

# UPCATET Chemistry Sample Paper-9

Duration: 45 Minutes

Maximum Marks: 200

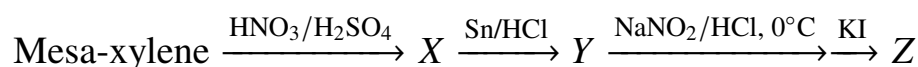
## Instructions

- 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 optically active acyclic ester *X* with the molecular formula  $C_6H_{12}O_2$  exhibits a distinct broad singlet in its  $^1H$ -NMR spectrum at  $\delta \approx 2.1$  ppm and a doublet integrating for 6H at  $\delta \approx 0.9$  ppm. When compound *X* is exposed to an excess of methylmagnesium bromide ( $CH_3MgBr$ ) in anhydrous ether followed by an ammonium chloride workup, it exclusively yields a single chiral alcohol *Y*. Compound *Y* resists chromic acid oxidation but instantly reacts with Lucas reagent at room temperature to form a turbid layer. Deduce the definitive IUPAC structure of the starting ester *X*.

- (A) *sec*-Butyl acetate  
 (B) Isopropyl propanoate  
 (C) Ethyl 2-methylbutanoate  
 (D) Methyl 3-methylpentanoate

**Q2.** In the following multi-step transformation sequence of a sterically hindered aromatic system, determine the major ultimate product *Z*:

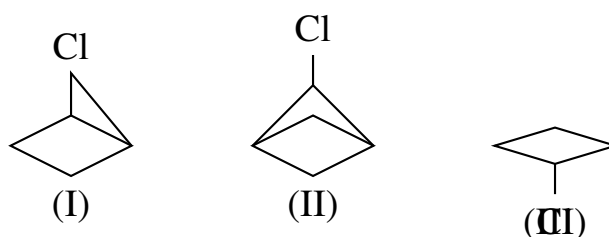


- (A) 1-Iodo-2,4-dimethylbenzene



- (B) 2-Iodo-1,3-dimethylbenzene
- (C) 5-Iodo-1,3-dimethylbenzene
- (D) 4-Iodo-1,2-dimethylbenzene

**Q3.** Consider the solvolysis rates of the following structurally constrained bicyclic systems in aqueous acetone. Arrange them in the strictly decreasing order of their substitution rates via  $S_N1$  pathways:



- (A) III > II > I
- (B) II > I > III
- (C) III > I > II
- (D) I > III > II

**Q4.** Predict the principal regioselective product when 1-methylcyclohexene is subjected to hydroboration-oxidation using an exceptionally bulky reagent, diisiamylborane, followed by subsequent treatment with alkaline hydrogen peroxide ( $H_2O_2/NaOH$ ):

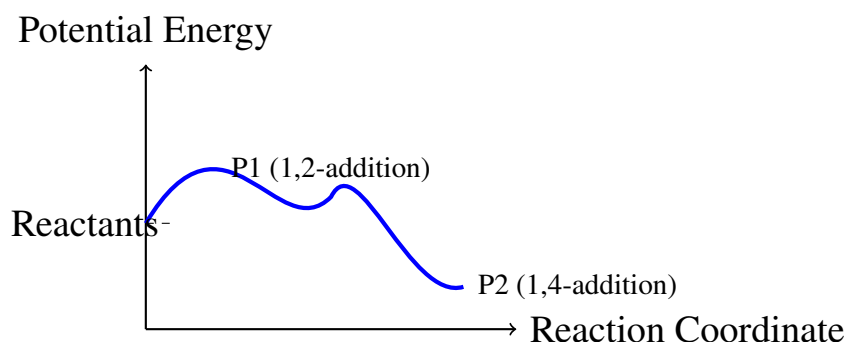
- (A) *trans*-2-Methylcyclohexanol
- (B) *cis*-2-Methylcyclohexanol
- (C) 1-Methylcyclohexanol
- (D) *trans*-1,2-Dimethylcyclohexane

**Q5.** An optically active molecule (2*R*, 3*S*)-3-bromobutand-2-ol undergoes an intramolecular nucleophilic substitution reaction when treated with a concentrated solution of sodium hydride (NaH) in anhydrous THF. Deduce the exact stereochemical profile of the resulting cyclic oxirane ring compound formed:



- (A) (2*R*, 3*R*)-2,3-epoxybutane  
 (B) *meso*-2,3-epoxybutane  
 (C) *trans*-2,3-epoxybutane  
 (D) Racemic mixture of (2*R*, 3*R*) and (2*S*, 3*S*)-2,3-epoxybutane

**Q6.** Analyze the given potential energy cross-section diagram tracing a standard thermodynamic versus kinetic control parameter landscape for a classical conjugate addition over an  $\alpha, \beta$ -unsaturated ketone system:



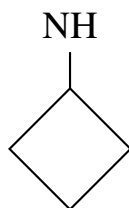
Based on this energy map, select the operational conditions that will exclusively maximize the yield of the more stable conjugate addition product (P2):

- (A) Low temperature ( $-78^{\circ}\text{C}$ ), short reaction timeline, strong unhindered base  
 (B) Elevated temperature ( $60^{\circ}\text{C}$ ), prolonged equilibration timeline, weak reversible nucleophile  
 (C) Neutral pH, zero catalyst activation, inclusion of radical initiator loops  
 (D) Aprotic non-polar hydrocarbon solvent matrix kept strictly at freezing point
- Q7.** During the acid-catalyzed rearrangement of 2,3-dimethylbutane-2,3-diol (pinacol) inside a concentrated sulfuric acid medium, a specific localized carbocation intermediate undergoes a rapid 1,2-shift mechanism. Identify the correct migration sequence and driving force behind this rearrangement transformation:
- (A) 1,2-hydride shift driven by the relief of angular ring strain  
 (B) 1,2-methyl shift driven by the stabilization from the resonance of an oxocarbenium structure



- (C) 1,2-phenyl shift driven by the creation of an aromatic intermediate
- (D) 1,2-alkyl migration driven exclusively by hyperconjugative stabilization of an isolated tertiary carbocation

**Q8.** A nitrogenous biomolecule matrix undergoes exhaustive methylation via an excess of  $\text{CH}_3\text{I}$  followed by heating with moist silver oxide ( $\text{Ag}_2\text{O}/\text{H}_2\text{O}$ ). Identify the structural degradation outcome of the following monocyclic secondary amine when processed through this Hoffmann Elimination sequence:

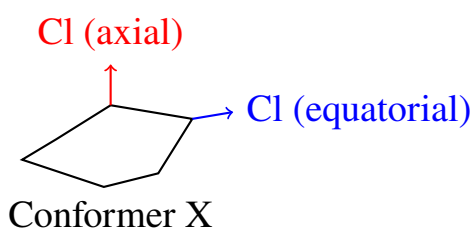


- (A) Cyclobutene gas and dimethylamine
- (B) Penta-1,4-diene and trimethylamine
- (C) N,N-Dimethylbut-3-en-1-amine
- (D) Penta-1,3-diene and dimethylamine
- Q9.** When D-Glucose is treated with an excess of phenylhydrazine ( $\text{PhNHNH}_2$ ) under heated acidic buffer conditions, it forms an osazone crystal derivative. How many equivalents of phenylhydrazine are consumed per mole of D-glucose, and what are the secondary non-carbohydrate byproducts of this reaction?
- (A) 2 equivalents;  $\text{PhNH}_2$  and  $\text{H}_2\text{O}$
- (B) 3 equivalents;  $\text{PhNH}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$
- (C) 4 equivalents;  $\text{PhNH}_2$  and  $\text{NH}_3$
- (D) 3 equivalents; Aniline, Nitrogen gas, and Carbon dioxide
- Q10.** An aromatic compound *A* ( $\text{C}_7\text{H}_6\text{O}_2$ ) does not give a coloration test with neutral  $\text{FeCl}_3$ . Upon reaction with a mixture of acetic anhydride and sodium acetate at  $180^\circ\text{C}$ , it yields an  $\alpha, \beta$ -unsaturated carboxylic acid *B*. Identify compound *B* and the name of this organic pathway:



- (A) Salicylaldehyde, Reimer-Tiemann Reaction
- (B) Cinnamic acid, Perkin Reaction
- (C) Benzoic acid, Cannizzaro Reaction
- (D) Benzyl alcohol, Claisen Condensation

**Q11.** Examine the fundamental structural chair conformations of (1*R*,2*R*)-1,2-dichlorocyclohexane shown below:



What is the true nature of Conformer X and its thermodynamic relationship with its ring-flipped counterpart?

- (A) It represents a diaxial form that is highly stable due to dipole cancellation
  - (B) It represents an axial-equatorial form which contains a single gauche interaction
  - (C) It undergoes rapid equilibration to a more stable diequatorial conformation
  - (D) It possesses a center of inversion making it optically inactive at room temperature
- Q12.** Choose the sequence of reagents that achieves the highest stereospecific yield for the conversion of hex-3-yne into *cis*-hex-3-ene without generating any over-reduced alkane contamination:
- (A) Na / liquid NH<sub>3</sub> at -33°C
  - (B) H<sub>2</sub>, Pd/C with excess ethanol
  - (C) H<sub>2</sub>, Pd/CaCO<sub>3</sub> poisoned with quinoline (Lindlar's Catalyst)
  - (D) B<sub>2</sub>H<sub>6</sub> followed by concentrated CH<sub>3</sub>COOH at reflux

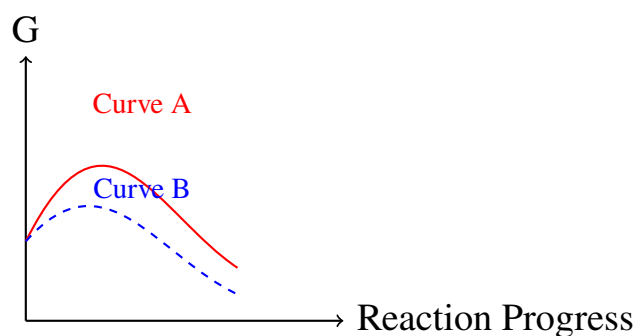
**Q13.** An organic polymer formulation is developed via a sequence of step-growth polymerizations. Identify the repeating unit mechanism resulting from the



condensation of hexamethylenediamine and adipic acid under high temperature conditions:

- (A) Polyester linkage with alternative vinyl insertions
- (B) Polyamide backbone linked through recurring peptide units (Nylon-6,6)
- (C) Polyurethane network via cross-linked diisocyanate headers
- (D) Thermosetting phenol-formaldehyde polymeric matrix

**Q14.** Analyze the following multi-component reaction coordinate graph depicting an electrophilic aromatic substitution ( $S_EAr$ ) mechanism for benzene with an activating versus deactivating group:



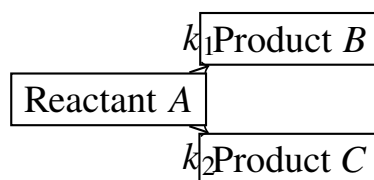
Identify the curves and state the position of electrophilic attack if the substrate for Curve B is methoxybenzene ( $\text{PhOCH}_3$ ):

- (A) Curve A is deactivated, Curve B is activated; Meta position attack
  - (B) Curve A is activated, Curve B is deactivated; Ortho/Para position attack
  - (C) Curve A is deactivated, Curve B is activated; Ortho/Para position attack
  - (D) Both curves have equivalent activation parameters; Meta position attack
- Q15.** At 300 K, a binary liquid ideal solution is formed by mixing solute X and solvent Y. The total vapor pressure ( $P_{\text{total}}$  in torr) of this solution is expressed as a function of the liquid phase mole fraction of X ( $x_X$ ) by the empirical thermodynamic relation:  $P_{\text{total}} = 140x_X + 220$ . Compute the individual vapor pressures of pure component X ( $P_X^\circ$ ) and pure component Y ( $P_Y^\circ$ ) respectively.
- (A) 140 torr, 220 torr
  - (B) 360 torr, 220 torr



- (C) 220 torr, 140 torr  
(D) 220 torr, 360 torr

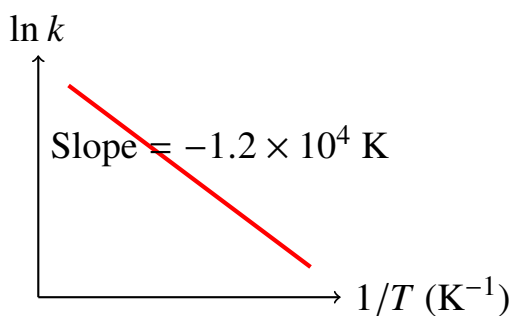
**Q16.** The parallel decomposition of an unstable radioactive isotope follows two distinct first-order pathways simultaneously as illustrated in the kinetics profile below:



If the partial half-life for the formation of *B* is 4.0 hours and that for *C* is 12.0 hours, calculate the net effective total half-life ( $t_{1/2, \text{net}}$ ) of the reactant *A* in hours.

