **Peroxodiphosphoric acid (H₄P₂O₈):** This acid contains a peroxide bridge (P – O – O – P), and its phosphorus atoms have an oxidation state of +5.
- **Cyclotrimetaphosphoric acid (H₃P₃O₉):** This is a cyclic trimer with alternating phosphorus and oxygen atoms (P – O – P) forming a six-membered ring, where each phosphorus atom has an oxidation state of +5.

Thus, hypophosphoric acid contains a direct P – P bond and has a central oxidation state of +4.

Final Answer: Hypophosphoric acid (H₄P₂O₆)

Answer: (B)

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Q33.

Solution

Concept: The lanthanide contraction refers to the steady, gradual decrease in the atomic and ionic radii of the lanthanide elements (atomic numbers 58 to 71) as their atomic number increases. This effect is caused by the poor shielding efficiency of the $4f$ electrons, which allows the increasing nuclear charge to pull the outer electron shells closer to the nucleus. This contraction balances out the expected size increase that normally occurs when moving down a group in the periodic table.

Solution:

1. In the transition metal series, moving down a group from the $3d$ series (Period 4) to the $4d$ series (Period 5) results in a noticeable increase in atomic and ionic radii due to the addition of a new principal electron shell (e.g., from Ti to Zr).
2. However, the 14 lanthanide elements are located between the $4d$ and $5d$ transition series in Groups 4, 5, and 6. The lanthanide contraction reduces the sizes of the subsequent $5d$ elements (Hf, Ta, W, etc.).
3. This contraction counteracts the size increase expected from adding a new electron shell. As a result, adjacent $4d$ and $5d$ transition pairs in the same group display almost identical atomic and ionic radii:
 - **Group 4 pair:** Zirconium (Zr, $4d$) and Hafnium (Hf, $5d$) have nearly identical radii (Zr \approx 160 pm, Hf \approx 159 pm).
 - **Group 5 pair:** Niobium (Nb, $4d$) and Tantalum (Ta, $5d$) also share nearly identical radii (Nb \approx 146 pm, Ta \approx 146 pm).
4. Therefore, both the Zr/Hf and Nb/Ta pairs exhibit this physical overlap due to the lanthanide contraction.

Final Answer: Both Zr/Hf and Nb/Ta pairs

Answer: (D)

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Q34.

Solution

Concept: Disproportionation is a specific type of redox reaction where a single chemical species undergoes simultaneous oxidation and reduction, transforming into two separate products with different oxidation states. The manganate ion (MnO_4^{2-}) contains manganese in a +6 oxidation state and is stable only in highly alkaline solutions; it readily disproportionates when exposed to acidic conditions.

Solution:

1. In an acidic medium, the dark green manganate oxoanion (MnO_4^{2-} , oxidation state = +6) becomes unstable and undergoes a rapid disproportionation reaction.
2. One portion of the manganate ions is reduced to solid manganese dioxide (MnO_2), where the manganese atom drops to a +4 oxidation state.
3. Concurrently, the remaining portion of the manganate ions is oxidized to form the permanganate oxoanion, labeled as **Anion Oxo-Species Y**, where the manganese atom reaches its highest stable oxidation state of +7.
4. Write the balanced chemical equation for this disproportionation pathway:



5. The permanganate anion (MnO_4^-) gives the solution a characteristic intense purple color and acts as a powerful oxidizing agent.

Final Answer: MnO_4^- (Purple color)

Answer: (A)

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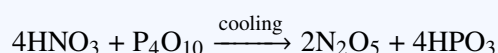
Q35.

Solution

Concept: Phosphorus pentoxide (P_4O_{10}) is a powerful dehydrating agent that can strip water or hydroxyl groups from chemical compounds, including strong mineral acids. Treating pure concentrated nitric acid (HNO_3) with P_4O_{10} removes water from the acid molecules, converting them into their corresponding acid anhydride.

