

# WBJEE Chemistry Sample Paper-16

Duration: 60 Minutes

Maximum Marks: 50

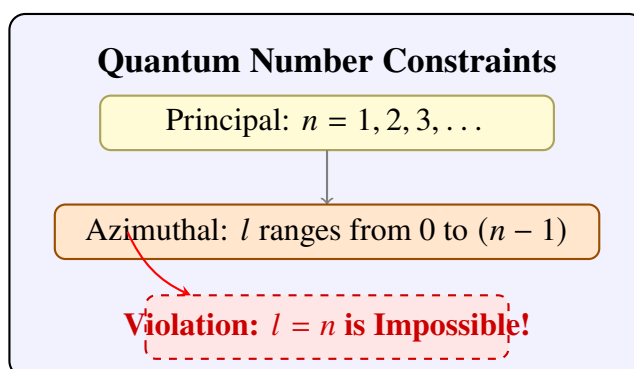
## Instructions

- 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]**

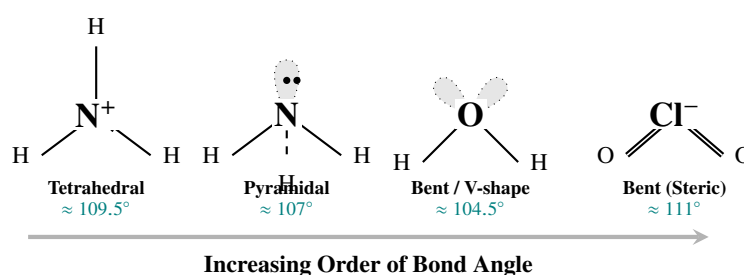
- Q1.** Equal volumes of 0.1 M  $\text{H}_2\text{SO}_4$  and 0.1 M NaOH solutions are mixed together. The normality of the resulting solution and its nature will be:
- (A) 0.05 N, acidic  
(B) 0.05 N, basic  
(C) 0.1 N, acidic  
(D) 0.025 N, basic
- Q2.** Which of the following sets of quantum numbers represents an impossible arrangement for an electron in a ground-state atom?





- (A)  $n = 3, l = 2, m_l = -2, m_s = +1/2$
- (B)  $n = 4, l = 0, m_l = 0, m_s = -1/2$
- (C)  $n = 3, l = 3, m_l = -1, m_s = +1/2$
- (D)  $n = 5, l = 1, m_l = 0, m_s = -1/2$

**Q3.** The correct increasing order of bond angles in the following species is:



- (A)  $ClO_2^- < H_2O < NH_3 < NH_4^+$
- (B)  $H_2O < ClO_2^- < NH_3 < NH_4^+$
- (C)  $H_2O < NH_3 < ClO_2^- < NH_4^+$
- (D)  $H_2O < NH_3 < NH_4^+ < ClO_2^-$

**Q4.** A certain mass of an ideal gas occupies a volume of 4.0 L at 27°C and 1 atm pressure. If the gas is compressed to 2.0 L at constant temperature, its final pressure will be:

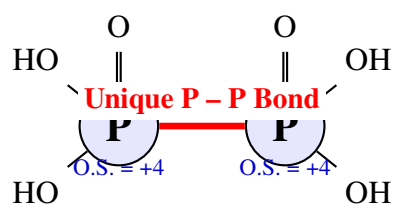
- (A) 0.5 atm
- (B) 1.5 atm
- (C) 2.0 atm
- (D) 4.0 atm



- Q5.** For the isothermal reversible expansion of an ideal gas into a vacuum (free expansion), which of the following conditions is entirely correct?
- (A)  $w = 0, q > 0, \Delta U = 0$   
(B)  $w < 0, q > 0, \Delta U = 0$   
(C)  $w = 0, q = 0, \Delta U = 0$   
(D)  $w < 0, q = 0, \Delta U < 0$
- Q6.** The solubility product ( $K_{sp}$ ) of a sparingly soluble salt  $\text{MX}_2$  is  $4 \times 10^{-12}$  at 298 K. Its solubility in mol/L in a 0.01 M solution of NaX is:
- (A)  $4 \times 10^{-10}$   
(B)  $1 \times 10^{-4}$   
(C)  $4 \times 10^{-8}$   
(D)  $2 \times 10^{-6}$
- Q7.** For a first-order reaction  $A \rightarrow \text{products}$ , the concentration of A decreases from 0.8 M to 0.2 M in 40 minutes. The rate constant ( $k$ ) of this reaction is:
- (A)  $0.0346 \text{ min}^{-1}$   
(B)  $0.0173 \text{ min}^{-1}$   
(C)  $0.0693 \text{ min}^{-1}$   
(D)  $0.0519 \text{ min}^{-1}$
- Q8.** In the standardization of  $\text{KMnO}_4$  using oxalic acid in an acidic medium, 20 mL of 0.1 M oxalic acid requires a specific volume of 0.02 M  $\text{KMnO}_4$ . What is this volume?
- (A) 20 mL  
(B) 40 mL  
(C) 50 mL  
(D) 10 mL



- Q9.** The standard reduction potentials of three metallic elements  $A$ ,  $B$ , and  $C$  are  $+0.34\text{ V}$ ,  $-0.76\text{ V}$ , and  $-0.44\text{ V}$  respectively. The correct arrangement showing their decreasing reducing power is:
- (A)  $A > C > B$   
 (B)  $B > C > A$   
 (C)  $C > B > A$   
 (D)  $B > A > C$
- Q10.** When sodium metal is dissolved in liquid ammonia, a deep blue colored solution is obtained. This intense color is fundamentally due to the presence of:
- (A) Sodium atoms  
 (B) Sodium hydride formation  
 (C) Ammoniated electrons  
 (D) Amide ions
- Q11.** Which of the following oxoacids of phosphorus contains a direct, unique P - P bond along with a +4 formal oxidation state on its phosphorus atoms?



*Symmetrical Chemical Structure of  $H_4P_2O_6$*

- (A) Hypophosphoric acid ( $H_4P_2O_6$ )  
 (B) Pyrophosphoric acid ( $H_4P_2O_7$ )  
 (C) Orthophosphoric acid ( $H_3O_4$ )  
 (D) Pyrophosphorous acid ( $H_4P_2O_5$ )
- Q12.** Which of the following ions is expected to exhibit the maximum spin-only magnetic moment in an aqueous medium?



- (A)  $\text{Ti}^{3+}$
- (B)  $\text{Cr}^{3+}$
- (C)  $\text{Mn}^{2+}$
- (D)  $\text{Fe}^{2+}$

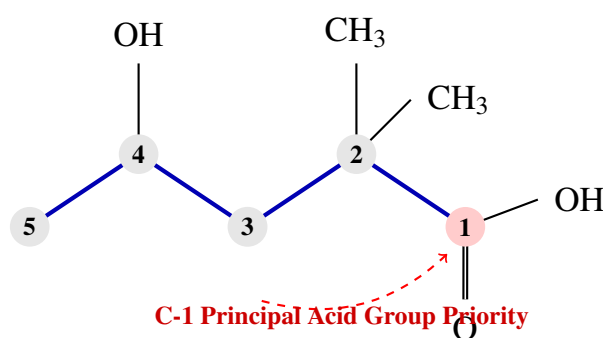
**Q13.** The total number of possible stereoisomers (including optical enantiomers) for the coordination complex compound  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is:

- (A) 2
- (B) 3
- (C) 4
- (D) 1

**Q14.** Which of the following gas-phase pollutants is predominantly responsible for the phenomenon of classical (London) smog rather than photochemical smog?

- (A)  $\text{NO}_2$
- (B)  $\text{O}_3$
- (C)  $\text{SO}_2$
- (D) Hydrocarbons

**Q15.** The correct IUPAC name for the organic molecular structure  $\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{COOH}$  is:



- (A) 4-Hydroxy-2,2-dimethylpentanoic acid
- (B) 2,2-Dimethyl-4-hydroxypentanoic acid



- (C) 4-Hydroxy-2,2,2-trimethylbutanoic acid
- (D) 2-Hydroxy-4,4-dimethylpentanoic acid

- Q16.** Ozonolysis of an alkene  $X$  followed by treatment with  $Zn/H_2O$  yields a clean equimolar mixture of propan-2-one and formaldehyde. The structural identity of alkene  $X$  is:
- (A) 2-Methylprop-1-ene
  - (B) But-2-ene
  - (C) 3-Methylbut-1-ene
  - (D) 2-Methylbut-2-ene
- Q17.** Which of the following alkyl halides undergoes nucleophilic substitution via the  $S_N1$  pathway at the fastest absolute rate when exposed to aqueous ethanol?
- (A)  $CH_3CH_2CH_2Cl$
  - (B)  $(CH_3)_3C - Cl$
  - (C)  $(CH_3)_2CH - Cl$
  - (D)  $CH_3CH_2CH_2Br$
- Q18.** When phenol is systematically treated with an excess of bromine water ( $Br_2/H_2O$ ), the major organic product obtained is a precipitate of:
- (A) 2-Bromophenol
  - (B) 4-Bromophenol
  - (C) 2,4,6-Tribromophenol
  - (D) 2,4-Dibromophenol
- Q19.** The major organic product formed in the acid-catalyzed reaction of benzaldehyde with an excess of acetophenone in the presence of dilute base is an example of:
- (A) Benzoin condensation
  - (B) Claisen-Schmidt reaction
  - (C) Cannizzaro reaction



(D) Gattermann-Koch reaction

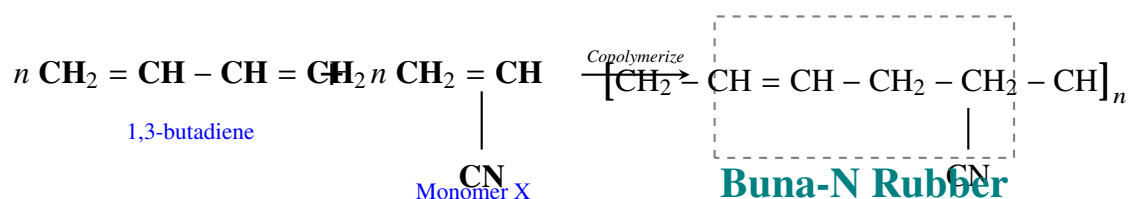
**Q20.** Which of the following primary amines will not produce a stable diazonium salt or clear solution even at  $0 - 5^{\circ}\text{C}$  and will immediately evolve nitrogen gas when treated with  $\text{NaNO}_2 + \text{HCl}$ ?