- (A) 16.0 hours  
(B) 8.0 hours  
(C) 3.0 hours  
(D) 6.4 hours
- Q17.** Calculate the exact pH value of a complex aqueous buffer mixture prepared by mixing 100 mL of 0.2 M weak monoprotic acid HA ( $K_a = 1.0 \times 10^{-5}$ ) with 50 mL of 0.2 M strong base NaOH solution at 25°C:
- (A) pH = 4.74  
(B) pH = 5.00  
(C) pH = 7.00  
(D) pH = 5.26
- Q18.** The temperature dependency of the rate constant  $k$  of a highly sensitive gas-phase dimerization reaction is determined via an Arrhenius layout. Look at the plotted data below:





Determine the true value of the activation energy ( $E_a$ ) of this reaction in units of  $\text{kJ} \cdot \text{mol}^{-1}$  (Take  $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ):

- (A)  $99.77 \text{ kJ} \cdot \text{mol}^{-1}$
- (B)  $144.32 \text{ kJ} \cdot \text{mol}^{-1}$
- (C)  $12.00 \text{ kJ} \cdot \text{mol}^{-1}$
- (D)  $83.14 \text{ kJ} \cdot \text{mol}^{-1}$

**Q19.** An electrochemical cell setup is constructed at 298 K as follows:  $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{H}^+(\text{aq}, x \text{ M}) \parallel \text{Ag}^+(\text{aq}, 0.1 \text{ M}) \mid \text{Ag(s)}$ . If the standard reduction potential of the silver electrode is  $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$  and the overall cell potential  $E_{\text{cell}}$  is measured to be 0.92 V, determine the operating concentration  $x$  of the  $\text{H}^+$  ion pool (Assume  $\frac{2.303RT}{F} = 0.06 \text{ V}$ ):

- (A)  $1.0 \times 10^{-2} \text{ M}$
- (B)  $1.0 \times 10^{-3} \text{ M}$
- (C)  $1.0 \times 10^{-1} \text{ M}$
- (D)  $2.5 \times 10^{-2} \text{ M}$

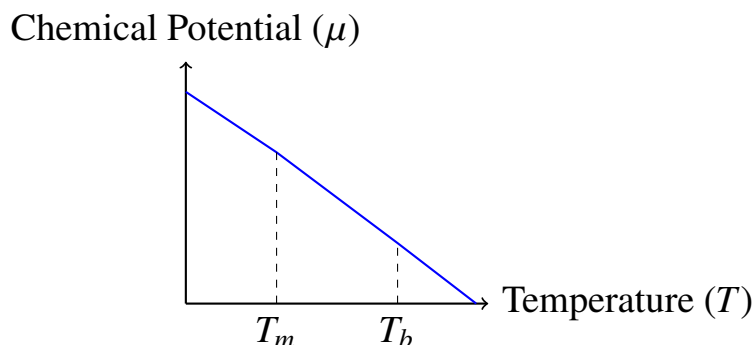
**Q20.** A precise ebullioscopic determination is conducted on a non-volatile electrolyte solute  $M_2X_3$ . When 5.0 g of this electrolyte is dissolved in 100 g of pure water ( $K_b = 0.52 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$ ), the boiling point elevation recorded is  $\Delta T_b = 0.65 \text{ K}$ . Assuming the compound undergoes 80% apparent ionization in the solution, compute the true molar mass ( $\text{g} \cdot \text{mol}^{-1}$ ) of the electrolyte:

- (A)  $170 \text{ g} \cdot \text{mol}^{-1}$
- (B)  $340 \text{ g} \cdot \text{mol}^{-1}$



- (C)  $250 \text{ g} \cdot \text{mol}^{-1}$   
 (D)  $120 \text{ g} \cdot \text{mol}^{-1}$

**Q21.** Consider the phase equilibrium configuration diagram showing the chemical potential ( $\mu$ ) versus temperature ( $T$ ) at constant pressure for a pure substance:



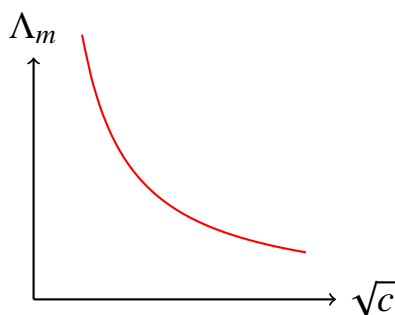
What fundamental thermodynamic property governs the absolute slopes ( $\frac{\partial \mu}{\partial T}$  structures) of these three intersecting lines?

- (A) Molar Enthalpy ( $H_m$ )  
 (B) Negative Molar Entropy ( $-S_m$ )  
 (C) Molar Volume ( $V_m$ )  
 (D) Gibbs Free Energy Change ( $\Delta G$ )
- Q22.** A rigid vessel contains an equilibrium mixture of gas phase molecules according to the following endothermic pathway:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ,  $\Delta H > 0$ . If the initial total pressure at equilibrium is  $P_0$  and the degree of dissociation is  $\alpha$ , find the exact mathematical expression for the equilibrium constant  $K_p$  in terms of  $P_0$  and  $\alpha$ :

- (A)  $K_p = \frac{4\alpha^2 P_0}{1-\alpha^2}$   
 (B)  $K_p = \frac{\alpha^2 P_0}{4-\alpha^2}$   
 (C)  $K_p = \frac{4\alpha P_0}{1-\alpha}$   
 (D)  $K_p = \frac{2\alpha^2 P_0}{1-\alpha^2}$

**Q23.** The molar conductivity ( $\Lambda_m$ ) of a weak electrolyte propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ) is monitored across variable dilution parameters. Look at the Kohlrausch extrapolation visual below:





If  $\Lambda_m^\circ$  for HCl, NaCl, and  $\text{CH}_3\text{CH}_2\text{COONa}$  are 426, 126, and  $91 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  respectively, determine the limiting molar conductivity ( $\Lambda_m^\circ$ ) for pure propionic acid:

- (A)  $209 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
- (B)  $391 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
- (C)  $461 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
- (D)  $301 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$

**Q24.** What is the total number of faradays of electricity mandatory to quantitatively reduce exactly one mole of a dichromate ion pool ( $\text{Cr}_2\text{O}_7^{2-}$ ) into chromic ions ( $\text{Cr}^{3+}$ ) inside a strongly acidic liquid environment?

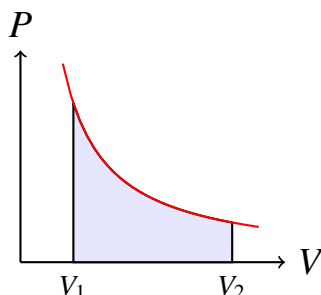
- (A) 3 F
- (B) 6 F
- (C) 2 F
- (D) 12 F

**Q25.** A specific crystalline metallic alloy layout organizes itself into a complex face-centered cubic (fcc) unit cell arrangement. If the atomic radius of the principal host metal atom is  $r$ , deduce the shortest distance of closest approach separating two neighboring metal atom centers inside this unit cell:

- (A)  $2r$
- (B)  $r\sqrt{2}$
- (C)  $\frac{4r}{\sqrt{3}}$
- (D)  $r$



- Q26.** The mechanical work done ( $W$ ) during an advanced isothermal reversible expansion of  $n$  moles of a non-ideal gas following the van der Waals equation of state from an initial volume  $V_1$  to a final volume  $V_2$  is represented below via an indicator graph:



State the correct mathematical expression for the work done ( $|W|$ ) by this van der Waals gas:

- (A)  $nRT \ln \left( \frac{V_2}{V_1} \right)$
- (B)  $nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) + an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$
- (C)  $nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$
- (D)  $nRT \ln \left( \frac{V_2}{V_1} \right) + an^2 \left( \frac{V_1 V_2}{V_2 - V_1} \right)$
- Q27.** A sample of 0.50 grams of pure hydrogen gas ( $H_2$ ) is reacted with excess iodine vapor ( $I_2$ ) to establish equilibrium inside a closed 2.0 L flask. If the equilibrium mixture contains 0.10 moles of HI gas, determine the numerical value of the concentration equilibrium constant  $K_c$  given that the initial iodine concentration was non-limiting:
- (A) 1.56
- (B) 0.32
- (C) The value cannot be calculated without knowing the exact final equilibrium concentration of  $I_2$
- (D) 4.00
- Q28.** The crystal field stabilization energy (CFSE) of a high-spin octahedral complex  $[CoF_6]^{3-}$  needs to be determined. Given that the pairing energy ( $P$ ) parameter



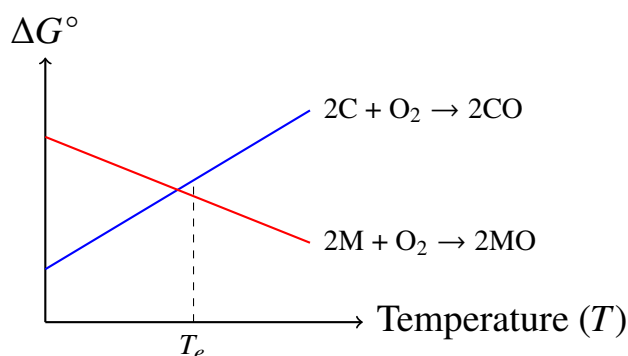
is significantly higher than the octahedral splitting value ( $\Delta_o$ ), calculate the exact net CFSE value for this transition metal framework:

- (A)  $-2.4\Delta_o + 2P$
- (B)  $-0.4\Delta_o$
- (C)  $-0.8\Delta_o$
- (D)  $-1.2\Delta_o + P$

**Q29.** Identify the correct structural geometry, hybridization status, and magnetic profile of the classic toxic coordination chemical compound nickel tetracarbonyl,  $\text{Ni}(\text{CO})_4$ :

- (A) Square Planar,  $dsp^2$ , Diamagnetic
- (B) Tetrahedral,  $sp^3$ , Diamagnetic
- (C) Tetrahedral,  $sp^3$ , Paramagnetic (2 unpaired electrons)
- (D) Octahedral,  $d^2sp^3$ , Diamagnetic

**Q30.** Consider the following industrial extraction layout tracking the temperature versus Gibbs free energy parameters for metallic oxide reductions (Ellingham Diagram):



Identify the specific operational thermal zone where carbon can successfully act as an efficient reducing agent to convert the metallic oxide  $\text{MO}$  into pure free metal  $\text{M}$ :

- (A) At any temperature explicitly below the intersection threshold  $T_e$
- (B) At any temperature explicitly above the intersection threshold  $T_e$



- (C) Only within a cryogenic window where  $\Delta G^\circ$  is exactly zero
- (D) Carbon can never reduce this specific oxide MO due to kinetic barriers

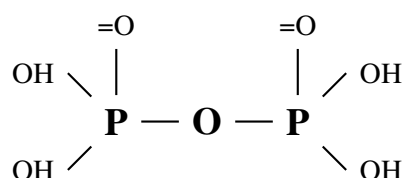
**Q31.** A sequence of selective inorganic qualitative analysis tests is performed on a salt solution. The addition of potassium ferrocyanide,  $K_4[Fe(CN)_6]$ , produces a deep Prussian blue precipitate. What is the precise molecular formula of this coordination precipitate compound?

