WBJEE 2024 Chemistry Question Paper with Solutions

Time Allowed :180 minutes	**Maximum Marks :**200	**Total Questions :**155

General Instructions

Read the following instructions very carefully and strictly follow them:

1. The test is of 3 hours duration.
2. The question paper consists of 155 questions. The maximum marks are 200.
3. There are three parts in the question paper consisting of Physics, Chemistry and Mathematics.
4. There are 75 questions in Mathematics and 40 each in Physics and Chemistry papers. 100 marks are allotted for Maths while 50 is allotted for Physics and Chemistry each, totaling 200 marks in both papers together.
5. There are three categories of WBJEE questions asked in the exam.
   (i) Category 1: 1 mark is awarded for choosing the correct option. 1/4th mark is deducted for an incorrect answer.
   (ii) Category 2: only 1 option is correct. 2 marks are awarded for each correct answer. $\frac{1}{2}$ mark is deducted for an incorrect answer. (iii) Category 3: Category 3: more than 1 option is correct and all correct answers are to be chosen to receive 2 marks.

1. Identify the incorrect statement among the following:
Options:

1. Viscosity of liquid always decreases with increase in temperature.
2. Surface tension of liquid always decreases with increase in temperature.
3. Viscosity of liquid always increases in presence of impurity.
4. Surface tension of liquid always increases in presence of impurity.

Correct Answer: 3. Viscosity of liquid always increases in presence of impurity.
Solution: This question assesses the understanding of how temperature and impurities affect the physical properties of liquids, specifically viscosity and surface tension.

Step 1: Analyze Each Statement

1. Option 1: Viscosity decreases with increasing temperature.
   - Correct. Higher temperatures provide more kinetic energy to molecules, reducing intermolecular forces and thus viscosity.
2. Option 2: Surface tension decreases with increasing temperature.
   - Correct. Increased temperature disrupts cohesive forces at the liquid surface, lowering surface tension.

3. Option 3: Viscosity always increases with impurities.
   - Incorrect. While impurities can disrupt the flow, leading to increased viscosity, this is not always the case. Some impurities may decrease viscosity depending on their nature and interactions.

4. Option 4: Surface tension always increases with impurities.
   - Incorrect. The effect of impurities on surface tension varies. Surfactants, for example, decrease surface tension, whereas other types of impurities might increase it.

Step 2: Identify the Incorrect Statement
Option 3 is incorrect because the presence of impurities does not invariably increase viscosity; it depends on the specific interactions between the impurity and the liquid.

> Quick Tip
>
> Impurities can have varying effects on liquid properties. Surfactants typically reduce surface tension, while other impurities may either increase or decrease viscosity based on their chemical nature.

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2. Which of the following statements is true about the equilibrium constant and rate constant of a single-step chemical reaction?
Options:

1. Equilibrium constant may increase or decrease, but rate constant always increases with temperature.
2. Both equilibrium constant and rate constant increase with temperature.
3. Rate constant may increase or decrease, but equilibrium constant always increases with temperature.
4. Both equilibrium constant and rate constant decrease with temperature.

Correct Answer: 1. Equilibrium constant may increase or decrease, but rate constant always increases with temperature.
Solution: This question explores the relationship between temperature and both the equilibrium constant (K) and the rate constant (k) in the context of a single-step chemical reaction.

Step 1: Understand the Rate Constant
The rate constant (k) is governed by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

where:

- A = frequency factor
- E_a = activation energy
- R = gas constant
- T = temperature in Kelvin

As temperature (T) increases, the exponential term increases, leading to an increase in the rate constant (k). Therefore, k always increases with temperature.

Step 2: Analyze the Equilibrium Constant

The equilibrium constant (K) is related to the standard Gibbs free energy change (ΔG°) by:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where:

- ΔH = enthalpy change
- ΔS = entropy change

- For Exothermic Reactions ($\Delta H < 0$): Increasing temperature decreases K. - For Endothermic Reactions ($\Delta H > 0$): Increasing temperature increases K. Thus, the equilibrium constant (K) can either increase or decrease with temperature depending on whether the reaction is endothermic or exothermic.

Step 3: Determine the Correct Statement

Based on the above analysis:

- The rate constant (k) always increases with temperature.
- The equilibrium constant (K) may increase or decrease with temperature.

Therefore, the correct statement is:

Equilibrium constant may increase or decrease, but rate constant always increases with temperature.

> Quick Tip
>
> While the rate of a reaction consistently speeds up with rising temperature due to increased molecular collisions, the equilibrium position shifts based on the reaction's enthalpy change—enhancing or reducing the equilibrium constant accordingly.

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3. Equal volumes of aqueous solutions of 0.1 M HCl and 0.2 M H_2SO_4 are mixed. The concentration of H^+ ions in the resulting solution is:

Options:

1. 0.15 M
2. 0.30 M
3. 0.10 M
4. 0.25 M

Correct Answer: 4. 0.25 M.

Solution: This problem involves calculating the resulting concentration of hydrogen ions (H^+) when equal volumes of two acidic solutions are mixed.

Step 1: Determine the Initial H^+ Contributions

- HCl:

$$\text{Concentration} = 0.1\,\text{M}$$

HCl is a strong monoprotic acid, so it dissociates completely:

$$\text{HCl} \rightarrow H^+ + Cl^-$$

$$\text{Concentration of } H^+ = 0.1\,\text{M}$$

- H_2SO_4:

$$\text{Concentration} = 0.2\,\text{M}$$

H_2SO_4 is a strong diprotic acid, so it dissociates completely:

$$\text{H}_2\text{SO}_4 \rightarrow 2H^+ + SO_4^{2-}$$

$$\text{Concentration of } H^+ = 2 \times 0.2\,\text{M} = 0.4\,\text{M}$$

Step 2: Account for Dilution Upon Mixing
Equal volumes of the two solutions are mixed, effectively diluting each by half:

$$\text{Final concentration of } HCl = \frac{0.1\,\text{M}}{2} = 0.05\,\text{M}$$

$$\text{Final concentration of } H^+ \text{ from HCl} = 0.05\,\text{M}$$

$$\text{Final concentration of } H_2SO_4 = \frac{0.2\,\text{M}}{2} = 0.1\,\text{M}$$

$$\text{Final concentration of } H^+ \text{ from H}_2\text{SO}_4 = 2 \times 0.1\,\text{M} = 0.2\,\text{M}$$

Step 3: Calculate Total H^+ Concentration

$$\text{Total } H^+ \text{ concentration} = 0.05\,\text{M} + 0.2\,\text{M} = 0.25\,\text{M}$$

Therefore, the concentration of H^+ ions in the resulting solution is 0.25 M.

> Quick Tip
>
> When mixing solutions, always account for dilution by considering the change in volume. Additionally, remember the stoichiometry of acid dissociation to determine the total H^+ concentration.

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4. The correct order of boiling points of the given aqueous solutions is:
Options:

1. 1 N KNO_3 > 1 N NaCl > 1 N CH_3COOH > 1 N sucrose
2. 1 N KNO_3 = 1 N NaCl > 1 N CH_3COOH > 1 N sucrose
3. Same for all
4. 1 N KNO_3 = 1 N NaCl = 1 N CH_3COOH > 1 N sucrose

Correct Answer: 2. 1 N KNO_3 = 1 N NaCl > 1 N CH_3COOH > 1 N sucrose.
Solution: This problem requires us to determine the order of boiling points for different aqueous solutions based on their nature and concentration.