Solution:

1. When pure concentrated nitric acid is mixed with solid phosphorus pentoxide under cooling conditions, a clean dehydration reaction takes place. The P_4O_{10} removes the elements of water from the acid, turning into metaphosphoric acid (HPO_3):



2. The nitrogen oxide produced by this dehydration is dinitrogen pentoxide (N_2O_5).

3. Let us evaluate the physical properties and molecular structure of N_2O_5 :

- In its solid state, dinitrogen pentoxide exists as a colorless, crystalline ionic compound composed of nitronium cations and nitrate anions: $[NO_2]^+ [NO_3]^-$.
- All the electrons within the chemical framework are paired up, making the compound entirely diamagnetic.

4. Therefore, the product is a colorless, diamagnetic crystalline solid with the chemical formula N_2O_5 .

Final Answer: Colorless diamagnetic crystalline solid, N_2O_5

Answer: (C)

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Q36.

Solution

Concept: For an octahedral coordination complex of the type $[M(AA)_2b_2c_2]$, where AA is a symmetrical bidentate ligand like ethylenediamine (en), and b and c are monodentate ligands (NO_2^- and Cl^- respectively), we evaluate geometric isomers by the relative spatial positions of the ligand pairs. Each geometric configuration is then tested for molecular chirality (lack of an alternating axis of symmetry or plane of symmetry) to determine if it exists as a pair of non-superimposable optical enantiomers.

Solution:

1. Let the bidentate ligand en occupy adjacent (cis) coordination sites, since it cannot span a trans position (180°) due to steric constraints.

2. We can group the remaining monodentate ligands (NO_2^- and Cl^-) relative to each other:

- **Configuration 1:** Cl^- ligands are trans to each other, and NO_2^- ligands are cis to each other. This isomer possesses a plane of symmetry containing the en ring and the NO_2^- groups, making it achiral (1 meso-like form).
- **Configuration 2:** NO_2^- ligands are trans to each other, and Cl^- ligands are cis to each other. This isomer similarly possesses a vertical mirror plane, rendering it achiral (1 meso-like form).
- **Configuration 3:** Both Cl^- ligands are cis to each other, and both NO_2^- ligands are cis to each other. This fully cis arrangement lacks any plane or center of inversion symmetry, making it asymmetric and chiral. It exists as a pair of non-superimposable d- and l-enantiomers (2 stereoisomers).

3. Adding up all forms gives $1 + 1 + 2 = 4$ total stereoisomers.

Final Answer: 4 stereoisomers

Answer: (C)

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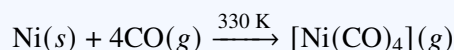
Q37.

Solution

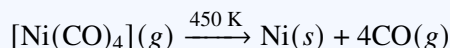
Concept: The metallurgical extraction and refining of nickel to a high degree of purity relies on its selective, reversible interaction with carbon monoxide (CO) gas. Transition metals readily form volatile neutral coordination carbonyl compounds when treated with specific gaseous ligands at moderate temperatures, which can then be thermally dissociated at a higher temperature threshold to yield the pure element.

Solution:

1. Crude elemental nickel is treated with a stream of carbon monoxide gas at approximately 330 – 350 K. It reacts selectively to generate a volatile, highly toxic, tetrahedral coordination complex called nickel tetracarbonyl, $[\text{Ni}(\text{CO})_4]$, leaving non-volatile impurities behind:



2. The volatile gas X ($[\text{Ni}(\text{CO})_4]$) is piped into a separate decomposition chamber heated to a higher temperature threshold around 450 – 470 K. At this energy state, the metal-carbonyl coordinate bonds break cleanly, depositing ultra-pure nickel metal crystals and regenerating carbon monoxide gas:



3. This specific chemical vapor transport purification protocol is universally termed Mond's process.

Final Answer: $[\text{Ni}(\text{CO})_4]$, Mond's process

Answer: (B)

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Q38.

Solution

Concept: Interstitial compounds are formed when small non-metal atoms like B, C, or N lodge inside the vacant interstitial spaces (such as octahedral or tetrahedral voids) present within the close-packed crystal lattices of transition metals. These chemical matrices do not follow standard stoichiometric valence relationships and exhibit distinct physical and chemical modifications compared to the host metals.

