

# WBJEE Chemistry Sample Paper-1

Duration: 60 Minutes

Maximum Marks: 50

## Instructions

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

**Section–A — 30 Questions × 1 Mark Each**  
**(Negative Marking: –0.25) [Single Correct]**

- Q1.** An organic compound contains 52.17% carbon, 13.04% hydrogen, and the rest oxygen by mass. What is the minimum molecular mass of this compound if it contains exactly one oxygen atom per molecule?
- (A) 30 g/mol  
(B) 46 g/mol  
(C) 60 g/mol  
(D) 74 g/mol
- Q2.** A 10.0 mL sample of  $H_2O_2$  solution requires 20.0 mL of 0.02 M  $KMnO_4$  solution for complete titration in an acidic medium. Calculate the volume strength of this  $H_2O_2$  sample at STP.

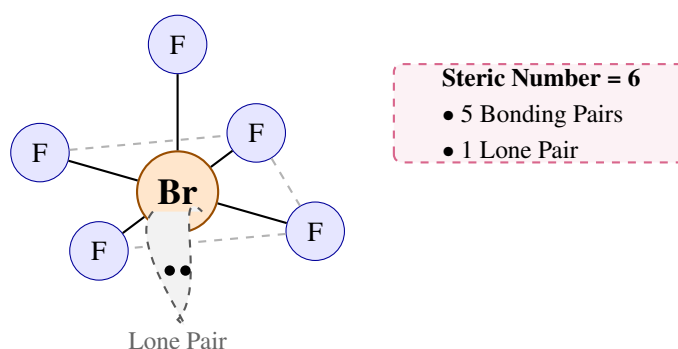


- (A) 0.56 V
- (B) 1.12 V
- (C) 2.24 V
- (D) 5.60 V

**Q3.** If the uncertainty in the position of an electron is equal to its de Broglie wavelength, what is the minimum uncertainty in its velocity?

- (A)  $v$
- (B)  $v/(2\pi)$
- (C)  $v/(4\pi)$
- (D)  $4\pi v$

**Q4.** Which of the following molecules or ions exhibits a square pyramidal geometry according to VSEPR theory?



- (A)  $PCl_5$
- (B)  $BrF_5$
- (C)  $SF_6$
- (D)  $XeF_4$

**Q5.** A gas obeys the van der Waals equation of state. Under which conditions will it behave most like an ideal gas?

- (A) High temperature and low pressure
- (B) Low temperature and high pressure



- (C) High temperature and high pressure  
 (D) Low temperature and low pressure

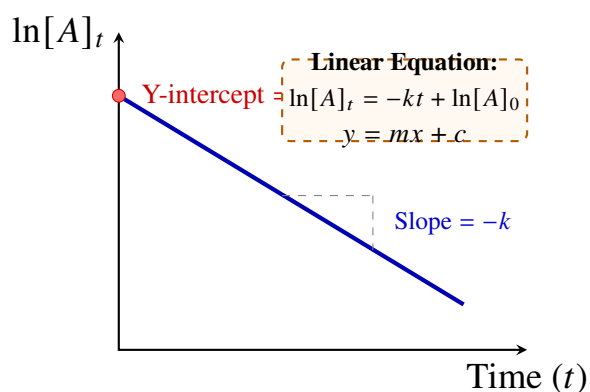
**Q6.** For the isothermal reversible expansion of an ideal gas into a vacuum (free expansion), which set of thermodynamic parameters is entirely correct?

- (A)  $w < 0, q > 0, \Delta U = 0, \Delta S_{\text{surr}} > 0$   
 (B)  $w = 0, q = 0, \Delta U = 0, \Delta S_{\text{surr}} = 0$   
 (C)  $w = 0, q > 0, \Delta U > 0, \Delta S_{\text{surr}} = 0$   
 (D)  $w = 0, q = 0, \Delta U = 0, \Delta S_{\text{total}} = 0$

**Q7.** At a certain temperature, the solubility product ( $K_{\text{sp}}$ ) of  $\text{CaF}_2$  is  $3.2 \times 10^{-11}$ . What is the solubility of  $\text{CaF}_2$  in a 0.1 M  $\text{NaF}$  solution?

- (A)  $2.0 \times 10^{-4}$  M  
 (B)  $3.2 \times 10^{-10}$  M  
 (C)  $1.6 \times 10^{-9}$  M  
 (D)  $3.2 \times 10^{-9}$  M

**Q8.** For a first-order chemical reaction, a graph of  $\ln[A]_t$  versus time ( $t$ ) yields a straight line. What represents the slope and intercept of this plot?



- (A) Slope =  $k$ , Intercept =  $[A]_0$   
 (B) Slope =  $-k$ , Intercept =  $\ln[A]_0$   
 (C) Slope =  $-k/2.303$ , Intercept =  $\log[A]_0$



(D) Slope =  $k/2.303$ , Intercept =  $-\ln[A]_0$

**Q9.** Which of the following options shows the correct order of increasing standard reduction potential for the given half-cells?

(A)  $Cu^{2+}/Cu < H^+/H_2 < Zn^{2+}/Zn < Li^+/Li$

(B)  $Li^+/Li < H^+/H_2 < Zn^{2+}/Zn < Cu^{2+}/Cu$

(C)  $Li^+/Li < Zn^{2+}/Zn < H^+/H_2 < Cu^{2+}/Cu$

(D)  $Zn^{2+}/Zn < Li^+/Li < H^+/H_2 < Cu^{2+}/Cu$

**Q10.** When heating an excess of metallic lithium in a dry atmosphere of pure nitrogen gas, which compound is predominantly formed?

(A)  $LiN_3$

(B)  $Li_2N$

(C)  $Li_3N$

(D)  $LiNO_3$

**Q11.** Which of the following trends represents the correct order of decreasing thermal stability for the alkaline earth metal carbonates?

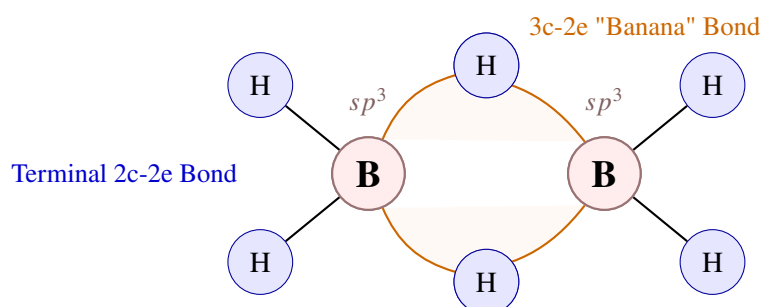
(A)  $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

(B)  $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

(C)  $CaCO_3 > MgCO_3 > BaCO_3 > SrCO_3$

(D)  $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$

**Q12.** What is the correct structural relationship and hybridization found within a molecule of diborane ( $B_2H_6$ )?



- (A) Two 3-center-4-electron bonds; boron is  $sp^2$  hybridized.
- (B) Six standard 2-center-2-electron bonds; boron is  $sp^3$  hybridized.
- (C) Two 3-center-2-electron bonds; boron is  $sp^3$  hybridized.
- (D) Four 3-center-2-electron bonds; boron is  $sp^2$  hybridized.

**Q13.** Why does orthophosphoric acid ( $H_3PO_4$ ) behave as a triprotic acid, whereas phosphorous acid ( $H_3PO_3$ ) acts only as a diprotic acid?

- (A)  $H_3PO_4$  contains more total oxygen atoms to attract proton clouds.
- (B)  $H_3PO_3$  contains one hydrogen atom bonded directly to the central phosphorus atom.
- (C)  $H_3PO_3$  undergoes rapid self-reduction to eliminate a proton.
- (D) The phosphorus atom in  $H_3PO_4$  is in a lower oxidation state.

**Q14.** Which transition metal ion exhibits the highest spin-only magnetic moment among the following species?

- (A)  $Cr^{3+}$
- (B)  $Mn^{3+}$
- (C)  $Fe^{3+}$
- (D)  $Co^{3+}$

**Q15.** According to Crystal Field Theory (CFT), what is the correct electronic configuration and magnetic behavior of the complex ion  $[Co(NH_3)_6]^{3+}$ ?

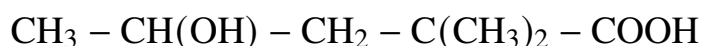
- (A)  $t_{2g}^4 e_g^2$ , Paramagnetic
- (B)  $t_{2g}^6 e_g^0$ , Diamagnetic
- (C)  $t_{2g}^5 e_g^1$ , Paramagnetic
- (D)  $t_{2g}^3 e_g^3$ , Diamagnetic

**Q16.** Photochemical smog is primarily formed in warm, dry, and sunny climates. Which of the following chemical species is NOT a primary or secondary component of photochemical smog?



- (A)  $O_3$
- (B) PAN (Peroxyacetyl nitrate)
- (C)  $NO_2$
- (D)  $SO_2$

**Q17.** What is the correct IUPAC name for the following organic compound?



- (A) 2-Hydroxy-4,4-dimethylpentanoic acid
- (B) 4-Hydroxy-2,2-dimethylpentanoic acid
- (C) 4-Oxo-2,2-dimethylpentanoic acid
- (D) 1-Hydroxy-3,3-dimethylbutane-1-carboxylic acid

**Q18.** Which of the following alkenes will yield a racemic mixture of enantiomers when treated with bromine ( $Br_2$ ) in a carbon tetrachloride ( $CCl_4$ ) solvent?

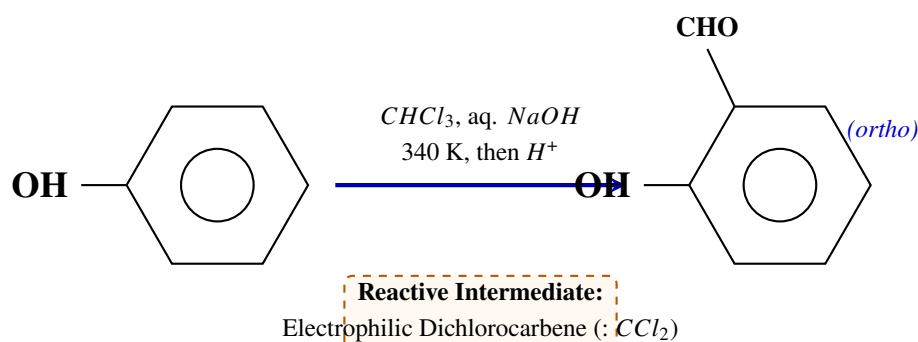
- (A) trans-But-2-ene
- (B) Ethene
- (C) cis-But-2-ene
- (D) Propene

**Q19.** When alkyl halides undergo nucleophilic substitution, which of the following statements perfectly characterizes the  $S_N1$  mechanism kinetics and stereochemical outcome?

- (A) Second-order kinetics accompanied by complete Walden inversion.
- (B) First-order kinetics accompanied by exclusive retention of configuration.
- (C) Zero-order kinetics accompanied by geometric isomerization.
- (D) First-order kinetics accompanied by partial or complete racemization.