Step 1: Understand Colligative Properties
Boiling point elevation is a colligative property, meaning it depends on the number of solute particles in the solution, not their identity.
Step 2: Analyze Each Solution

- 1 N KNO_3:

$$KNO_3 \text{ is a strong electrolyte and dissociates into } K^+ \text{ and } NO_3^-.$$

$$\text{Total particles} = 2 \times 1\,\text{N} = 2\,\text{N}$$

- 1 N NaCl:

$$\text{NaCl is a strong electrolyte and dissociates into } Na^+ \text{ and } Cl^-.$$

$$\text{Total particles} = 2 \times 1\,\text{N} = 2\,\text{N}$$

- 1 N CH_3COOH:

$$CH_3COOH \text{ is a weak electrolyte and partially dissociates into } CH_3COO^- \text{ and } H^+.$$

$$\text{Total particles} < 2 \times 1\,\text{N}$$

- 1 N Sucrose:

$$\text{Sucrose is a non-electrolyte and does not dissociate in solution.}$$

$$\text{Total particles} = 1 \times 1\,\text{N} = 1\,\text{N}$$

Step 3: Rank the Solutions Based on Particle Count
Boiling point increases with the number of dissolved particles:

$$1\text{ N } KNO_3 = 1\text{ N NaCl} > 1\text{ N } CH_3COOH > 1\text{ N sucrose}$$

Therefore, the correct order of boiling points is 1 N KNO_3 = 1 N NaCl > 1 N CH_3COOH > 1 N sucrose.

Quick Tip

Colligative properties like boiling point elevation depend on the number of solute particles. Strong electrolytes dissociate completely, contributing more particles and resulting in higher boiling points compared to weak electrolytes and non-electrolytes.

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5. After the emission of a β-particle followed by an α-particle from $^{214}_{83}$Bi, the number of neutrons in the atom is:
Options:

1. 210
2. 128
3. 129
4. 82

Correct Answer: 2. 128.
Solution: In this problem, we are determining the number of neutrons in a bismuth ($^{214}_{83}$Bi) atom after it undergoes the emission of a β-particle followed by an α-particle.

Step 1: Analyze the Initial Nucleus
The initial nucleus is $^{214}_{83}$Bi, where:

$$\text{Atomic number (Z)} = 83 \quad \text{and} \quad \text{Mass number (A)} = 214$$

$$\text{Number of neutrons} = A - Z = 214 - 83 = 131$$

Step 2: Emission of a β-Particle
A β-particle (β^-) emission involves the transformation of a neutron into a proton, releasing an electron (β^-) and an antineutrino. This process increases the atomic number by 1 while keeping the mass number unchanged.

$$Z : 83 \to 84 \quad (83 + 1 = 84)$$

$$A : 214 \quad \text{(unchanged)}$$

$$\text{New nucleus: } ^{214}_{84}\text{Po}$$

$$\text{Number of neutrons} = A - Z = 214 - 84 = 130$$

Step 3: Emission of an α-Particle
An α-particle (α) emission involves the loss of 2 protons and 2 neutrons from the nucleus. This decreases both the atomic number and the mass number.

$$Z : 84 \to 82 \quad (84 - 2 = 82)$$

$$A : 214 \to 210 \quad (214 - 4 = 210)$$

$$\text{New nucleus: } ^{210}_{82}\text{Pb}$$

$$\text{Number of neutrons} = A - Z = 210 - 82 = 128$$

Thus, after the emission of a β-particle followed by an α-particle, the number of neutrons in the atom is 128.

Quick Tip

In nuclear reactions, remember that β-decay increases the atomic number by converting a neutron to a proton, while α-decay decreases both the atomic and mass numbers by two and four, respectively.

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6. Which hydrogen-like species will have the same radius as the 1$^{\text{st}}$ Bohr orbit of a hydrogen atom?
Options:

1. $n = 2$, Li^{2+}
2. $n = 2$, Be^{3+}
3. $n = 2$, He^{+}
4. $n = 3$, Li^{2+}

Correct Answer: 2. $n = 2$, Be^{3+}.
Solution: In this problem, we aim to find which hydrogen-like species has a Bohr radius equivalent to that of the first orbit of a hydrogen atom.

Step 1: Recall the Bohr Radius Formula for Hydrogen-like Ions
The radius of the n^{th} Bohr orbit for a hydrogen-like ion is given by:

$$r_n = \frac{n^2 a_0}{Z}$$

where:

- n = principal quantum number
- a_0 = Bohr radius for hydrogen (5.29177×10^{-11} meters)
- Z = atomic number

Step 2: Calculate the Radius for Each Option
We need to find the species where $r_n = a_0$ (radius of the first Bohr orbit of hydrogen).

1. Option 1: $n = 2$, Li^{2+} ($Z = 3$)

$$r_n = \frac{2^2 a_0}{3} = \frac{4}{3} a_0 \neq a_0$$

2. Option 2: $n = 2$, Be^{3+} ($Z = 4$)

$$r_n = \frac{2^2 a_0}{4} = \frac{4a_0}{4} = a_0$$

3. Option 3: $n = 2$, He^{+} ($Z = 2$)

$$r_n = \frac{2^2 a_0}{2} = \frac{4a_0}{2} = 2a_0 \neq a_0$$

4. Option 4: $n = 3$, Li^{2+} ($Z = 3$)

$$r_n = \frac{3^2 a_0}{3} = \frac{9a_0}{3} = 3a_0 \neq a_0$$

Step 3: Identify the Correct Species
Only Option 2 results in $r_n = a_0$, matching the first Bohr orbit radius of hydrogen.

Therefore, the hydrogen-like species with the same radius as the first Bohr orbit of a hydrogen atom is $n = 2$, Be^{3+}.

> Quick Tip
>
> The Bohr radius for hydrogen-like ions depends on both the principal quantum number and the atomic number. To match hydrogen's first orbit, adjust these parameters accordingly.

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7. For a first-order reaction with rate constant k, the slope of the plot of log **(reactant concentration) against time is:**
Options:

1. $\frac{k}{2.303}$
2. k
3. $-\frac{k}{2.303}$
4. $-k$

Correct Answer: 3. $-\frac{k}{2.303}$.
Solution: In this problem, we are determining the slope of a plot for a first-order reaction when plotting the logarithm of reactant concentration against time.

Step 1: Recall the Integrated Rate Law for a First-Order Reaction
For a first-order reaction, the integrated rate law is:

$$\ln[A] = -kt + \ln[A]_0$$

where:

- $[A]$ = concentration of reactant at time t
- k = rate constant
- $[A]_0$ = initial concentration

Step 2: Convert Natural Logarithm to Common Logarithm
To express the equation in terms of log, we use the conversion:

$$\log[A] = \frac{\ln[A]}{2.303}$$

Substituting the integrated rate law:

$$\log[A] = \frac{-kt + \ln[A]_0}{2.303} = -\frac{k}{2.303}t + \frac{\ln[A]_0}{2.303}$$

Step 3: Identify the Slope
The equation now resembles the slope-intercept form $y = mx + c$, where:

- $y = \log[A]$
- $x = t$
- $m = -\frac{k}{2.303}$ (slope)
- $c = \frac{\ln[A]_0}{2.303}$

Step 4: Conclusion
Thus, the slope of the plot of $\log[A]$ against time is $-\frac{k}{2.303}$.

Therefore, the slope is $-\frac{k}{2.303}$.

Quick Tip

For first-order reactions, plotting log concentration versus time yields a straight line with a slope of $-k/2.303$. This relationship helps in determining the rate constant k experimentally.

8. Number of moles of ions produced by the complete dissociation of one mole of Mohr's salt in water is:
Options:

1. 3
2. 4
3. 5
4. 6

Correct Answer: 3. 5.
Solution: In this problem, we need to determine the total number of moles of ions produced when one mole of Mohr's salt dissociates completely in water.