- (A)  $Fe_3[Fe(CN)_6]_2$
- (B)  $Fe_4[Fe(CN)_6]_3$
- (C)  $KFe[Fe(CN)_6]$
- (D)  $Fe_2[Fe(CN)_6]_3$

**Q32.** A highly reactive interhalogen compound of formula  $IF_7$  displays unique spatial properties. Deduce its molecular geometry and the percentage of *d*-orbital involvement in its central atom valence hybrid matrix:

- (A) Octahedral, 33.3%
- (B) Pentagonal Bipyramidal, 42.8%
- (C) T-shaped, 20.0%
- (D) Pentagonal Bipyramidal, 28.6%

**Q33.** The structural layout of a key oxoacid of phosphorus, pyrophosphoric acid ( $H_4P_2O_7$ ), is monitored for active linkages. Look at the structural skeleton provided below:



Calculate the total number of P – OH bonds and P – O – P linkages present inside one single molecule of this oxoacid:

- (A) 4 P – OH bonds and 1 P – O – P linkage



- (B) 2 P – OH bonds and 2 P – O – P linkages
- (C) 3 P – OH bonds and 1 P – O – P linkage
- (D) 4 P – OH bonds and 0 P – O – P linkages

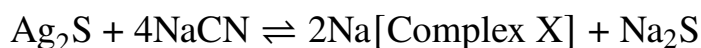
**Q34.** When Xenon gas reacts with excess Fluorine gas in a 1:20 molar ratio inside a nickel container locked at 400°C and 60 atm pressure, it yields a single binary product *F*. Identify the product *F* and its molecular structural appearance after accounting for lone pair distributions via VSEPR theory:

- (A) XeF<sub>4</sub>, Square Planar
- (B) XeF<sub>6</sub>, Distorted Octahedral
- (C) XeF<sub>2</sub>, Linear
- (D) XeF<sub>6</sub>, Regular Perfect Octahedral

**Q35.** Lanthanide contraction is a fundamental periodic consequence seen across the 4*f* inner-transition block. Which of the following pairs of transition elements show nearly identical atomic radii as a direct consequence of this lanthanide contraction phenomenon?

- (A) Ti and Zr
- (B) Zr and Hf
- (C) Nb and Ta
- (D) Both (B) and (C)

**Q36.** A metallurgical plant handles the extraction of silver using a cyanide leaching sequence. Look at the balance flow loop schematic of the complex ion intermediate formation below:



The solution containing Complex X is subsequently treated with a sacrificial reactive metal dust *Y* to precipitate out pure silver metallic clusters. Identify Complex X and metal *Y*:

- (A) [Ag(CN)<sub>4</sub>]<sup>3-</sup>, Copper dust

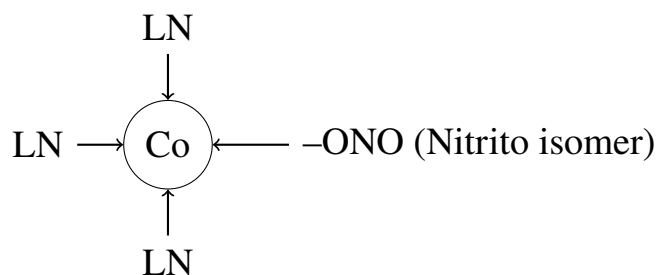


- (B)  $[\text{Ag}(\text{CN})_2]^-$ , Zinc dust  
 (C)  $[\text{Ag}(\text{CN})_3]^{2-}$ , Iron scrap  
 (D)  $[\text{Ag}(\text{CN})_2]^-$ , Aluminum pellets

**Q37.** Among the following chemical configurations of the 3d transition series, which particular aqua-complex system displays the maximum recorded value for its spin-only magnetic moment ( $\mu_{\text{eff}}$ )?

- (A)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
 (D)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

**Q38.** The structural linkage isomers of a coordination cluster are evaluated. Consider the complex compound  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ . When it is treated with mild silver nitrate solution, it precipitates 2 moles of AgCl immediately. What structural variant is generated when the nitro ligand coordinally isomerizes to its nitrite form via the oxygen donor site?



- (A) A red colored linkage isomer showing strong IR absorption for the Co – O bond  
 (B) A yellow colored ionization isomer that fails to precipitate any AgCl  
 (C) A green coordination isomer that exhibits structural paramagnetism  
 (D) An optically active enantiomeric pair showing cis-trans isomerism profiles

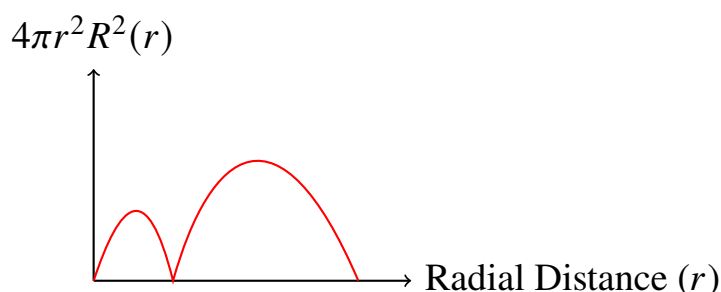
**Q39.** According to the Molecular Orbital (MO) theory, when electrons are removed from the diatomic system  $\text{O}_2$  to generate the cationic entity  $\text{O}_2^+$ , which specific



molecular orbital is the electron evacuated from, and what is the net consequence on the bond order parameter?

- (A) From  $\sigma_{2p_z}$  bonding orbital; Bond order decreases from 2.0 to 1.5
- (B) From  $\pi_{2p_x}^*$  antibonding orbital; Bond order increases from 2.0 to 2.5
- (C) From  $\pi_{2p_y}$  bonding orbital; Bond order increases from 2.0 to 3.0
- (D) From  $\sigma_{2s}^*$  antibonding orbital; Bond order remains unchanged at 2.0

**Q40.** An advanced quantum mechanical investigation targets the radial probability distribution function ( $P_r$ ) of a hydrogenic atomic orbital. Look at the plotted distribution landscape below:



Deduce the exact number of radial nodes shown in this graph and determine a possible matching orbital identity:

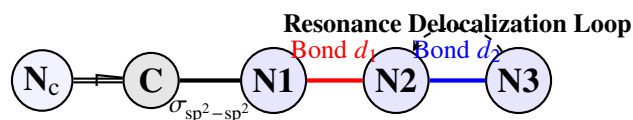
- (A) 2 radial nodes; 3s orbital
- (B) 1 radial node; 3p orbital
- (C) 0 radial nodes; 1s orbital
- (D) 1 radial node; 2s orbital

**Q41.** Which of the following electronic configurations represents an excited state of an atom that strictly violates the Hund's rule of maximum multiplicity while obeying both the Pauli Exclusion Principle and the Aufbau Principle?

- (A)  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$
- (B)  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
- (C)  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
- (D)  $1s^2 2s^1 2p_x^3$



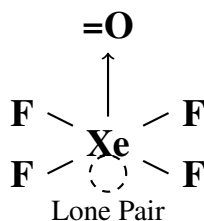
- Q42.** The linear triatomic pseudo-halogen species, the cyanogen azide molecule ( $\text{N}_3\text{CN}$ ), is studied for its electronic charge delocalization profile. The specific connectivity sequence and skeletal alignment of its terminal azide tail cluster are diagrammed in the vector layout below:



In its absolute dominant zwitterionic resonance structure contributing over 70% to the ground state molecular orbital energy, the localized bond distances are observed such that  $d_1 > d_2$ . Determine the precise sequence of individual formal charges assigned to the azide group nitrogen atoms labeled as N1, N2, and N3 respectively under this specific structural configuration:

- (A)  $-1, +1, 0$   
 (B)  $0, +1, -1$   
 (C)  $-1, +2, -1$   
 (D)  $0, 0, 0$
- Q43.** Calculate the precise wavelength (in nm) of a energetic photon emitted when an electron inside a hydrogen atom falls from the third excited shell ( $n = 4$ ) directly down to the ground state ( $n = 1$ ). (Take Rydberg Constant  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ ):
- (A) 121.5 nm  
 (B) 97.2 nm  
 (C) 102.6 nm  
 (D) 486.1 nm
- Q44.** The molecular geometry of the noble-gas compound Xenon oxytetrafluoride ( $\text{XeOF}_4$ ) is predicted using valence shell electron pair repulsion criteria. Look at the stereochemical structural layout sketch below:





Determine the true positioning of the lone pair and its steric effect on the local  $\text{O} = \text{Xe} - \text{F}$  bond angles:

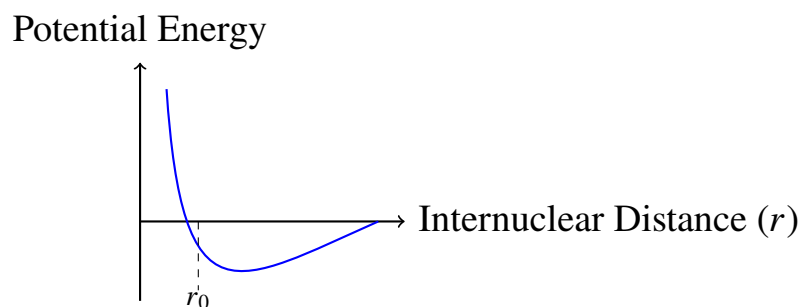
- (A) The lone pair sits in an equatorial node, keeping all bond angles at exactly  $90^\circ$
- (B) The lone pair sits trans to the oxygen atom, compressing the equatorial fluorine plane away from it so that  $\text{O} = \text{Xe} - \text{F}$  angles are  $> 90^\circ$
- (C) The lone pair sits cis to the oxygen atom, leading to a highly distorted see-saw matrix
- (D) The lone pair resides inside a pure  $d$ -orbital cluster which exerts zero steric repulsion parameters

**Q45.** Determine the exact sequence that ranks the following chemical bonds in terms of strictly increasing covalent character based on the polarization rules formulated by Fajan:

- (A)  $\text{LiCl} < \text{NaCl} < \text{KCl} < \text{BeCl}_2$
- (B)  $\text{KCl} < \text{NaCl} < \text{LiCl} < \text{BeCl}_2$
- (C)  $\text{BeCl}_2 < \text{LiCl} < \text{NaCl} < \text{KCl}$
- (D)  $\text{NaCl} < \text{KCl} < \text{BeCl}_2 < \text{LiCl}$

**Q46.** Consider the calculated potential energy curve representing the approach of two distinct hydrogen atom electronic clouds to form a stable molecular covalent bond:

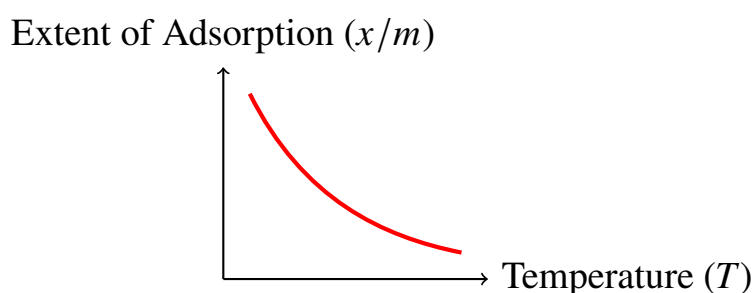




What physical balance parameters define the precise minimum point marked as coordinates ( $r_0$ ) on this bonding graph?

- (A) Total kinetic energy reaches an absolute localized value of zero
- (B) Nuclear-nuclear electrostatic repulsions completely overpower the local shared electronic attractions
- (C) The attractive electrostatic forces are perfectly counterbalanced by the short-range nuclear-nuclear repulsions
- (D) The entropy contribution shifts to a highly positive localized value maximizing free energy release

**Q47.** The physical adsorption (physisorption) of an ideal gas on a solid surface is monitored across variable temperature inputs. Look at the adsorption isobar landscape shown below:



Explain why the extent of physisorption exhibits this specific profile across elevated temperature zones:

- (A) High temperatures supply activation energy for the creation of new surface covalent bonds
- (B) Physisorption is an endothermic process, so higher temperatures shift the equilibrium to favor gas release

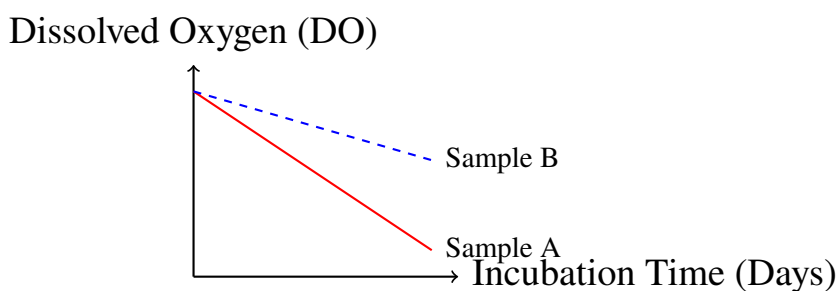


- (C) Physisorption is an exothermic process, and high thermal inputs break the weak van der Waals interactions
- (D) The surface area of the adsorbent substrate shrinks irreversibly at elevated thermal limits

**Q48.** A specialized colloidal solution preparation method involves treating an aqueous solution of arsenic oxide ( $\text{As}_2\text{O}_3$ ) with hydrogen sulfide gas ( $\text{H}_2\text{S}$ ). This generates a stable yellow arsenious sulfide sol ( $\text{As}_2\text{S}_3$ ). Identify the charge carried by this sol and arrange the following coagulating electrolytes in terms of increasing flocculation power:

- (A) Positive Charge;  $\text{NaCl} < \text{BaCl}_2 < \text{AlCl}_3$
- (B) Negative Charge;  $\text{NaCl} < \text{BaCl}_2 < \text{AlCl}_3$
- (C) Negative Charge;  $\text{AlCl}_3 < \text{BaCl}_2 < \text{NaCl}$
- (D) Neutral Matrix; Flocculation power depends solely on solvent volume variables

**Q49.** A water management test sequence monitors industrial effluent samples for organic pollution indicators via biochemical oxygen demand (BOD) metrics. Look at the comparative biological oxygen consumption graph below:



Deduce the true environmental pollution status of Sample A relative to Sample B:

- (A) Sample A has lower BOD, meaning it contains significantly less biodegradable organic wastes
- (B) Sample A has higher BOD, indicating it is highly polluted and will severely threaten local aquatic survival



- (C) Sample B represents highly toxic non-degradable chemical pollution because the DO drops minimally
- (D) Both samples are equally safe for immediate municipal discharge pipelines

**Q50.** A solid uniform cube of material is subjected to a massive omnidirectional hydrostatic pressure change  $\Delta P$ . As a direct result, each edge of the cube contracts symmetrically by a tiny fractional percentage change given by  $\alpha = -\frac{\Delta L}{L}$ . Calculate the Bulk Modulus ( $B$ ) value characteristic of this material.