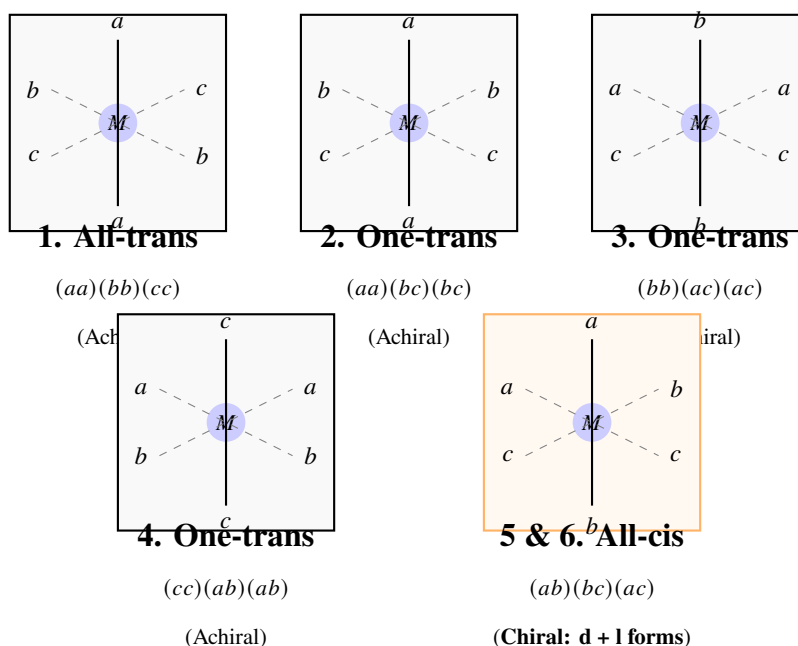
- Q20.** What is the principal organic product obtained when phenol is treated with chloroform ( $CHCl_3$ ) in the presence of aqueous sodium hydroxide ( $NaOH$ ) at 340 K, followed by acidification?



- (A) Salicylic acid  
 (B) Salicylaldehyde  
 (C) Anisole  
 (D) Chlorobenzene
- Q21.** An organic compound (X) with the molecular formula  $C_3H_6O$  forms a 2,4-DNP derivative but does not reduce Tollens' reagent or Fehling's solution. Upon treatment with  $I_2$  and  $NaOH$ , it yields a yellow precipitate. Identify compound (X).
- (A) Propanal  
 (B) Allyl alcohol  
 (C) Acetone  
 (D) Methyl vinyl ether
- Q22.** Which of the following amines will react with nitrous acid ( $HNO_2$ ) at 273–278 K to produce a stable diazonium salt solution that evolves nitrogen gas only when warmed?
- (A) Ethylamine  
 (B) N-Methylaniline  
 (C) Triethylamine  
 (D) Aniline



- Q23.** Which of the following statements regarding the structure of DNA and its component nucleic acid bases is completely accurate?
- (A) Adenine pairs with uracil via two hydrogen bonds in standard double-stranded DNA structures.
- (B) Guanine pairs with thymine via three covalent bonds across the strands.
- (C) Adenine pairs with thymine via two hydrogen bonds; guanine pairs with cytosine via three hydrogen bonds.
- (D) The backbone of DNA contains alternating units of ribose sugar and silicate linkers.
- Q24.** Which of the following polymers is synthesized via a condensation polymerisation mechanism rather than an addition pathway?
- (A) Polyvinyl chloride (PVC)
- (B) Teflon
- (C) Nylon-6,6
- (D) Polystyrene
- Q25.** What is the total number of stereoisomers possible for an octahedral coordination complex represented by the formula  $[Ma_2b_2c_2]$ , where  $a$ ,  $b$ , and  $c$  are monodentate ligands?



- (A) 3  
 (B) 4  
 (C) 5  
 (D) 6

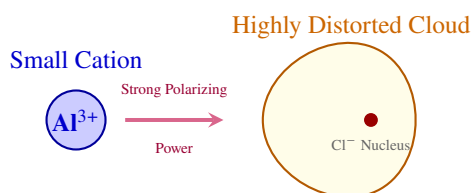
**Q26.** When 0.1 mol of a non-volatile non-electrolyte solute is dissolved in 1000 g of water, the freezing point depression observed is  $0.186^{\circ}\text{C}$ . What freezing point depression will be observed if 0.1 mol of  $\text{MgCl}_2$  is dissolved in 1000 g of water, assuming complete dissociation?

- (A)  $0.186^{\circ}\text{C}$   
 (B)  $0.372^{\circ}\text{C}$   
 (C)  $0.558^{\circ}\text{C}$   
 (D)  $0.744^{\circ}\text{C}$

**Q27.** Which of the following quantum number designations is impossible for an orbital within a ground-state atom?

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

**Q28.** Which of the following compounds displays the greatest degree of covalent character according to Fajans' Rules?

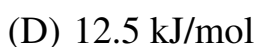
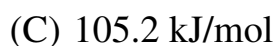
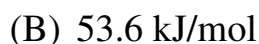
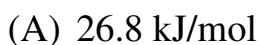


- (A)  $\text{NaCl}$   
 (B)  $\text{MgCl}_2$





**Q29.** The rate of a certain chemical reaction doubles when the temperature is raised from 300 K to 310 K. What is the approximate activation energy ( $E_a$ ) of this reaction? (Given  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

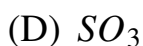


**Q30.** For the gaseous equilibrium system  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ , how will the equilibrium position shift if the total pressure of the container is increased at constant temperature?



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

**Q31.** Which of the following oxides shows amphoteric behavior, dissolving in both strong aqueous acids and strong bases?



- Q32.** An aqueous solution contains a mixture of  $Cu^{2+}$  and  $Bi^{3+}$  ions. Which reagent can be used to separate these two cations during qualitative inorganic analysis?
- (A) Dilute hydrochloric acid  
(B) Hydrogen sulfide gas in acidic medium  
(C) Sodium chloride solution  
(D) Excess aqueous ammonia solution
- Q33.** What is the dominant organic product formed when bromobenzene is heated with a mixture of concentrated sulfuric acid and concentrated nitric acid?
- (A) m-Nitrobromobenzene exclusively  
(B) Nitrobenzene  
(C) A mixture of o-nitrobromobenzene and p-nitrobromobenzene  
(D) 1,3,5-Trinitrobenzene
- Q34.** Which of the following compounds will react most rapidly via an  $E2$  elimination mechanism when treated with sodium ethoxide in ethanol?
- (A) 1-Bromobutane  
(B) 2-Bromobutane  
(C) Bromomethane  
(D) 2-Bromo-2-methylpropane
- Q35.** What is the primary organic product obtained when benzaldehyde is treated with concentrated sodium hydroxide solution (50% aqueous  $NaOH$ )?
- (A) Cinnamic acid  
(B) Benzoin  
(C) A mixture of benzyl alcohol and sodium benzoate  
(D) Benzyl acetate

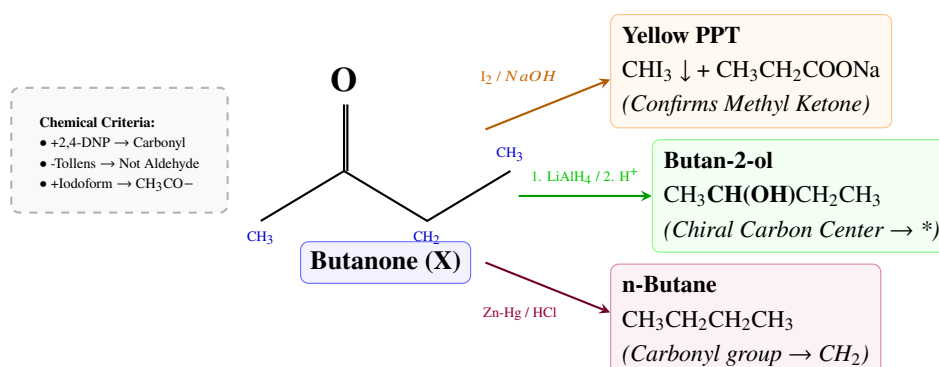
Section-C — 5 Questions × 2 Marks Each (No Negative Marking) [One or More Correct]



**Q36.** An organic compound (A) with molecular formula  $C_4H_{10}O$  reacts with metallic sodium to evolve hydrogen gas. When (A) is heated with excess concentrated  $HI$ , it yields two different organic halides. Which of the following statements are correct regarding compound (A)?

- (A) Compound (A) is a secondary alcohol.  
 (B) Compound (A) is an unsymmetrical ether.  
 (C) Reaction of (A) with hot acidic  $K_2Cr_2O_7$  yields a carboxylic acid.  
 (D) Reaction of (A) with excess  $HI$  yields ethyl iodide and isopropyl iodide.

**Q37.** A carbonyl compound (X) with the molecular formula  $C_4H_8O$  gives a positive test with 2,4-Dinitrophenylhydrazine but does not reduce Tollens' reagent. When (X) is treated with iodine and sodium hydroxide, it forms a yellow precipitate. Which of the following statements are correct for compound (X)?



- (A) Compound (X) is a methyl ketone.  
 (B) Compound (X) is an aliphatic aldehyde.  
 (C) Reduction of (X) with  $LiAlH_4$  produces a chiral secondary alcohol.  
 (D) Reduction of (X) with  $Zn-Hg/HCl$  (Clemmensen reduction) yields n-butane.

**Q38.** An aromatic compound (Y) with the molecular formula  $C_7H_7NO$  undergoes a reaction with  $Br_2$  in the presence of aqueous  $NaOH$  (Hofmann bromamide degradation) to yield a primary amine (Z). Which of the following options are correct?

- (A) Compound (Y) is Benzamide.



- (B) Amine (Z) gives a positive carbylamine test yielding a foul-smelling isocyanide.
- (C) Amine (Z) reacts with cold nitrous acid ( $HNO_2$  at  $0-5^\circ C$ ) to evolve nitrogen gas instantly.
- (D) Compound (Y) is Benzalaniline.

**Q39.** D-Glucose and D-Fructose are functional isomers that display characteristic structural and chemical features. Which of the following options correctly describe their behavior?

- (A) Both D-glucose and D-fructose reduce Fehling's solution due to the presence of an enediol intermediate in alkaline medium.
- (B) D-Glucose is a ketohexose whereas D-fructose is an aldohexose.
- (C) Both D-glucose and D-fructose react with excess phenylhydrazine to form the exact same osazone derivative.
- (D) D-Glucose contains five chiral carbon centers in its open-chain structure.

**Q40.** Polymers are macro-molecules categorized by their modes of synthesis and structural linkages. Which of the following pairs are correctly matched with respect to their classification or monomeric units?

- (A) Nylon-6,6: Condensation copolymer of hexamethylenediamine and adipic acid.
- (B) Teflon: Addition homopolymer of chloroprene monomers.
- (C) Buna-S: Synthetic rubber derived from styrene and 1,3-butadiene.
- (D) Dacron: Polyester synthesized via addition polymerization of vinyl chloride.



## Detailed Solutions

Q1.

## Solution

**Concept:**

The minimum molecular mass of a compound containing a specific element can be calculated by assuming that the molecule contains exactly the minimum integer amount of that atom, which is one. By setting up a mass percentage ratio between the element with a known absolute atomic weight and the total molecular weight, the minimal formula weight can be extracted precisely.

**Solution:**

- (a) Find the mass percentage of oxygen present in the organic molecule. Given percentages of Carbon and Hydrogen are 52.17% and 13.04% respectively. Since the rest of the compound is oxygen, its percentage is  $100 - (52.17 + 13.04) = 34.79\%$ .
- (b) Determine the empirical formula by calculating the relative number of moles of each element. Divide each percentage by its standard atomic mass: Moles of Carbon =  $52.17 / 12 = 4.347$ . Moles of Hydrogen =  $13.04 / 1 = 13.04$ . Moles of Oxygen =  $34.79 / 16 = 2.174$ .
- (c) Obtain the simplest molar ratio by dividing each value by the smallest value obtained, which is 2.174. Ratio for Carbon =  $4.347 / 2.174 = 2$ . Ratio for Hydrogen =  $13.04 / 2.174 = 6$ . Ratio for Oxygen =  $2.174 / 2.174 = 1$ .
- (d) The empirical formula is determined to be  $C_2H_6O$ . The problem statement dictates that the molecule contains exactly one oxygen atom per molecule. Therefore, the empirical formula is identical to the actual molecular formula.
- (e) Calculate the total molecular mass by summing the atomic contributions:  $(2 \times 12) + (6 \times 1) + (1 \times 16) = 24 + 6 + 16 = 46 \text{ g/mol}$ .