Solution:

1. Let us analyze each given statement systematically:

- **Statement A:** Interstitial trapping does not alter the delocalized conduction bands of the host d-block lattice. Thus, they retain their characteristic metallic electrical and thermal conductivity completely invariant. (Correct statement)
- **Statement B:** The newly established guest-host interactions lock the lattice framework in place, meaning they exhibit significantly higher melting points than the corresponding pure host transition metals. (Correct statement)
- **Statement C:** Interstitial compounds are well-noted for becoming chemically inert. They demonstrate remarkable resistance to rapid mineral acid corrosion and oxidation compared to the native pure metals. Thus, stating that they are much more reactive is chemically false. (Incorrect statement)
- **Statement D:** The inclusion of these small covalent atoms increases friction against lattice plane slippage, making them exceptionally hard, with some approaching the hardness of diamond on the Mohs scale. (Correct statement)

2. Therefore, the incorrect statement is option C.

Final Answer: They are chemically much more reactive and prone to rapid mineral acid corrosion

Answer: (C)

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Q39.

Solution

Concept: The spatial probability distribution of an electron in a hydrogenic atomic orbital is dictated by its quantum mechanical wavefunction. Nodes represent positions of zero electron density. The total number of nodes is subdivided into radial nodes (which depend on distance from the nucleus) and angular nodes (which depend on orientation and correspond to planar or conical boundaries).

- Number of Angular Nodes = l
- Number of Radial Nodes = $n - l - 1$

Solution:

1. The problem specifies that the electronic state contains exactly zero angular nodes. Setting the angular node equation equal to this value gives the azimuthal quantum number:

$$l = 0 \quad (\text{denoting an } s\text{-orbital})$$

2. The problem also states that the state contains exactly two radial nodes. Using the value found for l , substitute into the radial node expression:

$$\text{Radial Nodes} = n - l - 1 = 2 \implies n - 0 - 1 = 2$$

3. Solving for the principal quantum number n :

$$n - 1 = 2 \implies n = 3$$

4. Hence, the unique quantum number values describing this specific electronic orbital state ($3s$) are $n = 3, l = 0$.

Final Answer: $n = 3, l = 0$

Answer: (B)

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Q40.

Solution

Concept: In Molecular Orbital Theory (MOT), atomic orbitals combine linearly (LCAO) to generate molecular orbitals. When two p_z atomic orbitals align collinearly along the internuclear axis (z -axis), they can combine in-phase to form a bonding σ_{2p_z} orbital or out-of-phase to yield an antibonding $\sigma_{2p_z}^*$ orbital.

Solution:

1. Examine the provided computational boundary contour schematic: there are four alternating phase lobes aligned end-to-end along the horizontal axis, with signs matching (+), (-), (+), (-).
2. A critical vertical nodal plane passes right through the center between the two nuclei, slicing directly across the internuclear bonding region where electron density drops to zero due to destructive wave interference.
3. This specific layout is the characteristic fingerprint of an out-of-phase head-on combination of two $2p_z$ orbitals, which explicitly identifies it as a $\sigma_{2p_z}^*$ antibonding molecular orbital.

Final Answer: $\sigma_{2p_z}^*$ antibonding molecular orbital

Answer: (B)

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Q41.

Solution

Concept: According to Molecular Orbital Theory, the electronic configuration of homonuclear diatomic molecules containing more than 14 electrons (like O_2 and its charged variants) follows the specific energy level ordering:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < (\pi_{2p_x} = \pi_{2p_y}) < (\pi_{2p_x}^* = \pi_{2p_y}^*) < \sigma_{2p_z}^*$$

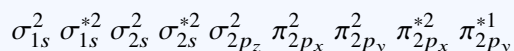
The absolute bond order parameter is evaluated from the net imbalance between bonding electrons (N_b) and antibonding electrons (N_a):

$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

Solution:

1. A neutral oxygen molecule (O_2) possesses 16 electrons. The superoxide radical anion (O_2^-) gains one extra electron, bringing its total to 17 valence/core electrons.