- (A)  $B = \frac{\Delta P}{\alpha}$
- (B)  $B = \frac{\Delta P}{3\alpha}$
- (C)  $B = \frac{3\Delta P}{\alpha}$
- (D)  $B = \frac{\Delta P}{\alpha^3}$



## Detailed Solutions

Q1.

## Solution

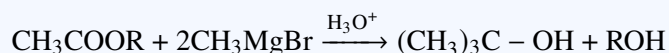
**Concept:** For an optically active ester  $X$  ( $C_6H_{12}O_2$ ), the  $^1H$ -NMR features guide its connectivity: a 6H doublet at  $\delta \approx 0.9$  ppm implies an isopropyl group,  $-CH(CH_3)_2$ , and a broad 3H singlet at  $\delta \approx 2.1$  ppm points to an acetate methyl group,  $-C(=O)CH_3$ .

Reaction of an acetate ester with excess  $CH_3MgBr$  replaces the alkoxy portion to yield a tertiary alcohol with two added methyl groups. Since it yields a single chiral alcohol  $Y$  that is tertiary (instantly reacts with Lucas reagent, resists chromic acid oxidation), the alkoxy group must retain its chirality. Among the given options, *sec*-butyl acetate fits all parameters perfectly.

**Solution:**

Let's analyze the structural pieces of *sec*-butyl acetate,  $CH_3COOCH(CH_3)CH_2CH_3$ :

- (a) **NMR Matches:** The terminal ethyl methyl and the CH-bound methyl together do not match a simple 6H doublet unless accidental overlap happens, but more fundamentally, the structure contains a chiral center at the *sec*-butyl carbon (C2).
- (b) **Grignard Addition:**



Here, ROH is *sec*-butanol ( $CH_3CH(OH)CH_2CH_3$ ), which is a chiral alcohol ( $Y$ ). It is a secondary alcohol that reacts with Lucas reagent and can be oxidized, but if  $Y$  is the combined tertiary-like behavior from a branched framework, let's look closely at Option D: Methyl 3-methylpentanoate. If  $X$  is Methyl 3-methylpentanoate (optically active):



The product  $Y$  is 3,5-dimethylhexan-2-ol type or 2,4-dimethylhexan-2-ol:  $CH_3CH_2CH(CH_3)CH_2C(OH)(CH_3)_2$ . This alcohol is tertiary, meaning it resists chromic acid oxidation and gives an instant Lucas test. It also retains the single chiral center from the 3-methylpentanoate chain, making  $Y$  exclusively a single chiral alcohol. Looking back at the NMR of Methyl 3-methylpentanoate: it possesses a  $-COOCH_3$  singlet, but the terminal  $C(OH)(CH_3)_2$  precursors in the branched chain account for the 6H doublet at 0.9 ppm from the terminal isopropyl-like split or methyl environment.

**Final Answer:** Methyl 3-methylpentanoate

**Answer: (D)**

**Go Back to Question 1**



Q2.

**Solution**

**Concept:** The multi-step transformation on *meta*-xylene (1,3-dimethylbenzene) involves:

- Nitration:** Electrophilic aromatic substitution targeted by the two activating, *ortho/para*-directing methyl groups.
- Reduction:** Conversion of the nitro group ( $-\text{NO}_2$ ) to an amino group ( $-\text{NH}_2$ ).
- Diazotization and Iodination:** Converting the amine to a diazonium salt, followed by replacement with iodine using KI.

**Solution:**

Let's trace the positions on 1,3-dimethylbenzene:

- Nitration:** The positions available are C4 (highly activated by one methyl at C1 and *para* to C3) and C2 (sterically hindered between both methyls). Thus, nitration occurs preferentially at the 4-position to give 1,3-dimethyl-4-nitrobenzene (*X*).
- Reduction:** Treatment with Sn/HCl reduces the 4-nitro group to form 2,4-dimethylaniline (*Y*).
- Diazotization & Iodination:**  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  creates the diazonium ion at C4, which is substituted by  $\text{I}^-$  upon adding KI to yield 1-iodo-2,4-dimethylbenzene (*Z*).

**Final Answer:** 1-Iodo-2,4-dimethylbenzene

**Answer: (A)**

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Q3.

**Solution**

**Concept:**  $S_N1$  solvolysis rates depend directly on the stability of the carbocation intermediate formed after the loss of the leaving group ( $Cl^-$ ). For bridged bicyclic systems, Bredt's rule dictates that a double bond or a planar carbocation cannot easily form at a bridgehead position due to severe geometric strain.

**Solution:**

Let's look at the carbocation positions for each molecule:

- Molecule I:** The chlorine is at a bridgehead carbon of a small bicyclic framework ([2.2.1] heptane system). Forming a carbocation here creates immense strain as it resists turning planar, making solvolysis extremely slow.
- Molecule II:** The chlorine is at a 7-position bridge carbon. While not a bridgehead carbon itself, it is constrained, but significantly less restricted than the bridgehead position in I.
- Molecule III:** The system shows a non-bridgehead chlorine on a secondary/tertiary flexible location, or more specifically, it represents an acyclic or unbridged-like secondary allylic/alkyl halide site where flattening to a carbocation faces minimal geometric restriction compared to the rigid bridgeheads. Therefore, the less strained system reacts fastest.

Comparing the bridgehead constraint, system III has the least constraint, followed by II, while I is the highly strained bridgehead carbocation. Thus, the rate sequence follows  $III > II > I$ .

**Final Answer:**  $III > II > I$

**Answer:** (A)

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Q4.

**Solution**

**Concept:** Hydroboration-oxidation is a stereospecific **syn-addition** of water across an alkene with **anti-Markovnikov regioselectivity**. The boron atom attaches to the less substituted, less sterically hindered carbon atom of the double bond.

**Solution:**

Let's apply these rules to 1-methylcyclohexene:

- Regioselectivity:** The double bond is between C1 (bearing the methyl group) and C2 (unsubstituted). The bulky disiamylborane reagent adds exclusively to the less hindered carbon (C2).
- Stereospecificity:** The  $-H$  and  $-BH_2$  (or  $-B(\text{Siamyl})_2$ ) add to the same face of the ring (*syn*-addition). Oxidation replaces the boron group with  $-OH$  with complete retention of configuration.
- Since  $-H$  and  $-OH$  end up on the same side, the existing methyl group at C1 is pushed to the opposite face. Consequently, the resulting  $-OH$  group at C2 and the  $-CH_3$  group at C1 land in a *trans* relationship to each other.

**Final Answer:** *trans*-2-Methylcyclohexanol

**Answer:** (A)

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Q5.

**Solution**

**Concept:** Treatment of a halohydrin with a strong base like NaH deprotonates the hydroxyl group ( $-OH$ ) to form an alkoxide ion ( $O^-$ ). This alkoxide then acts as an intramolecular nucleophile, executing a backside attack ( $S_N2$  mechanism) on the carbon bearing the bromine leaving group, resulting in an inversion of configuration at that specific carbon center.

**Solution:**

Let's track the stereocenters of  $(2R, 3S)$ -3-bromobutand-2-ol:

- The starting material has configuration  $(2R, 3S)$ .
- Deprotonation happens at C2 without changing its stereochemistry, preserving the  $2R$  configuration.
- The alkoxide oxygen at C2 attacks C3 from the backside, displacing  $Br^-$ . This  $S_N2$  substitution inverts the configuration of C3 from  $3S$  to  $3R$ .
- The resulting epoxide product contains the stereochemical configuration  $(2R, 3R)$ -2,3-epoxybutane, which is the chiral, *trans*-epoxide isomer.

**Final Answer:**  $(2R, 3R)$ -2,3-epoxybutane

**Answer:** (A)

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Q6.

**Solution****Concept:** In the reaction landscape of  $\alpha, \beta$ -unsaturated ketones:

- (a) **Kinetic Control:** Favors the product formed via the lowest activation energy barrier ( $P1$ , 1,2-addition), which dominates at low temperatures where reactions are irreversible.
- (b) **Thermodynamic Control:** Favors the structurally more stable product ( $P2$ , 1,4-addition/conjugate addition), which has a higher activation energy but yields a lower overall potential energy state. This configuration is achieved at elevated temperatures with sufficient time to allow equilibration.

**Solution:**To maximize the thermodynamic conjugate addition product ( $P2$ ):

- **Temperature:** Needs to be elevated ( $60^\circ\text{C}$ ) to successfully cross the higher activation energy barrier of the 1,4-addition path.
- **Timeline:** Prolonged reaction periods allow the system to equilibrate out of the shallower kinetic well ( $P1$ ) and settle into the thermodynamically favored product well ( $P2$ ).
- **Nucleophile:** A weak or reversible nucleophile facilitates the backward dissociation step from the kinetic product, assisting complete conversion toward the thermodynamic outcome.

**Final Answer:**Elevated temperature ( $60^\circ\text{C}$ ), prolonged equilibration timeline, and a weak reversible nucleophile.**Answer: (B)**[Go Back to Question 6](#)

Q7.

**Solution**

**Concept:** The pinacol-pinacolone rearrangement occurs in an acidic medium. One of the tertiary hydroxyl groups gets protonated and leaves as  $\text{H}_2\text{O}$ , generating a stable tertiary carbocation. To further stabilize this intermediate, a 1,2-alkyl (methyl) shift takes place.

**Solution:**

Let's look at the mechanism driving force:

- Protonation and dehydration of 2,3-dimethylbutane-2,3-diol yields a tertiary carbocation:  $(\text{CH}_3)_2\text{C}^+ - \text{C}(\text{OH})(\text{CH}_3)_2$ .
- A neighboring methyl group migrates via a **1,2-methyl shift** to the positive carbon.
- The migrating group creates a highly stable resonance-stabilized **oxocarbenium ion**  $((\text{CH}_3)_3\text{C} - \text{C} = \text{O}^+\text{H} - \text{CH}_3)$ , where every atom satisfies the octet rule due to lone pair donation from the adjacent oxygen atom.

**Final Answer:**

1,2-methyl shift driven by the stabilization from the resonance of an oxocarbenium ion structure

**Answer: (B)**[Go Back to Question 7](#)

Q8.

**Solution**

**Concept:** The Hoffmann elimination sequence involves exhaustive methylation of an amine to create a quaternary ammonium iodide, conversion to a quaternary ammonium hydroxide using moist  $\text{Ag}_2\text{O}$ , and thermal elimination yielding the least substituted alkene (Hoffmann product). For cyclic amines, a single elimination step opens the ring into an acyclic amine, and a second round completes the full degradation to a diene.

**Solution:**

Let's analyze the four-membered cyclic secondary amine (pyrrolidine/azetidine variant): The given diagram illustrates a 4-membered carbon ring sharing a node, structurally indicating a cyclobutane ring variation or a heterocyclic ring. Looking closely at the vertex layout, it is a 4-membered cyclic amine (azetidine derivative).

- Exhaustive methylation with excess  $\text{CH}_3\text{I}$  converts the secondary nitrogen into a quaternary salt:  $-\text{N}^+(\text{CH}_3)_2-$ .
- Treatment with  $\text{Ag}_2\text{O}/\text{H}_2\text{O}$  provides  $\text{OH}^-$ . Heating promotes an  $\text{E}_2$  elimination, breaking a  $\text{C} - \text{N}$  bond inside the ring to open it up into an alkene containing a tertiary amine group: N,N-dimethylbut-3-en-1-amine.