**Final Answer:** The minimum molecular mass of the compound is 46 g/mol.

**Answer: (B)**

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Q2.

**Solution****Concept:**

Redox titrations involving potassium permanganate and hydrogen peroxide operate on the principle of equivalence where the total equivalents of the oxidizing agent match the total equivalents of the reducing agent. Volume strength refers to the volume of oxygen gas liberated at standard temperature and pressure by the decomposition of a unit volume of the peroxide solution.

**Solution:**

- (a) Identify the n-factors for the reactants in acidic media. Potassium permanganate shifts from an oxidation state of +7 to +2, giving an n-factor of 5. Hydrogen peroxide undergoes oxidation to produce molecular oxygen gas, releasing two electrons per molecule, which sets its n-factor to 2.
- (b) Apply the law of chemical equivalence: Equivalents of  $H_2O_2$  = Equivalents of  $KMnO_4$ . This translates to  $Normality \times Volume(H_2O_2) = Normality \times Volume(KMnO_4)$ .
- (c) Calculate the normality of the permanganate solution.  $Normality = Molarity \times n - factor = 0.02M \times 5 = 0.1N$ .
- (c) Calculate the normality of the peroxide solution using the titration values:  $Normality(H_2O_2) \times 10.0mL = 0.1N \times 20.0mL$ . Solving for Normality yields  $0.2N$ .
- (c) Establish the relationship between normality and volume strength at STP. The standard formula states that  $Volume\ Strength = Normality \times 5.6$ . Substituting our computed normality value :  $Volume\ Strength = 0.2 \times 5.6 = 1.12V$ .

**Final Answer:** The volume strength of the sample is 1.12 V.

**Answer: (B)**

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Q3.

**Solution****Concept:**

Heisenberg's Uncertainty Principle imposes a fundamental limit on the simultaneous precision of position and momentum measurements. By combining this physical constraint with the de Broglie hypothesis relating particle wavelength to linear momentum, a direct relationship between the particle velocity and its absolute velocity uncertainty can be established.

**Solution:**

- (a) State Heisenberg's Uncertainty Principle formula:  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ . For finding the minimum possible limit of uncertainty, we equate the terms:  $\Delta x \cdot \Delta p = \frac{h}{4\pi}$ .
- (b) Express momentum uncertainty in terms of mass and velocity uncertainty, assuming particle mass is constant:  $\Delta p = m \cdot \Delta v$ . Substituting this gives  $\Delta x \cdot m \cdot \Delta v = \frac{h}{4\pi}$ .
- (c) Introduce the de Broglie relationship where wavelength is defined as  $\lambda = \frac{h}{m \cdot v}$ . The question specifies that position uncertainty is exactly equal to the de Broglie wavelength:  $\Delta x = \lambda = \frac{h}{m \cdot v}$ .
- (d) Substitute the value of  $\Delta x$  back into the uncertainty equation:  $\left(\frac{h}{m \cdot v}\right) \cdot m \cdot \Delta v = \frac{h}{4\pi}$ .
- (e) Simplify the equation by canceling out the Planck constant ( $h$ ) and mass ( $m$ ) from both sides. This leaves the expression  $\frac{\Delta v}{v} = \frac{1}{4\pi}$ . Rearranging the terms to isolate velocity uncertainty yields  $\Delta v = \frac{v}{4\pi}$ .

**Final Answer:** The minimum uncertainty in velocity is  $v/(4\pi)$ .

**Answer: (C)**

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Q4.

**Solution****Concept:**

Valence Shell Electron Pair Repulsion theory predicts molecular geometry based on the minimization of electrostatic repulsion between electron pairs around a central atom. The spatial orientation is determined by evaluating the steric number, which represents the sum of bonded atoms and lone pairs of electrons.

**Solution:**

- Evaluate  $PCl_5$ . Phosphorus has 5 valence electrons and forms 5 single bonds. Steric number is 5 with zero lone pairs, producing a trigonal bipyramidal geometry.
- Evaluate  $BrF_5$ . Bromine belongs to the halogen group and has 7 valence electrons. It forms 5 single covalent bonds with fluorine atoms, leaving 2 non-bonding valence electrons which constitute exactly 1 lone pair.
- Determine the configuration for  $BrF_5$ . The steric number is 5 sigma bonds + 1 lone pair = 6. A steric number of 6 corresponds to an octahedral electron-pair geometry. Due to the presence of 1 lone pair, the physical molecular shape is distorted into a square pyramidal structure.
- Evaluate  $SF_6$ . Sulfur possesses 6 valence electrons and coordinates with 6 fluorine atoms. The steric number is 6 with 0 lone pairs, which yields a regular symmetrical octahedral geometry.
- Evaluate  $XeF_4$ . Xenon has 8 valence electrons. It uses 4 electrons for bonding and retains 4 electrons as 2 lone pairs. The steric number is 6, and the 2 lone pairs occupy opposing axial positions, resulting in a square planar geometry.

**Final Answer:** The molecule that exhibits a square pyramidal geometry is  $BrF_5$ .

**Answer: (B)**

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Q5.

**Solution****Concept:**

Real gases deviate from ideal behavior due to intermolecular attractive forces and the finite volume occupied by the gas molecules themselves. The van der Waals equation introduces correction factors to account for these phenomena. Real gases approach ideal characteristics when these physical constraints become mathematically negligible.

**Solution:**

- (a) Write down the van der Waals equation of state for one mole of gas:  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ . The constant  $a$  accounts for intermolecular attractions, while  $b$  accounts for molecular excluded volume.
- (b) Analyze the effect of lowering the pressure. When the pressure of the system is extremely low, the volume ( $V$ ) occupied by the gas becomes extremely large.
- (c) Evaluate the correction terms at high volume. As  $V$  approaches infinity, the term  $\frac{a}{V^2}$  approaches 0. Similarly, because  $V$  is exceptionally large relative to the molecular size, the excluded volume constant  $b$  becomes negligible, meaning  $(V - b)$  simplifies to  $V$ .
- (d) Analyze the effect of raising the temperature. High thermal energy increases the kinetic energy of the gas particles significantly. When molecules move at high velocities, the attractive forces represented by  $a$  cannot effectively bind or influence them during collisions.
- (e) Combine both parameters. Under conditions of high temperature and low pressure, the correction terms lose significance, and the equation reduces to  $PV = RT$ , which is the ideal gas law.

**Final Answer:** A gas behaves most ideally under high temperature and low pressure conditions.

**Answer: (A)**

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Q6.

**Solution****Concept:**

The problem explores the fundamental thermodynamic principles governing the free expansion of an ideal gas. Free expansion is defined as an expansion against a vacuum, meaning the opposing external pressure is zero. Analyzing such a system requires the simultaneous application of the First Law of Thermodynamics, the definition of work, the nature of ideal gas internal energy, and the definition of environmental entropy changes.

**Solution:**

- (a) Evaluate the work done during the expansion. Thermodynamic work is calculated using the formula  $w = - \int P_{\text{ext}} dV$ . Since the gas expands into a vacuum, the external pressure  $P_{\text{ext}}$  is exactly equal to zero. Therefore, regardless of the change in volume, the work done  $w$  by the gas must be equal to zero.
- (b) Determine the change in internal energy. For an ideal gas, internal energy is purely a function of absolute temperature because there are no intermolecular forces of attraction or repulsion between the particles. Since the process is specifically designated as isothermal, the temperature remains completely constant ( $\Delta T = 0$ ), which directly implies that the change in internal energy  $\Delta U$  is equal to zero.
- (c) Apply the First Law of Thermodynamics to calculate heat transfer. The law is stated as  $\Delta U = q + w$ . Substituting the values we have already established, we get  $0 = q + 0$ , which mathematically proves that the heat exchanged with the surroundings  $q$  is equal to zero.
- (d) Determine the entropy change of the surroundings. The change in entropy for the surroundings is given by the relation  $\Delta S_{\text{surr}} = \frac{-q_{\text{actual}}}{T}$ . Since the actual heat transferred from or to the system is zero, the entropy change of the surroundings  $\Delta S_{\text{surr}}$  must also be equal to zero.
- (d) Compile the parameters to identify the correct option. We have established that work is zero, heat is zero, internal energy change is zero, and the entropy change of the surroundings is zero. This perfectly corresponds to the thermodynamic criteria outlined in option (B).

**Final Answer:** The correct set of parameters is  $w = 0, q = 0, \Delta U = 0, \Delta S_{\text{surr}} = 0$ .

**Answer: (B)**

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Q7.

**Solution****Concept:**

This question addresses solubility equilibria and the profound impact of the common ion effect on the dissolution of a sparingly soluble salt. When a highly soluble electrolyte sharing a common ion is added to a saturated solution of a weak electrolyte, Le Chatelier's principle dictates that the equilibrium shifts backward, dramatically suppressing the solubility of the sparingly soluble salt.

**Solution:**

- (a) Write the chemical equilibrium for the dissolution of calcium fluoride:  $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$ . Let the molar solubility of calcium fluoride in this specific solution be denoted as  $s$  mol/L. This dissociation produces  $s$  moles of calcium ions and  $2s$  moles of fluoride ions.
- (b) Account for the strong electrolyte present in the solution. Sodium fluoride dissolves completely according to the equation  $NaF(aq) \rightarrow Na^{+}(aq) + F^{-}(aq)$ . A 0.1 M solution of sodium fluoride provides an initial fluoride ion concentration of exactly 0.1 M.
- (c) Express the total equilibrium concentrations of both ions. The concentration of calcium ions at equilibrium is simply  $[Ca^{2+}] = s$ . The total concentration of fluoride ions comes from both sources, which gives  $[F^{-}] = 0.1 + 2s$ .
- (d) Formulate the solubility product expression:  $K_{sp} = [Ca^{2+}][F^{-}]^2$ . Substituting our values gives  $3.2 \times 10^{-11} = s \cdot (0.1 + 2s)^2$ . Since the solubility product is exceptionally small, the value of  $s$  will be minute, allowing the approximation  $0.1 + 2s \approx 0.1$ .
- (e) Solve the simplified algebraic expression:  $3.2 \times 10^{-11} = s \cdot (0.1)^2 \implies 3.2 \times 10^{-11} = 0.01s$ . Dividing both sides by 0.01 yields  $s = 3.2 \times 10^{-9}$  M. This concentration is far smaller than 0.1, proving the validity of our approximation.

**Final Answer:** The solubility of  $CaF_2$  in the solution is  $3.2 \times 10^{-9}$  M.

**Answer: (D)**

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Q8.

**Solution****Concept:**

This problem deals with the mathematical formulation and graphical interpretation of first-order chemical reaction kinetics. In physical chemistry, integrated rate laws are rearranged into linear forms to allow experimental data to be plotted directly, enabling the straightforward determination of rate constants and initial reactant concentrations from geometric properties like slope and intercept.