Step 1: Understand the Composition of Mohr's Salt
Mohr's salt is ammonium iron(II) sulfate with the formula $(NH_4)_2[Fe(SO_4)_2] \cdot 6H_2O$.
When dissolved in water, it dissociates completely as follows:

$$(NH_4)_2[Fe(SO_4)_2] \cdot 6H_2O \rightarrow 2\mathrm{NH_4^+} + \mathrm{Fe^{2+}} + 2\mathrm{SO_4^{2-}}$$

From this dissociation, the ions produced are:

- $2\,\mathrm{NH_4^+}$ (ammonium ions),
- $1\,\mathrm{Fe^{2+}}$ (iron(II) ion),
- $2\,\mathrm{SO_4^{2-}}$ (sulfate ions).

Step 2: Calculate Total Moles of Ions
Adding these, the total number of moles of ions produced from one mole of Mohr's salt is:

$$2 + 1 + 2 = 5\,\text{moles of ions.}$$

Therefore, one mole of Mohr's salt produces 5 moles of ions upon complete dissociation.

> **Quick Tip**
>
> When dealing with ionic salts, account for all ions produced during dissociation, including those from polyatomic ions and multiple cations or anions.

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9. Which of the following species exhibits both LMCT and paramagnetism?
Options:

1. $\mathrm{MnO_4^-}$
2. $\mathrm{MnO_4^{2-}}$
3. $\mathrm{Cr_2O_7^{2-}}$
4. $\mathrm{CrO_4^{2-}}$

Correct Answer: 2. $\mathrm{MnO_4^{2-}}$.
Solution: In this problem, we need to identify which of the given species exhibits both Ligand-to-Metal Charge Transfer (LMCT) and paramagnetism.

Step 1: Understand LMCT and Paramagnetism

- LMCT (Ligand-to-Metal Charge Transfer): Occurs when electrons are transferred from ligand orbitals to metal orbitals. This typically happens in complexes where ligands have lone pairs that can donate electrons to the metal.
- Paramagnetism: Arises from unpaired electrons in a species. A species with unpaired electrons will be paramagnetic.

Step 2: Analyze Each Species for LMCT and Unpaired Electrons

1. MnO_4^- (Permanganate ion):

   Mn is in +7 oxidation state (d^0).

   - LMCT: Possible due to high oxidation state.
   - Paramagnetism: No unpaired electrons (d^0).

2. MnO_4^{2-} (Manganate ion):

   Mn is in +6 oxidation state (d^1).

   - LMCT: Possible as ligands can transfer electrons to Mn.
   - Paramagnetism: One unpaired electron (d^1).

3. $Cr_2O_7^{2-}$ (Dichromate ion):

   Each Cr is in +6 oxidation state (d^0).

   - LMCT: Possible due to high oxidation state.
   - Paramagnetism: No unpaired electrons (d^0).

4. CrO_4^{2-} (Chromate ion):

   Cr is in +6 oxidation state (d^0).

   - LMCT: Possible due to high oxidation state.
   - Paramagnetism: No unpaired electrons (d^0).

Step 3: Identify the Correct Species
Only MnO_4^{2-} exhibits both LMCT and paramagnetism due to the presence of one unpaired electron and the ability of oxygen ligands to transfer charge to Mn.

Therefore, the species that exhibits both LMCT and paramagnetism is MnO_4^{2-}.

Quick Tip

Paramagnetism is due to unpaired electrons, while LMCT involves electron transfer from ligands to metal centers. A species must have unpaired electrons to be paramagnetic and suitable ligands for LMCT.

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10. Correct solubility order of AgF, AgCl, AgBr, AgI in water is:
Options:

1. AgF < AgCl > AgBr > AgI
2. AgI < AgBr < AgCl < AgF
3. AgF < AgCl < AgBr < AgI
4. AgCl > AgBr > AgF > AgI

Correct Answer: 2. AgI < AgBr < AgCl < AgF.
Solution: In this problem, we are determining the solubility order of silver halides (AgF, AgCl, AgBr, AgI) in water. The solubility of these compounds is influenced by the lattice energy of the crystal lattice and the hydration energy of the ions.

Step 1: Understand Factors Affecting Solubility
The solubility of ionic compounds in water depends on the balance between lattice energy and hydration energy:

$$\text{Solubility} \propto \frac{\text{Hydration Energy}}{\text{Lattice Energy}}$$

- Lattice Energy: The energy required to separate the ions in the solid lattice. Higher lattice energy means lower solubility.
- Hydration Energy: The energy released when ions are solvated by water molecules. Higher hydration energy favors greater solubility.

Step 2: Analyze Silver Halides
Silver halides (AgF, AgCl, AgBr, AgI) vary in their solubility based on the size of the halide ion:

- AgF: Contains the smallest halide ion (F^-), leading to the highest lattice energy due to strong electrostatic attraction.
- AgCl: Contains Cl^-, larger than F^-, resulting in lower lattice energy than AgF.
- AgBr: Contains Br^-, larger than Cl^-, leading to even lower lattice energy.
- AgI: Contains the largest halide ion (I^-), resulting in the lowest lattice energy among the silver halides.

Step 3: Determine Solubility Order
Since lattice energy decreases with increasing halide ion size, and hydration energy increases with decreasing ion size, the overall solubility decreases as the halide ion size increases. Therefore:

$$\text{Solubility Order: AgI} < \text{AgBr} < \text{AgCl} < \text{AgF}$$

Therefore, the correct solubility order is AgI < AgBr < AgCl < AgF.

Quick Tip

Solubility of ionic compounds is inversely related to the lattice energy. Larger ions typically form less tightly bound lattices, resulting in lower solubility.

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11. What will be the change in acidity if: (i) $CuSO_4$ is added to saturated $(NH_4)_2SO_4$ solution, (ii) SbF_5 is added to anhydrous HF?
Options:

1. Increases, Increases
2. Decreases, Decreases
3. Increases, Decreases
4. Decreases, Increases

Correct Answer: 1. Increases, Increases.
Solution: In this problem, we are evaluating how the addition of certain compounds affects the acidity of specific solutions.

Part (i): Addition of $CuSO_4$ to Saturated $(NH_4)_2SO_4$ Solution

- Copper Sulfate ($CuSO_4$): Copper sulfate is a strong electrolyte and dissociates completely in water to form Cu^{2+} and SO_4^{2-} ions.
- Effect on Acidity: The addition of Cu^{2+} ions introduces a Lewis acid into the solution. Cu^{2+} can accept electron pairs, leading to increased formation of H^+ ions through hydrolysis:

$$Cu^{2+} + 6H_2O \leftrightarrow [Cu(H_2O)_6]^{2+} \leftrightarrow [Cu(H_2O)_5(OH)]^+ + H^+$$

- Conclusion for Part (i): The concentration of H^+ ions increases, thereby increasing the acidity.

Part (ii): Addition of SbF_5 to Anhydrous HF

- Antimony Pentafluoride (SbF_5): SbF_5 is a strong Lewis acid and can form complexes with HF.
- Formation of Superacid: When SbF_5 is added to HF, it reacts to form the superacid combination HF-SbF_5, which greatly enhances acidity:

$$SbF_5 + HF \rightarrow HSbF_6$$

- Effect on Acidity: The formation of $HSbF_6$ stabilizes the fluoride ions (F^-), effectively increasing the concentration of free H^+ ions in the solution.
- Conclusion for Part (ii): The acidity of the solution increases.