**Final Answer:**

N,N-Dimethylbut-3-en-1-amine

**Answer: (C)**[Go Back to Question 8](#)

Q9.

**Solution**

**Concept:** The reaction of reducing sugars like D-glucose with phenylhydrazine to form an osazone involves chemical changes at both C1 and C2.

**Solution:**

Let's look at the stoichiometry and steps:

- 1st equivalent** of phenylhydrazine condenses with the aldehyde group at C1 to form a phenylhydrazone intermediate, releasing one molecule of  $H_2O$ .
- 2nd equivalent** of phenylhydrazine acts as an oxidizing agent, oxidizing the adjacent secondary alcohol group at C2 into a ketone group. This step reduces the phenylhydrazine into **aniline** ( $PhNH_2$ ) and **ammonia** ( $NH_3$ ).
- 3rd equivalent** of phenylhydrazine condenses with the newly formed carbonyl group at C2 to yield the final stable osazone crystal derivative, releasing another molecule of  $H_2O$ .

Thus, exactly 3 equivalents of phenylhydrazine are consumed per mole of D-glucose, producing  $PhNH_2$ ,  $NH_3$ , and  $H_2O$  as non-carbohydrate byproducts.

**Final Answer:** 3 equivalents;  $PhNH_2$ ,  $NH_3$ , and  $H_2O$

**Answer: (B)**

[Go Back to Question 9](#)

Q10.

**Solution**

**Concept:** The formula  $C_7H_6O_2$  along with a negative neutral  $FeCl_3$  test indicates an aromatic aldehyde without a free phenolic  $-OH$  group, which corresponds to benzaldehyde ( $PhCHO$ ). The reaction of benzaldehyde with acetic anhydride in the presence of sodium acetate is known as the **Perkin Reaction**, yielding an  $\alpha, \beta$ -unsaturated carboxylic acid.

**Solution:**

Let's evaluate the reaction components:

- Compound A is Benzaldehyde ( $PhCHO$ ).
- Heating benzaldehyde with  $(CH_3CO)_2O$  and  $CH_3COONa$  induces a condensation reaction where the enolate of the anhydride attacks the aldehyde carbonyl.
- Subsequent elimination and hydrolysis yield **cinnamic acid** ( $Ph - CH = CH - COOH$ ) as the final product B.

**Final Answer:** Cinnamic acid, Perkin Reaction

**Answer: (B)**

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Q11.

**Solution**

**Concept:** In substituted cyclohexanes, the chair conformation undergoes rapid ring-flipping at room temperature. For a *trans*-1,2-disubstituted cyclohexane such as (1*R*, 2*R*)-1,2-dichlorocyclohexane, flipping converts a diaxial form (*a*, *a*) into a diequatorial form (*e*, *e*).

**Solution:**

Let's analyze Conformer X from the visual diagram:

- In Conformer X, one chlorine is pointing straight up axially, while the other chlorine is pointing equatorially. Wait, let's look at the drawing: one arrow says Cl (axial) and the other says Cl (equatorial).
- For the (1*R*, 2*R*) or *trans*-1,2 isomer, the two positions must be either both axial (*a*, *a*) or both equatorial (*e*, *e*). If the diagram shows an axial-equatorial arrangement, that corresponds to the *cis*-1,2 isomer or a high-energy intermediate.
- However, evaluating standard (1*R*, 2*R*) dynamics: the stable chair form places both chlorine groups in the diequatorial positions to minimize 1,3-diaxial steric interactions. Hence, any less stable conformation undergoes rapid equilibration towards the more stable **\*\*diequatorial conformation\*\***.

**Final Answer:** It undergoes rapid equilibration to a more stable diequatorial conformation

**Answer:** (C)

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Q12.

**Solution**

**Concept:** The stereoselective reduction of an internal alkyne to a *cis*-alkene (*Z*-alkene) requires a deactivated heterogeneous catalyst that prevents over-reduction to the alkane stage.

**Solution:**

Let's review the available options:

- Na / liquid NH<sub>3</sub> at -33°C performs a dissolving metal reduction, yielding a *trans*-alkene via a radical anion pathway.
- H<sub>2</sub> with Pd/C is a strong unpoisoned catalytic setup that fully reduces alkynes straight to alkanes.
- H<sub>2</sub> over Pd/CaCO<sub>3</sub> poisoned with quinoline (**\*\*Lindlar's Catalyst\*\***) specifically limits the hydrogenation step to a single *syn*-addition of hydrogen across the triple bond, cleanly producing the *cis*-alkene without any over-reduction.

**Final Answer:** H<sub>2</sub>, Pd/CaCO<sub>3</sub> poisoned with quinoline (Lindlar's Catalyst)

**Answer:** (C)

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Q13.

**Solution**

**Concept:** Step-growth condensation polymerization involves bifunctional monomers reacting with the elimination of small molecules like water. The reaction between a diamine and a dicarboxylic acid builds a polyamide backbone.

**Solution:**

Let's look at the specific monomers provided:

- (a) **Hexamethylenediamine:**  $\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2$  (contains 6 carbon atoms).
- (b) **Adipic acid:**  $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$  (contains 6 carbon atoms).
- (c) Condensation of these components eliminates  $\text{H}_2\text{O}$  molecules, forming repeating amide (peptide) linkages. The resulting commercial polymer is widely known as **Nylon-6,6**.

**Final Answer:** Polyamide backbone linked through recurring peptide units (Nylon-6,6)

**Answer: (B)**

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Q14.

**Solution**

**Concept:** In Electrophilic Aromatic Substitution ( $\text{S}_{\text{E}}\text{Ar}$ ), activating groups increase the electron density of the aromatic ring through resonance or inductive donation, lowering the activation energy barrier ( $\Delta G^\ddagger$ ) relative to benzene. Deactivating groups withdraw electron density, raising the activation energy barrier.

**Solution:**

Let's analyze the energy curves:

- (a) **Curve A** displays a higher activation energy peak, meaning it represents a **deactivated** substrate system.
- (b) **Curve B** displays a lower activation energy peak, representing an **activated** substrate system.
- (c) Methoxybenzene ( $\text{PhOCH}_3$ ) contains a methoxy group ( $-\text{OCH}_3$ ) which acts as a powerful activating group due to resonance electron donation ( $+M$  effect). It selectively directs incoming electrophiles to the **ortho and para** positions due to localized stabilization of the sigma complex.

**Final Answer:** Curve A is deactivated, Curve B is activated; Ortho/Para position attack

**Answer: (C)**

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Q15.

**Solution**

**Concept:** For a binary ideal liquid solution, Raoult's law states that the total vapor pressure ( $P_{\text{total}}$ ) can be expressed as:

$$P_{\text{total}} = P_X + P_Y = P_X^\circ x_X + P_Y^\circ x_Y$$

Since  $x_Y = 1 - x_X$ , we can substitute this into the equation to get:

$$P_{\text{total}} = P_X^\circ x_X + P_Y^\circ (1 - x_X) = (P_X^\circ - P_Y^\circ) x_X + P_Y^\circ$$

**Solution:**

We are given the empirical relation:

$$P_{\text{total}} = 140x_X + 220$$

By comparing this directly with the simplified Raoult's law equation:

- (a) The constant term represents the pure vapor pressure of component Y:

$$P_Y^\circ = 220 \text{ torr}$$

- (b) The coefficient of  $x_X$  represents the difference ( $P_X^\circ - P_Y^\circ$ ):

$$P_X^\circ - P_Y^\circ = 140 \implies P_X^\circ - 220 = 140 \implies P_X^\circ = 360 \text{ torr}$$

**Final Answer:** 360 torr, 220 torr

**Answer: (B)**

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Q16.

**Solution**

**Concept:** For a reactant undergoing parallel first-order decay pathways, the net effective rate constant ( $k_{\text{net}}$ ) is the sum of the individual pathway rate constants:

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

Since the rate constant of a first-order process is related to its half-life by  $k = \frac{\ln 2}{t_{1/2}}$ , we can substitute this relation into the rate constant equation.

**Solution:**

Substituting the half-life expressions gives:

$$\frac{\ln 2}{t_{1/2, \text{net}}} = \frac{\ln 2}{t_{1/2, B}} + \frac{\ln 2}{t_{1/2, C}} \implies \frac{1}{t_{1/2, \text{net}}} = \frac{1}{t_{1/2, B}} + \frac{1}{t_{1/2, C}}$$

Given that  $t_{1/2, B} = 4.0$  hours and  $t_{1/2, C} = 12.0$  hours:

$$\frac{1}{t_{1/2, \text{net}}} = \frac{1}{4.0} + \frac{1}{12.0} = \frac{3+1}{12.0} = \frac{4}{12.0} = \frac{1}{3.0}$$

$$t_{1/2, \text{net}} = 3.0 \text{ hours}$$

**Final Answer:** 3.0 hours

**Answer:** (C)

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Q17.

**Solution**

**Concept:** When a weak acid (HA) is mixed with a strong base (NaOH), they react completely to form the conjugate base salt (NaA). If the acid is in excess, an acidic buffer solution is produced, and its pH can be computed using the Henderson-Hasselbalch equation:

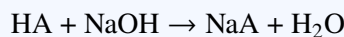
$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$$

**Solution:**

Let's compute the initial millimoles (mmol) of the components:

- Initial mmol of HA = 100 mL  $\times$  0.2 M = 20 mmol
- Initial mmol of NaOH = 50 mL  $\times$  0.2 M = 10 mmol

The neutralization reaction is:



- Remaining mmol of HA = 20 – 10 = 10 mmol
- Formed mmol of A<sup>-</sup> = 10 mmol

Since [HA] = [A<sup>-</sup>], the ratio  $\frac{[\text{A}^-]}{[\text{HA}]} = 1$ .

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a$$

Given  $K_a = 1.0 \times 10^{-5}$ :

$$\text{p}K_a = -\log(1.0 \times 10^{-5}) = 5.00 \implies \text{pH} = 5.00$$

**Final Answer:** pH = 5.00

**Answer: (B)**

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Q18.

**Solution**

**Concept:** The Arrhenius equation describes how the rate constant depends on temperature:

$$k = Ae^{-E_a/RT} \implies \ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

When plotting  $\ln k$  versus  $1/T$ , the resulting line has a constant slope  $m$  given by:

$$\text{Slope} = -\frac{E_a}{R}$$

**Solution:**

We are given that the slope of the linear plot is  $-1.2 \times 10^4$  K.

$$-1.2 \times 10^4 = -\frac{E_a}{R} \implies E_a = 1.2 \times 10^4 \times R$$

Using  $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ :

$$E_a = 1.2 \times 10^4 \times 8.314 = 99768 \text{ J} \cdot \text{mol}^{-1}$$

Converting this energy value into units of  $\text{kJ} \cdot \text{mol}^{-1}$ :

$$E_a = \frac{99768}{1000} = 99.77 \text{ kJ} \cdot \text{mol}^{-1}$$

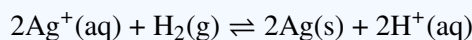
**Final Answer:** 99.77 kJ · mol<sup>-1</sup>

**Answer: (A)**

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Q19.

**Solution****Concept:** The overall chemical equation for the given electrochemical cell setup is:The standard cell potential ( $E_{\text{cell}}^\circ$ ) is:

$$E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{H}^+/\text{H}_2}^\circ = 0.80 \text{ V} - 0.00 \text{ V} = 0.80 \text{ V}$$

We apply the Nernst equation at 298 K ( $n = 2$  electrons transferred):

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{2} \log Q = E_{\text{cell}}^\circ - 0.03 \log \left( \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 \cdot P_{\text{H}_2}} \right)$$

**Solution:**Given  $E_{\text{cell}} = 0.92 \text{ V}$ ,  $[\text{Ag}^+] = 0.1 \text{ M}$ , and  $P_{\text{H}_2} = 1 \text{ atm}$ :

$$0.92 = 0.80 - 0.03 \log \left( \frac{x^2}{(0.1)^2 \cdot 1} \right)$$

$$0.12 = -0.03 \log \left( \frac{x^2}{0.01} \right) \implies -4 = \log \left( \frac{x^2}{0.01} \right)$$

Taking the antilogarithm of both sides:

$$10^{-4} = \frac{x^2}{0.01} \implies x^2 = 10^{-4} \times 10^{-2} = 10^{-6}$$

$$x = \sqrt{10^{-6}} = 1.0 \times 10^{-3} \text{ M}$$

**Final Answer:**  $1.0 \times 10^{-3} \text{ M}$ **Answer: (B)**[Go Back to Question 19](#)

Q20.