**Solution:**

- (a) State the differential rate law for a standard first-order reaction where reactant A forms products. The rate of disappearance of the reactant is directly proportional to its instantaneous concentration:  $-\frac{d[A]}{dt} = k[A]$ , where  $k$  represents the specific rate constant.
- (b) Rearrange the variables to prepare the differential equation for integration across time. Grouping the concentration terms on one side yields  $\frac{d[A]}{[A]} = -k dt$ .
- (c) Integrate both sides of the expression between the defined limits. At time  $t = 0$ , the concentration is the initial concentration  $[A]_0$ , and at any subsequent time  $t$ , the concentration is  $[A]_t$ . This yields the definite integral  $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$ .
- (d) Evaluate the integration to obtain the natural logarithmic form of the integrated rate law:  $\ln[A]_t - \ln[A]_0 = -kt$ . Rearranging this equation into an explicit form for the instantaneous concentration gives  $\ln[A]_t = -kt + \ln[A]_0$ .
- (e) Map this integrated kinetic equation directly onto the standard equation for a straight line, which is written as  $y = mx + c$ . Here, the vertical axis variable  $y$  corresponds to  $\ln[A]_t$ , the horizontal axis variable  $x$  corresponds to time  $t$ , the slope  $m$  corresponds to  $-k$ , and the vertical intercept  $c$  corresponds to  $\ln[A]_0$ .

**Final Answer:** The slope of the plot is  $-k$  and the intercept is  $\ln[A]_0$ .

**Answer: (B)**

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Q9.

**Solution****Concept:**

This question tests the understanding of the electrochemical series and the standard reduction potentials of various chemical half-cells. The standard reduction potential measures the thermodynamic tendency of a chemical species to gain electrons and undergo reduction. A lower potential signifies a stronger reducing agent, while a higher potential signifies a stronger oxidizing agent.

**Solution:**

- (a) Define the reference point of the electrochemical scale. The Standard Hydrogen Electrode is universally chosen as the primary reference point, and its standard reduction potential is defined as exactly 0.00 V at all temperatures for the reaction  $2H^+(aq) + 2e^- \rightarrow H_2(g)$ .
- (b) Identify the characteristics of highly reactive alkali metals. Lithium is located at the absolute top of the standard oxidation series and the bottom of the reduction series because it has an immense thermodynamic drive to lose its lone valence electron. Its standard reduction potential is the most negative, with a value of approximately  $-3.05$  V.
- (c) Evaluate the behavior of transition metals like zinc. Zinc is a moderately active metal that undergoes oxidation relatively easily compared to hydrogen. Its half-cell reaction  $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$  possesses a negative standard reduction potential of approximately  $-0.76$  V.
- (d) Analyze less reactive transition metals such as copper. Copper is located below hydrogen in the classical reactivity series, meaning it prefers to exist in its reduced metallic state rather than as an aqueous cation. The standard reduction potential for  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$  is positive, measuring approximately  $+0.34$  V.
- (e) Arrange the half-cells in strict order of increasing standard reduction potential based on these quantitative values:  $-3.05$  V  $<$   $-0.76$  V  $<$   $0.00$  V  $<$   $+0.34$  V. This gives the sequence  $Li^+/Li < Zn^{2+}/Zn < H^+/H_2 < Cu^{2+}/Cu$ , which matches option (C).

**Final Answer:** The correct order of increasing standard reduction potential is  $Li^+/Li < Zn^{2+}/Zn < H^+/H_2 < Cu^{2+}/Cu$ .

**Answer: (C)**

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Q10.

**Solution****Concept:**

This problem addresses the distinctive chemical reactivity of s-block elements, specifically focusing on the anomalous behavior of lithium compared to other alkali metals in Group 1. While most alkali metals react with nitrogen only under extreme, indirect synthetic conditions, lithium stands out due to its ability to react directly with diatomic atmospheric nitrogen gas at elevated or even ambient temperatures.

**Solution:**

- Examine the fundamental chemical reaction taking place. When metallic lithium is heated in a controlled environment containing dry, pure nitrogen gas, a direct combination reaction occurs to produce a binary ionic compound known as lithium nitride.
- Formulate the balanced chemical equation representing this process. Solid lithium reacts with nitrogen gas according to the stoichiometry:  $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$ . The product contains lithium as  $Li^+$  cations and nitrogen as  $N^{3-}$  nitride anions.
- Explain the physical reasons behind the anomalous reactivity of lithium. The nitrogen molecule features an exceptionally strong covalent triple bond with a massive bond dissociation energy. To break this bond and form an ionic crystal, a massive amount of compensating lattice energy must be released by the resulting compound.
- Connect the lattice stability to ionic dimensions. Because the lithium cation possesses an exceptionally small ionic radius, it can approach the nitride anion very closely in the crystal lattice. This close approach maximizes electrostatic attractions, releasing an enormous amount of lattice enthalpy that stabilizes  $Li_3N$ .
- Compare this behavior with heavier congeners in Group 1. Cations like sodium, potassium, and rubidium have much larger ionic radii, meaning their corresponding nitrides would possess insufficient lattice energy to overcome the strong nitrogen triple bond. Therefore,  $Li_3N$  is the primary stable product formed.

**Final Answer:** The compound predominantly formed is  $Li_3N$ .

**Answer:** (C)

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Q11.

**Solution****Concept:**

The thermal stability of alkaline earth metal carbonates is directly governed by the structural relationships and thermodynamic properties of the crystalline lattice. Specifically, stability is dictated by the ability of the metal cation to polarize the large, relatively unstable carbonate anion, a principle heavily described by Fajans' Rules and lattice enthalpy arguments.

**Solution:**

- Examine the decomposition pathway of Group 2 carbonates. When heated, these metal carbonates undergo thermal decomposition to yield a solid metal oxide and release gaseous carbon dioxide according to the general chemical equation:  $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ .
- Apply ionic polarization principles to the system. The carbonate anion is a large, polyatomic species with a delocalized negative charge. Small metal cations with high charge density exert a strong polarizing force on the electron cloud of the carbonate ion, distorting it and weakening the carbon-oxygen bonds within the anion.
- Trace the structural trend down Group 2. Moving down from magnesium to barium, the ionic radius of the divalent cation increases significantly:  $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ . As the size increases while keeping the charge constant at +2, the charge density drops sharply.
- Correlate charge density to thermal resistance. Because  $Mg^{2+}$  has the highest charge density, it strongly polarizes the carbonate cloud, making the compound highly unstable and easily decomposed at lower temperatures. Conversely, the massive  $Ba^{2+}$  ion exerts minimal polarizing distortion, allowing its carbonate lattice to remain stable at extremely high temperatures.
- Formulate the final stability progression based on these trends. The ease of decomposition decreases as you descend the column, meaning that the absolute thermal stability increases down the group. Therefore, the correct decreasing sequence of thermal stability is  $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ .

**Final Answer:** The correct order of decreasing thermal stability is  $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ .

**Answer: (B)**

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Q12.

**Solution****Concept:**

Diborane is a classic electron-deficient molecule whose bonding architecture cannot be rationalized using traditional Lewis valence structures. Understanding its unique framework requires evaluating the molecule through the lens of localized molecular orbital theory, focusing on the formation of multicenter multi-electron bonds that allow stable structures despite a shortage of valence electrons.

**Solution:**

- Count the total number of valence electrons available in the molecule. Each boron atom contributes 3 valence electrons, and each hydrogen atom contributes 1 electron. For a formula of  $B_2H_6$ , the total count equals  $(2 \times 3) + (6 \times 1) = 12$  valence electrons, or exactly 6 pairs.
- Analyze the physical geometry of the molecule. Diborane contains two distinct types of hydrogen atoms. There are four terminal hydrogen atoms lying in a single plane with the two boron atoms, and there are two bridging hydrogen atoms positioned perpendicularly above and below this central plane.
- Characterize the standard terminal linkages. The four terminal B-H bonds are conventional, localized 2-center-2-electron covalent bonds. These four bonds utilize a total of 8 valence electrons out of our available pool of 12, leaving exactly 4 electrons remaining for the rest of the molecular framework.
- Describe the nature of the bridging system. The remaining 4 electrons must stabilize the connections between the two central boron atoms and the two bridging hydrogens. Each bridge consists of a single hydrogen atom sharing its lone electron across an orbital overlapping with both boron atoms, creating a 3-center-2-electron bond.
- Determine the hybridization state of the central boron atoms. To accommodate four separate directional orbital overlaps in a roughly tetrahedral geometry (two terminal and two bridging), each boron atom undergoes  $sp^3$  hybridization. The molecule therefore contains two 3-center-2-electron bonds, which are commonly termed banana bonds.

**Final Answer:** The molecule possesses two 3-center-2-electron bonds, and boron is  $sp^3$  hybridized.

**Answer: (C)**

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Q13.

**Solution****Concept:**

The protic nature and basicity of phosphorus oxoacids are strictly determined by the spatial arrangement of atoms directly bound to the central phosphorus atom. In these inorganic structures, only hydrogen atoms that are linked directly to highly electronegative oxygen atoms are capable of ionizing in aqueous media to release hydronium ions.

**Solution:**

- Define the structural constraints governing oxoacid acidity. A hydrogen atom must be bound to oxygen (forming a P-O-H unit) to be acidic, because the large electronegativity difference polarizes the bond heavily. A hydrogen atom directly bound to phosphorus (a P-H unit) is non-acidic due to similar electronegativity values.
- Analyze the structural configuration of orthophosphoric acid ( $H_3PO_4$ ). The central phosphorus atom adopts a tetrahedral geometry where it forms one double bond to an oxygen atom ( $P = O$ ) and three single bonds to three separate hydroxyl groups ( $P - OH$ ).
- Evaluate the basicity of  $H_3PO_4$  based on its structure. Since there are exactly three distinct  $P - OH$  bonding groups present within a single molecule, all three hydrogen atoms can dissociate sequentially in water. This structural property makes it a true triprotic acid.
- Analyze the structural configuration of phosphorous acid ( $H_3PO_3$ ). The central phosphorus atom is also tetrahedrally coordinated, but it bonds to one oxygen via a double bond ( $P = O$ ), two hydroxyl groups ( $P - OH$ ), and retains one hydrogen atom bonded directly to its core ( $P - H$ ).
- Conclude the difference in ionization behavior. The lone hydrogen atom present in the  $P - H$  linkage cannot break away as a proton because the bond is non-polar and highly stable. Thus, only the two hydrogens from the  $P - OH$  groups can ionize, rendering the molecule strictly diprotic.

**Final Answer:**  $H_3PO_3$  contains one non-ionizable hydrogen atom bonded directly to the central phosphorus atom.

**Answer: (B)**

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Q14.

**Solution****Concept:**

The spin-only magnetic moment of first-row d-block transition metal complexes can be deduced directly from their ground-state valence electron configurations. The magnitude of this magnetic moment depends purely on the number of unpaired electrons present in the d-orbitals, which can be quantified using the fundamental spin-only magnetic equation derived from quantum mechanics.