Overall Conclusion: Both additions lead to an increase in acidity, making the correct answer Increases, Increases.

> Quick Tip
>
> Lewis acids like Cu^{2+} and SbF_5 can increase the acidity of a solution by accepting electron pairs and promoting the formation of H^+ ions.

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12. Which of the following contains the maximum number of lone pairs on the central atom?
Options:

1. ClO_3^-
2. XeF_4
3. SF_4
4. I_3^-

Correct Answer: 4. I_3^-.
Solution: In this problem, we are identifying which of the given species has the highest number of lone pairs on its central atom.

Step 1: Analyze Each Species

1. ClO_3^- (Chlorate ion):

   Chlorine is the central atom.

   Valence electrons: Cl (7) + 3 $\times O(6) \times 3 + 1$negative charge $= 7 + 18 + 1 = 26$Valence electrons: Cl

   Number of lone pairs on Cl: 1

2. XeF_4 (Xenon Tetrafluoride):

   Xenon is the central atom.

   Valence electrons: Xe (8) + 4 $\times F(7) = 8 + 28 = 36$ electronsValence electrons: Xe (8) + 4 $\times F(7) =$

   Number of lone pairs on Xe: 2

3. SF_4 (Sulfur Tetrafluoride):

   Sulfur is the central atom.

   Valence electrons: S (6) + 4 $\times F(7) = 6 + 28 = 34$ electronsValence electrons: S (6) + 4 $\times F(7) = 6$

   Number of lone pairs on S: 1

4. I_3^- (Triiodide ion):

   Central atom: Iodine.

   Valence electrons: I (7) $\times 3 + 1(negativecharge) = 21 + 1 = 22$ electronsValence electrons: I (7) $\times 3$

   Number of lone pairs on central I: 3

Step 2: Compare the Number of Lone Pairs

- ClO_3^-: 1 lone pair
- XeF_4: 2 lone pairs
- SF_4: 1 lone pair
- I_3^-: 3 lone pairs

Conclusion: The triiodide ion (I_3^-) has the maximum number of lone pairs (3) on its central atom.

Therefore, the species with the maximum number of lone pairs on the central atom is I_3^-.

Quick Tip

To determine lone pairs on the central atom, calculate total valence electrons, subtract bonding electrons, and divide the remaining electrons by two.

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13. Metallic conductors and semiconductors are heated separately. What are the changes in conductivity?
Options:

1. Increase, Increase
2. Decrease, Decrease
3. Increase, Decrease
4. Decrease, Increase

Correct Answer: 4. Decrease, Increase

Solution: The behavior of metals and semiconductors under heat can be explained as follows:

- **Metals:** Conductivity decreases with temperature because the lattice vibrations increase, leading to more frequent collisions of electrons with ions.
- **Semiconductors:** Conductivity increases with temperature as more electrons gain sufficient energy to cross the band gap from the valence band to the conduction band, increasing charge carriers.

Quick Tip

In metals, resistivity increases with temperature due to lattice vibrations. In semiconductors, higher temperatures excite more electrons, enhancing conductivity.

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14. The equivalent weight of $Na_2S_2O_3$ (Gram molecular weight = M) in the given reaction is:
$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$
Options:

1. M/2
2. M
3. 2M
4. M/4

Correct Answer: 2. M

Solution: The equivalent weight of $Na_2S_2O_3$ depends on the number of electrons transferred during the reaction.

Step 1: Reaction Overview.

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$$

In this reaction, each molecule of $Na_2S_2O_3$ donates one electron.
Step 2: Equivalent Weight Calculation. The formula for equivalent weight is:

$$\text{Equivalent Weight} = \frac{\text{Molecular Weight (M)}}{\text{Number of Electrons Transferred (n)}}$$

Since $n = 1$, the equivalent weight of $Na_2S_2O_3$ is:

$$\text{Equivalent Weight} = \frac{M}{1} = M$$

Final Answer: The equivalent weight of $Na_2S_2O_3$ in this reaction is M.

QuickTip
The equivalent weight of a compound is its molecular weight divided by the number of electrons transferred during the reaction.

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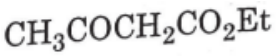
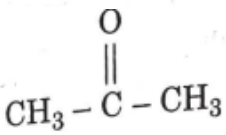
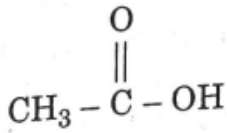
15. In the following sequence of reactions, compound 'M' is:

$$M \xrightarrow{CH_3MgBr} N + CH_4\uparrow \xrightarrow{H^+} CH_3COCH_2COCH_3$$

1. 
2. 
3. 
4. 

Correct Answer: 1. $CH_3COCH_2COCH_3$

Solution: The reaction sequence can be understood as follows:

- **Reaction with Grignard reagent:** The Grignard reagent CH_3MgBr reacts with a carbonyl group in compound M, producing an intermediate. During this reaction, a new carbon-carbon bond forms, and CH_4 gas evolves due to the abstraction of a proton by the Grignard reagent.

- **Hydrolysis:** The intermediate undergoes acid hydrolysis, converting it into $CH_3COCH_2COCH_3$, a β-diketone. This confirms the structure of M as a precursor to β-diketones.

Structural Insight: The structure of $CH_3COCH_2COCH_3$ clearly indicates that compound M must have a similar backbone that facilitates the formation of a β-diketone after reaction with CH_3MgBr and subsequent hydrolysis.

Quick Tip

Grignard reagents add to carbonyl groups to form alcohol intermediates, which can undergo further reactions like hydrolysis to produce ketones or β-diketones.

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16. Identify the ion having $4f^6$ electronic configuration.
Options:

1. Gd^{3+}
2. Sm^{3+}
3. Sm^{2+}
4. Tb^{3+}

Correct Answer: 3. Sm^{2+}

Solution: The electronic configuration of the lanthanides can be deduced as follows:

- **Gd^{3+}:** Gadolinium has the configuration [Xe] $4f^7$ $5d^1$ $6s^2$. Removal of three electrons results in [Xe] $4f^7$, which does not match $4f^6$.
- **Sm^{3+}:** Samarium has the configuration [Xe] $4f^6$ $6s^2$. Removal of three electrons gives [Xe] $4f^5$, which does not match $4f^6$.
- **Sm^{2+}:** Removing two electrons from Sm gives [Xe] $4f^6$, matching the given configuration.
- **Tb^{3+}:** Terbium forms [Xe] $4f^8$, which is not correct.

Thus, Sm^{2+} is the ion with $4f^6$ configuration.

Quick Tip

For lanthanides, the f-electron configuration depends on the oxidation state and the number of electrons removed.

---

17. Toluene reacts with mixed acid at 25°C to produce:
Options:

1. Nearly equal amounts of o- and m-nitrotoluene
2. p-Nitrotoluene (only)
3. Predominantly o-nitrotoluene and p-nitrotoluene
4. 2, 4, 6-Trinitrotoluene (only)

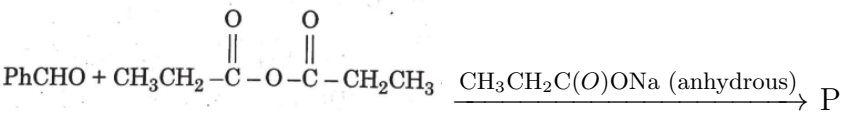
Correct Answer: 3. Predominantly o-nitrotoluene and p-nitrotoluene

Solution:
Step 1: Reaction Mechanism.
- The nitration of toluene with mixed acid (HNO_3 and H_2SO_4) involves an electrophilic substitution reaction.
- The methyl group in toluene is an electron-donating group, which activates the ortho and para positions.
Step 2: Product Distribution.
At 25°C, the reaction produces both ortho- and para-nitrotoluene as the major products, with the para isomer predominating due to steric and electronic factors.
Final Answer: The major products are ortho- and para-nitrotoluene.