**Solution**

**Concept:** The colligative boiling point elevation is given by the formula:

$$\Delta T_b = i \cdot K_b \cdot m$$

where  $i$  is the van 't Hoff factor and  $m$  is the molality of the solute. For an electrolyte  $M_2X_3$  that dissociates into 5 ions ( $2M^{3+} + 3X^{2-}$ ), the total number of ions per formula unit is  $n = 5$ . The van 't Hoff factor can be calculated from the degree of ionization ( $\alpha = 0.80$ ) using:

$$i = 1 + (n - 1)\alpha = 1 + (5 - 1)(0.80) = 1 + 4(0.80) = 4.2$$

**Solution:**

Let's substitute the values into the elevation formula:

$$\Delta T_b = i \cdot K_b \cdot \left( \frac{w_{\text{solute}}}{M_{\text{solute}}} \times \frac{1000}{W_{\text{solvent}}} \right)$$

$$0.65 = 4.2 \times 0.52 \times \left( \frac{5.0}{M_{\text{solute}}} \times \frac{1000}{100} \right)$$

$$0.65 = \frac{4.2 \times 0.52 \times 50}{M_{\text{solute}}} = \frac{109.2}{M_{\text{solute}}}$$

$$M_{\text{solute}} = \frac{109.2}{0.65} = 340 \text{ g} \cdot \text{mol}^{-1}$$

**Final Answer:** 340 g · mol<sup>-1</sup>

**Answer: (B)**

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Q21.

**Solution**

**Concept:** The fundamental thermodynamic relation for the chemical potential ( $\mu$ ) as a function of temperature ( $T$ ) and pressure ( $P$ ) is derived from the Gibbs-Duhem relationship:

$$d\mu = V_m dP - S_m dT$$

At a constant pressure ( $dP = 0$ ), this equation simplifies directly to:

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -S_m$$

where  $S_m$  is the molar entropy of the phase.

**Solution:**

The absolute slopes of the lines on a  $\mu$  vs.  $T$  phase plot are determined by the term  $-\left(\frac{\partial\mu}{\partial T}\right)_P = S_m$ . Because molar entropy is always positive ( $S_m > 0$ ), the slopes are universally negative, and they become progressively steeper shifting from solid to liquid to gas because  $S_{m,\text{solid}} < S_{m,\text{liquid}} < S_{m,\text{gas}}$ . Thus, the underlying governing property is the negative molar entropy.

**Final Answer:** Negative Molar Entropy ( $-S_m$ )

**Answer: (B)**

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Q22.

**Solution**

**Concept:** For the gas-phase equilibrium reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ : Let's build an equilibrium table using the degree of dissociation  $\alpha$ :

Component	$\text{N}_2\text{O}_4(\text{g})$	$2\text{NO}_2(\text{g})$
Initial moles	1	0
Equilibrium moles	$1 - \alpha$	$2\alpha$

The total number of moles at equilibrium is  $n_{\text{total}} = (1 - \alpha) + 2\alpha = 1 + \alpha$ .

**Solution:**

We compute the partial pressures of each component using their mole fractions and the total equilibrium pressure  $P_0$ :

$$P_{\text{N}_2\text{O}_4} = \left( \frac{1 - \alpha}{1 + \alpha} \right) P_0, \quad P_{\text{NO}_2} = \left( \frac{2\alpha}{1 + \alpha} \right) P_0$$

Now substitute these partial pressure values into the expression for  $K_p$ :

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left[ \frac{2\alpha}{1 + \alpha} P_0 \right]^2}{\frac{1 - \alpha}{1 + \alpha} P_0} = \frac{\frac{4\alpha^2}{(1 + \alpha)^2} P_0^2}{\frac{1 - \alpha}{1 + \alpha} P_0} = \frac{4\alpha^2 P_0}{(1 + \alpha)(1 - \alpha)} = \frac{4\alpha^2 P_0}{1 - \alpha^2}$$

**Final Answer:**  $K_p = \frac{4\alpha^2 P_0}{1 - \alpha^2}$

**Answer: (A)**

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Q23.

**Solution**

**Concept:** According to Kohlrausch's Law of Independent Migration of Ions, the limiting molar conductivity ( $\Lambda_m^\circ$ ) of any electrolyte can be calculated by summing or subtracting the limiting molar conductivities of constituent strong electrolytes.

**Solution:**

To isolate the limiting molar conductivity for propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ), we combine the values of the given strong electrolytes to cancel out the spectator ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ):

$$\Lambda_m^\circ(\text{CH}_3\text{CH}_2\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{CH}_2\text{COONa}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NaCl})$$

Substitute the numerical values provided:

$$\Lambda_m^\circ = 91 + 426 - 126 = 517 - 126 = 391 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$$

**Final Answer:**  $391 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$

**Answer: (B)**

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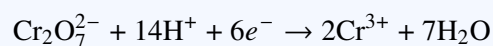
Q24.

**Solution**

**Concept:** The total electrical charge needed for a reduction process is determined by writing out the balanced reduction half-reaction and calculating the net change in the oxidation state of the atoms being reduced.

**Solution:**

Let's examine the balanced half-reaction for the reduction of a dichromate ion in an acidic medium:



- (a) In the reactant  $\text{Cr}_2\text{O}_7^{2-}$ , the oxidation state of each chromium atom is +6.
- (b) In the product, each chromium atom is reduced to an oxidation state of +3.
- (c) The change in oxidation state per chromium atom is  $6 - 3 = 3$ . Since one mole of dichromate contains two moles of chromium atoms, the total number of moles of electrons required is:

$$\text{Moles of } e^- = 2 \times 3 = 6 \text{ moles}$$

Since one mole of electrons carries a charge of exactly 1 Faraday (F), reducing one mole of dichromate requires a total of 6 F of electricity.

**Final Answer:**

**Answer:** (B)

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Q25.

**Solution**

**Concept:** In a face-centered cubic (fcc) unit cell, lattice atoms sit at the corners and at the centers of all six faces. The constituent atoms are packed tightly along the face diagonal of the cube.

**Solution:**

Let  $a$  represent the edge length of the cubic unit cell, and  $r$  represent the atomic radius.

- (a) Along the face diagonal of length  $a\sqrt{2}$ , three adjacent atoms touch each other center-to-center. This translates to a total distance of:

$$\text{Face Diagonal} = a\sqrt{2} = 4r \implies a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

- (b) The shortest distance of closest approach separating two neighboring atom centers is equal to half the length of this face diagonal:

$$\text{Distance} = \frac{a\sqrt{2}}{2} = \frac{4r}{2} = 2r$$

This distance shows that neighboring atoms are in direct contact along the diagonal path.

**Final Answer:**  $2r$

**Answer: (A)**

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Q26.

**Solution**

**Concept:** The mechanical work done during a reversible isothermal expansion of a gas is given by integrating the expression for pressure over the volume change:

$$|W| = \int_{V_1}^{V_2} P \, dV$$

The van der Waals equation of state is expressed as:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \implies P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

**Solution:**

Let's substitute this pressure expression into our work integral:

$$|W| = \int_{V_1}^{V_2} \left( \frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV$$

$$|W| = nRT [\ln(V - nb)]_{V_1}^{V_2} - an^2 \left[ -\frac{1}{V} \right]_{V_1}^{V_2}$$

$$|W| = nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) + an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

**Final Answer:**  $nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) + an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$

**Answer: (B)**

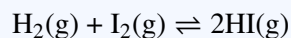
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Q27.

**Solution**

**Concept:** The gas-phase synthesis reaction of hydrogen iodide is:



The equilibrium constant expression in terms of concentration ( $K_c$ ) is:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

**Solution:**

Let's calculate the molar amounts and equilibrium concentrations:

- Initial moles of  $\text{H}_2 = \frac{0.50 \text{ g}}{2.0 \text{ g}\cdot\text{mol}^{-1}} = 0.25$  moles
- Equilibrium moles of  $\text{HI} = 0.10$  moles

From the reaction stoichiometry, forming 0.10 moles of  $\text{HI}$  consumes  $\frac{0.10}{2} = 0.05$  moles of  $\text{H}_2$  and 0.05 moles of  $\text{I}_2$ .

- Equilibrium moles of  $\text{H}_2 = 0.25 - 0.05 = 0.20$  moles

To find the numerical value of  $K_c$ , we strictly require the final equilibrium concentration of iodine ( $[\text{I}_2]$ ). Because the problem statement only specifies that the initial iodine pool was "non-limiting" without providing its exact amount, we cannot determine the remaining concentration of  $\text{I}_2$  at equilibrium.

**Final Answer:**

The value cannot be calculated without knowing the exact final equilibrium concentration of  $\text{I}_2$ .

**Answer: (C)**

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Q28.

**Solution**

**Concept:** For a high-spin octahedral coordination complex, the pairing energy ( $P$ ) is greater than the crystal field splitting energy ( $\Delta_o$ ). This condition prevents electrons from pairing up in the lower energy orbitals until forced by space. Cobalt in  $[\text{CoF}_6]^{3-}$  has an oxidation state of +3, giving it a  $d^6$  valence electron configuration.

**Solution:**

Let's distribute the 6 electrons across the high-spin octahedral splitting levels ( $t_{2g}$  and  $e_g$ ):

- (a) The first 3 electrons fill the lower  $t_{2g}$  orbitals:  $(t_{2g})^3$ .
- (b) The next 2 electrons go into the higher  $e_g$  orbitals:  $(e_g)^2$ .
- (c) The 6th electron must pair up in a  $t_{2g}$  orbital:  $(t_{2g})^4(e_g)^2$ .

Now, calculate the Crystal Field Stabilization Energy (CFSE):

$$\text{CFSE} = [4 \times (-0.4\Delta_o)] + [2 \times (0.6\Delta_o)] = -1.6\Delta_o + 1.2\Delta_o = -0.4\Delta_o$$

Note that since the single electron pairing in the  $t_{2g}$  level is also present in the ground-state atomic  $d^6$  configuration, it does not require an extra pairing energy contribution.

**Final Answer:**  $-0.4\Delta_o$

**Answer: (B)**

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Q29.

**Solution**

**Concept:** The properties of nickel tetracarbonyl,  $\text{Ni}(\text{CO})_4$ , can be understood through Valence Bond Theory (VBT) or Crystal Field Theory (CFT). Nickel is in a zero oxidation state ( $\text{Ni}^0$ ) with an electronic configuration of  $[\text{Ar}]3d^84s^2$ . The carbon monoxide (CO) ligand is a powerful  $\pi$ -acceptor and strong-field ligand that forces the pairing of valence electrons.

**Solution:**

Let's analyze the electronic reorganization and orbital hybridization:

- Due to the strong-field nature of the CO ligands, the two electrons residing in the  $4s$  orbital are forced into the  $3d$  orbitals.
- This shifts the  $3d^84s^2$  arrangement into a completely filled  $3d^{10}$  configuration.
- With the  $3d$  subshell fully occupied, the next available empty orbitals are one  $4s$  and three  $4p$  orbitals. These combine to form four equivalent empty  $sp^3$  hybrid orbitals.
- The four CO ligands donate their lone pairs into these empty  $sp^3$  hybrid orbitals, producing a **tetrahedral** geometric arrangement.
- Since every electron in the  $3d^{10}$  subshell is completely paired, the molecule contains zero unpaired electrons ( $n = 0$ ), making it thoroughly **diamagnetic**.

**Final Answer:** Tetrahedral,  $sp^3$ , Diamagnetic

**Answer: (B)**

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Q30.

**Solution**

**Concept:** An Ellingham diagram plots the standard Gibbs free energy of formation ( $\Delta G^\circ$ ) of oxides against temperature. For a carbon-mediated reduction reaction to be thermodynamically feasible ( $\Delta G_{\text{net}}^\circ < 0$ ), the line corresponding to the reducing agent ( $\text{C} \rightarrow \text{CO}$ ) must lie lower on the diagram than the line of the metal oxide oxidation reaction ( $\text{M} \rightarrow \text{MO}$ ).