- (A) Aniline
- (B) *p*-Toluidine
- (C) Benzylamine
- (D) Cyclohexylamine

**Q21.** Which of the following specific chemical components represents a non-reducing disaccharide sugar?

- (A) Maltose
- (B) Lactose
- (C) Sucrose
- (D) Cellobiose

**Q22.** The structure of Buna-N synthetic rubber is derived from the copolymerization of 1,3-butadiene with which of the following monomers?



- (A) Styrene
- (B) Acrylonitrile
- (C) Vinyl chloride
- (D) Chloroprene

**Q23.** An organic compound containing carbon, hydrogen, and oxygen contains 40.0% Carbon and 6.67% Hydrogen by mass. What is its empirical formula?



- (A)  $\text{CH}_2\text{O}$
- (B)  $\text{CHO}$
- (C)  $\text{C}_2\text{H}_4\text{O}$
- (D)  $\text{CHO}_2$

**Q24.** According to the Bohr theory of the hydrogen atom, the radius of the electron's orbit is directly proportional to:

- (A)  $n$
- (B)  $n^2$
- (C)  $1/n$
- (D)  $1/n^2$

**Q25.** Which of the following compounds displays the highest magnitude of covalent character according to Fajans' rules?

- (A)  $\text{LiCl}$
- (B)  $\text{NaCl}$
- (C)  $\text{KCl}$
- (D)  $\text{RbCl}$

**Q26.** The critical temperature values of four different real gases  $W$ ,  $X$ ,  $Y$ , and  $Z$  are 33 K, 126 K, 154 K, and 304 K respectively. Which of these gases will be most easily liquefied upon cooling?

- (A)  $W$
- (B)  $X$
- (C)  $Y$
- (D)  $Z$

**Q27.** For a spontaneous process at all temperatures, the thermodynamic criteria that must be satisfied are:

- (A)  $\Delta H < 0$  and  $\Delta S > 0$



- (B)  $\Delta H > 0$  and  $\Delta S > 0$   
(C)  $\Delta H < 0$  and  $\Delta S < 0$   
(D)  $\Delta H > 0$  and  $\Delta S < 0$

**Q28.** If the rate of a chemical reaction doubles for every  $10^\circ\text{C}$  rise in temperature, by what total factor will the rate increase when the temperature is raised from  $25^\circ\text{C}$  to  $65^\circ\text{C}$ ?

- (A) 4  
(B) 8  
(C) 16  
(D) 32

**Q29.** In a balanced acidic redox equation:  $x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \rightarrow a\text{Mn}^{2+} + b\text{CO}_2 + c\text{H}_2\text{O}$ , the stoichiometric coefficients  $x$ ,  $y$ , and  $z$  are:

- (A) 2, 5, 16  
(B) 5, 2, 16  
(C) 2, 5, 8  
(D) 1, 5, 8

**Q30.** Which of the following statements regarding interstitial hydrides formed by  $d$ -block transition metals is fundamentally incorrect?

- (A) They retain metallic conductivity.  
(B) They are highly non-stoichiometric.  
(C) They are significantly harder than the parent metals.  
(D) They are chemical compounds with fixed ionic bonds.

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



- Q31.** The standard EMF ( $E^\circ$ ) of a cell involving the cell reaction:  $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s)$  is 1.10 V at 25°C. The equilibrium constant ( $K_c$ ) for this cell reaction is approximately of the order of:
- (A)  $10^{28}$   
(B)  $10^{37}$   
(C)  $10^{18}$   
(D)  $10^{45}$
- Q32.** An aqueous solution contains a mixture of  $\text{Ca}(\text{NO}_3)_2$  and an unknown non-volatile non-electrolyte solute. The boiling point of this combined solution is measured to be 100.52°C. If the molality of  $\text{Ca}(\text{NO}_3)_2$  is 0.1 m (assuming complete 100% dissociation), what is the molality of the non-electrolyte solute? (Given  $K_b$  for water = 0.52 K kg mol<sup>-1</sup>)
- (A) 0.7 m  
(B) 0.5 m  
(C) 0.9 m  
(D) 0.3 m
- Q33.** Consider the transition element complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Which of the following statements matches its crystal field splitting parameter ( $\Delta_o$ ) description and electronic distribution inside the  $d$ -orbitals?
- (A)  $\Delta_o < P$ , high spin,  $t_{2g}^4 e_g^2$   
(B)  $\Delta_o > P$ , low spin,  $t_{2g}^6 e_g^0$   
(C)  $\Delta_o < P$ , high spin,  $t_{2g}^3 e_g^3$   
(D)  $\Delta_o > P$ , high spin,  $t_{2g}^5 e_g^1$
- Q34.** An organic aromatic compound A ( $\text{C}_7\text{H}_8$ ) on reaction with  $\text{Cl}_2$  in the presence of  $\text{FeCl}_3$  gives compound B. Compound A on heating with  $\text{Cl}_2$  at boiling point in the absence of a catalyst gives compound C. Compounds B and C are respectively:



- (A) Benzyl chloride and *o*-chlorotoluene
- (B) *m*-Chlorotoluene and Benzyl chloride
- (C) *o*-/*p*-Chlorotoluene and Benzyl chloride
- (D) Benzyl chloride and *m*-chlorotoluene

**Q35.** Xenon fluorides react readily with selective covalent fluoride ion acceptors to form crystalline salts. When  $\text{XeF}_4$  reacts with  $\text{SbF}_5$ , the molecular configurations of the cationic and anionic parts produced in the product adduct are respectively:

- (A) T-shaped and Octahedral
- (B) Square planar and Trigonal bipyramidal
- (C) See-saw and Octahedral
- (D) T-shaped and Square pyramidal

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

**Q36.** Which of the following statements are correct regarding the molecular orbital (MO) configuration of the  $\text{O}_2^+$  ion?

- (A) It is paramagnetic in nature.
- (B) Its bond order is equal to 2.5.
- (C) The unpaired electron resides in an antibonding  $\pi^*$  molecular orbital.
- (D) It has a shorter bond length than the neutral  $\text{O}_2$  molecule.

**Q37.** For the ideal gas chemical equilibrium reaction:  $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ , which of the following alterations will cause the equilibrium position to shift toward the right-hand side (forward direction)?

- (A) Increasing the total pressure of the system at constant temperature.
- (B) Adding an inert gas like Helium at constant volume.

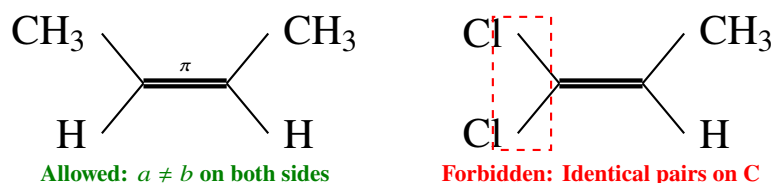


- (C) Decreasing the partial pressure of  $\text{Cl}_2$  gas.  
 (D) Increasing the volume of the reaction container.

**Q38.** Which of the following standard chemical reagents or reactions can be used to cleanly differentiate between Benzaldehyde and Acetaldehyde?

- (A) Tollen's reagent test  
 (B) Fehling's solution test  
 (C) Iodoform test  
 (D) 2,4-DNP test

**Q39.** Which of the following compounds will exhibit geometrical isomerism (cis/trans or E/Z)?



- (A) But-2-ene  
 (B) 1,2-Dimethylcyclopropane  
 (C) 1,1-Dichloroprop-1-ene  
 (D) 2-Methylbut-2-ene

**Q40.** Which of the following properties are characteristics of transition metals ( $d$ -block elements) and their compounds?

- (A) Ability to show variable oxidation states due to small energy gaps between  $(n - 1)d$  and  $ns$  subshells.  
 (B) Formation of catalytic active centers due to empty  $d$ -orbitals.  
 (C) Diamagnetism across almost all +2 oxidation state ions.  
 (D) Formation of deeply colored complexes via  $d - d$  electronic transitions.



## Detailed Solutions

Q1.

## Solution

**Concept:**

To determine the normality and chemical nature of a mixed solution, we analyze the equivalents of acidic hydrogen ions ( $\text{H}^+$ ) and basic hydroxyl ions ( $\text{OH}^-$ ) that neutralize each other. Normality (N) represents the number of gram-equivalents of solute per liter of solution. The species present in higher equivalent amounts dictates the final nature of the solution, while the unreacted excess concentration determines the final normality.

**Solution:**

- (a) First, we calculate the normality of each initial solution. For  $\text{H}_2\text{SO}_4$ , which has an  $n$ -factor of 2 because it releases two  $\text{H}^+$  ions per molecule, the normality is  $N = \text{Molarity} \times n\text{-factor} = 0.1 \text{ M} \times 2 = 0.2 \text{ N}$ . For  $\text{NaOH}$ , which has an  $n$ -factor of 1, the normality remains equal to its molarity,  $N = 0.1 \text{ N}$ .
- (b) Let the mixed volume of each solution be  $V \text{ mL}$ . The milliequivalents (meq) of  $\text{H}_2\text{SO}_4$  are calculated as  $N_1 V_1 = 0.2 \times V = 0.2V \text{ meq}$ . The milliequivalents of  $\text{NaOH}$  are calculated as  $N_2 V_2 = 0.1 \times V = 0.1V \text{ meq}$ .
- (c) Comparing the values shows that the milliequivalents of acid exceed those of the base ( $0.2V > 0.1V$ ), which means the resulting solution is inherently acidic in nature.
- (d) The excess milliequivalents of acid remaining after neutralization are  $\text{meq}_{\text{excess}} = 0.2V - 0.1V = 0.1V \text{ meq}$ .
- (e) The total combined volume of the final mixture is  $V_1 + V_2 = V + V = 2V \text{ mL}$ .
- (f) The normality of the resulting solution is the excess milliequivalents divided by the total volume:  $N_{\text{final}} = \frac{0.1V}{2V} = 0.05 \text{ N}$ .

**Final Answer:** The resulting solution is 0.05 N and acidic.

**Answer: (A)**

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Q2.

**Solution****Concept:**

Quantum numbers govern the allowed energy states and arrangements of electrons in atomic orbitals. The four quantum numbers must follow strict hierarchical mathematical definitions based on the wave equations of quantum mechanics. For any given principal quantum number  $n$ , the permissible values for the azimuthal quantum number  $l$  range strictly from 0 up to  $n - 1$ . An arrangement violating this restriction is physically impossible.