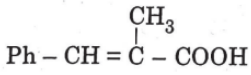
QuickTip
Activating groups like methyl direct electrophilic substitution to the ortho and para positions.

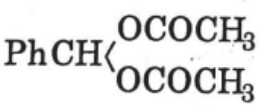
---

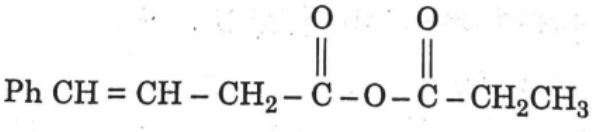
18. The product 'P' in the above reaction is:

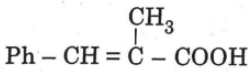


Options:

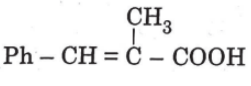
1. Ph CH = $CHCH_2COOH$
2. 

3. 

4. 

Correct Answer: 2. 

Solution:
Step 1: Reaction Type.
This reaction is a Perkin condensation reaction, which synthesizes α, β-unsaturated carboxylic acids.
Step 2: Mechanism.
Benzaldehyde reacts with acetic anhydride in the presence of sodium ethoxide, forming an enolate ion. This intermediate undergoes aldol-like condensation and dehydration to yield cinnamic acid.

Final Answer: The product P is cinnamic acid,  .

QuickTip
Perkin condensation is a useful method to synthesize α, β-unsaturated carboxylic acids.

---

19. The reactivity order of the following molecules towards SN1 reaction is:
Allyl chloride (I), Chlorobenzene (II), Ethyl chloride (III)
Options:

1. I > II > III
2. I > III > II
3. II > I > III
4. III > I > II

Correct Answer: 2. I > III > II

Solution:
Step 1: Determine Carbocation Stability.
- Allyl chloride (I) forms an allylic carbocation, which is resonance-stabilized, making it highly reactive in SN1 reactions.
- Ethyl chloride (III) forms a primary carbocation, which is less stable than the allylic carbocation.
- Chlorobenzene (II) does not undergo SN1 reactions easily due to the instability of the carbocation in an aromatic system.
Step 2: Order Reactivity Based on Stability.
The reactivity towards SN1 reactions directly depends on carbocation stability. Hence, the order is:

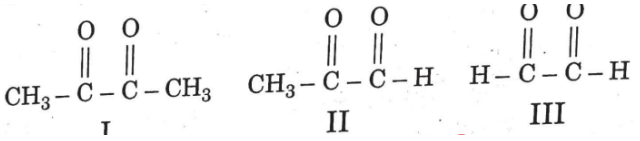
$$\text{I} > \text{III} > \text{II}$$

Final Answer: The reactivity order is I > III > II.

QuickTip
The stability of the carbocation intermediate is the key factor influencing the rate of SN1 reactions.

---

20. Ozonolysis of o-xylene produces:



Options:

1. I:III = 1:2
2. II:III = 2:1
3. I:II:III = 1:2:3
4. I:II:III = 3:2:1

Correct Answer: 3. I:II:III = 1:2:3

Solution:
Step 1: Product Identification.
Ozonolysis of o-xylene cleaves double bonds, yielding carbonyl compounds: - Compound I: CH_3–C(O)–C(O)–CH_3 (1 part).
- Compound II: CH_3–C(O)–C(O)–H (2 parts).
- Compound III: H–C(O)–C(O)–H (3 parts).
Step 2: Product Ratio.
The ratio of products depends on symmetry and substituents. For o-xylene, the ratio is:

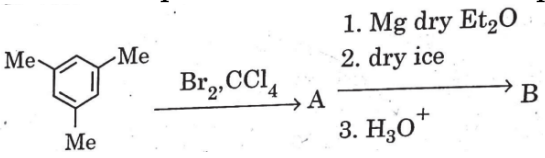
$$\text{I:II:III} = 1:2:3$$

Final Answer: The product ratio is I:II:III = 1:2:3.

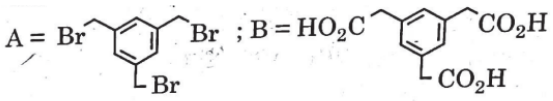
QuickTip
Ozonolysis cleaves double bonds, producing products based on the substituent distribution and symmetry of the molecule.

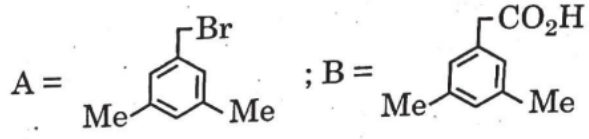
---

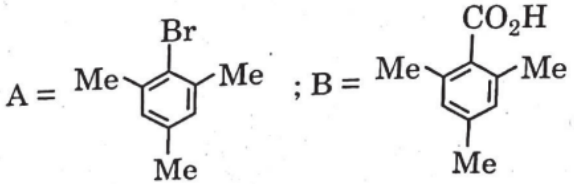
21. The compounds A and B are respectively:

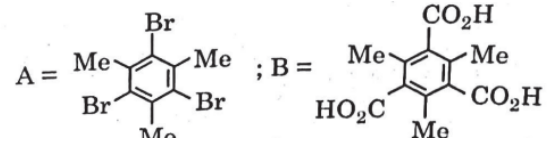


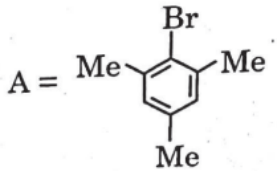
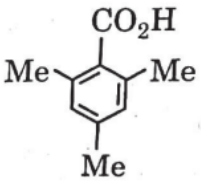
Options:

1. 

2. 

3. 

4. 

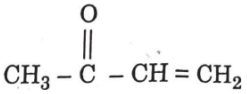
Correct Answer: 3. A =  ; B = 

Solution:
Step 1: Formation of Grignard Reagent.
- Methyl bromide (Me Br) reacts with magnesium (Mg) in dry ether to form the Grignard reagent (CH_3MgBr).
Step 2: Reaction with CO_2.
- The Grignard reagent reacts with carbon dioxide (CO_2) to produce a magnesium carboxylate intermediate.
Step 3: Acidic Hydrolysis.
- The magnesium carboxylate intermediate undergoes protonation with dilute acid (H_3O^+) to form the final carboxylic acid product.
Final Answer: The structures of compounds A and B correspond to option (3).

QuickTip
Grignard reagents are powerful nucleophiles that can react with carbon dioxide to form carboxylic acids, providing a reliable method for extending carbon chains.

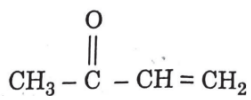
---

22. The decreasing order of reactivity of the following alkenes towards HBr addition is:

CH_3–CH=CH_2 (I), CF_3–CH=CH_2 (II), MeOCH=CH_2 (III),  (IV)
Options:

1. I > II > III > IV
2. II > IV > I > III
3. III > IV > I > II
4. III > I > II > IV

Correct Answer: 4. III > I > II > IV

Solution:
Step 1: Carbocation Stability.
- Methoxy group in MeOCH=CH_2 (III) is electron-donating and stabilizes the carbocation, making it highly reactive.
- CH_3–CH=CH_2 (I) forms a secondary carbocation, which is moderately stable.
- CF_3–CH=CH_2 (II) is destabilized by the electron-withdrawing CF_3 group.
-  (IV) has steric hindrance, reducing reactivity.