2. Distribute these 17 electrons across the molecular orbital energy hierarchy:



3. Count the total number of bonding and antibonding electrons:

$$N_b = 2(\sigma_{1s}) + 2(\sigma_{2s}) + 2(\sigma_{2p_z}) + 4(\pi_{2p}) = 10$$

$$N_a = 2(\sigma_{1s}^*) + 2(\sigma_{2s}^*) + 3(\pi_{2p}^*) = 7$$

4. Compute the bond order value:

$$\text{Bond Order} = \frac{10 - 7}{2} = \frac{3}{2} = 1.5$$

5. Because there is one unpaired electron remaining in the degenerate $\pi_{2p_y}^*$ antibonding orbital level, the superoxide anion exhibits a paramagnetic performance profile.

Final Answer: Bond order = 1.5, Paramagnetic performance

Answer: (B)

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Q42.

Solution

Concept: The number of valence electrons of an element is determined by analyzing successive ionization energies (IE). A massive, disproportionate step jump in required ionization energy occurs when an electron is removed from a stable, lower-energy inner core shell (noble gas configuration) rather than a valence shell.

Solution:

1. Examine the given experimental data values:

- $IE_1 = 738 \text{ kJ mol}^{-1}$ (Removal of the first valence electron)
- $IE_2 = 1450 \text{ kJ mol}^{-1}$ (Removal of the second valence electron)
- $IE_3 = 7733 \text{ kJ mol}^{-1}$ (Removal of a core electron)

2. The energy required to strip away the third electron (IE_3) is more than five times larger than the second ionization energy (IE_2). This abrupt threshold jump indicates that the element possesses exactly two easily removable valence electrons in its outermost shell.

3. An outer shell with 2 valence electrons (ns^2 configuration) corresponds to Group 2 of the modern periodic table, which is the Alkaline Earth Metal family (specifically matching magnesium, Mg).

Final Answer: Group 2 (Alkaline Earth Metal)

Answer: (B)

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Q43.

Solution

Concept: The formal charge (FC) tracking matrix evaluates the apparent electrical charge assigned to an individual atomic node within a Lewis structure configuration, assuming all bonding electrons are shared equally. It is calculated using the relation:

$$FC = V - L - \frac{1}{2}B$$

where V is the number of valence electrons of the isolated neutral atom, L is the number of localized non-bonding lone pair electrons, and B is the number of shared bonding electrons.

Solution:

1. Draw the valid resonant Lewis structure framework for the ozone (O_3) molecule. It consists of a central oxygen atom connected to one terminal oxygen atom by a double bond and to the other terminal oxygen atom by a single bond:



2. Apply the formal charge formula to each individual oxygen atom node ($V = 6$ for oxygen):

- **Central Oxygen Atom:** It forms 3 total bonds (6 bonding electrons) and retains 1 lone pair (2 electrons).

$$FC = 6 - 2 - \frac{1}{2}(6) = 6 - 2 - 3 = +1$$

- **Double-Bonded Terminal Oxygen:** It forms 2 bonds (4 bonding electrons) and retains 2 lone pairs (4 electrons).

$$FC = 6 - 4 - \frac{1}{2}(4) = 6 - 4 - 2 = 0$$

- **Single-Bonded Terminal Oxygen:** It forms 1 bond (2 bonding electrons) and retains 3 lone pairs (6 electrons).

$$FC = 6 - 6 - \frac{1}{2}(2) = 6 - 6 - 1 = -1$$

3. This gives a formal charge of +1 on the central atom, and charges of 0 and -1 on the terminal atoms.

Final Answer: Central atom: +1; Terminal atoms: 0, -1

Answer: (B)

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Q44.

Solution

Concept: According to Valence Shell Electron Pair Repulsion (VSEPR) guidelines, the steric number (SN) determines the hybridization state and coordination geometry of the central atom. The steric number is calculated by summing the number of bonded atoms (σ -bonds) and the number of localized non-bonding lone pairs on that central node:

$$SN = \frac{V + M - C + A}{2}$$

where V is the valence electron count of the neutral central atom, M is the number of monovalent ligands, C is the net cationic charge, and A is the net anionic charge.