**Solution:**

- (a) Let us analyze each given configuration step-by-step against standard rules. In option (A),  $n = 3, l = 2$  represents a valid  $3d$  orbital. The magnetic quantum number  $m_l = -2$  falls within the permitted range from  $-l$  to  $+l$  ( $-2$  to  $+2$ ), and  $m_s = +1/2$  is a standard spin value.
- (b) In option (B),  $n = 4, l = 0$  corresponds to a valid  $4s$  orbital. The value  $m_l = 0$  is correct since  $m_l$  can only be 0 when  $l = 0$ , and  $m_s = -1/2$  is valid.
- (c) In option (C), the values specified are  $n = 3$  and  $l = 3$ . This configuration violates the fundamental quantum mechanical rule stating that the maximum value of  $l$  must always be strictly less than  $n$  ( $l \leq n - 1$ ). For  $n = 3$ , the allowed values of  $l$  are only 0, 1, or 2 (corresponding to  $3s, 3p$ , and  $3d$  subshells). A subshell with  $l = 3$  would be a  $3f$  orbital, which does not exist in any atom.
- (d) In option (D),  $n = 5, l = 1$  describes a valid  $5p$  orbital, where  $m_l = 0$  and  $m_s = -1/2$  are fully allowed values.

**Final Answer:** The configuration  $n = 3, l = 3, m_l = -1, m_s = +1/2$  is impossible.

**Answer:** (C)

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Q3.

**Solution****Concept:**

According to the Valence Shell Electron Pair Repulsion (VSEPR) theory, the spatial arrangement and bond angles of a molecule or polyatomic ion depend on its steric number, which is the total number of bonding atom groups and lone pairs surrounding the central atom. Repulsions follow the trend: lone pair-lone pair > lone pair-bond pair > bond pair-bond pair. Consequently, the presence of lone pairs compresses the adjacent bond angles away from ideal geometries.

**Solution:**

- (a) We evaluate the hybridization, lone pairs, and structural geometry for each chemical species. In  $\text{NH}_4^+$ , the central nitrogen atom has 4 bonding pairs and 0 lone pairs. This yields a regular tetrahedral geometry with a perfect, uncompressed ideal bond angle of  $109.5^\circ$ .
- (b) In  $\text{NH}_3$ , the central nitrogen atom possesses 3 bonding pairs and 1 lone pair. The lone pair-bond pair repulsion compresses the ideal tetrahedral angle down to approximately  $107^\circ$ .
- (c) In  $\text{H}_2\text{O}$ , the central oxygen atom has 2 bonding pairs and 2 lone pairs. The presence of two strong lone pairs causes even greater structural compression, shrinking the internal H – O – H bond angle down to about  $104.5^\circ$ .
- (d) In  $\text{ClO}_2^-$ , the central chlorine atom is surrounded by 2 bonding groups and 2 lone pairs. While it shares a similar steric environment with water, chlorine belongs to the third period and has larger, more polarizable lone pairs and larger bonding oxygen atoms. This causes its internal bond angle to expand slightly to about  $111^\circ$ , which is larger than the angles in water and ammonia.
- (e) Arranging these values in ascending order gives:  $\text{H}_2\text{O}$  ( $104.5^\circ$ ) <  $\text{NH}_3$  ( $107^\circ$ ) <  $\text{NH}_4^+$  ( $109.5^\circ$ ) <  $\text{ClO}_2^-$  ( $111^\circ$ ).

**Final Answer:** The correct increasing order is  $\text{H}_2\text{O} < \text{NH}_3 < \text{NH}_4^+ < \text{ClO}_2^-$ .

**Answer: (D)**

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Q4.

**Solution****Concept:**

Gas behavior under varying physical constraints is governed by the classical gas laws derived from the kinetic molecular theory. For a fixed mass of an ideal gas kept at a constant, uniform temperature, the relationship between its volume and pressure is described by Boyle's Law. This law states that the pressure of an ideal gas is inversely proportional to its volume, meaning the product of pressure and volume remains constant throughout the process.

**Solution:**

- We identify the initial parameters given in the problem statement. The initial pressure ( $P_1$ ) of the ideal gas system is 1 atm, and the initial volume ( $V_1$ ) occupied by the gas is 4.0 L.
- The gas undergoes a compression process that changes its volume to a new final volume ( $V_2$ ) of 2.0 L.
- Since the problem explicitly states that this compression occurs at a constant temperature, we apply the mathematical expression for Boyle's Law:  $P_1V_1 = P_2V_2$ .
- Substituting our known parameters into the formula gives the equation:  $1 \text{ atm} \times 4.0 \text{ L} = P_2 \times 2.0 \text{ L}$ .
- Isolating the final unknown pressure variable ( $P_2$ ), we solve the algebraic equation:  
$$P_2 = \frac{1 \times 4.0}{2.0} = 2.0 \text{ atm.}$$
- As expected from an inverse relationship, reducing the physical space to half its original volume causes the internal pressure of the gas to double.

**Final Answer:** The final pressure of the gas will be 2.0 atm.

**Answer: (C)**

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Q5.

**Solution****Concept:**

Thermodynamics provides a framework for analyzing energy transformations during gas expansion. Free expansion refers to the expansion of a gas into an unresisting vacuum. The work done ( $w$ ) by a gas depends on the opposing external pressure ( $P_{\text{ext}}$ ). If there is no external pressure resisting the movement of the gas boundaries, no mechanical work can be performed.

**Solution:**

- (a) The expansion takes place into an absolute vacuum, meaning the external pressure is zero ( $P_{\text{ext}} = 0$ ). Because the mechanical work for expansion is defined by the integral  $w = - \int P_{\text{ext}} dV$ , the total work done during this process is exactly zero ( $w = 0$ ).
- (b) The problem states that the expansion is entirely isothermal, which means the temperature of the system remains constant ( $\Delta T = 0$ ).
- (c) For an ideal gas, the total internal energy ( $U$ ) depends solely on its absolute temperature. Because the temperature does not change during an isothermal process, the change in internal energy must also be zero ( $\Delta U = 0$ ).
- (d) We can now apply the First Law of Thermodynamics, which is expressed by the mathematical equation:  $\Delta U = q + w$ .
- (e) Substituting our known values ( $\Delta U = 0$  and  $w = 0$ ) into this equation gives:  $0 = q + 0$ , which means that the heat exchanged ( $q$ ) must also be exactly zero ( $q = 0$ ).
- (f) Combining these three results shows that during the isothermal free expansion of an ideal gas, no heat is absorbed, no work is performed, and the internal energy remains unchanged.

**Final Answer:** The correct set of thermodynamic conditions is  $w = 0, q = 0, \Delta U = 0$ .

**Answer:** (C)

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Q6.

**Solution****Concept:**

The solubility of a sparingly soluble salt is governed by its solubility product constant ( $K_{sp}$ ). When a strong electrolyte sharing a common ion is introduced into the aqueous mixture, it alters the ionic equilibrium. According to Le Chatelier's principle, the addition of the common ion shifts the dissociation equilibrium backward, significantly reducing the solubility of the sparingly soluble salt. This phenomenon is known as the common ion effect.

**Solution:**

- (a) Let us assume the molar solubility of the sparingly soluble salt  $\text{MX}_2$  in the salt solution is  $S$  mol/L. The dissociation of  $\text{MX}_2$  in water can be written as:  $\text{MX}_2(s) \rightleftharpoons \text{M}^{2+}(aq) + 2\text{X}^-(aq)$ .
- (b) From this dissociation, the concentration of metal ions produced is  $[\text{M}^{2+}] = S$ , and the concentration of halide ions produced is  $[\text{X}^-] = 2S$ .
- (c) The solution also contains 0.01 M  $\text{NaX}$ , which is a strong electrolyte that dissociates completely:  $\text{NaX}(aq) \rightarrow \text{Na}^+(aq) + \text{X}^-(aq)$ . This adds an additional 0.01 M to the halide ion concentration.
- (d) Therefore, the total concentration of  $\text{X}^-$  ions in the final mixture is  $[\text{X}^-] = 2S + 0.01$ .
- (e) Because the solubility product  $K_{sp} = 4 \times 10^{-12}$  is extremely small, the value of  $S$  will be negligible compared to 0.01. This allows us to approximate the total halide concentration as  $[\text{X}^-] \approx 0.01$  M.
- (f) We substitute these concentrations into the equilibrium expression:  $K_{sp} = [\text{M}^{2+}][\text{X}^-]^2 \Rightarrow 4 \times 10^{-12} = S \times (0.01)^2$ .
- (g) Solving for  $S$  gives:  $S = \frac{4 \times 10^{-12}}{10^{-4}} = 4 \times 10^{-8}$  mol/L.

**Final Answer:** The solubility of the salt is  $4 \times 10^{-8}$  mol/L.

**Answer: (C)**

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Q7.

**Solution****Concept:**

Chemical kinetics deals with the rates of chemical processes and the factors that influence them. For a first-order chemical reaction, the rate of the reaction depends directly on the concentration of a single reactant. The integrated rate law for a first-order process provides a mathematical relationship between the initial concentration of the reactant, its remaining concentration at any given time, and the specific rate constant.

**Solution:**

- (a) We identify the initial parameters given in the question. The initial concentration of the reactant at time  $t = 0$  is  $[A]_0 = 0.8$  M.
- (b) The remaining concentration of the reactant after the specified time interval has elapsed is  $[A]_t = 0.2$  M. The time elapsed for this concentration decrease is  $t = 40$  minutes.
- (c) The integrated rate equation for a first-order reaction is given by the formula:  $k = \frac{2.303}{t} \log \left( \frac{[A]_0}{[A]_t} \right)$ .
- (d) Alternatively, using natural logarithms, the expression can be written as:  $k = \frac{1}{t} \ln \left( \frac{[A]_0}{[A]_t} \right)$ .
- (e) Substituting our concentration values into the ratio gives:  $\frac{[A]_0}{[A]_t} = \frac{0.8}{0.2} = 4$ .
- (f) Substituting this ratio and the time into the rate equation yields:  $k = \frac{1}{40} \ln(4)$ . Since  $\ln(4) = 2 \ln(2)$  and  $\ln(2) \approx 0.693$ , we can simplify the equation to:  $k = \frac{2 \times 0.693}{40} = \frac{1.386}{40} = 0.03465 \text{ min}^{-1}$ .

**Final Answer:** The rate constant of the reaction is  $0.0346 \text{ min}^{-1}$ .

**Answer: (A)**

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Q8.

**Solution****Concept:**

Volumetric redox titrations involve calculating equivalent amounts based on electron transfer between an oxidizing agent and a reducing agent. According to the law of equivalence, reacting chemical species always combine in equal gram-equivalent amounts at the stoichiometric end point. The number of equivalents is calculated by multiplying the molarity of a solution by its volume and its specific valence factor ( $n$ -factor).