Final Answer: The reactivity order is III > I > II > IV.

QuickTip

Electron-donating groups increase carbocation stability, enhancing reactivity, while electron-withdrawing groups decrease reactivity.

---

23. The correct acidity order of phenol (I), 4-hydroxybenzaldehyde (II), and 3-hydroxybenzaldehyde (III) is:
Options:

1. I < II < III
2. I < III < II
3. II < I < III
4. III < I < II

Correct Answer: 2. I < III < II.
Solution: The acidity of these compounds is influenced by the electron-withdrawing effects of substituents and their positions relative to the hydroxyl group.
- Phenol (I): Has only the hydroxyl group, providing resonance stabilization to the phenoxide ion, but no additional electron-withdrawing groups.
- 3-Hydroxybenzaldehyde (III): Contains a formyl group (-CHO) at the meta position, which exerts an electron-withdrawing effect through induction, increasing acidity compared to phenol.
- 4-Hydroxybenzaldehyde (II): The formyl group is at the para position, allowing for both inductive and resonance electron-withdrawing effects, making it the most acidic among the three.
Thus, the acidity order is I < III < II.

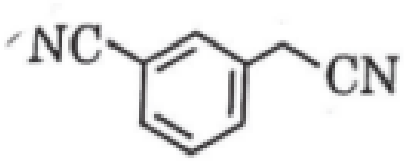
Quick Tip

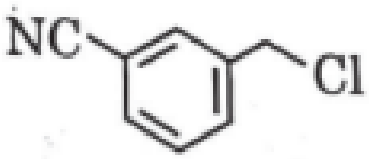
Electron-withdrawing groups enhance acidity by stabilizing the negative charge on the phenoxide ion. Their position relative to the hydroxyl group significantly affects their influence.

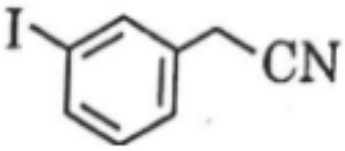
---

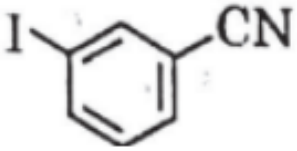
24. The major product of the following reaction is:

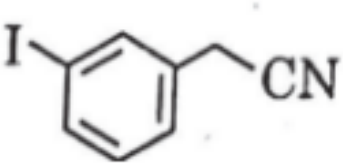
Options:

1. 

2. 

3. 

4. 



Correct Answer: 3. .

Solution: The reaction involves nucleophilic substitution (S_N2) where sodium cyanide (NaCN) acts as the nucleophile, replacing the leaving group on the substrate.
Analyzing the mechanism:

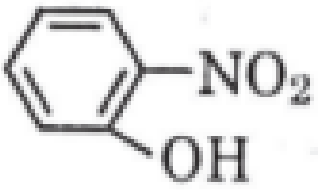
1. The cyanide ion (CN^-) attacks the electrophilic carbon bonded to the leaving group (Cl or I).
2. The leaving group departs, resulting in the formation of a nitrile group (CN) attached to the benzene ring.

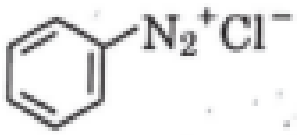
Given the structure of the reactant and the nature of the reaction, the major product formed is **(C) Iodobenzene with one CN group attached to the benzene ring**.

> Quick Tip
>
> In S_N2 reactions, the nucleophile attacks the carbon bearing the leaving group from the opposite side, leading to inversion of configuration.

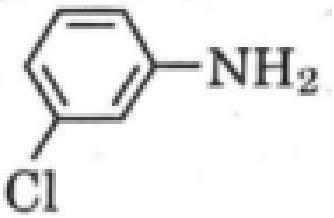
---

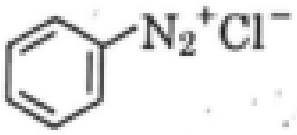
25. The compound that does not give a positive test for nitrogen in Lassaigne's test is:
Options:

1. 

2. 

3. 

4. 



Correct Answer: 2.

Solution: In Lassaigne's test, the presence of nitrogen in a compound is detected by its reaction with sodium to form sodium nitride, which then reacts with ferrous sulfate to produce a characteristic blue or purple color. Compounds containing nitrogen will give a positive test. Analyzing the given compounds:

1. Nitro phenol ($C_6H_4NO_2OH$) contains nitrogen and will give a positive test.
2. Chlorobenzene (C_6H_5Cl) does not contain nitrogen and will not give a positive test.
3. Aniline ($C_6H_4NH_2$) contains nitrogen and will give a positive test.
4. Aminobenzene ($C_6H_4NH_2$) contains nitrogen and will give a positive test.

Therefore, the compound that does not give a positive test for nitrogen is **2. Chlorobenzene**.

Quick Tip

Lassaigne's test specifically detects elements like nitrogen, sulfur, and halogens by converting them into their respective ions using sodium fusion.

---

26. The compressibility factor for a van der Waals gas at high pressure is:
Options:

1. $1 + \frac{RT}{Pb}$
2. $1 + \frac{Pb}{RT}$
3. $1 - \frac{Pb}{RT}$
4. 1

Correct Answer: 2. $1 + \frac{Pb}{RT}$.
Solution: This problem involves determining the compressibility factor (Z) for a van der Waals gas under high-pressure conditions. The compressibility factor is a measure of how much a real gas deviates from ideal gas behavior.

Step 1: Recall the Compressibility Factor
The compressibility factor is defined as:

$$Z = \frac{PV}{RT}$$

where:

- P = pressure
- V = volume
- R = gas constant
- T = temperature

Step 2: Consider the van der Waals Equation
The van der Waals equation adjusts the ideal gas law to account for intermolecular forces and finite molecular sizes:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where:

- a = measure of intermolecular attraction
- b = measure of the volume occupied by gas molecules

Step 3: Simplify for High Pressure
At high pressures, the volume V becomes very small, making the term b significant. However, the intermolecular attraction term $\frac{a}{V^2}$ becomes negligible compared to the pressure P. Thus, the equation simplifies to:

$$(P + 0)(V - b) \approx PV - Pb = RT \Rightarrow PV \approx RT + Pb$$

$$Z = \frac{PV}{RT} \approx \frac{RT + Pb}{RT} = 1 + \frac{Pb}{RT}$$

Quick Tip

At high pressures, the volume occupied by gas molecules (b) significantly affects the compressibility factor, while intermolecular attractions (a) become less impactful.

---

27. For a spontaneous process, the incorrect statement is:
Options:

1. $(\Delta G_{\text{system}})_{T,P} > 0$
2. $(\Delta S_{\text{system}}) + (\Delta S_{\text{surroundings}}) > 0$
3. $(\Delta G_{\text{system}})_{T,P} < 0$
4. $(\Delta U_{\text{system}})_{S,V} < 0$

Correct Answer: 1. $(\Delta G_{\text{system}})_{T,P} > 0$.
Solution: This question tests the understanding of the thermodynamic criteria for spontaneity in a process.