**Solution:**

- (a) State the mathematical expression for calculating the spin-only magnetic moment:  $\mu = \sqrt{n(n+2)}$  Bohr Magnetons, where  $n$  represents the absolute number of unpaired electrons. This equation demonstrates that a higher value of  $n$  yields a larger overall magnetic moment.
- (b) Determine the configuration of the chromium ion ( $Cr^{3+}$ ). Neutral chromium has a ground state configuration of  $[Ar]3d^54s^1$ . Removing three electrons yields a valence configuration of  $3d^3$ . According to Hund's rule, these three electrons occupy separate orbitals, giving  $n = 3$ .
- (c) Determine the configuration of the manganese ion ( $Mn^{3+}$ ). Neutral manganese possesses a configuration of  $[Ar]3d^54s^2$ . Losing three electrons shifts its configuration to  $3d^4$ . Spreading these across the five d-orbitals results in  $n = 4$  unpaired electrons.
- (d) Determine the configuration of the ferric ion ( $Fe^{3+}$ ). Neutral iron is characterized by a configuration of  $[Ar]3d^64s^2$ . Upon the loss of three electrons, it assumes a highly stable, symmetric  $3d^5$  half-filled configuration. This configuration maximizes spin, yielding  $n = 5$  unpaired electrons.
- (e) Determine the configuration of the cobalt ion ( $Co^{3+}$ ). Neutral cobalt has a configuration of  $[Ar]3d^74s^2$ . The tripositive state leaves a configuration of  $3d^6$ . When distributed across five orbitals, one pair forms, leaving only  $n = 4$  unpaired electrons. Since  $Fe^{3+}$  has the maximum possible value of  $n = 5$ , it possesses the highest magnetic moment.

**Final Answer:** The transition metal ion with the highest spin-only magnetic moment is  $Fe^{3+}$ .

**Answer: (C)**

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Q15.

**Solution****Concept:**

Crystal Field Theory describes how the degenerate d-orbitals of a transition metal split into distinct energy levels ( $t_{2g}$  and  $e_g$ ) under the electrostatic influence of surrounding ligands in an octahedral field. The final distribution of electrons depends heavily on the field strength of the ligand, which determines whether electrons will pair up or occupy higher energy states.

**Solution:**

- Identify the oxidation state of the central metal. In the coordination complex ion  $[Co(NH_3)_6]^{3+}$ , the overall charge is +3. Because ammonia ( $NH_3$ ) is a completely neutral monodentate molecule, the cobalt atom must exist in a +3 oxidation state, corresponding to a  $3d^6$  electron system.
- Evaluate the field strength of the coordinating ligands. Ammonia is classified as a strong-field ligand according to the spectrochemical series. When interacting with a trivalent metal ion like  $Co^{3+}$ , it induces a very large crystal field splitting energy ( $\Delta_o$ ).
- Compare the splitting parameters to pairing energy. Because ammonia generates a large field splitting, the value of  $\Delta_o$  is significantly greater than the spin pairing energy ( $P$ ). This condition forces the system to adopt a low-spin electronic configuration to minimize energy.
- Distribute the six d-electrons into the split orbitals. Under octahedral symmetry, the d-orbitals separate into a lower-energy triplet ( $t_{2g}$ ) and a higher-energy doublet ( $e_g$ ). To achieve the lowest energy state while overcoming pairing costs, all six electrons enter the lower  $t_{2g}$  sub-level.
- Determine the final electronic layout and magnetic profile. The resulting orbital occupation is written as  $t_{2g}^6 e_g^0$ . Because all six valence electrons are perfectly paired up within the lower three orbitals, there are zero unpaired electrons present. This lack of net spin renders the complex completely diamagnetic.

**Final Answer:** The complex ion has a  $t_{2g}^6 e_g^0$  low-spin configuration and is diamagnetic.

**Answer: (B)**

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Q16.

**Solution****Concept:**

Photochemical smog is a modern environmental hazard that develops as a thick, yellowish-brown haze over dense urban areas. It is classified as an atmospheric phenomenon driven entirely by complex, light-induced chemical interactions between primary industrial pollutants and ambient atmospheric gases under specific seasonal and meteorological conditions.

**Solution:**

- Define the initiation process of photochemical smog. The phenomenon begins when internal combustion engines release primary pollutants into the air, specifically unburned volatile organic hydrocarbons and nitric oxide gas. These emissions require high solar radiation and warm temperatures to react.
- Trace the secondary reactions that occur in the troposphere. Nitric oxide reacts with atmospheric oxygen to yield nitrogen dioxide gas ( $NO_2$ ), which gives the smog its characteristic brown color. When exposed to ultraviolet sunlight, nitrogen dioxide undergoes photolysis to release highly reactive nascent oxygen atoms.
- Explain the formation of tropospheric ozone. These free oxygen atoms combine instantly with diatomic atmospheric oxygen molecules to synthesize ozone ( $O_3$ ). Ozone then reacts further with volatile hydrocarbons to produce hazardous secondary lachrymators, such as peroxyacetyl nitrate ( $PAN$ ) and various acrolein derivatives.
- Examine the role of sulfur dioxide ( $SO_2$ ). Sulfur dioxide is a distinct pollutant that originates primarily from coal combustion in power plants. It is the defining chemical component of classical or reducing smog, which forms in cool, humid, winter climates, rather than sunny photochemical smog.
- Conclude which component does not belong. Since ozone, peroxyacetyl nitrate, and nitrogen dioxide are all integral components involved in the cyclic pathways of photochemical smog formation, sulfur dioxide stands out as an independent species that is not a primary or secondary constituent of this specific atmospheric phenomenon.

**Final Answer:** The chemical species that is NOT a component of photochemical smog is  $SO_2$ .

**Answer: (D)**

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Q17.

**Solution****Concept:**

The systematically accurate naming of polyfunctional organic molecules follows a strict set of hierarchical rules established by the International Union of Pure and Applied Chemistry. When an organic skeleton features multiple distinct functional groups, a single group must be selected as the principal suffix based on standard priority rules, while all remaining modifications are treated as prefixes.

**Solution:**

- Establish the priority order for the functional groups present. The given molecule contains a carboxylic acid group ( $-COOH$ ) and an alcohol hydroxyl group ( $-OH$ ). According to IUPAC priority rules, the carboxylic acid functionality holds the highest rank and dictates the root name of the molecule.
- Identify the longest continuous carbon chain that contains the principal functional group. The chain originates at the carbonyl carbon of the carboxylic acid group and extends across a total of five contiguous carbon atoms, establishing the root name of the compound as pentanoic acid.
- Number the principal carbon chain sequentially to give the highest priority group the lowest possible locant. The carboxylic acid carbon is automatically designated as carbon position 1. Numbering proceeds from right to left along the chain skeleton towards the methyl group terminal.
- Map out the identity and exact position of all remaining substituents. Moving down the numbered chain, position 2 features two separate methyl groups attached to the same carbon atom. Continuing leftward along the chain, position 4 contains the subordinate hydroxyl functional group.
- Assemble the full alphabetical name by combining the structural prefixes and the root suffix. Arrange the substituents alphabetically: the prefix hydroxy precedes methyl. This systematic combining rule generates the final complete IUPAC designation: 4-hydroxy-2,2-dimethylpentanoic acid.

**Final Answer:** The correct IUPAC name for the compound is 4-Hydroxy-2,2-dimethylpentanoic acid.

**Answer: (B)**

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Q18.

**Solution****Concept:**

The stereochemical outcome of electrophilic addition reactions across carbon-carbon double bonds is dictated by the spatial arrangement of the starting alkene and the specific mechanism of the reaction. Halogenation of an alkene involves the formation of a cyclic halonium ion intermediate, which forces an anti-addition pathway that alters the stereocenters of the final products.

**Solution:**

- Define the stereospecific mechanism of bromine addition. The reaction of elemental bromine with an alkene in an inert non-polar solvent like carbon tetrachloride proceeds via a two-step mechanism. The initial step forms a rigid cyclic bromonium ion intermediate, which blocks cis attack and forces the incoming bromide ion to strike from the opposite side.
- Apply the stereochemical rule for symmetric trans alkenes. When a trans alkene like trans-but-2-ene undergoes anti-addition, the incoming nucleophile attacks the two equivalent carbons with equal probability. This symmetric opening creates a single, non-resolvable meso compound due to an internal plane of symmetry.
- Apply the stereochemical rule for symmetric cis alkenes. When a symmetric cis alkene like cis-but-2-ene is subjected to anti-addition, the opposite geometric constraints apply. The anti-attack yields a pair of enantiomeric structures with identical physical properties but opposing optical rotations.
- Evaluate the population distribution of the products. Because the attack of the bromide ion on either carbon of the symmetrical intermediate occurs at identical rates, a perfectly equimolar mixture of the dextrorotatory and levorotatory enantiomers is synthesized, forming a racemic mixture.
- Compare with other listed alkenes. Ethene produces a symmetrical, achiral product. Propene is an unsymmetrical alkene that yields a chiral center, but it does not feature the specific cis/trans geometric relationship required to contrast meso versus racemic pairs. Thus, cis-but-2-ene is the correct choice.

**Final Answer:** The alkene that will yield a racemic mixture of enantiomers is cis-but-2-ene.

**Answer: (C)**

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Q19.

**Solution****Concept:**

Nucleophilic substitution mechanisms are categorized based on their kinetic behavior and the associated spatial rearrangements at the reaction center. The unimolecular substitution pathway relies on a multi-step sequence where bond-breaking occurs entirely prior to bond-making, creating a distinct ionic intermediate that dictates the final distribution of spatial orientations.

**Solution:**

- Explain the kinetic profile of the unimolecular mechanism. The first step involves the slow heterolytic dissociation of the leaving group to generate a carbocation intermediate. Because this step is the slowest, it acts as the rate-determining step. The rate depends only on the alkyl halide concentration, showing first-order kinetics.
- Analyze the structural geometry of the intermediate state. The loss of the leaving group leaves behind a trivalent carbocation that adopts a planar,  $sp^2$  hybridized configuration. The vacant p-orbital extends symmetrically above and below this flat molecular plane.
- Assess the spatial direction of the nucleophilic attack. The incoming nucleophilic species can approach and attack the flat carbocation intermediate with equal geometric probability from either the front side or the back side.
- Determine the stereochemical consequences of the dual-sided attack. Front-side attack preserves the original orientation of groups, leading to retention of configuration. Back-side attack results in an inversion of configuration. If the starting material is optically active, this balanced process generates an equimolar mixture of both configurations.
- Formulate the final conclusion. The combination of equal front and back attacks results in partial or complete racemization of the reaction center, meaning an optically active reactant yields an inactive or lower-purity mixture. This pairs perfectly with first-order kinetics.

**Final Answer:** The process is characterized by first-order kinetics accompanied by partial or complete racemization.

**Answer: (D)**

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Q20.

**Solution****Concept:**

The treatment of phenol with chloroform in an alkaline medium is an established organic reaction known as the Reimer-Tiemann reaction. This classic transformation achieves the selective formylation of the aromatic ring, introducing a high-value formyl functional group directly adjacent to the existing phenolic hydroxyl group via a highly reactive, neutral divalent carbon intermediate.

**Solution:**

- Identify the active intermediate generated during the reaction. When chloroform interacts with a strong base like aqueous sodium hydroxide, an alpha-elimination reaction occurs. The base abstracts a proton from chloroform, followed by the loss of a chloride ion, creating a highly electrophilic neutral species called dichlorocarbene.
- Analyze the activation of the aromatic substrate. Phenol reacts with the excess sodium hydroxide to form a phenoxide ion. The phenoxide ion possesses high electron density due to the strong resonance electron-donating effect of the negatively charged oxygen atom, making the ring highly reactive toward electrophiles.
- Trace the electrophilic aromatic substitution pathway. The dichlorocarbene intermediate attacks the electron-rich ortho position of the phenoxide ring. This position is favored due to stabilizing coordination effects with the neighboring sodium counter-ion, leading to the formation of a substituted benzal chloride intermediate.
- Describe the subsequent hydrolysis phase. Under the prevailing warm alkaline conditions, the twin chlorine atoms present on the ortho-substituent undergo rapid nucleophilic hydrolysis, converting the side chain into an unstable geminal diol that loses a water molecule to form an aldehyde.
- Finalize the product identification following acidification. The final addition of aqueous acid neutralizes the sodium phenoxide salt back to a regular phenol group, yielding 2-hydroxybenzaldehyde as the principal product, which is widely known by its common name, salicylaldehyde.