**Solution:**

- (a) We determine the  $n$ -factor for both reacting molecules based on how they behave in an acidic medium. Potassium permanganate ( $\text{KMnO}_4$ ) acts as a strong oxidizing agent, and its manganese atom is reduced from an oxidation state of +7 to +2. This gain of five electrons means its  $n$ -factor is  $n_1 = 5$ .
- (b) Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) acts as a reducing agent, and its carbon atoms are oxidized from an oxidation state of +3 to +4 in carbon dioxide. Since each oxalic acid molecule contains two carbon atoms, it loses two electrons, giving it an  $n$ -factor of  $n_2 = 2$ .
- (c) We apply the law of equivalence at the endpoint:  $\text{Molarity}_1 \times \text{Volume}_1 \times n_1 = \text{Molarity}_2 \times \text{Volume}_2 \times n_2$ .
- (d) Substituting the known values for the permanganate and oxalic acid solutions gives the equation:  $0.02 \text{ M} \times V_1 \times 5 = 0.1 \text{ M} \times 20 \text{ mL} \times 2$ .
- (e) Simplifying both sides of the expression yields:  $0.1 \times V_1 = 4$ .
- (f) Solving for the unknown volume shows that  $V_1 = \frac{4}{0.1} = 40 \text{ mL}$ .

**Final Answer:** The required volume of potassium permanganate solution is 40 mL.

**Answer: (B)**

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Q9.

**Solution****Concept:**

The electrochemical series arranges chemical elements based on their standard reduction potentials ( $E^\circ$ ). The standard reduction potential measures how easily an element gains electrons and undergoes reduction. A lower or more negative reduction potential indicates that an element loses electrons more easily, making it a stronger reducing agent.

**Solution:**

- (a) We list and compare the standard reduction potentials provided for the three metallic elements. The reduction potential for element  $A$  is  $E^\circ = +0.34 \text{ V}$ , for element  $B$  is  $E^\circ = -0.76 \text{ V}$ , and for element  $C$  is  $E^\circ = -0.44 \text{ V}$ .
- (b) A lower standard reduction potential indicates a greater tendency to undergo oxidation, which corresponds to a stronger reducing power.
- (c) Comparing these numerical values shows that element  $B$  has the lowest, most negative reduction potential ( $-0.76 \text{ V}$ ), meaning it is the most powerful reducing agent among the three.
- (d) Element  $C$  has the next lowest reduction potential ( $-0.44 \text{ V}$ ), placing it second in terms of reducing capability.
- (e) Element  $A$  has a positive standard reduction potential ( $+0.34 \text{ V}$ ), which means it has the lowest tendency to lose electrons and is the weakest reducing agent.
- (f) Arranging the elements in order of decreasing reducing power gives:  $B > C > A$ .

**Final Answer:** The correct arrangement showing decreasing reducing power is  $B > C > A$ .

**Answer:** (B)

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Q10.

**Solution****Concept:**

When alkali metals dissolve in liquid ammonia, they undergo a unique chemical process that produces a conducting, deeply colored solution. Liquid ammonia acts as a ionizing solvent that stabilizes free ions through solvation. The dissolving metal atoms lose their outer valence electrons to the solvent, creating solvated metal cations and free electrons trapped in cavities formed by the ammonia molecules.

**Solution:**

- When sodium metal is added to liquid ammonia, it dissolves and ionizes according to the following chemical equation:  $\text{Na} + (x + y)\text{NH}_3 \rightarrow [\text{Na}(\text{NH}_3)_x]^+ + [e(\text{NH}_3)_y]^-$ .
- This process produces ammoniated sodium cations and ammoniated electrons that are stabilized by the surrounding polar ammonia molecules.
- The intense deep blue color of dilute solutions is caused by these ammoniated electrons. They absorb light in the red region of the visible spectrum, which excites them to higher electronic energy levels.
- Because red light is absorbed, the transmitted light appears as a deep blue color.
- These free ammoniated electrons move easily through the solvent cavities, which also makes the solution highly paramagnetic and an excellent conductor of electricity.

**Final Answer:** The intense color is due to the presence of ammoniated electrons.

**Answer: (C)**

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Q11.

**Solution****Concept:**

The structural chemistry of phosphorus oxoacids is determined by the element's ability to form stable bonds with oxygen and hydrogen, as well as catenated bonds with other phosphorus atoms. In these structures, each phosphorus atom is tetrahedrally coordinated, forming a strong double bond with an oxygen atom and single bonds with hydroxyl groups. When two phosphorus atoms couple directly without an intervening oxygen atom, it forms a distinct homonuclear covalent bond that lowers the average oxidation state of the phosphorus atoms.

**Solution:**

- (a) Hypophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_6$ ) has a symmetrical molecular structure that contains a direct phosphorus-phosphorus (P – P) bond. Its structural arrangement can be written as  $(\text{HO})_2\text{P}(=\text{O}) - \text{P}(=\text{O})(\text{OH})_2$ .
- (b) Let us calculate the formal oxidation state of phosphorus in hypophosphoric acid. Hydrogen has an oxidation state of +1 and oxygen has an oxidation state of -2. Setting up the charge balance equation gives:  $4(+1) + 2(x) + 6(-2) = 0 \implies 4 + 2x - 12 = 0 \implies 2x = 8 \implies x = +4$ .
- (c) Pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) features a bridging oxygen atom that links the two phosphorus atoms, forming a P – O – P bond anhydride linkage. The oxidation state of phosphorus in this molecule is +5.
- (d) Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) contains a single phosphorus atom bonded to one oxo oxygen atom and three hydroxyl groups, giving it an oxidation state of +5.
- (e) Pyrophosphorous acid ( $\text{H}_4\text{P}_2\text{O}_5$ ) contains a bridging P – O – P linkage along with direct P – H bonds, giving its phosphorus atoms an oxidation state of +3.

**Final Answer:** The oxoacid is Hypophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_6$ ).

**Answer:** (A)

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Q12.

**Solution****Concept:**

The magnetic properties of transition metal complexes are governed by the distribution of electrons within their  $d$ -orbitals. According to the spin-only formula, the magnetic moment ( $\mu_s$ ) depends directly on the number of unpaired electrons ( $n$ ) present in the metal ion. A higher number of unpaired electrons results in a larger spin-only magnetic moment, which can be calculated using the mathematical relationship  $\mu_s = \sqrt{n(n+2)}$  Bohr Magnetons (BM).

**Solution:**

- (a) We determine the ground-state electronic configuration and number of unpaired electrons for each transition metal ion in its aqueous form. Titanium has an atomic number of 22. The  $\text{Ti}^{3+}$  ion has a  $d^1$  electronic configuration, which means it contains 1 unpaired electron ( $n = 1$ ).
- (b) Chromium has an atomic number of 24. The  $\text{Cr}^{3+}$  ion has a  $d^3$  electronic configuration, which means it contains 3 unpaired electrons ( $n = 3$ ).
- (c) Manganese has an atomic number of 25. The  $\text{Mn}^{2+}$  ion has a  $d^5$  electronic configuration. Water acts as a weak field ligand that does not cause electron pairing in the  $d$ -orbitals, leaving all 5 electrons unpaired ( $n = 5$ ).
- (d) Iron has an atomic number of 26. The  $\text{Fe}^{2+}$  ion has a  $d^6$  electronic configuration. In the presence of weak field water ligands, these 6 electrons are distributed to maximize spin, resulting in 4 unpaired electrons ( $n = 4$ ).
- (e) Comparing these values shows that the  $\text{Mn}^{2+}$  ion has the highest number of unpaired electrons ( $n = 5$ ). This configuration gives it a maximum spin-only magnetic moment of  $\sqrt{5(5+2)} = \sqrt{35} \approx 5.92$  BM.

**Final Answer:** The ion that exhibits the maximum magnetic moment is  $\text{Mn}^{2+}$ .

**Answer:** (C)

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Q13.

**Solution****Concept:**

Coordination chemistry uses stereoisomerism to describe complexes that share the same chemical formula and atom connectivity but differ in how their ligands are arranged in space. For octahedral coordination geometries, stereoisomers can be divided into geometric isomers (such as cis and trans arrangements) and optical isomers (enantiomeric pairs that form non-superimposable mirror images).

**Solution:**

- (a) The coordination complex compound  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  features a central cobalt metal ion surrounded by two bidentate ethylenediamine (en) ligands and two monodentate chloride ligands. This complex forms two distinct geometric isomers: a cis isomer and a trans isomer.
- (b) In the trans-isomer configuration, the two monodentate chloride ligands are positioned exactly opposite each other at an angle of  $180^\circ$ . This symmetrical arrangement introduces an internal plane of symmetry into the molecule, making the trans-isomer achiral and optically inactive.
- (c) In the cis-isomer configuration, the two chloride ligands are positioned adjacent to each other at an angle of  $90^\circ$ . This asymmetrical arrangement lacks an internal plane of symmetry, making the cis-isomer chiral.
- (d) Because it is chiral, the cis-isomer exists as a pair of non-superimposable mirror images, forming a dextrorotatory (*d*) enantiomer and a levorotatory (*l*) enantiomer.
- (e) Counting the total number of stereoisomers gives: 1 optically inactive trans-isomer + 2 optically active cis-enantiomers = 3 stereoisomers.

**Final Answer:** The total number of possible stereoisomers is 3.

**Answer: (B)**

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Q14.

**Solution****Concept:**

Environmental chemistry distinguishes between different air pollution phenomena based on their chemical composition, meteorological conditions, and formation mechanisms. Smog is generally categorized into two main types: classical (London) smog and photochemical (Los Angeles) smog. Classical smog forms in cool, humid climates and is chemically reducing because it contains high concentrations of sulfur compounds.

**Solution:**

- (a) Classical smog was first identified in London during industrial periods characterized by heavy coal combustion. Burning coal releases large amounts of sulfur dioxide gas ( $\text{SO}_2$ ) and particulate soot into the atmosphere.
- (b) The high concentration of sulfur dioxide gives classical smog its characteristic reducing chemical nature. It thrives in cool, damp winter conditions where moisture helps convert sulfur gases into acidic aerosols.
- (c) Photochemical smog forms in warm, dry, and sunny urban environments with heavy automobile traffic. Its formation is driven by solar radiation, which triggers photochemical reactions among nitrogen oxides ( $\text{NO}_x$ ) and volatile hydrocarbons.
- (d) This solar-driven process generates highly oxidizing secondary pollutants such as ozone ( $\text{O}_3$ ), peroxyacetyl nitrates (PAN), and nitrogen dioxide ( $\text{NO}_2$ ).
- (e) Since  $\text{NO}_2$ ,  $\text{O}_3$ , and hydrocarbons are primary components or drivers of photochemical smog, sulfur dioxide ( $\text{SO}_2$ ) is the component responsible for classical smog.