Solution:

1. For the interhalogen anion species BrF_4^- , bromine (Br) is the central atom ($V = 7$). It is bonded to four monovalent fluorine atoms ($M = 4$), carries no cationic charge ($C = 0$), and has a single negative charge ($A = 1$).
2. Compute the steric number:

$$SN = \frac{7 + 4 - 0 + 1}{2} = \frac{12}{2} = 6$$

3. A steric number of 6 corresponds to an octahedral electron-pair geometry, which requires a valence shell orbital hybridization assignment of sp^3d^2 .
4. Determine the number of lone pairs localized on the central bromine atom:

$$\text{Lone Pairs} = SN - \text{Number of Bonded Atoms} = 6 - 4 = 2 \text{ lone pairs}$$

These two lone pairs sit trans to each other to minimize electron-electron repulsion, giving the anion a square planar molecular shape.

Final Answer: sp^3d^2 hybridization with 2 lone pairs

Answer: (B)

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Q45.

Solution

Concept: A potential energy curve diagram tracks the continuous balance between attractive and repulsive electrostatic forces operating between two approaching atomic nuclei. As the inter-nuclear distance r decreases from infinity, attractive forces dominate initially, causing the potential energy $V(r)$ of the system to decrease and stabilize.

Solution:

1. The potential energy drops steadily until it reaches a sharp global minimum point at a specific inter-nuclear separation distance, labeled here as r_0 .
2. At this exact configuration point, the attractive forces exactly balance the repulsive forces, resulting in the most stable state for the chemical bond. The distance r_0 corresponds to the stable equilibrium bond length of the molecule.
3. Decreasing the distance past r_0 ($r < r_0$) causes core nuclear and electron-electron repulsions to grow exponentially, driving the potential energy up sharply. Thus, point r_0 represents the equilibrium bond distance where potential energy is minimized.

Final Answer: Equilibrium bond distance where potential energy is minimized

Answer: (C)

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Q46.

Solution

Concept: The net permanent molecular dipole moment (μ) of a polyatomic molecule is the vector sum of its individual localized polar bond dipoles. A molecule can contain highly polar individual bonds but still possess a net zero dipole moment ($\mu = 0$) if its structural geometry is highly symmetrical, causing the individual bond dipole vectors to cancel each other out completely.

Solution:

1. Let us analyze the symmetrical structural profiles of the given compounds:

- **Boron trifluoride (BF_3):** It has a trigonal planar geometry (sp^2). The three polar B – F bond vectors point toward the corners of an equilateral triangle at 120° angles, cancelling out completely ($\mu = 0$).
- **Carbon tetrachloride (CCl_4):** It has a regular tetrahedral geometry (sp^3). The four polar C – Cl vectors cancel out completely due to its high symmetry ($\mu = 0$).
- **Sulfur tetrafluoride (SF_4):** It has a steric number of 5 (sp^3d), containing 4 bonding pairs and 1 lone pair. This creates an asymmetric "see-saw" molecular shape. The polar S – F bond vectors cannot cancel each other out due to this asymmetry, resulting in a non-vanishing net permanent molecular dipole moment ($\mu \neq 0$).
- **Trans-1,2-dichloroethene:** The two polar C – Cl bond dipoles point in exactly equal and opposite directions across the double bond, cancelling each other out completely ($\mu = 0$).

2. Therefore, only sulfur tetrafluoride retains a net non-zero dipole moment.

Final Answer: Sulfur tetrafluoride (SF_4)

Answer: (C)

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Q47.

Solution

Concept: The gold number is a quantitative parameter used to evaluate the protective efficiency of hydrophilic protective colloids. It is defined as the minimum mass in milligrams of a protective colloid that must be added to prevent the coagulation of 10 mL of a standard red gold sol when 1 mL of a 10% sodium chloride (NaCl) solution is introduced.