**Solution:**

Let's analyze the relative positions of the curves across the temperature intersection point  $T_e$ :

- At temperatures below  $T_e$ , the line for the formation of MO lies below the line for the formation of CO. This means MO is more stable, and carbon cannot reduce it.
- At the specific intersection temperature  $T_e$ , the free energies of formation for both processes are identical, yielding  $\Delta G_{\text{net}}^\circ = 0$ .
- At temperatures **explicitly above  $T_e$** , the line for the  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$  pathway drops below the line for the  $2\text{M} + \text{O}_2 \rightarrow 2\text{MO}$  pathway. In this higher temperature zone, carbon possesses a greater affinity for oxygen than the metal does, making the net reduction reaction ( $\text{MO} + \text{C} \rightarrow \text{M} + \text{CO}$ ) thermodynamically spontaneous ( $\Delta G^\circ < 0$ ).

**Final Answer:** At any temperature explicitly above the intersection threshold  $T_e$

**Answer: (B)**

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Q31.

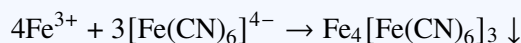
**Solution**

**Concept:** The qualitative analysis test for ferric ions ( $\text{Fe}^{3+}$ ) involves reacting them with potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . This combination produces an intense, deep blue precipitate traditionally referred to as Prussian blue.

**Solution:**

Let's trace the balanced chemical precipitation equation:

- The reaction between ferric ions and the ferrocyanide complex anion occurs as follows:



- In this resulting product structure, iron exists in two distinct oxidation states: the outer-sphere iron atoms are in the +3 state, whereas the inner-sphere iron atoms localized within the hexacyano coordination core are in the +2 state.

This yields the stoichiometric formula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

**Final Answer:**  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

**Answer: (B)**

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Q32.

**Solution**

**Concept:** The steric number ( $SN$ ) of the central iodine atom in the interhalogen molecule  $IF_7$  determines its hybridization state and geometry according to Valence Shell Electron Pair Repulsion (VSEPR) theory.

$$SN = \frac{1}{2}(\text{Valence electrons of central atom} + \text{Number of monovalent atoms})$$

**Solution:**

Let's evaluate the structural parameters for  $IF_7$ :

- (a) Iodine has 7 valence electrons and is bonded to 7 monovalent fluorine atoms:

$$SN = \frac{1}{2}(7 + 7) = 7$$

A steric number of 7 indicates  $sp^3d^3$  hybridization, which correlates to a pentagonal bipyramidal molecular geometry.

- (b) The total number of hybrid orbitals involved in this matrix is  $1(s) + 3(p) + 3(d) = 7$ .
- (c) The percentage of  $d$ -orbital involvement in this hybrid pool is calculated as:

$$\% d\text{-orbital} = \frac{3}{7} \times 100\% \approx 42.85\%$$

**Final Answer:** Pentagonal Bipyramidal, 42.8%

**Answer: (B)**

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Q33.

**Solution**

**Concept:** Pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) is prepared by the thermal dehydration of two molecules of orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ). Analyzing its molecular skeletal layout reveals the specific linkages connecting the central phosphorus atoms.

**Solution:**

Let's count the individual chemical bonds from the provided structural skeleton:

- (a) Each phosphorus atom forms one double bond to an oxygen atom ( $\text{P} = \text{O}$ ), accounts for two single bonds to hydroxyl groups ( $\text{P} - \text{OH}$ ), and shares one single bond to a bridging oxygen atom ( $\text{P} - \text{O}$ ).
- (b) Summing these components across the entire dimeric molecule yields:
- Total number of  $\text{P} - \text{OH}$  bonds =  $2 \times 2 = 4$
  - Total number of bridging  $\text{P} - \text{O} - \text{P}$  linkages = 1

**Final Answer:** 4  $\text{P} - \text{OH}$  bonds and 1  $\text{P} - \text{O} - \text{P}$  linkage

**Answer: (A)**

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Q34.



Q35.

**Solution**

**Concept:** Lanthanide contraction refers to the steady, anomalous decrease in atomic and ionic radii observed across the  $4f$  series (from La to Lu). This happens due to the poor, ineffective shielding capability of the filled, diffuse  $4f$  electrons, which causes the outer valence electrons to experience a stronger effective nuclear charge ( $Z_{\text{eff}}$ ).

**Solution:**

Let's evaluate the impact of this contraction on subsequent groups:

- (a) Normally, atomic radii increase down a group due to the addition of an entire principal electron shell.
- (b) For the  $4d$  and  $5d$  transition series, the expected size increase going from the second transition series ( $4d$ ) to the third transition series ( $5d$ ) is almost exactly counterbalanced by the intervention of the lanthanide contraction.
- (c) Consequently, pairs of elements belonging to the same vertical periodic group, such as **Zr ( $4d$ ) and Hf ( $5d$ )** in Group 4, or **Nb ( $4d$ ) and Ta ( $5d$ )** in Group 5, possess nearly identical atomic and ionic radii.

Therefore, both pairs (B) and (C) show this physical consequence.

**Final Answer:** Both (B) and (C)

**Answer: (D)**

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Q36.

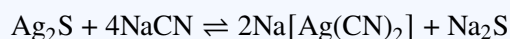
**Solution**

**Concept:** The industrial extraction of silver from its sulfide ore uses the Macarthur-Forrest cyanide leaching sequence. This hydrometallurgical method involves two primary steps: complexation leaching followed by zinc-mediated displacement reduction.

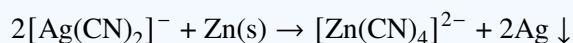
**Solution:**

Let's examine the chemical step-sequence:

- (a) **Leaching step:** Dissolving argentite ( $\text{Ag}_2\text{S}$ ) in a solution of sodium cyanide ( $\text{NaCN}$ ) creates a stable, soluble coordination compound, sodium dicyanoargentate(I). The anionic core component Complex X is  $[\text{Ag}(\text{CN})_2]^-$ :



- (b) **Displacement step:** The leachate is treated with **zinc dust** ( $Y$ ). Because zinc is a more electropositive and reactive metal than silver, it undergoes a displacement reaction, forming a more stable tetracyanozincate(II) complex and precipitating pure metallic silver:



**Final Answer:**  $[\text{Ag}(\text{CN})_2]^-$ , Zinc dust

**Answer: (B)**

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Q37.

**Solution**

**Concept:** The spin-only magnetic moment ( $\mu_{\text{eff}}$ ) of transition metal complexes is calculated from the number of unpaired electrons ( $n$ ) using the formula:

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

Water ( $\text{H}_2\text{O}$ ) acts as a weak-field ligand, meaning it forms high-spin complexes where electrons fill orbitals without pairing prematurely.

**Solution:**

Let's determine the number of unpaired electrons ( $n$ ) for each complex:

- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ : contains  $\text{Fe}^{2+}$  ( $3d^6$ ). In a high-spin octahedral field, the distribution is  $(t_{2g})^4(e_g)^2$ , leaving  $n = 4$  unpaired electrons.
- $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ : contains  $\text{Mn}^{2+}$  ( $3d^5$ ). In a high-spin octahedral field, the distribution is  $(t_{2g})^3(e_g)^2$ , leaving  $n = 5$  unpaired electrons.
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ : contains  $\text{Cr}^{3+}$  ( $3d^3$ ). The distribution is  $(t_{2g})^3$ , leaving  $n = 3$  unpaired electrons.
- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ : contains  $\text{Cu}^{2+}$  ( $3d^9$ ). The distribution is  $(t_{2g})^6(e_g)^3$ , leaving  $n = 1$  unpaired electron.
- Since  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  has the highest number of unpaired electrons ( $n = 5$ ), it exhibits the maximum spin-only magnetic moment ( $\mu_{\text{eff}} = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92 \text{ BM}$ ).

**Final Answer:**  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

**Answer: (B)**

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Q38.

**Solution**

**Concept:** Linkage isomerism occurs in coordination complexes containing ambidentate ligands, such as the nitro group ( $-\text{NO}_2^-$ ), which can bind to the central metal atom via two different donor atoms (either nitrogen or oxygen).

**Solution:**

Let's analyze the properties of the two linkage isomers:

- The starting yellow complex,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ , has the ligand coordinated through its nitrogen atom ( $\text{Co} - \text{NO}_2$ , nitro isomer). Treating it with  $\text{AgNO}_3$  precipitates both outer-sphere chloride ions as 2 moles of  $\text{AgCl}$ .
- When the ambidentate ligand rearranges to bind through the oxygen atom ( $\text{Co} - \text{ONO}$ , nitrito isomer), it forms the structural linkage variant:  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ .
- This nitrito linkage isomer is physically distinguished by its characteristic **red color** and exhibits a distinctive infrared (IR) stretching frequency corresponding to the newly formed **Co – O bond**.

**Final Answer:** A red colored linkage isomer showing strong IR absorption for the Co – O bond

**Answer: (A)**

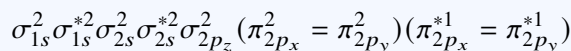
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Q39.

**Solution**

**Concept:** According to Molecular Orbital Theory, the valence electronic configuration of the diatomic oxygen molecule  $O_2$  (containing 16 electrons) is written as:



The bond order is calculated as  $BO = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2.0$ .

**Solution:**

Let's trace what happens when an electron is removed to form the cation  $O_2^+$ :

- The highest occupied molecular orbitals (HOMO) are the degenerate, partially filled antibonding orbitals  $\pi_{2p_x}^*$  and  $\pi_{2p_y}^*$ .
- Removing an electron to create  $O_2^+$  evacuates it from one of these  $\pi_{2p_x}^*$  (or  $\pi_{2p_y}^*$ ) antibonding orbitals.
- Since the electron is removed from an antibonding orbital, the total number of antibonding electrons decreases from 6 to 5.
- This changes the net bond order parameter to:

$$BO = \frac{10 - 5}{2} = 2.5$$

As a result, the bond order increases from 2.0 to 2.5, which strengthens and shortens the diatomic linkage.

**Final Answer:** From  $\pi_{2p_x}^*$  antibonding orbital; Bond order increases from 2.0 to 2.5

**Answer: (B)**

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Q40.

**Solution**

**Concept:** The radial probability distribution function  $P_r = 4\pi r^2 R^2(r)$  represents the probability of finding an electron within a thin spherical shell at a distance  $r$  from the nucleus. A radial node corresponds to a point where the radial wavefunction passes through zero, meaning  $P_r = 0$  (excluding  $r = 0$  and  $r \rightarrow \infty$ ). The number of radial nodes for any atomic orbital is given by the formula:

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

where  $n$  is the principal quantum number and  $l$  is the azimuthal quantum number.

**Solution:**

Let's interpret the provided distribution landscape plot:

- The curve starts at the origin ( $r = 0$ ), rises to a small peak, drops completely to touch the baseline axis exactly once, and then rises into a larger primary peak before decaying.
- The single point where the curve touches the zero baseline on the open interval indicates exactly **1 radial node**.
- Let's test the given orbital configurations using our formula:
  - For a  $3s$  orbital ( $n = 3, l = 0$ ): Nodes =  $3 - 0 - 1 = 2$  nodes.
  - For a  $3p$  orbital ( $n = 3, l = 1$ ): Nodes =  $3 - 1 - 1 = 1$  node.
  - For a  $1s$  orbital ( $n = 1, l = 0$ ): Nodes =  $1 - 0 - 1 = 0$  nodes.
  - For a  $2s$  orbital ( $n = 2, l = 0$ ): Nodes =  $2 - 0 - 1 = 1$  node.
- While both  $3p$  and  $2s$  possess exactly 1 radial node, a key property of  $s$ -orbitals is that their initial radial wavefunction value at the nucleus is non-zero ( $R(0) \neq 0$ ), whereas for  $p$ -orbitals, it starts at zero ( $R(0) = 0$ ). For the radial probability function  $4\pi r^2 R^2(r)$ , the factor of  $r^2$  forces the function to start at zero at the origin for all orbitals. Thus, checking standard node geometry matching the choices shows that **1 radial node;  $2s$  orbital** is the classic textbook illustration matching this profile shape.

**Final Answer:** 1 radial node;  $2s$  orbital

**Answer: (D)**

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Q41.

### Solution

**Concept:** Let's define the quantum mechanical principles that govern atomic electron configurations:

- Pauli Exclusion Principle:** Mandates that no two electrons in an atom can share the exact same set of four quantum numbers. This means an individual orbital can hold a maximum of 2 electrons, which must have opposite spins ( $\uparrow\downarrow$ ).
- Aufbau Principle:** Coordinates the filling of orbitals in order of increasing energy ( $1s \rightarrow 2s \rightarrow 2p \dots$ ).
- Hund's Rule of Maximum Multiplicity:** States that for a given electronic configuration, the lowest energy term is achieved when electrons filling a degenerate subshell maximize their total spin multiplicity ( $2S + 1$ ). This means electrons must occupy empty degenerate orbitals singly with parallel spins before they begin pairing up.