**Final Answer:** The pollutant responsible for classical smog is  $\text{SO}_2$ .

**Answer: (C)**

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Q15.

**Solution****Concept:**

The systematic nomenclature of organic compounds follows rules established by the International Union of Pure and Applied Chemistry (IUPAC). To determine the correct name of a multi-functional organic molecule, we must establish a hierarchy of principal functional groups, identify the longest continuous carbon chain containing those groups, number the chain to give the principal group the lowest locant, and list all substituents alphabetically.

**Solution:**

- (a) We examine the given organic structure:  $\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{COOH}$ . The molecule contains two functional groups: a carboxylic acid group ( $-\text{COOH}$ ) and a hydroxyl group ( $-\text{OH}$ ).
- (b) According to IUPAC priority rules, the carboxylic acid group has higher priority than the hydroxyl alcohol group. This means the acid group serves as the principal functional group, which defines the suffix of the molecule as "-anoic acid".
- (c) The longest continuous carbon chain containing the carboxylic acid carbon atom consists of 5 carbon atoms, making the parent alkane name pentane.
- (d) We number the carbon chain starting directly with the carboxylic acid carbon atom as C-1 to give it the lowest possible locant:  $\text{C}^5\text{H}_3 - \text{C}^4\text{H}(\text{OH}) - \text{C}^3\text{H}_2 - \text{C}^2(\text{CH}_3)_2 - \text{C}^1\text{OOH}$ .
- (e) We identify and locate the substituents on this numbered chain. Carbon-2 holds two methyl groups ( $-\text{CH}_3$ ), which are designated as "2,2-dimethyl". Carbon-4 holds the lower-priority hydroxyl group, which is treated as a prefix designated as "4-hydroxy".
- (f) Combining these parts alphabetically ("hydroxy" comes before "methyl") gives the full systematic name: 4-Hydroxy-2,2-dimethylpentanoic acid.

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

**Answer: (A)**

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## Q16.

**Solution****Concept:**

Ozonolysis is an organic reaction that cleaves the unsaturated bonds of alkenes, alkynes, or azo compounds using ozone ( $O_3$ ). The oxidative cleavage of an alkene breaks both the  $\sigma$  and  $\pi$  bonds of the carbon-carbon double bond, replacing them with two distinct carbon-oxygen double bonds. By analyzing the carbonyl fragments produced after reductive workup with zinc and water ( $Zn/H_2O$ ), we can deduce the structure of the original alkene through a retro-synthetic approach.

**Solution:**

- The problem states that the reductive ozonolysis of alkene  $X$  yields an equimolar mixture of two specific carbonyl compounds: propan-2-one (acetone) and formaldehyde (methanal).
- We write out the chemical structures of these two product molecules. Propan-2-one is a ketone with the structure  $(CH_3)_2C = O$ , and formaldehyde is an aldehyde with the structure  $H_2C = O$ .
- To reconstruct the original alkene  $X$ , we remove the two oxygen atoms from these carbonyl groups and join the remaining fragments together with a carbon-carbon double bond ( $C = C$ ).
- Aligning the carbonyl carbons facing each other gives:  $(CH_3)_2C = O + O = CH_2$ . Connecting them directly yields the alkene structure:  $(CH_3)_2C = CH_2$ .
- We name this reconstructed alkene according to systematic IUPAC nomenclature rules. The longest continuous carbon chain containing the double bond has three carbon atoms, making the parent alkene prop-1-ene.
- There is a methyl substituent located on the second carbon atom. This gives the full systematic name: 2-Methylprop-1-ene.

**Final Answer:** The structural identity of alkene  $X$  is 2-Methylprop-1-ene.

**Answer: (A)**

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Q17.

**Solution****Concept:**

Nucleophilic substitution reactions of alkyl halides can proceed via two primary mechanistic pathways: the  $S_N1$  mechanism or the  $S_N2$  mechanism. The  $S_N1$  pathway is a two-step process whose rate is determined by the ionization step, where the leaving group departs to form a carbocation intermediate. The absolute rate of an  $S_N1$  reaction depends primarily on the thermodynamic stability of this carbocation intermediate and the leaving group ability.

**Solution:**

- Aqueous ethanol is a polar protic solvent mixture. Polar protic solvents stabilize ionic intermediates through hydrogen bonding, which favors the  $S_N1$  ionization mechanism.
- We evaluate the carbocation intermediate formed by each alkyl halide option upon ionization. Option (A) is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ , a primary alkyl chloride that ionizes to form a highly unstable  $1^\circ$  propyl carbocation.
- Option (B) is  $(\text{CH}_3)_3\text{C} - \text{Cl}$  (tert-butyl chloride), a tertiary alkyl halide that ionizes to form a  $3^\circ$  tert-butyl carbocation. This carbocation is highly stabilized by nine hyperconjugative hydrogens and electron-donating inductive effects.
- Option (C) is  $(\text{CH}_3)_2\text{CH} - \text{Cl}$  (isopropyl chloride), a secondary alkyl halide that forms a moderately stable  $2^\circ$  carbocation.
- Option (D) is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ , which forms an unstable  $1^\circ$  carbocation despite having a better leaving group than the chlorides.
- Because tertiary carbocations are much more stable than secondary and primary carbocations, tert-butyl chloride forms its intermediate with a significantly lower activation energy. This allows it to react via the  $S_N1$  pathway at the fastest absolute rate.

**Final Answer:** The alkyl halide that reacts fastest via the  $S_N1$  pathway is  $(\text{CH}_3)_3\text{C} - \text{Cl}$ .

**Answer: (B)**

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Q18.

**Solution****Concept:**

Electrophilic aromatic substitution is a reaction where an atom attached to an aromatic ring is replaced by an electrophile. The reactivity of the aromatic ring depends heavily on the substituents already present. Phenol contains a hydroxyl group ( $-\text{OH}$ ) attached directly to the benzene ring. The lone pairs on the oxygen atom undergo strong resonance donation into the ring system, making the hydroxyl group a highly activating substituent and a strong ortho/para-director.

**Solution:**

- Water is a highly polar solvent that can ionize phenol into a phenoxide ion ( $\text{C}_6\text{H}_5\text{O}^-$ ). The negatively charged oxygen atom in the phenoxide ion donates electron density into the aromatic ring even more strongly than a neutral hydroxyl group.
- This high electron density strongly activates the ortho and para positions of the aromatic ring toward electrophilic attack.
- Bromine water ( $\text{Br}_2/\text{H}_2\text{O}$ ) provides a high concentration of electrophilic bromine species. Because the aromatic ring is so highly activated, bromination occurs rapidly and repeatedly without needing a Lewis acid catalyst like  $\text{FeBr}_3$ .
- Substitution happens simultaneously at all available activated positions, which include both ortho positions (carbon-2 and carbon-6) and the single para position (carbon-4) relative to the hydroxyl group.
- This multiple substitution reaction replaces three hydrogen atoms on the ring with bromine atoms, forming 2,4,6-tribromophenol.
- 2,4,6-Tribromophenol has a symmetrical, non-polar structure that is insoluble in water. It precipitates out of the aqueous reaction mixture as a characteristic white solid.

**Final Answer:** The major organic product obtained is 2,4,6-Tribromophenol.

**Answer:** (C)

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Q19.

**Solution****Concept:**

Carbonyl condensation reactions involve the addition of an enol or enolate ion from one carbonyl compound to the carbonyl carbon of another. The Claisen-Schmidt reaction is a specialized crossed aldol condensation that occurs between an aromatic aldehyde lacking  $\alpha$ -hydrogens and an aliphatic ketone or alkyl aryl ketone that possesses accessible  $\alpha$ -hydrogens.

**Solution:**

- We examine the two reacting structures. Benzaldehyde ( $C_6H_5CHO$ ) is an aromatic aldehyde that does not contain any  $\alpha$ -hydrogens, meaning it cannot form an enol or enolate ion in the presence of a base.
- Acetophenone ( $C_6H_5COCH_3$ ) is an alkyl aryl ketone that contains three highly acidic  $\alpha$ -hydrogens on its methyl group.
- In the presence of a dilute base, a hydroxide ion removes one of these acidic  $\alpha$ -hydrogens from acetophenone to form a resonance-stabilized nucleophilic enolate ion:  $C_6H_5COCH_2^-$ .
- This enolate ion attacks the electrophilic carbonyl carbon atom of benzaldehyde. This addition forms a  $\beta$ -hydroxyketone intermediate known as an aldol product.
- Under the reaction conditions, this intermediate undergoes spontaneous dehydration (loss of a water molecule) driven by the formation of an extended conjugated system. This produces a stable  $\alpha, \beta$ -unsaturated ketone called chalcone ( $C_6H_5CH = CHCOCH_3$ ).
- This specific condensation between an aromatic aldehyde and a ketone is called the Claisen-Schmidt reaction.

**Final Answer:** The reaction described is an example of the Claisen-Schmidt reaction.

**Answer: (B)**

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Q20.

**Solution****Concept:**

The stability of diazonium salts ( $R - N_2^+X^-$ ) formed during the diazotization of primary amines depends heavily on the organic group (R) attached to the diazonium function. Aromatic diazonium salts are stabilized at low temperatures ( $0 - 5^\circ\text{C}$ ) because the positive charge on the nitrogen atom can be delocalized into the  $\pi$ -system of the benzene ring through resonance. Aliphatic diazonium salts lack this resonance stabilization and are highly unstable.

**Solution:**

- When a primary amine is treated with nitrous acid (generated in situ from  $\text{NaNO}_2 + \text{HCl}$ ), it undergoes diazotization to form a diazonium cation.
- In aniline and *p*-toluidine, the amino group is attached directly to an aromatic benzene ring. This creates an aryl diazonium ion that is stabilized by resonance, allowing it to remain stable in solution at  $0 - 5^\circ\text{C}$ .
- In benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ), the nitrogen atom is bonded to an  $\text{sp}^3$  hybridized benzylic carbon rather than directly to the aromatic ring. This isolates the diazonium group from the ring's  $\pi$ -system, preventing resonance stabilization.
- Cyclohexylamine ( $\text{C}_6\text{H}_{11}\text{NH}_2$ ) is a primary aliphatic amine that forms a purely aliphatic diazonium salt upon diazotization.
- Aliphatic diazonium salts are highly unstable even at  $0^\circ\text{C}$ . They decompose rapidly to release nitrogen gas ( $\text{N}_2$ ) and form a highly reactive carbocation intermediate.
- This carbocation reacts immediately with the aqueous solvent to produce a mixture of alcohols, alkenes, and alkyl chlorides, along with the visible evolution of nitrogen gas bubbles.