Solution:

1. The protective efficiency of a biopolymer stabilizer is inversely proportional to its gold number value. A smaller gold number means that a much lower mass of the protective colloid is required to stabilize the sol, which indicates a higher protective efficiency:

$$\text{Protective Efficiency} \propto \frac{1}{\text{Gold Number}}$$

2. Examine the given experimental gold numbers:

$$\text{Gelatin (0.01)} < \text{Gum Arabic (0.15)} < \text{Egg Albumin (0.25)} < \text{Starch (25.0)}$$

3. Inverting these values to arrange them by protective efficiency yields:

$$\text{Gelatin} > \text{Gum Arabic} > \text{Egg Albumin} > \text{Starch}$$

Final Answer: Gelatin > Gum Arabic > Egg Albumin > Starch

Answer: (B)

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Q48.

Solution

Concept: Colloidal particles carry a net surface electrical charge (either positive or negative) that stabilizes the dispersion by generating mutual electrostatic repulsions, which prevents the particles from aggregating. In an industrial electrostatic precipitator (such as a Cottrell precipitator), smoke or effluent containing charged colloidal dust particles is passed through an intensive electric field.

Solution:

1. When these charged colloidal particles travel through the core channels and encounter high-voltage metal collector plates carrying an opposite electrical charge, they discharge.
2. The loss of their stabilizing surface charge eliminates the mutual electrostatic repulsion between the particles.
3. Without these repulsive forces, the neutral particles aggregate upon collision due to attractive van der Waals forces, leading to rapid coagulation and precipitation out of the gas stream.

Final Answer: Charge neutralization leading to rapid Coagulation/Precipitation

Answer: (B)

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Q49.

Solution

Concept: The Freundlich adsorption isotherm models the relationship between the mass of gas adsorbed per unit mass of solid adsorbent (x/m) and the equilibrium pressure (P) of the gas:

$$\frac{x}{m} = kP^{1/n}$$

Taking the base-10 logarithm of both sides transforms this expression into a linear equation ($y = mx + c$):

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log P$$

Solution:

1. Identify the parameters by matching the linear equation to the experimental plot values:

- Slope ($1/n$) = 0.50
- Vertical Intercept ($\log k$) = 0.3010 $\implies k = 10^{0.3010} = 2.0$

2. Write out the specific isotherm model with the calculated constants:

$$\frac{x}{m} = 2.0 \cdot P^{0.50} = 2.0 \cdot \sqrt{P}$$

3. Compute the mass of gas adsorbed per gram of adsorbent (x/m) at an equilibrium pressure of $P = 4.0$ atm:

$$\frac{x}{m} = 2.0 \cdot \sqrt{4.0} = 2.0 \times 2.0 = 4.0 \text{ g}$$

Final Answer:

Answer: (B)

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Q50.

Solution

Concept: Chlorofluorocarbons (CFCs), such as freons, are exceptionally stable chemical compounds in the troposphere. However, when they diffuse upward into the stratospheric layer, they are exposed to high-energy solar ultraviolet (UV-C) radiation.

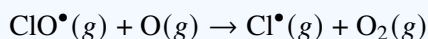
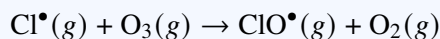
Solution:

1. Exposure to short-wavelength UV radiation triggers homolytic cleavage of the relatively weaker carbon-chlorine covalent bonds within the CFC molecule:



2. This photolytic cleavage releases a highly reactive, un-paired chlorine free radical (Cl^\bullet).

3. The Cl^\bullet radical attacks ozone (O_3), breaking it down into an oxygen molecule and a chlorine monoxide radical (ClO^\bullet). The ClO^\bullet radical subsequently reacts with atomic oxygen to regenerate the reactive Cl^\bullet radical:



4. This catalytic cycle allows a single chlorine radical to continuously destroy thousands of ozone molecules.

Final Answer: Chlorine free radical (Cl^\bullet)

Answer: (B)

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Answer Key

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