Step 1: Recall Spontaneity Criteria
For a process to be spontaneous at constant temperature and pressure:

- The change in Gibbs Free Energy (ΔG) of the system must be negative:

$$(\Delta G_{\text{system}})_{T,P} < 0$$

- The total entropy change of the universe (system + surroundings) must be positive:

$$(\Delta S_{\text{system}}) + (\Delta S_{\text{surroundings}}) > 0$$

Step 2: Analyze Each Option

1. Option 1: $(\Delta G_{\text{system}})_{T,P} > 0$
   - This implies that the Gibbs Free Energy of the system increases, which is non-spontaneous.
2. Option 2: $(\Delta S_{\text{system}}) + (\Delta S_{\text{surroundings}}) > 0$
   - This aligns with the second law of thermodynamics for spontaneity.
3. Option 3: $(\Delta G_{\text{system}})_{T,P} < 0$
   - This correctly indicates a spontaneous process.
4. Option 4: $(\Delta U_{\text{system}})_{S,V} < 0$
   - While not a direct criterion for spontaneity under constant temperature and pressure, a negative internal energy change can contribute to spontaneity under certain conditions.

Step 3: Identify the Incorrect Statement
Option 1 is incorrect because a positive ΔG indicates a non-spontaneous process, which contradicts the definition of spontaneity.

> Quick Tip
>
> Remember that a negative Gibbs Free Energy change ($\Delta G < 0$) is a primary indicator of spontaneity in processes occurring at constant temperature and pressure.

---

28. Which of the following statements is correct for a spontaneous polymerization reaction?
Options:

1. $\Delta G < 0, \Delta H < 0, \Delta S < 0$
2. $\Delta G < 0, \Delta H > 0, \Delta S > 0$
3. $\Delta G > 0, \Delta H < 0, \Delta S > 0$
4. $\Delta G > 0, \Delta H > 0, \Delta S > 0$

Correct Answer: 1. $\Delta G < 0, \Delta H < 0, \Delta S < 0$.
Solution: For a reaction to be spontaneous, the Gibbs free energy change (ΔG) must be negative:

$$\Delta G = \Delta H - T\Delta S$$

Where:

- ΔH is the enthalpy change.
- ΔS is the entropy change.
- T is the temperature in Kelvin.

In spontaneous polymerization:

- $\Delta H < 0$: The reaction is exothermic, releasing energy as monomers form polymer chains.
- $\Delta S < 0$: The system becomes more ordered as monomers link together, decreasing entropy.

Despite the decrease in entropy, the exothermic nature ($\Delta H < 0$) ensures that ΔG remains negative, satisfying the condition for spontaneity.
Therefore, the correct statement is:

$$\boxed{\Delta G < 0, \Delta H < 0, \Delta S < 0.}$$

Quick Tip

Spontaneous reactions can occur even if entropy decreases, provided the enthalpy term compensates sufficiently to keep ΔG negative.

---

29. At 25°C, the ionic product of water is 10^{-14}. The free energy change for the self-ionization of water in kcal mol^{-1} is:
Options:

1. 20.5
2. 14.0
3. 19.1
4. 25.3

Correct Answer: 3. 19.1.
Solution: The Gibbs free energy change (ΔG°) for a reaction is related to the equilibrium constant (K) by the equation:

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

Where:

- $R = 1.987\,\text{cal mol}^{-1}\text{K}^{-1}$ (universal gas constant).
- $T = 298\,\text{K}$ (25°C in Kelvin).
- $K = 10^{-14}$ (ionic product of water).

Substituting the values:

$$\Delta G^\circ = -1.987 \times 298 \times \ln(10^{-14})$$

$$\ln(10^{-14}) = -14 \ln(10) \approx -14 \times 2.303 = -32.242$$

$$\Delta G^\circ = -1.987 \times 298 \times (-32.242) \approx 19,100 \,\text{cal mol}^{-1} = 19.1 \,\text{kcal mol}^{-1}$$

Thus, the free energy change for the self-ionization of water is approximately 19.1 kcal mol^{-1}.

> **Quick Tip**
>
> Use the equation $\Delta G^\circ = -RT \ln K$ to relate free energy changes to equilibrium constants. Ensure consistent units throughout the calculation.

---

30. Consider an electron moving in the first Bohr orbit of a He^+ ion with a velocity v_1. If it is allowed to move in the third Bohr orbit with a velocity v_3, indicate the correct $v_3 : v_1$ ratio:
Options:

1. 3:1
2. 2:1
3. 1:3
4. 1:2

Correct Answer: 3. 1:3.
Solution: In this problem, we are analyzing the relationship between the velocities of an electron in different Bohr orbits of a He^+ ion. Specifically, we aim to determine the ratio of the electron's velocity in the third orbit (v_3) to its velocity in the first orbit (v_1).

Step 1: Understand the Bohr Model
According to the Bohr model of the atom, the velocity of an electron in a given orbit is inversely proportional to the principal quantum number (n). The formula representing this relationship is:

$$v_n \propto \frac{1}{n}$$

where v_n is the velocity in the n^{th} orbit.
Step 2: Apply the Proportionality
For the first orbit ($n = 1$):

$$v_1 \propto \frac{1}{1} = 1$$

For the third orbit ($n = 3$):

$$v_3 \propto \frac{1}{3}$$

Step 3: Determine the Ratio
To find the ratio $v_3 : v_1$, we set up the proportion:

$$\frac{v_3}{v_1} = \frac{\frac{1}{3}}{1} = \frac{1}{3}$$

Thus, the ratio $v_3 : v_1$ is $1 : 3$.

Quick Tip

In the Bohr model, remember that as the principal quantum number increases, the electron's velocity decreases. This inverse relationship is crucial for comparing velocities across different orbits.

---

31. The degree of dissociation of acetic acid is:
Options:

1. 0.021
2. 0.21
3. 0.012
4. 0.12

Correct Answer: 1. 0.021.
Solution: This problem involves calculating the degree of dissociation (α) of acetic acid using given conductivity data.

Given Data:

- Molar conductivity (Λ_m) = 1.65×10^{-4} S cm^{-1}
- Concentration (C) = 0.02 M
- Molar conductivity at infinite dilution (Λ°) = $\lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-} = 349.1 + 40.9 = 390$ S cm^2 mol^{-1}

Step 1: Calculate Molar Conductivity of the Solution (Λ_m)

$$\Lambda_m = \frac{k}{C} = \frac{1.65 \times 10^{-4}\,\text{S cm}^{-1}}{0.02\,\text{M}} = 0.00825\,\text{S cm}^2\,\text{mol}^{-1}$$

Step 2: Determine the Degree of Dissociation (α)

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ} = \frac{0.00825}{390} \approx 0.021$$

Conclusion: The degree of dissociation (α) of acetic acid is 0.021.

Quick Tip

The degree of dissociation (α) indicates the extent to which an acid dissociates in solution. It is calculated by comparing the measured molar conductivity to the limiting molar conductivity.

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32. The number(s) of -OH group(s) present in H_3PO_3 and H_3PO_4 is/are:
Options:

1. 3 and 3 respectively
2. 3 and 4 respectively
3. 2 and 3 respectively
4. 1 and 3 respectively

Correct Answer: 3. 2 and 3 respectively

Solution:
H_3PO_3: Comprises two -OH groups and a single hydrogen atom bonded directly to phosphorus.
H_3PO_4: Comprises three -OH groups along with a phosphorus-oxygen double bond (P=O).

> Quick Tip
>
> The structure of phosphorus oxyacids is key in determining the number of -OH groups. Pay attention to the presence of P-H and P=O bonds.

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33. How many P–O–P linkages are there in P_4O_{10}?
Options:

1. Six
2. Four
3. Five
4. One

Correct Answer: 1. Six.
Solution: In this problem, we are tasked with determining the number of P–O–P linkages in the molecule P_4O_{10}.