**Final Answer:** Cyclohexylamine immediately evolves nitrogen gas because it forms an unstable aliphatic diazonium salt.

**Answer: (D)**

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Q21.

**Solution****Concept:**

Carbohydrates are classified as reducing or non-reducing sugars based on their ability to act as reducing agents in the presence of mild oxidizing solutions like Tollen's or Fehling's reagents. A sugar acts as a reducing sugar if it contains a free, unlinked anomeric carbon atom that can undergo mutarotation to open into a reactive chain form with a free aldehyde or ketone group. In disaccharides, if the glycosidic bond links the anomeric carbons of both monosaccharide units, the sugar loses its reducing capability.

**Solution:**

- We evaluate the structural linkage of the listed disaccharides. Maltose is composed of two glucose units connected by an  $\alpha(1 \rightarrow 4)$  glycosidic bond. This leaves the anomeric carbon of the second glucose unit free, making maltose a reducing sugar.
- Lactose consists of galactose and glucose units joined by a  $\beta(1 \rightarrow 4)$  glycosidic linkage. The anomeric carbon at position 1 of the glucose residue remains unbonded, allowing it to reduce mild oxidizing agents.
- Sucrose is a disaccharide formed by joining a glucose unit and a fructose unit. The glycosidic bond connects the anomeric carbon 1 of  $\alpha$ -D-glucose with the anomeric carbon 2 of  $\beta$ -D-fructose.
- Because both reactive anomeric centers are locked within the glycosidic bond, neither ring can open into a chain form containing a free carbonyl group. This structural feature prevents sucrose from reducing Tollen's or Fehling's reagents, making it a non-reducing sugar.
- Cellobiose consists of two glucose units joined by a  $\beta(1 \rightarrow 4)$  bond, leaving one anomeric center free to act as a reducing site.

**Final Answer:** The non-reducing disaccharide sugar is Sucrose.

**Answer:** (C)

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Q22.

**Solution****Concept:**

Synthetic rubbers are high-molecular-weight polymers engineered through polymerization mechanisms to mimic or improve upon the mechanical properties of natural rubber. Elastomers like Buna-N are copolymer products, meaning they are synthesized by polymerizing a mixture of two or more distinct monomer species. The name itself serves as an abbreviation that reflects its chemical composition and polymerization catalyst.

**Solution:**

- We break down the nomenclature of the synthetic elastomer Buna-N to identify its components. The syllable "Bu" represents 1,3-butadiene, which serves as the primary conjugated diene monomer in the structure.
- The syllable "Na" denotes sodium metal (Na), which was historically used as the chemical initiator or catalyst to drive the addition polymerization reaction.
- The letter "N" signifies the presence of a nitrile group, which comes from the specific co-monomer acrylonitrile.
- Therefore, Buna-N is chemically classified as a butadiene-acrylonitrile copolymer. It is produced by combining 1,3-butadiene ( $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ ) and acrylonitrile ( $\text{CH}_2 = \text{CH} - \text{CN}$ ) in a typical ratio of approximately three to one.
- Styrene is copolymerized with 1,3-butadiene to produce Buna-S rubber. Chloroprene is the single monomer used to synthesize neoprene rubber, and vinyl chloride polymerizes to form polyvinyl chloride.

**Final Answer:** The structure of Buna-N is derived from the copolymerization of 1,3-butadiene with Acrylonitrile.

**Answer: (B)**

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Q23.

**Solution****Concept:**

The empirical formula represents the simplest whole-number ratio of the different atoms present in a chemical compound. To find this formula from mass percent data, we determine the relative number of moles of each element by dividing its mass percentage by its atomic mass. We then divide each mole value by the smallest value in the set to obtain the simplest atomic ratio.

**Solution:**

- (a) We list the given mass percentages for the elements in the organic compound. The compound contains 40.0% Carbon and 6.67% Hydrogen by mass.
- (b) Since the compound is composed entirely of carbon, hydrogen, and oxygen, we calculate the remaining mass percentage for oxygen by subtracting the values of carbon and hydrogen from one hundred: Percent Oxygen =  $100.0\% - (40.0\% + 6.67\%) = 53.33\%$ .
- (c) We calculate the relative number of moles for each element in a 100 g sample. For Carbon, moles =  $\frac{40.0}{12.01} \approx 3.33$ . For Hydrogen, moles =  $\frac{6.67}{1.008} \approx 6.62$ . For Oxygen, moles =  $\frac{53.33}{16.00} \approx 3.33$ .
- (d) To find the simplest whole-number ratio, we divide each calculated mole value by the smallest value in the group, which is 3.33.
- (e) For Carbon, the ratio value is  $\frac{3.33}{3.33} = 1$ . For Hydrogen, the ratio value is  $\frac{6.62}{3.33} \approx 2$ . For Oxygen, the ratio value is  $\frac{3.33}{3.33} = 1$ .
- (f) This gives an atomic ratio of 1 : 2 : 1 for Carbon, Hydrogen, and Oxygen, which corresponds to the empirical formula  $\text{CH}_2\text{O}$ .

**Final Answer:** The empirical formula of the compound is  $\text{CH}_2\text{O}$ .

**Answer: (A)**

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Q24.

**Solution****Concept:**

The Bohr model of the atom introduces a quantized framework to describe the behavior of an electron orbiting a hydrogen nucleus. According to Bohr's postulates, an electron moves around the nucleus only in specific allowed circular orbits without radiating energy. The angular momentum of the electron in these orbits is restricted to integer multiples of Planck's constant divided by  $2\pi$ , which leads to quantized expressions for the allowable orbital radii.

**Solution:**

- (a) We use the mathematical derivation for the radius of an electron orbit from Bohr's theory. The balancing force required to maintain a circular orbit is provided by the electrostatic attraction between the positively charged nucleus and the negatively charged electron.
- (b) Combining the electrostatic force equation with the quantized angular momentum condition ( $mvr = \frac{nh}{2\pi}$ ) yields an explicit mathematical formula for the radius of the  $n$ -th orbit.
- (c) The mathematical expression for the radius is written as:  $r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 Z}$ .
- (d) In this equation,  $h$  represents Planck's constant,  $\epsilon_0$  is the permittivity of free space,  $m$  is the mass of an electron,  $e$  is the elementary electron charge,  $Z$  is the atomic number of the atom, and  $n$  is the principal quantum number.
- (e) For a hydrogen atom, the atomic number is constant ( $Z = 1$ ). All other terms in the equation except  $n$  are fundamental physical constants. This allows us to simplify the expression to:  $r_n = a_0 n^2$ , where  $a_0 \approx 0.529 \text{ \AA}$  is the Bohr radius.
- (f) This mathematical relationship demonstrates that the radius of the electron's orbit is directly proportional to the square of the principal quantum number ( $n^2$ ).

**Final Answer:** The radius of the orbit is directly proportional to  $n^2$ .

**Answer: (B)**

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Q25.

**Solution****Concept:**

Fajans' rules help predict whether a chemical bond will have predominantly ionic or covalent character by analyzing the polarizing power of the cation and the polarizability of the anion. When a cation approaches an anion, its positive charge attracts the electron cloud of the anion, distorting its shape. A higher degree of electron cloud distortion increases the sharing of electron density, which introduces greater covalent character into the chemical bond.

**Solution:**

- According to Fajans' rules, several factors favor high polarization and increased covalent character: a small cation size, a large anion size, and high ionic charges on either species.
- We examine the given series of compounds: LiCl, NaCl, KCl, and RbCl. All four compounds share the same chloride anion ( $\text{Cl}^-$ ), so the anion size and charge remain constant across the series.
- We compare the properties of the cations, which all carry a identical +1 charge:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$ .
- Moving down the first group of the periodic table, the ionic radius increases steadily:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$ . This means the lithium ion ( $\text{Li}^+$ ) is the smallest cation in the series.
- Because of its exceptionally small ionic radius, the lithium ion has the highest charge density (charge-to-size ratio) among the alkali metal cations. This high charge density gives it the strongest polarizing power.
- The highly polarizing  $\text{Li}^+$  ion strongly distorts the adjacent electron cloud of the chloride anion, which introduces the highest magnitude of covalent character in LiCl.

**Final Answer:** The compound displaying the highest covalent character is LiCl.

**Answer:** (A)

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Q26.

**Solution****Concept:**

The liquefaction of real gases depends on their intermolecular attractive forces, which can be quantified using the van der Waals constants or evaluated using critical constants. The critical temperature ( $T_c$ ) is defined as the maximum temperature at which a gas can be converted into its liquid state by the application of external pressure. Above this temperature, the kinetic energy of the gas molecules is too high to be overcome by pressure alone, meaning the gas cannot be liquefied regardless of how much pressure is applied.

**Solution:**

- (a) A higher critical temperature indicates that a gas has stronger intermolecular attractive forces (such as dipole-dipole interactions or London dispersion forces) holding its molecules together.
- (b) When a real gas possesses strong internal attractive forces, its molecules tend to cluster together more easily at higher temperatures. This makes the gas much easier to liquefy by standard cooling and compression techniques.
- (c) We compare the critical temperature values given for the four real gases:  $W$  (33 K),  $X$  (126 K),  $Y$  (154 K), and  $Z$  (304 K).
- (d) Gas  $Z$  has the highest critical temperature (304 K), which corresponds to  $31^\circ\text{C}$ . This indicates that gas  $Z$  has the strongest intermolecular attractions among the group, allowing it to remain in a liquid state at or near room temperature.
- (e) Because its molecules aggregate easily, gas  $Z$  requires the least amount of cooling to undergo a phase transition, making it the most easily liquefied gas in the series.
- (f) Conversely, gas  $W$  has the lowest critical temperature (33 K), meaning it has very weak attractive forces and must be cooled close to absolute zero before it can be liquefied.

**Final Answer:** The gas that will be most easily liquefied is  $Z$ .

**Answer: (D)**

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Q27.