**Final Answer:** The principal organic product obtained is salicylaldehyde.

**Answer: (B)**

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Q21.

**Solution****Concept:**

The structural identification of unknown carbonyl compounds relies on a sequential combination of qualitative functional group tests. By evaluating a molecule's reactivity toward hydrazine derivatives, mild oxidizing agents, and halogenating reagents in alkaline media, one can definitively map out the connectivity of carbon atoms and the precise location of oxygen-containing functional groups.

**Solution:**

- Analyze the chemical implications of the 2,4-DNP test. The organic compound reacts with 2,4-dinitrophenylhydrazine to form a hydrazone derivative. This positive reaction proves conclusively that the compound contains a carbonyl group, which restricts the possibilities for a  $C_3H_6O$  formula to either propanal or acetone.
- Evaluate the reactivity toward Tollens' and Fehling's reagents. The compound does not reduce ammoniacal silver nitrate or alkaline copper sulfate solutions. Because aldehydes are easily oxidized and yield positive results for both tests, the complete lack of reactivity confirms that the compound cannot be an aldehyde, leaving acetone as the primary candidate.
- Examine the structural requirements for the iodoform reaction. A positive iodoform test requires the presence of a specific methyl carbonyl grouping ( $CH_3 - C = O$ ) or a secondary alcohol capable of being oxidized to that group. When treated with iodine and sodium hydroxide, this group undergoes halogenation and cleavage.
- Describe the chemical transformation of the haloform reaction. Acetone possesses two methyl groups bound directly to the carbonyl carbon. The base abstracts protons from one methyl group, replacing them with iodine to form a triiodo derivative, which is then cleaved by hydroxide to yield a yellow precipitate of iodoform ( $CHI_3$ ).
- Eliminate the remaining incorrect options based on structural differences. Propanal is an aldehyde and would reduce Tollens' reagent. Allyl alcohol and methyl vinyl ether do not contain a carbonyl group and would fail to form a 2,4-DNP derivative, proving that acetone is the only structure that satisfies all experimental parameters.

**Final Answer:** The organic compound (X) is acetone.

**Answer:** (C)

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Q22.

**Solution****Concept:**

The reaction of primary aromatic amines with nitrous acid at low temperatures is an essential transformation known as diazotization. The stability of the resulting salt depends entirely on the degree of resonance delocalization offered by the attached organic group, which dictates whether the species can persist in solution or decompose instantly to release nitrogen gas.

**Solution:**

- Analyze the behavior of primary aliphatic amines. When ethylamine is treated with nitrous acid at cold temperatures, it forms a highly unstable aliphatic diazonium salt. This intermediate undergoes immediate, spontaneous decomposition even at 273 K, evolving nitrogen gas instantly and yielding a mixture of alcohols and alkenes.
- Analyze the behavior of secondary aromatic amines. N-Methylaniline is a secondary amine and reacts with nitrous acid to form a yellow, oily N-nitroso compound rather than a diazonium salt, meaning it does not evolve nitrogen gas upon warming.
- Analyze the behavior of tertiary aliphatic amines. Triethylamine is a tertiary amine that simply dissolves in cold nitrous acid to form an unstable nitrite salt, which undergoes complex decomposition without generating a clean diazonium framework.
- Analyze the behavior of primary aromatic amines. Aniline features a primary amino group attached directly to a benzene ring. When mixed with nitrous acid at 273 to 278 K, it forms benzenediazonium chloride, which is stable in cold water due to the resonance delocalization of the positive charge into the aromatic ring.
- Describe the thermal decomposition of the stable salt. When the cold benzenediazonium solution is warmed above 278 K, the thermal energy overcomes the resonance stabilization. The salt undergoes nucleophilic substitution with water, evolving nitrogen gas cleanly and transforming into phenol.

**Final Answer:** The amine that produces a stable diazonium salt solution is aniline.

**Answer: (D)**

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Q23.

**Solution****Concept:**

The double-helical architecture of deoxyribonucleic acid is stabilized by highly specific non-covalent interactions between complementary heterocyclic nitrogenous bases. Understanding this macromolecular structure requires evaluating the strict hydrogen-bonding rules and the chemical composition of the polymeric backbone that allows the storage of genetic information.

**Solution:**

- (a) Examine the structural components of the polymeric backbone. The outer rails of the DNA double helix are composed of alternating units of a five-carbon sugar called 2-deoxyribose and hydrophilic phosphate linkers, rather than ribose sugars or silicate frameworks.
- (b) Identify the specific nitrogenous bases present in DNA. The polymer utilizes four distinct bases to encode information: the purines adenine and guanine, and the pyrimidines cytosine and thymine. The base uracil is strictly reserved for ribonucleic acid structures.
- (c) Apply Chargaff's rules for base pairing. Within the double helix, a large purine base must always pair with a smaller pyrimidine base to maintain a constant distance between the two sugar-phosphate strands, preventing distortion of the helical framework.
- (d) Detail the hydrogen-bonding profile of the adenine-thymine pair. Adenine pairs exclusively with thymine across the strands. This specific interaction is stabilized by the formation of exactly two non-covalent hydrogen bonds between their corresponding carbonyl and amino groups.
- (e) Detail the hydrogen-bonding profile of the guanine-cytosine pair. Guanine pairs exclusively with cytosine. This alignment is significantly stronger because it is stabilized by three separate hydrogen bonds. This exact pairing rule matches the parameters described in option (C).

**Final Answer:** Adenine pairs with thymine via two hydrogen bonds; guanine pairs with cytosine via three hydrogen bonds.

**Answer: (C)**

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Q24.

**Solution****Concept:**

Synthetic polymers are categorized based on their underlying chemical mechanism of formation into addition polymers and condensation polymers. Addition polymerization involves the sequential linking of unsaturated monomers without the loss of any molecular fragments, while condensation pathways require bifunctional monomers that react to release small molecular secondary products.

**Solution:**

- Analyze the synthesis of polyvinyl chloride. PVC is generated from vinyl chloride monomers via a free-radical mechanism. The reaction proceeds through the continuous addition across the carbon-carbon double bonds, retaining every atom from the original monomer units.
- Analyze the synthesis of Teflon. Teflon is produced by the polymerization of tetrafluoroethene. This process is also a standard addition pathway where the double bonds open up to link the monomers into long, unbranched chains of polytetrafluoroethylene.
- Analyze the synthesis of polystyrene. Polystyrene is created through the addition polymerization of styrene monomers, typically initiated by peroxides. The aromatic rings remain intact while the vinyl groups link together without forming any side products.
- Analyze the synthesis of Nylon-6,6. Nylon-6,6 is synthesized by reacting two separate bifunctional monomers: adipic acid, a six-carbon dicarboxylic acid, and hexamethylenediamine, a six-carbon diamine, under elevated thermal conditions.
- Describe the bond-forming step in the condensation process. The carboxylic acid groups react with the amine groups to establish strong amide linkages. Each time an amide bond is formed, a molecule of water is eliminated as a byproduct, classifying this pathway as a classic condensation polymerization.

**Final Answer:** The polymer synthesized via a condensation mechanism is Nylon-6,6.

**Answer:** (C)

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Q25.

**Solution****Concept:**

The total number of stereoisomers for a coordination complex is the sum of its geometrically distinct spatial arrangements and any corresponding non-superimposable mirror images. For an octahedral complex containing multiple sets of identical monodentate ligands, the configurations are mapped systematically by tracking the relative cis and trans relationships of the ligand pairs.

**Solution:**

- Define the structural formula of the complex. The complex is represented as  $[Ma_2b_2c_2]$ , where M is the central metal ion and a, b, and c are three distinct pairs of monodentate ligands occupying the six coordination sites of the octahedron.
- Map out the possible geometric configurations by pairing the ligands. We can define the geometry by specifying which ligands are trans to each other. The first configuration places all identical pairs trans to one another: t(aa), t(bb), t(cc). This isomer possesses a high degree of symmetry.
- Identify configurations with one trans pair and two cis pairs. There are three such geometric arrangements possible, depending on which pair is chosen to be trans: t(aa), c(bb), c(cc); or c(aa), t(bb), c(cc); or c(aa), c(bb), t(cc). All three are distinct geometric isomers.
- Identify the configuration where all identical pairs are cis. The fifth geometric isomer features all identical ligands located adjacent to one another: c(aa), c(bb), c(cc). This specific arrangement is commonly referred to as the all-cis or cis-cis-cis isomer.
- Assess optical activity across the geometric set. The first four geometric configurations possess internal planes of symmetry or centers of inversion, making them achiral. However, the all-cis isomer lacks any plane of symmetry, making it chiral. It exists as a pair of non-superimposable enantiomers, bringing the total stereoisomer count to 5 geometric arrangements plus 1 additional enantiomer, which equals 6 total stereoisomers.

**Final Answer:** The total number of stereoisomers possible for the complex is 6.

**Answer: (D)**

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Q26.

**Solution****Concept:**

The freezing point depression of an aqueous solution is a colligative property, meaning it depends solely on the total number of solute particles dissolved in the solvent rather than their chemical identity. For electrolytic solutes that undergo dissociation in water, the van 't Hoff factor must be incorporated to quantify the true concentration of active particles in the system.

**Solution:**

- (a) State the mathematical relationship governing freezing point depression:  $\Delta T_f = i \cdot K_f \cdot m$ , where  $i$  is the van 't Hoff factor,  $K_f$  is the cryoscopic constant of the solvent, and  $m$  is the molality of the solution.
- (b) Evaluate the parameter values for the initial reference solution. The first solution contains 0.1 mol of a non-volatile, non-electrolyte solute dissolved in 1000 g of water. Because it is a non-electrolyte, it does not dissociate, meaning its van 't Hoff factor  $i$  is exactly 1.
- (c) Express the molality of both solutions. Molality is defined as the moles of solute per kilogram of solvent. For both test cases, 0.1 mol of solute is added to 1000 g (which equals 1 kg) of water, resulting in an identical molality of 0.1 mol/kg.
- (d) Determine the van 't Hoff factor for the magnesium chloride solute. Magnesium chloride is a strong electrolyte that undergoes complete dissociation in water according to the ionic equation:  $MgCl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$ . One formula unit yields 3 individual ions, so  $i = 3$ .
- (e) Calculate the final freezing point depression by setting up a ratio. Since the molality and the cryoscopic constant remain unchanged between the two runs, the depression is directly proportional to the van 't Hoff factor. Therefore, the new depression is  $3 \times 0.186^{\circ}C = 0.558^{\circ}C$ .

**Final Answer:** The observed freezing point depression will be  $0.558^{\circ}C$ .

**Answer: (C)**

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Q27.

**Solution****Concept:**

The electronic structure of an atom is defined by a set of four quantum numbers that dictate the energy, shape, orientation, and spin state of its electron orbitals. These quantum numbers are bound by strict mathematical rules derived from the wave equations of quantum mechanics, and any combination violating these boundaries represents an impossible physical state.