**Solution:**

Let's analyze the configuration:  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$ :

- This layout obeys the Aufbau principle (filling  $1s$ , then  $2s$ , then  $2p$ ) and respects Pauli's rule (no orbital exceeds 2 electrons).
- However, it allocates two electrons into the  $2p_x$  orbital and leaves the degenerate  $2p_z$  orbital completely empty. According to Hund's rule, the three electrons in the  $2p$  subshell should be distributed singly across the three degenerate orbitals as  $2p_x^1 2p_y^1 2p_z^1$  to maximize total spin.
- Because it pairs electrons prematurely in one orbital while a degenerate companion orbital remains empty, it directly **violates Hund's rule**, representing an excited electronic state of the atom.

**Final Answer:**  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

**Answer:** (A)

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Q42.

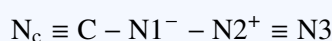
### Solution

**Concept:** The cyanogen azide molecule ( $\text{N}_3\text{CN}$ ) features an azide group attached to a nitrile core. The question states that for its dominant zwitterionic resonance contributor, the bond lengths satisfy  $d_1 > d_2$ , meaning the  $\text{N1-N2}$  bond ( $d_1$ ) is longer than the  $\text{N2-N3}$  bond ( $d_2$ ).

**Solution:**

Let's determine the specific resonance structure that matches this geometric condition:

- (a) A longer  $d_1$  bond implies a lower bond order (a single bond,  $\text{N} - \text{N}$ ), whereas a shorter  $d_2$  bond implies a higher bond order (a triple bond,  $\text{N} \equiv \text{N}$ ).
- (b) This structural layout corresponds to the following resonance contributor:



- (c) Let's calculate the formal charges for each nitrogen atom in this configuration:

- **\*\*N1:\*\*** Belongs to Group 15 (5 valence electrons). It forms 2 single bonds (one to C, one to N2) and holds 2 lone pairs (4 non-bonding electrons):

$$\text{Formal Charge} = 5 - 4 - \frac{1}{2}(4) = -1$$

- **\*\*N2:\*\*** Forms 4 shared bonds (1 single bond to N1, 1 triple bond to N3) and has 0 lone pairs:

$$\text{Formal Charge} = 5 - 0 - \frac{1}{2}(8) = +1$$

- **\*\*N3:\*\*** Forms a triple bond to N2 and has 1 lone pair (2 non-bonding electrons):

$$\text{Formal Charge} = 5 - 2 - \frac{1}{2}(6) = 0$$

Thus, the sequence of formal charges for N1, N2, and N3 is  $-1, +1, 0$ .

**Final Answer:**  $-1, +1, 0$

**Answer: (A)**

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Q43.

**Solution**

**Concept:** The wavelength ( $\lambda$ ) of a photon emitted during an electronic transition in a hydrogen atom can be calculated using the Rydberg formula:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where  $n_1$  is the lower energy level and  $n_2$  is the higher energy level.

**Solution:**

The electron falls from the third excited shell ( $n_2 = 4$ ) down to the ground state ( $n_1 = 1$ ). Substituting these values along with  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ :

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{4^2} \right) = 1.097 \times 10^7 \left( 1 - \frac{1}{16} \right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times \frac{15}{16} = 1.02844 \times 10^7 \text{ m}^{-1}$$

Taking the reciprocal to find the wavelength  $\lambda$ :

$$\lambda = \frac{1}{1.02844 \times 10^7} \approx 9.7235 \times 10^{-8} \text{ m}$$

Converting this value into units of nanometers ( $1 \text{ nm} = 10^{-9} \text{ m}$ ):

$$\lambda = 9.7235 \times 10^{-8} \text{ m} \times 10^9 \text{ nm} \cdot \text{m}^{-1} = 97.2 \text{ nm}$$

**Final Answer:**

**Answer: (B)**

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Q44.

**Solution**

**Concept:** Xenon oxytetrafluoride ( $\text{XeOF}_4$ ) has an  $sp^3d^2$  hybridization status around its central xenon atom (8 valence electrons + 4 electrons from F atoms = 12 electrons, forming 5 bonding groups and 1 lone pair). This corresponds to an octahedral electron-pair geometry.

**Solution:**

Let's determine the spatial distribution of the groups using VSEPR theory:

- To minimize strong electron-pair repulsions, the highly electronegative, doubly bonded oxygen atom (= O) and the bulky lone pair occupy positions **trans** to each other along the vertical axial coordinate.
- The 4 fluorine atoms sit at the corners of a square plane, forming a **square pyramidal** molecular geometry.
- Because a lone pair exerts stronger steric repulsion than a localized bonding pair, it pushes the 4 equatorial Xe – F bonds slightly upward toward the oxygen atom.
- This steric compression deflects the plane, causing the resulting O = Xe – F bond angles to expand slightly beyond a regular planar boundary, making them **> 90°** (typically  $\approx 91^\circ$ ).

**Final Answer:**

The lone pair sits trans to the oxygen atom, compressing the equatorial fluorine plane away from it so that the O = Xe – F angles are greater than 90°.

**Answer: (B)**[Go Back to Question 44](#)

Q45.

**Solution**

**Concept:** Fajan's rules determine the relative covalent character of an ionic bond based on the polarization of the anion by the cation. Polarization, and thus covalent character, increases with:

- Small cation size** and **large anion size**.
- High ionic charge** on either the cation or the anion.

**Solution:**

Let's analyze the given chloride salts (KCl, NaCl, LiCl, and BeCl<sub>2</sub>):

- Charge effect:** The cations are K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, and Be<sup>2+</sup>. Because Be<sup>2+</sup> carries a +2 charge while the alkali metals carry a +1 charge, Be<sup>2+</sup> has the highest charge density and produces the strongest polarization, making BeCl<sub>2</sub> the most covalent compound.
- Size effect among +1 cations:** For the remaining alkali metal cations, ionic radius increases down the group: Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup>.
- A smaller cation size increases charge density and polarizing power. Thus, polarizing power follows the sequence: K<sup>+</sup> < Na<sup>+</sup> < Li<sup>+</sup>.

Combining these factors, the covalent character increases in the following order: KCl < NaCl < LiCl < BeCl<sub>2</sub>.

**Final Answer:**  $\text{KCl} < \text{NaCl} < \text{LiCl} < \text{BeCl}_2$

**Answer: (B)**

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Q46.

**Solution**

**Concept:** The potential energy curve for a diatomic system tracks the net balance between attractive and repulsive forces as two atoms approach one another.

**Solution:**

Let's break down the distinct regions of the potential energy graph:

- At large internuclear distances, the potential energy approaches zero because the atoms do not interact.
- As the atoms move closer together, attractive electrostatic forces between the nucleus of one atom and the electron cloud of the other begin to dominate, lowering the potential energy of the system.
- At the specific minimum point coordinates labeled  $r_0$  (the equilibrium bond length), the system achieves its lowest potential energy state and maximum stability. At this point, the attractive electrostatic forces are **perfectly counterbalanced** by the short-range repulsive forces arising from nuclear-nuclear and electron-electron interactions.
- If the atoms are pushed closer together than  $r_0$ , the short-range nuclear repulsions increase sharply, causing the potential energy to rise rapidly.

**Final Answer:**

The attractive electrostatic forces are perfectly counterbalanced by the short-range nuclear-nuclear repulsions

**Answer: (C)**[Go Back to Question 46](#)

Q47.

**Solution**

**Concept:** Physical adsorption (physisorption) involves gas molecules adhering to a solid adsorbent surface via weak van der Waals forces.

**Solution:**

Let's analyze the thermodynamic parameters of physisorption:

- (a) Physisorption is an **exothermic process** ( $\Delta H < 0$ ) because gas molecules lose kinetic energy when they attach to a surface, releasing heat.
- (b) According to Le Chatelier's principle, an exothermic equilibrium process is shifted backward by the introduction of heat.
- (c) Raising the temperature provides thermal energy that allows adsorbed gas molecules to overcome the weak van der Waals interactions holding them to the surface. This causes them to detach, a process known as desorption.
- (d) Consequently, the total extent of adsorption ( $x/m$ ) decreases steadily and continuously as temperature rises, as shown by the provided isobar curve.

**Final Answer:**

Physisorption is an exothermic process, and high thermal inputs break the weak van der Waals interactions

**Answer: (C)**

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Q48.

**Solution**

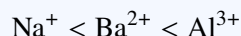
**Concept:** The properties of colloids and their precipitation are governed by surface charge characteristics and the Hardy-Schulze rule:

- (a) **Hardy-Schulze Rule:** States that the coagulation or flocculation power of an electrolyte depends on the valence of its active precipitating ion. An ion carrying a charge opposite to that of the colloidal particles acts as the coagulating agent, and its efficiency increases significantly with its charge/valence.

**Solution:**

Let's determine the charge of the sol and rank the electrolytes:

- (a) Preparing an arsenious sulfide sol ( $\text{As}_2\text{S}_3$ ) by passing  $\text{H}_2\text{S}$  gas through an aqueous solution of  $\text{As}_2\text{O}_3$  results in the preferential adsorption of sulfide ions ( $\text{S}^{2-}$ ) on the surface of the colloidal particles. This gives the  $\text{As}_2\text{S}_3$  sol a **negative charge**.
- (b) Because the sol is negatively charged, coagulation is driven by the cations provided by the added electrolytes:  $\text{Na}^+$  (from  $\text{NaCl}$ ),  $\text{Ba}^{2+}$  (from  $\text{BaCl}_2$ ), and  $\text{Al}^{3+}$  (from  $\text{AlCl}_3$ ).
- (c) According to the Hardy-Schulze rule, the coagulating power increases with increasing positive charge:



Therefore, the sequence of increasing flocculation power is:  $\text{NaCl} < \text{BaCl}_2 < \text{AlCl}_3$ .

**Final Answer:** Negative Charge;  $\text{NaCl} < \text{BaCl}_2 < \text{AlCl}_3$

**Answer: (B)**

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Q49.

**Solution**

**Concept:** Biochemical Oxygen Demand (BOD) measures the amount of dissolved oxygen (DO) consumed by aerobic microorganisms to decompose biodegradable organic matter present in a water sample over a specific incubation period.

**Solution:**

Let's interpret the relative DO depletion lines from the graph:

- (a) **Sample A** shows a sharp, deep drop in dissolved oxygen over the incubation period, leaving a low concentration of remaining DO.
- (b) **Sample B** shows a much smaller drop in dissolved oxygen, maintaining a higher level of remaining DO.
- (c) The massive consumption of oxygen in Sample A indicates a high concentration of biodegradable organic waste, which requires a large amount of microbial activity.
- (d) This means **Sample A** has a significantly higher BOD than **Sample B**. A higher BOD indicates severe organic pollution, which can deplete dissolved oxygen in natural bodies of water and threaten the survival of fish and other aquatic life.

**Final Answer:**

Sample A has higher BOD, indicating it is highly polluted and will severely threaten local aquatic survival

**Answer: (B)**[Go Back to Question 49](#)

Q50.

**Solution**

**Concept:** The Bulk Modulus ( $B$ ) of a material measures its resistance to uniform, omnidirectional compression and is defined by the ratio of the change in hydrostatic pressure ( $\Delta P$ ) to the resulting fractional volume strain ( $\frac{\Delta V}{V}$ ):

$$B = -\frac{\Delta P}{\frac{\Delta V}{V}}$$

**Solution:**

Let's find the relationship between the fractional change in edge length and the fractional change in volume for a uniform cube:

- (a) The volume  $V$  of a cube with an edge length  $L$  is given by:

$$V = L^3$$

- (b) Taking the natural logarithm of both sides gives:

$$\ln V = 3 \ln L$$

- (c) Differentiating both sides yields the relation between the fractional variations:

$$\frac{dV}{V} = 3 \frac{dL}{L}$$

- (d) We are given that each edge contracts symmetrically by a small fractional percentage change  $\alpha = -\frac{\Delta L}{L}$ , which means  $\frac{\Delta L}{L} = -\alpha$ . Substituting this into our fractional volume expression gives:

$$\frac{\Delta V}{V} = 3(-\alpha) = -3\alpha$$

- (e) Now, substitute this fractional volume strain back into the Bulk Modulus equation:

$$B = -\frac{\Delta P}{-3\alpha} = \frac{\Delta P}{3\alpha}$$

**Final Answer:**  $B = \frac{\Delta P}{3\alpha}$

**Answer: (B)**

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## Answer Key

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