**Solution****Concept:**

The thermodynamic criterion for the spontaneity of a chemical or physical process is determined by the change in Gibbs Free Energy ( $\Delta G$ ), which is defined at a constant temperature and pressure by the Gibbs-Helmholtz equation:  $\Delta G = \Delta H - T\Delta S$ . For any process to occur spontaneously, the total change in Gibbs Free Energy must be strictly negative ( $\Delta G < 0$ ). This net value depends on the balance between the enthalpy factor ( $\Delta H$ ) and the entropy factor ( $\Delta S$ ).

**Solution:**

- Let us analyze how the mathematical terms in the Gibbs-Helmholtz equation behave under different algebraic conditions to ensure that  $\Delta G$  remains negative at all temperatures.
- First, we consider the enthalpy change ( $\Delta H$ ). If a process is exothermic, its enthalpy change is negative ( $\Delta H < 0$ ). A negative value directly contributes to making the overall free energy change negative.
- Next, we look at the entropy term, which enters the equation as  $-T\Delta S$ . The absolute temperature ( $T$ ) measured on the Kelvin scale is always positive ( $T > 0$ ).
- If a process leads to an increase in molecular randomness or disorder, its entropy change is positive ( $\Delta S > 0$ ). When  $\Delta S$  is positive, the product  $-T\Delta S$  becomes a negative value.
- When both conditions are met ( $\Delta H < 0$  and  $\Delta S > 0$ ), the Gibbs Free Energy equation combines two negative terms:  $\Delta G = (\text{negative value}) + (\text{negative value})$ .
- Because both components are negative, the resulting value for  $\Delta G$  will always be negative regardless of the magnitude of the absolute temperature ( $T$ ). Therefore, the process will be spontaneous under all conditions.

**Final Answer:** The thermodynamic criteria for a process to be spontaneous at all temperatures are  $\Delta H < 0$  and  $\Delta S > 0$ .

**Answer:** (A)

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Q28.

**Solution****Concept:**

The rate of a chemical reaction is sensitive to changes in the temperature of the system. This relationship is quantified by the temperature coefficient ( $\eta$ ), which represents the ratio of the rate constants measured at temperatures differing by exactly ten degrees Celsius. For many common reactions, the rate of reaction doubles or triples for every ten-degree rise in temperature. The total increase in the reaction rate over a larger temperature interval can be calculated using an exponential relationship.

**Solution:**

- The problem states that the rate of the chemical reaction doubles for every  $10^\circ\text{C}$  rise in temperature, which means the temperature coefficient for this reaction is  $\eta = 2$ .
- We calculate the total temperature change ( $\Delta T$ ) by subtracting the initial temperature from the final temperature:  $\Delta T = 65^\circ\text{C} - 25^\circ\text{C} = 40^\circ\text{C}$ .
- Next, we determine the number of ten-degree intervals ( $n$ ) contained within this total temperature change by dividing  $\Delta T$  by ten:  $n = \frac{40^\circ\text{C}}{10^\circ\text{C}} = 4$ .
- The final reaction rate ( $R_2$ ) is related to the initial reaction rate ( $R_1$ ) by an exponential formula based on the number of intervals:  $\frac{R_2}{R_1} = (\eta)^n$ .
- Substituting our values into this formula gives:  $\frac{R_2}{R_1} = (2)^4$ .
- Evaluating this power of two yields:  $2 \times 2 \times 2 \times 2 = 16$ .
- This means that raising the temperature from  $25^\circ\text{C}$  to  $65^\circ\text{C}$  causes the reaction rate to increase by a total factor of sixteen.

**Final Answer:** The reaction rate will increase by a total factor of 16.

**Answer:** (C)

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Q29.

**Solution****Concept:**

Balancing redox equations in an acidic medium requires tracking the transfer of electrons between the oxidizing agent and the reducing agent to ensure both mass and charge conservation. The ion-electron method divides the overall chemical reaction into two separate steps: an oxidation half-reaction and a reduction half-reaction. These individual steps are balanced independently for mass and charge before being combined into a single, balanced net ionic equation.

**Solution:**

- (a) We isolate and write out the reduction half-reaction for the permanganate ion. Manganese is reduced from an oxidation state of +7 in  $\text{MnO}_4^-$  to +2 in  $\text{Mn}^{2+}$ . The balanced reduction equation including hydrogen ions and water is:  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ .
- (b) Next, we isolate and write out the oxidation half-reaction for the oxalate ion. Carbon is oxidized from an oxidation state of +3 in  $\text{C}_2\text{O}_4^{2-}$  to +4 in  $\text{CO}_2$ . The balanced oxidation equation is:  $\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^-$ .
- (c) To balance the total electron transfer, the number of electrons lost during oxidation must equal the number of electrons gained during reduction. The least common multiple for the electron counts ( $5e^-$  and  $2e^-$ ) is ten.
- (d) We multiply the entire reduction half-reaction by a factor of two:  $2\text{MnO}_4^- + 16\text{H}^+ + 10e^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ .
- (e) We multiply the entire oxidation half-reaction by a factor of five:  $5\text{C}_2\text{O}_4^{2-} \rightarrow 10\text{CO}_2 + 10e^-$ .
- (f) Adding these two half-reactions together cancels the ten electrons from both sides, yielding the final balanced net ionic equation:  $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$ .
- (g) Matching this with the coefficients in the question gives  $x = 2$ ,  $y = 5$ , and  $z = 16$ .

**Final Answer:** The stoichiometric coefficients are 2, 5, and 16.

**Answer:** (A)

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Q30.

**Solution****Concept:**

Interstitial compounds form when small non-metal atoms, such as hydrogen, boron, carbon, or nitrogen, diffuse into the vacant interstitial spaces or cavities within the crystal lattices of transition metals. These substances do not adopt standard covalent or ionic geometries. Instead, they are unique materials whose properties are a blend of metallic behavior and altered physical constraints caused by the presence of the trapped atoms.

**Solution:**

- (a) We analyze the physical and chemical characteristics of interstitial hydrides to evaluate the accuracy of each statement. Statement (A) states that they retain metallic conductivity. This is fully correct; the host metal lattice maintains its free electron delocalization, allowing these hydrides to conduct electricity and heat efficiently.
- (b) Statement (B) states that they are highly non-stoichiometric. This is also correct; because the non-metal atoms simply occupy variable fractions of the available lattice holes, their formulas cannot be expressed by simple whole-number ratios (for example,  $\text{TiH}_{1.73}$  or  $\text{VnH}_{0.56}$ ).
- (c) Statement (C) notes that they are significantly harder than the parent metals. This is correct because the interstitial atoms lock the metal layers in place, preventing them from sliding past one another easily. This increases hardness and brittleness.
- (d) Statement (D) claims that they are chemical compounds held together by fixed ionic bonds. This statement is fundamentally incorrect. The binding forces in interstitial structures remain primarily metallic, and there is no fixed electron transfer or ionic bonding network between the atoms.

**Final Answer:** The incorrect statement is that they are chemical compounds with fixed ionic bonds.

**Answer: (D)**

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Q31.

**Solution****Concept:**

The standard electromotive force ( $E^\circ$ ) of an electrochemical cell is directly linked to the thermodynamic equilibrium constant ( $K_c$ ) of the underlying redox reaction. At equilibrium, the net chemical driving force of the cell drops to zero, making the cell potential ( $E_{\text{cell}}$ ) exactly zero. Under these conditions, the Nernst equation simplifies to a direct relationship where the standard cell potential determines the logarithm of the equilibrium constant.

**Solution:**

- (a) The given cell reaction is:  $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s)$ . In this redox process, a zinc atom undergoes a two-electron oxidation to form a zinc ion ( $\text{Zn}^{2+}$ ), while a copper ion ( $\text{Cu}^{2+}$ ) undergoes a two-electron reduction to form metallic copper. This gives a total number of transferred electrons of  $n = 2$ .
- (b) The standard cell potential at  $25^\circ\text{C}$  (298 K) is given as  $E^\circ = 1.10 \text{ V}$ .
- (c) We apply the simplified form of the Nernst equation at 298 K:  $E^\circ = \frac{0.0591}{n} \log(K_c)$ .
- (d) Substituting our known values into this equation gives:  $1.10 = \frac{0.0591}{2} \log(K_c)$ .
- (e) Rearranging the equation to isolate the logarithm term yields:  $\log(K_c) = \frac{1.10 \times 2}{0.0591} = \frac{2.20}{0.0591} \approx 37.22$ .
- (f) To solve for the equilibrium constant  $K_c$ , we take the inverse logarithm (base 10) of both sides:  $K_c = 10^{37.22} = 1.66 \times 10^{37}$ .
- (g) This mathematical result shows that the equilibrium constant for this spontaneous displacement reaction is approximately of the order of  $10^{37}$ .

**Final Answer:** The equilibrium constant is approximately of the order of  $10^{37}$ .

**Answer: (B)**

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Q32.

**Solution****Concept:**

The elevation of boiling point ( $\Delta T_b$ ) is a colligative property, meaning its magnitude depends entirely on the total number or concentration of solute particles present in the solution rather than their chemical identity. For solutions containing volatile or non-volatile electrolytes, we must account for ionic dissociation using the van 't Hoff factor ( $i$ ). When multiple solute species coexist in a single solution, the total boiling point elevation is determined by the combined effective molalities of all the solute particles.

**Solution:**

- (a) We calculate the net elevation in the boiling point of the solution. The measured boiling point of the combined aqueous mixture is  $100.52^\circ\text{C}$ , and the standard boiling point of pure water is  $100.00^\circ\text{C}$ . This gives a boiling point elevation of:  $\Delta T_b = 100.52^\circ\text{C} - 100.00^\circ\text{C} = 0.52^\circ\text{C}$ .
- (b) The mathematical equation for boiling point elevation is written as:  $\Delta T_b = K_b \times m_{\text{effective}}$ , where  $m_{\text{effective}}$  represents the total effective molality of all particles in the solution.
- (c) Substituting the given values ( $\Delta T_b = 0.52$  and  $K_b = 0.52$ ) into this formula gives:  $0.52 = 0.52 \times m_{\text{effective}} \implies m_{\text{effective}} = 1.0 \text{ m}$ .
- (d) The total effective molality is the sum of the particles contributed by the electrolyte calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , and the unknown non-electrolyte solute:  $m_{\text{effective}} = (i \times m_{\text{electrolyte}}) + m_{\text{non-electrolyte}}$ .
- (e) Calcium nitrate dissociates completely in water according to the equation:  $\text{Ca}(\text{NO}_3)_2 \rightarrow \text{Ca}^{2+} + 2\text{NO}_3^-$ . This produces three ions per formula unit, giving a van 't Hoff factor of  $i = 3$ .
- (f) The molality of the calcium nitrate is  $0.1 \text{ m}$ , so its effective particle concentration is  $3 \times 0.1 = 0.3 \text{ m}$ .
- (g) We substitute this value back into our total effective molality equation to find the concentration of the non-electrolyte:  $1.0 = 0.3 + m_{\text{non-electrolyte}} \implies m_{\text{non-electrolyte}} = 1.0 - 0.3 = 0.7 \text{ m}$ .