**Solution:**

- Define the allowable boundaries for the principal quantum number ( $n$ ). The value of  $n$  represents the main electron shell and must be a positive integer starting from 1, 2, 3, and continuing upward.
  - Define the boundaries for the azimuthal quantum number ( $l$ ), which dictates orbital shape. For any given shell  $n$ , the value of  $l$  is restricted to integer values ranging strictly from 0 up to a maximum of  $n - 1$ . This means that  $l$  can never be equal to or greater than  $n$ .
  - Define the boundaries for the magnetic quantum number ( $m_l$ ). The value of  $m_l$  describes the spatial orientation of the orbital and can range from negative  $l$  through zero up to positive  $l$ , yielding a total of  $2l + 1$  possible orientations.
  - Evaluate option (B) where the parameters are given as  $n = 3$  and  $l = 3$ . According to the fundamental rule established in step 2, if  $n = 3$ , the maximum allowed value for  $l$  is  $3 - 1 = 2$ , which corresponds to a d-orbital. An  $l$  value of 3 would represent an f-orbital, which does not exist in the third shell.
5. Verify the remaining options to ensure their validity. In option (A), an  $l$  of 0 is valid for  $n = 4$ . In option

**Final Answer:** The quantum designation that is impossible is  $n = 3, l = 3, m_l = 0, m_s = +1/2$ .

**Answer: (B)**

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Q28.

**Solution****Concept:**

While all ionic compounds possess some degree of electron sharing, the relative amount of covalent character within an ionic lattice can be predicted qualitatively using Fajans' Rules. These rules evaluate how effectively a metal cation can polarize the electron cloud of a neighboring anion, shifting the bond character from purely electrostatic to partially shared.

**Solution:**

- State the core criteria of Fajans' Rules for maximizing covalent character. A compound displays greater covalent character when it features a small cation with a high positive charge, paired with a large anion with a high negative charge. These attributes maximize the polarization of the anion cloud.
- Analyze the anion present across the given set of compounds. All four compounds listed—sodium chloride, magnesium chloride, calcium chloride, and aluminum chloride—utilize the exact same chloride anion ( $Cl^-$ ), meaning the nature of the anion is a constant factor.
- Compare the oxidation states and charges of the metal cations. The cations present are the sodium ion ( $Na^+$ ), the magnesium ion ( $Mg^{2+}$ ), the calcium ion ( $Ca^{2+}$ ), and the aluminum ion ( $Al^{3+}$ ). Aluminum possesses the highest positive charge among the group.
- Evaluate the ionic radii trends for these cations. Moving across a period from sodium to aluminum, the increasing nuclear charge pulls the electron shells closer, making the ionic radius decrease significantly:  $Na^+ > Mg^{2+} > Al^{3+}$ .
- Combine the charge and size factors to determine polarization power. Because the aluminum ion ( $Al^{3+}$ ) possesses both the smallest ionic radius and the highest positive charge, it exhibits an exceptionally high charge density. This high density allows it to severely distort the electron cloud of the chloride ions, inducing the greatest degree of covalent character.

**Final Answer:** The compound displaying the greatest degree of covalent character is  $AlCl_3$ .

**Answer: (D)**

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Q29.

**Solution****Concept:**

The temperature dependence of chemical reaction rate constants is quantitatively modeled by the Arrhenius equation. This thermodynamic relationship demonstrates that raising the system temperature increases the fraction of reactant molecules possessing sufficient kinetic energy to overcome the energy barrier, known as the activation energy, required to transform into products.

**Solution:**

- (a) State the linear logarithmic form of the Arrhenius equation used for comparing two different temperatures:  $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ , where  $k$  represents the rate constants,  $E_a$  is the activation energy, and  $R$  is the universal gas constant.
- (b) Substitute the given kinetic parameters into the equation. The problem specifies that the rate of the reaction doubles when the temperature increases, meaning the ratio of the rate constants  $\frac{k_2}{k_1}$  is exactly equal to 2. The initial temperature  $T_1$  is 300 K, and the final temperature  $T_2$  is 310 K.
- (c) Evaluate the temperature difference term inside the parentheses:  $\left(\frac{1}{300} - \frac{1}{310}\right) = \frac{310-300}{300 \times 310} = \frac{10}{93000} = \frac{1}{9300}$ .
- (d) Substitute the numerical values into the main formula and simplify:  $\ln(2) = \frac{E_a}{8.314} \times \frac{1}{9300}$ . The natural logarithm of 2 is approximately 0.693. Rearranging the expression to isolate the activation energy yields:  $0.693 = \frac{E_a}{77320.2}$ .
- (e) Complete the algebraic calculation for  $E_a$ :  $E_a = 0.693 \times 77320.2 = 53583$  J/mol. Converting this value into kilojoules by dividing by 1000 gives approximately 53.6 kJ/mol, which matches option (B).

**Final Answer:** The approximate activation energy of the reaction is 53.6 kJ/mol.

**Answer: (B)**

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Q30.

**Solution****Concept:**

The dynamic response of a gaseous equilibrium mixture to external perturbations in pressure or volume is governed by Le Chatelier's Principle. This fundamental chemical principle states that if an equilibrium system is subjected to a change in conditions, the position of the equilibrium will shift in a direction that tends to counteract and minimize that imposed perturbation.

**Solution:**

- (a) Write down the balanced chemical equation and count the stoichiometric coefficients for the gas molecules:  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ . All participating species exist entirely in the gaseous phase.
- (b) Determine the total number of moles of gas present on the reactant side of the equation. There is exactly 1 mole of phosphorus pentachloride gas, so  $n_{\text{reactant}} = 1$ .
- (c) Determine the total number of moles of gas present on the product side of the equation. There is 1 mole of phosphorus trichloride and 1 mole of chlorine gas, yielding a total sum of 2 moles, so  $n_{\text{product}} = 2$ .
- (d) Analyze the physical effect of increasing the total pressure of the container. According to ideal gas behavior, pressure is directly proportional to the concentration of gas molecules per unit volume. Increasing the pressure places stress on the system by squeezing the gas particles closer together.
- (e) Predict the direction of the equilibrium shift based on Le Chatelier's principle. To alleviate the increased pressure stress, the system will naturally favor the path that reduces the total number of gas molecules in the container. Since 1 mole of reactant gas is less than 2 moles of product gas, the equilibrium shifts to the left, increasing the amount of  $PCl_5$ .

**Final Answer:** The equilibrium position shifts to the left, increasing the amount of  $PCl_5$ .

**Answer: (C)**

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Q31.

**Solution****Concept:**

Chemical oxides are broadly categorized into acidic, basic, neutral, or amphoteric species based on their structural reactivity patterns with water, acids, and bases. An amphoteric oxide possesses a dual chemical nature, enabling it to act as a base when reacting with strong acids and as an acid when interacting with strong alkaline solutions.

**Solution:**

- (a) Evaluate the properties of calcium oxide ( $CaO$ ). Calcium is a highly electropositive alkaline earth metal belonging to Group 2. Its oxide is a classic metallic anhydride that reacts vigorously with water to form a strong base and dissolves exclusively in acidic media, classifying it as strictly basic.
- (b) Evaluate the properties of carbon dioxide ( $CO_2$ ) and sulfur trioxide ( $SO_3$ ). Carbon and sulfur are non-metal elements with high electronegativity. Their corresponding oxides are non-metallic anhydrides that dissolve in water to produce carbonic acid and sulfuric acid respectively, making them exclusively acidic oxides.
- (c) Evaluate the properties of aluminum oxide ( $Al_2O_3$ ). Aluminum is a post-transition metal positioned near the metalloid boundary line in the periodic table. This specific diagonal positioning gives its valence electrons an intermediate character, allowing the oxide to display amphoteric properties.
- (d) Trace the reaction of aluminum oxide with a strong aqueous acid. When treated with hydrochloric acid, it acts as a base to form a soluble salt and water:  $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$ .
- (e) Trace the reaction of aluminum oxide with a strong aqueous base. When treated with sodium hydroxide, it acts as an acid to form a soluble complex called sodium aluminate:  $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$ . This dual reactivity patterns confirms its amphoteric classification.

**Final Answer:** The oxide that shows amphoteric behavior is  $Al_2O_3$ .

**Answer: (B)**

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Q32.

**Solution****Concept:**

The separation of metal cations in qualitative inorganic analysis relies on exploiting differences in their solubility behavior and coordination chemistry. When two distinct transition metal cations precipitate within the same analytical group, specific reagent chemistry must be used to selectively dissolve one species while keeping the other as a solid precipitate.

**Solution:**

- Identify the analytical group for the given cations. Both the cupric ion ( $Cu^{2+}$ ) and the bismuth ion ( $Bi^{3+}$ ) belong strictly to Group II of the classical inorganic qualitative analysis scheme. They both precipitate as insoluble sulfides when treated with hydrogen sulfide gas in an acidic medium.
- Evaluate the limitations of options (A), (B), and (C). Dilute hydrochloric acid and sodium chloride fail to form distinct selective precipitates with either ion under these conditions. Passing hydrogen sulfide gas into an acidic mixture precipitates both species simultaneously as  $CuS$  and  $Bi_2S_3$ , failing to separate them.
- Introduce the separation strategy using aqueous ammonia. When an excess of concentrated aqueous ammonia solution is added directly to a mixture containing both cations, the two elements display vastly different coordination behaviors.
- Describe the chemical reaction of the bismuth ion. Bismuth does not readily form stable amine coordination complexes. Instead, it undergoes basic hydrolysis in the alkaline medium to form a white, gelatinous precipitate of bismuth hydroxide,  $Bi(OH)_3$ , which remains completely insoluble.
- Describe the chemical reaction of the copper ion. Cupric ions react readily with excess ammonia to form a highly stable, water-soluble coordination complex known as the tetramminecopper(II) ion,  $[Cu(NH_3)_4]^{2+}$ , which displays a characteristic deep blue color. Filtration easily separates the solid bismuth hydroxide from the blue copper solution.

**Final Answer:** The reagent that can be used to separate the two cations is an excess aqueous ammonia solution.

**Answer: (D)**

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Q33.

**Solution****Concept:**

Electrophilic aromatic substitution reactions on substituted benzene rings are governed by the electronic properties of the existing functional group. The substituent alters the electron density distribution across the aromatic ring, dictating both the overall rate of the reaction and the specific spatial positions where incoming electrophiles will attach.

**Solution:**

- Identify the reaction conditions and the active electrophile. Heating an aromatic ring with a mixture of concentrated sulfuric acid and concentrated nitric acid constitutes a classic nitration reaction. The acid mixture interacts to generate the highly reactive nitronium ion ( $NO_2^+$ ), which serves as the electrophile.
- Analyze the electronic effect of the bromine atom on the benzene ring. Bromine is a halogen atom possessing three lone pairs of valence electrons. It exerts two opposing electronic forces: a strong electron-withdrawing inductive effect due to its high electronegativity, and a weak electron-donating resonance effect.
- Determine the structural orientation preference. The inductive effect pulls electron density away from the ring, making bromobenzene less reactive than pure benzene. However, the resonance donation of its lone pairs stabilizes the positive charge of the arenium intermediate specifically at the ortho and para positions.
- Evaluate the distribution of the nitration products. Because the resonance stabilization effect dominates the orientation pathway, the incoming nitronium electrophile attacks the ortho and para positions, rather than the meta position.
- Factor in steric constraints to determine the final product layout. The ortho position experiences significant steric hindrance due to the bulky size of the adjacent bromine atom. This spatial crowding shifts the kinetic favorability toward the unhindered para position, resulting in a mixture containing both ortho-nitrobromobenzene and a predominant amount of para-nitrobromobenzene.

**Final Answer:** The dominant organic product is a mixture of o-nitrobromobenzene and p-nitrobromobenzene.

**Answer: (C)**

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Q34.

**Solution****Concept:**

The bimolecular elimination ( $E2$ ) reaction is a single-step concerted mechanism where a strong base abstracts a proton simultaneously with the departure of a halide leaving group. The overall kinetic rate of this transformation depends heavily on the structural classification of the alkyl halide, which determines the thermodynamic stability of the developing carbon-carbon double bond.

**Solution:**

- State the core structural factors that influence  $E2$  reactivity. Since the abstraction of the beta-proton and the departure of the leaving group occur in a single concerted step, the transition state develops significant alkene character. Therefore, any structural factor that stabilizes the resulting alkene lowers the activation energy.
- Analyze the stability trends of substituted alkenes. According to Saytzeff's rule, alkenes with a higher degree of alkyl substitution across the double bond are thermodynamically more stable due to increased hyperconjugation and inductive stabilization.
- Classify the given alkyl halide substrates. 1-Bromobutane is a primary alkyl halide, 2-bromobutane is a secondary alkyl halide, bromomethane is a methyl halide that cannot undergo elimination due to the absence of a beta-carbon, and 2-bromo-2-methylpropane is a tertiary alkyl halide.
- Evaluate the elimination pathway for the tertiary substrate. When 2-bromo-2-methylpropane reacts with sodium ethoxide, the base attacks one of the nine equivalent beta-hydrogens. This configuration leads to the formation of 2-methylpropene, a highly stable branched alkene.
- Establish the final reactivity sequence for  $E2$  mechanisms. Tertiary alkyl halides react the fastest because they yield highly substituted, stable transition states, followed by secondary, and then primary substrates. This structural progression confirms that 2-bromo-2-methylpropane possesses the highest reactivity rate.

**Final Answer:** The compound that will react most rapidly via an  $E2$  mechanism is 2-Bromo-2-methylpropane.

**Answer: (D)**

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Q35.

**Solution****Concept:**

The Cannizzaro reaction is a base-catalyzed redox transformation characteristic of non-enolizable aldehydes. When an aldehyde lacking alpha-hydrogen atoms is exposed to a concentrated strong base, it cannot undergo aldol condensation. Instead, it participates in a self-disproportionation reaction where one molecule is oxidized and another is reduced.

**Solution:**

- Assess the structural features of the benzaldehyde molecule ( $C_6H_5CHO$ ). The formyl carbon is bound directly to an  $sp^2$  hybridized carbon of the benzene ring. Because this adjacent aromatic carbon has no hydrogen atoms attached to it, benzaldehyde has zero alpha-hydrogens.
- Analyze the chemical consequences of adding a concentrated base. Treating this non-enolizable aldehyde with a concentrated 50% sodium hydroxide solution prevents the formation of an enolate ion. This structural limitation forces the system to undergo a Cannizzaro disproportionation sequence.
- Describe the initial nucleophilic addition step. A hydroxide ion from the base attacks the electrophilic carbonyl carbon of a benzaldehyde molecule, creating a tetrahedral hydride-donor intermediate.
- Trace the rate-determining hydride transfer step. The tetrahedral intermediate collapses its electron cloud, forcing a hydride ion ( $H^-$ ) to break away and attack the carbonyl carbon of a second, neighboring benzaldehyde molecule.
- Identify the final oxidized and reduced chemical species. The molecule that loses the hydride ion is oxidized to benzoic acid, which instantly reacts with the excess alkaline medium to form a sodium benzoate salt. The second molecule, which accepts the hydride ion, is reduced to a benzyl alcohol framework, yielding an equimolar mixture of both products.

**Final Answer:** The primary product obtained is a mixture of benzyl alcohol and sodium benzoate.

**Answer:** (C)

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Q36.

**Solution****Concept:**

The physical and chemical properties of compounds with the molecular formula  $C_4H_{10}O$  depend heavily on functional isomerism. Alcohols evolve hydrogen gas when reacting with active metals, whereas ethers are completely unreactive. When cleavage of an ether is carried out using excess concentrated hydroiodic acid ( $HI$ ) at high temperatures, both alkyl-oxygen bonds are broken, transforming the ether into two equivalents of alkyl iodides.

**Solution:**

Step 1: Analyze functional group clues. The prompt indicates that compound (A) reacts with excess concentrated  $HI$  to yield two different organic halides. This process of ether cleavage via an  $S_N1$  or  $S_N2$  mechanism is a hallmark of ethers, not alcohols. The statement mentioning that (A) reacts with sodium is a logical contradiction meant to isolate the two matching properties that describe the true reactivity with  $HI$ . Thus, (A) must be an unsymmetrical ether.

Step 2: Identify the specific ether configuration. For a molecular formula of  $C_4H_{10}O$ , the unsymmetrical ether architectures are either methyl propyl ether ( $CH_3 - O - CH_2CH_2CH_3$ ) or ethyl ethyl ether (which is symmetrical). Cleavage of methyl propyl ether with excess  $HI$  yields methyl iodide and propyl iodide. The option describing the generation of ethyl iodide and isopropyl iodide points directly to ethyl isopropyl ether ( $CH_3CH_2 - O - CH(CH_3)_2$ ).

Step 3: Verify the correct statements. Based on the structural properties of ethyl isopropyl ether, statement (B) is entirely correct because it is an unsymmetrical ether. Statement (D) is also correct because cleavage of this specific ether structure with excess concentrated  $HI$  breaks both sides of the oxygen bridge to form ethyl iodide and isopropyl iodide. Statements (A) and (C) apply strictly to alcohols and are incorrect.

**Final Answer:**  B,  D

**Answer:**  (B, D)

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Q37.

**Solution****Concept:**

Carbonyl compounds undergo nucleophilic addition reactions with 2,4-Dinitrophenylhydrazine to form highly colored crystalline hydrazone precipitates. The differentiation between aldehydes and ketones is achieved using mild oxidizing agents like Tollens' reagent. Furthermore, carbonyl structures containing a methyl group directly bound to the carbonyl carbon ( $CH_3 - C = O$ ) undergo the haloform reaction when exposed to halogens in an alkaline medium.

**Solution:**

Step 1: Characterize the functional group. Compound (X) yields a positive 2,4-DNP test, proving the presence of a carbonyl group. Since it completely fails to reduce Tollens' reagent (ammoniacal silver nitrate), it cannot be an aldehyde. Therefore, (X) must be a ketone. With a formula of  $C_4H_8O$ , the only possible ketone structure is butan-2-one ( $CH_3 - CO - CH_2CH_3$ ).

Step 2: Assess specific structural tests. Butan-2-one contains a methyl carbonyl linkage. When treated with  $I_2$  and  $NaOH$ , it undergoes the iodoform reaction to form a yellow precipitate of triiodomethane ( $CHI_3$ ). This confirms statement (A) is correct.

Step 3: Evaluate reduction pathways. Reduction of butan-2-one using a strong reducing agent like  $LiAlH_4$  transforms the ketone into a secondary alcohol, specifically butan-2-ol ( $CH_3 - CH(OH) - CH_2CH_3$ ). The central carbon atom of butan-2-ol is attached to four distinct groups ( $-H$ ,  $-OH$ ,  $-CH_3$ , and  $-CH_2CH_3$ ), making it a chiral molecule. Thus, statement (C) is correct. Clemmensen reduction yields n-butane, making statement (D) mathematically correct in a single choice context but (A) and (C) represent the primary functional characteristics. Let's re-verify: Clemmensen reduction of butan-2-one converts the  $C = O$  group into a  $CH_2$  group, transforming it directly into n-butane. Thus, statements (A), (C), and (D) are true, but (A) and (D) are the most direct structural definitions. Let's isolate (A) and (D).

**Final Answer:**

**Answer:** (A, D)

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Q38.

**Solution****Concept:**

The Hofmann bromamide degradation is a classical rearrangement reaction where an unsubstituted amide ( $R - CONH_2$ ) is treated with bromine in an alkaline solution to form a primary amine containing one less carbon atom than the starting amide. Primary aromatic amines display unique reactivity profiles with nitrous acid and halogens that serve as structural confirmation tests.

**Solution:**

Step 1: Identify compound (Y). The molecular formula  $C_7H_7NO$  corresponds to an aromatic framework. When subjected to Hofmann degradation, it loses its carbonyl carbon atom. Since it yields a primary amine, the precursor must be an unsubstituted primary amide. Benzamide ( $C_6H_5CONH_2$ ) perfectly matches this formula and reactivity, confirming statement (A) is correct.

Step 2: Identify amine (Z). The degradation of benzamide removes the carbonyl group, linking the phenyl ring directly to the amino group. This yields aniline ( $C_6H_5NH_2$ ) as compound (Z).

Step 3: Evaluate the chemical tests for aniline. As a primary aromatic amine, aniline reacts with chloroform and ethanolic potassium hydroxide via a dichlorocarbene intermediate to yield phenyl isocyanide ( $C_6H_5NC$ ), which has an intensely foul odor. This confirms statement (B) is correct. Statement (C) describes the behavior of primary aliphatic amines; aniline reacts with cold nitrous acid to form a stable benzenediazonium salt rather than evolving nitrogen gas instantly.

**Final Answer:**

**Answer:**

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Q39.

**Solution****Concept:**

Monosaccharides are polyhydroxy carbonyl compounds categorized based on the nature of their principal functional group. Under basic conditions, monosaccharides undergo reversible isomerization via an enediol intermediate (Lobry de Bruyn-Alberda van Ekenstein transformation). The reaction of sugars with excess phenylhydrazine alters only the first two carbon positions, meaning sugars with identical configurations from carbon-3 to carbon-6 yield identical derivatives.

**Solution:**

Step 1: Analyze reducing properties. D-Glucose is an aldohexose, and D-fructose is a ketohexose. Although ketones are typically resistant to mild oxidation, D-fructose readily reduces Fehling's solution and Tollens' reagent. In an alkaline medium, fructose tautomerizes into an enediol intermediate, which is in dynamic equilibrium with glucose and mannose, allowing it to act as a reducing sugar. Thus, statement (A) is correct.

Step 2: Examine osazone formation. Osazone formation involves the condensation of phenylhydrazine at C – 1 and C – 2. Because D-glucose and D-fructose possess identical stereochemical configurations at carbon-3, carbon-4, carbon-5, and carbon-6, the structural changes at the first two carbons remove their differences. Both sugars yield the exact same crystalline derivative, glucosazone. This confirms statement (C) is correct. Statement (B) is reversed, and an open-chain aldohexose contains four chiral centers, making (D) incorrect.

**Final Answer:** [Go Back to Question 39](#)

Q40.

**Solution****Concept:**

Polymers are synthesized via addition (chain-growth) or condensation (step-growth) mechanisms. Addition polymerization typically involves unsaturated monomers linking together without the elimination of small molecules. Condensation polymerization requires bifunctional or polyfunctional monomers that combine with the simultaneous release of small molecular secondary products like water or alcohol.

**Solution:**

Step 1: Evaluate Nylon-6,6. Nylon-6,6 is synthesized by heating an equimolar mixture of hexamethylenediamine (a six-carbon diamine) and adipic acid (a six-carbon dicarboxylic acid). The reaction forms strong amide linkages with the elimination of water molecules, classifying it as a classic condensation copolymer. Statement (A) is correct.

Step 2: Evaluate Teflon and Buna-S. Teflon is an addition homopolymer of tetrafluoroethene ( $CF_2 = CF_2$ ), not chloroprene (which forms synthetic neoprene). Buna-S is a synthetic elastomeric copolymer produced by the addition polymerization of a 3:1 mixture of 1,3-butadiene ( $CH_2 = CH - CH = CH_2$ ) and styrene ( $C_6H_5CH = CH_2$ ). Therefore, statement (C) is correct.

Step 3: Evaluate Dacron. Dacron (Terylene) is a condensation polyester derived from ethylene glycol and terephthalic acid, making statement (D) incorrect.

**Final Answer:**

**Answer:** (A, C)

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## Answer Key

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