**Final Answer:** The molality of the non-electrolyte solute is  $0.7 \text{ m}$ .

**Answer: (A)**

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Q33.

**Solution****Concept:**

Crystal Field Theory (CFT) explains how the five d-orbitals of a transition metal ion split into different energy levels when surrounded by a sphere of electron-donating ligands. In an octahedral coordination field, the d-orbitals split into a lower-energy triplet state ( $t_{2g}$ ) and a higher-energy doublet state ( $e_g$ ). The distribution of electrons within these split levels depends on the relative magnitudes of the crystal field splitting energy ( $\Delta_o$ ) and the electron pairing energy ( $P$ ).

**Solution:**

- We look at the central transition metal ion in the complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Iron has an atomic number of 26. Since the water ligands are neutral, the iron atom has an oxidation state of +2, which corresponds to a  $d^6$  electronic configuration.
- Next, we evaluate the field strength of the surrounding ligands. According to the spectrochemical series, water ( $\text{H}_2\text{O}$ ) is classified as a weak-field ligand.
- Because water is a weak-field ligand, its crystal field splitting energy is smaller than the energy required to pair electrons within the same orbital ( $\Delta_o < P$ ).
- Since it is energetically easier for electrons to jump to the higher energy level than to pair up, the complex adopts a high-spin configuration. The six  $d$ -electrons are distributed to maximize the total spin, following Hund's rule of maximum multiplicity.
- The first five electrons enter the d-orbitals individually, placing three in the lower  $t_{2g}$  orbitals and two in the higher  $e_g$  orbitals. The remaining sixth electron must pair up in one of the lower  $t_{2g}$  orbitals.
- This distribution results in four electrons occupying the lower triplet state and two electrons occupying the higher doublet state, which is written as  $t_{2g}^4 e_g^2$ .

**Final Answer:** The complex matches the description  $\Delta_o < P$ , high spin,  $t_{2g}^4 e_g^2$ .

**Answer:** (A)

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Q34.

**Solution****Concept:**

The chemical reactivity of aromatic hydrocarbons depends on whether a reaction is conducted under catalytic conditions or radical-promoting conditions. Toluene ( $C_7H_8$ ) contains two potential reaction sites: the electron-rich aromatic benzene ring and the aliphatic methyl side chain ( $-CH_3$ ). The presence of a Lewis acid catalyst promotes electrophilic aromatic substitution on the ring, while heating or exposure to ultraviolet light in the absence of a catalyst promotes free-radical substitution along the side chain.

**Solution:**

- We identify compound *A* as toluene ( $C_6H_5CH_3$ ) based on its molecular formula,  $C_7H_8$ .
- In the first reaction, toluene is treated with chlorine gas ( $Cl_2$ ) in the presence of an iron(III) chloride catalyst ( $FeCl_3$ ). The Lewis acid catalyst polarizes the chlorine molecule to generate an electrophilic chloronium ion ( $Cl^+$ ).
- The methyl group on the toluene ring acts as an electron-donating substituent that activates the ring and directs substitution to the ortho and para positions. This electrophilic aromatic substitution produces a mixture of ortho-chlorotoluene and para-chlorotoluene, which represents compound *B*.
- In the second reaction, toluene is heated to its boiling point with chlorine gas without a Lewis acid catalyst. These thermal conditions cause the chlorine molecules to undergo homolytic cleavage, generating highly reactive chlorine free radicals.
- These radicals selectively abstract a hydrogen atom from the methyl side chain because the resulting benzyl radical is highly stabilized by resonance with the aromatic ring.
- This side-chain free-radical chlorination replaces one hydrogen atom on the methyl group with a chlorine atom, producing benzyl chloride ( $C_6H_5CH_2Cl$ ), which represents compound *C*.

**Final Answer:** Compounds *B* and *C* are *o/p*-chlorotoluene and benzyl chloride, respectively.

**Answer: (C)**

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Q35.

**Solution****Concept:**

Xenon fluorides are powerful fluorinating agents that undergo redox or halogen-exchange reactions when mixed with covalent inorganic Lewis acids or bases. When reacted with strong fluoride ion acceptors like antimony pentafluoride ( $\text{SbF}_5$ ), the xenon fluoride transfers a fluoride ion ( $\text{F}^-$ ) to the acceptor molecule. This ionic transformation generates a cationic xenon fluoride species and a stable polyfluorinated complex anion. The shapes of these resulting ions can be predicted using Valence Shell Electron Pair Repulsion (VSEPR) theory.

**Solution:**

- (a) When xenon tetrafluoride ( $\text{XeF}_4$ ) reacts with the strong Lewis acid antimony pentafluoride ( $\text{SbF}_5$ ), it transfers a fluoride ion to form an adduct compound. The chemical equation for this ionization reaction is written as:  $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$ .
- (b) We determine the spatial configuration of the resulting cationic part,  $[\text{XeF}_3]^+$ . The central xenon atom belongs to the noble gas group and initially has 8 valence electrons. Losing one electron to form the cation leaves it with 7 valence electrons.
- (c) Three of these valence electrons form single covalent bonds with three fluorine atoms, leaving four non-bonding electrons that form two distinct lone pairs. This gives the central xenon atom a steric number of 5 (3 bonding pairs + 2 lone pairs), which corresponds to a trigonal bipyramidal electron-pair geometry.
- (d) According to VSEPR rules, the two lone pairs occupy the more spacious equatorial positions to minimize electronic repulsion. This leaves the three fluorine atoms in the remaining positions, giving the  $[\text{XeF}_3]^+$  cation a T-shaped molecular geometry.
- (e) Next, we analyze the anionic part,  $[\text{SbF}_6]^-$ . The central antimony atom has 5 valence electrons. Gaining a fluoride ion provides an additional electron and forms 6 bonding pairs with no remaining lone pairs.
- (f) A steric number of 6 with zero lone pairs results in a symmetrical octahedral molecular geometry for the  $[\text{SbF}_6]^-$  anion.

**Final Answer:** The configurations of the cationic and anionic parts are T-shaped and Octahedral, respectively.

**Answer: (A)**

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Q36.

**Solution****Concept:**

Molecular Orbital Theory determines the bond order and magnetic nature of ions.

**Solution:**

The  $O_2^+$  ion contains 15 electrons. Its molecular orbital configuration is:  $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 (\pi_{2p_x}^2 = \pi_{2p_y}^2) (\pi_{2p_x}^{*1} = \pi_{2p_y}^{*0})$ . This configuration has 10 bonding electrons ( $N_b$ ) and 5 antibonding electrons ( $N_a$ ). The bond order is calculated as  $\frac{1}{2}(10 - 5) = 2.5$ . The single unpaired electron in the antibonding  $\pi^*$  orbital makes the ion paramagnetic. Because its bond order is higher than that of neutral  $O_2$  (2.0),  $O_2^+$  possesses a shorter bond length. Thus, statements (A), (B), (C), and (D) are correct.

**Final Answer:**

**Answer:** (A,B,C,D)

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Q37.

**Solution****Concept:**

Le Chatelier's principle shifts gaseous equilibria to oppose concentration or volume changes.

**Solution:**

For  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ , the gaseous mole change is  $\Delta n_g = 2 - 1 = +1$ . Increasing total pressure favors the reactant side with fewer gas moles. Adding an inert gas at constant volume leaves the concentrations unaltered, causing no shift. Decreasing the partial pressure of product  $Cl_2$  gas shifts the equilibrium forward to replace it. Increasing the container volume lowers total pressure, shifting the reaction forward toward more gas moles. Thus, modifications (C) and (D) shift the position to the right.

**Final Answer:**

**Answer:** (C,D)

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Q38.

**Solution****Concept:**

Distinct functional group tests differentiate aliphatic and aromatic aldehydes.

**Solution:**

Tollen's reagent oxidizes both acetaldehyde and benzaldehyde to form a silver mirror, failing to differentiate them. 2,4-DNP reacts with any carbonyl group to yield a hydrazone precipitate for both. However, Fehling's solution oxidizes aliphatic acetaldehyde to form a red  $\text{Cu}_2\text{O}$  precipitate, but it cannot oxidize resonance-stabilized aromatic benzaldehyde. The iodoform test ( $\text{I}_2/\text{NaOH}$ ) yields a yellow  $\text{CHI}_3$  precipitate with acetaldehyde due to its methyl carbonyl ( $\text{CH}_3\text{CO}-$ ) group, while benzaldehyde shows no reaction. Thus, tests (B) and (C) differentiate the two compounds.

**Final Answer:** **Answer:** (B,C)[Go Back to Question 38](#)

Q39.

**Solution****Concept:**

Geometrical isomerism requires restricted rotation where each center holds two distinct groups.

**Solution:**

In but-2-ene ( $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ ), each double-bonded carbon carries a distinct hydrogen atom and methyl group, enabling cis/trans forms. 1,2-Dimethylcyclopropane features a rigid ring with restricted single-bond rotation where carbon-1 and carbon-2 hold distinct substituents, allowing cis/trans isomers. Conversely, 1,1-dichloroprop-1-ene ( $\text{Cl}_2\text{C} = \text{CH} - \text{CH}_3$ ) has identical chlorine atoms on an alkene carbon, and 2-methylbut-2-ene has identical methyl groups on an alkene carbon, preventing isomerism. Thus, only molecules (A) and (B) exhibit geometrical isomerism.

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

Q40.

**Solution****Concept:**

Transition metal characteristics stem from a partially filled  $(n - 1)d$  subshell.

**Solution:**

The small energy gap between the  $(n - 1)d$  and  $ns$  subshells permits both to participate in bonding, leading to variable oxidation states. Empty or partially filled d-orbitals allow transition metals to serve as active catalytic centers by bonding with reactants. Most +2 transition metal ions contain unpaired d-electrons (like  $d^5 \text{Mn}^{2+}$ ), making them paramagnetic, not diamagnetic. Crystal field splitting splits the d-orbitals, enabling visible light absorption via  $d - d$  electronic transitions that create deeply colored complexes. Thus, statements (A), (B), and (D) are correct.

**Final Answer:**

**Answer:**

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## Answer Key

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