Step 1: Understand the Molecular Structure of P_4O_{10}
P_4O_{10}, also known as phosphorus pentoxide, has a structure based on a tetrahedral arrangement of phosphorus atoms. Each phosphorus atom is bonded to oxygen atoms, some of which bridge between phosphorus centers, forming P–O–P linkages.
Step 2: Analyze the Bridging Oxygen Atoms
In the P_4O_{10} molecule:

- There are a total of 10 oxygen atoms.
- Each P–O–P linkage involves one bridging oxygen atom connecting two phosphorus atoms.
- The remaining oxygen atoms are terminal, bonded to only one phosphorus atom.

Step 3: Count the P–O–P Linkages
Given that there are 10 oxygen atoms and some are bridging:

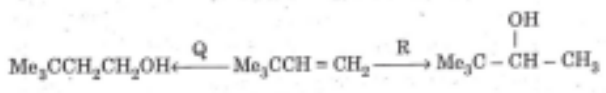
$$\text{Number of P–O–P linkages} = 6$$

This is because in the tetrahedral structure of P_4O_{10}, there are six bridging oxygen atoms that connect the phosphorus centers.

Therefore, P_4O_{10} contains six P–O–P linkages.

> Quick Tip
>
> In complex molecular structures, identifying bridging atoms is key to determining linkage counts. Visualizing or referring to molecular geometry can aid in accurate counting.

34. Q and R in the reaction sequences are respectively:



Options:

1. $Hg(OAc)_2$, $NaBH_4/OH^-$; B_2H_6, H_2O_2/OH^-
2. B_2H_6, H_2O_2/OH^-; H^+/H_2O
3. $Hg(OAc)_2$, $NaBH_4/OH^-$; H^+/H_2O
4. B_2H_6, H_2O_2/OH^-; $Hg(OAc)_2$, $NaBH_4/OH^-$

Correct Answer: 4. B_2H_6, H_2O_2/OH^-; $Hg(OAc)_2$, $NaBH_4/OH^-$.
Solution: This problem involves identifying the reagents used in specific reaction sequences, particularly in hydroboration-oxidation and reduction reactions.

Step 1: Identify the Reaction Sequences

- Sequence 1 (Q): Involves reagents B_2H_6 (diborane) and H_2O_2/OH^-.
- Sequence 2 (R): Involves reagents $Hg(OAc)_2$ (mercuric acetate) and $NaBH_4/OH^-$.

Step 2: Assign the Correct Reagents to Each Sequence

- Sequence Q: B_2H_6 and H_2O_2/OH^- are characteristic of the hydroboration-oxidation reaction, which adds water across a double bond with anti-Markovnikov regioselectivity.
- Sequence R: $Hg(OAc)_2$ and $NaBH_4/OH^-$ are characteristic of the reduction reaction, specifically the reduction of carbonyl compounds to alcohols.

Step 3: Match the Reagents to the Options
Reviewing the options, Option 4 correctly assigns B_2H_6 and H_2O_2/OH^- to Q, and $Hg(OAc)_2$, $NaBH_4/OH^-$ to R.

Therefore, Q and R in the reaction sequences are respectively B_2H_6, H_2O_2/OH^-; $Hg(OAc)_2$, $NaBH_4/OH^-$.

> **Quick Tip**
>
> Hydroboration-oxidation uses diborane and hydrogen peroxide with a base, while reduction reactions often involve mercuric salts and sodium borohydride.

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35. pH of 10^{-8} M HCl solution is:
Options:

1. 8
2. Greater than 7, less than 8
3. Greater than 8
4. Greater than 6, less than 7

Correct Answer: 4. Greater than 6, less than 7.
Solution: This problem requires calculating the pH of a very dilute HCl solution, considering both the HCl contribution and the autoionization of water.

Step 1: Recognize the Contributions to $[H^+]$
Given:

- Concentration of HCl = 10^{-8} M
- HCl is a strong acid and dissociates completely: $HCl \rightarrow H^+ + Cl^-$
- Autoionization of water: $2H_2O \rightleftharpoons H_3O^+ + OH^-$, contributing $[H^+] = 10^{-7}$ M

Step 2: Calculate Total $[H^+]$

$$\text{Total } [H^+] = [H^+ \text{ from HCl}] + [H^+ \text{ from water}] = 10^{-8}\,\text{M} + 10^{-7}\,\text{M} = 1.1 \times 10^{-7}\,\text{M}$$

Step 3: Determine the pH

$$\text{pH} = -\log[H^+] = -\log(1.1 \times 10^{-7}) \approx 6.96$$

Conclusion: The pH of the solution is approximately 6.96, which lies greater than 6 and less than 7.

> Quick Tip
>
> At very low acid concentrations, the autoionization of water significantly influences the pH. Always consider both acid contributions and water's autoionization in such cases.

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36. Which of the following ion/ions is/are diamagnetic?
Options:

1. $[CoF_6]^{3-}$
2. $[Co(NH_3)_6]^{3+}$
3. $[Fe(OH_2)_6]^{2+}$
4. $[Fe(CN)_6]^{4-}$

Correct Answer: 2, 4 **Solution:**

- $[CoF_6]^{3-}$: Paramagnetic due to the presence of unpaired electrons in the high-spin configuration.
- $[Co(NH_3)_6]^{3+}$: Diamagnetic as NH_3 is a strong field ligand, resulting in a low-spin configuration with all electrons paired.
- $[Fe(OH_2)_6]^{2+}$: Paramagnetic because of unpaired electrons.
- $[Fe(CN)_6]^{4-}$: Diamagnetic since CN^- is a strong field ligand, leading to a low-spin configuration with no unpaired electrons.

> Quick Tip
>
> Diamagnetic complexes have no unpaired electrons. Use crystal field theory to determine the spin state based on the strength of the ligand field.

37. Which of the following statement(s) is/are correct?
Options:

1. Solid I_2 is freely soluble in water.
2. Solid I_2 is freely soluble in water but only in the presence of excess KI.
3. Solid I_2 is freely soluble in CCl_4.
4. Solid I_2 is freely soluble in hot water.

Correct Answer: 2, 3 **Solution:**

Statement 1: False. Solid I_2 has only limited solubility in water.
Statement 2: True. The solubility of I_2 in water increases in the presence of KI, which promotes the formation of I_3^- complexes.
Statement 3: True. I_2 is highly soluble in non-polar solvents such as CCl_4.
Statement 4: False. I_2 is not freely soluble in hot water despite the increased solubility with higher temperatures.

Quick Tip

The solubility of iodine is influenced by the polarity of the solvent and the temperature. Adding excess KI increases solubility through the formation of complexes.

38. Which of the following statements about the SN2 reaction mechanism is/are true?
Options:

1. The rate of reaction increases with increasing nucleophilicity.
2. The number 2 denotes a second-order reaction.
3. Tertiary butyl substrates do not follow this mechanism.
4. The optical rotation of substrates always changes from (+) to (-) or from (-) to (+) in the products.

Correct Answer: 1, 2, 3

Solution:
The SN2 reaction mechanism is a bimolecular nucleophilic substitution, characterized by:
A single step in which the nucleophile attacks the electrophilic carbon and the leaving group departs simultaneously.
Statement 1: True. The rate of reaction depends on the concentration of both the nucleophile and the substrate, increasing with nucleophilicity.
Statement 2: True. The "2" in SN2 indicates that the reaction follows second-order kinetics, dependent on both reactants.
Statement 3: True. Tertiary substrates do not undergo SN2 reactions due to steric hindrance.
Statement 4: False. While optical rotation can change, it does not necessarily shift from (+) to (-) or vice versa, as this depends on the specific nucleophile and substrate involved.

Quick Tip

SN2 reactions are stereospecific and lead to inversion of configuration. Steric hindrance plays a significant role in determining whether the reaction can proceed.

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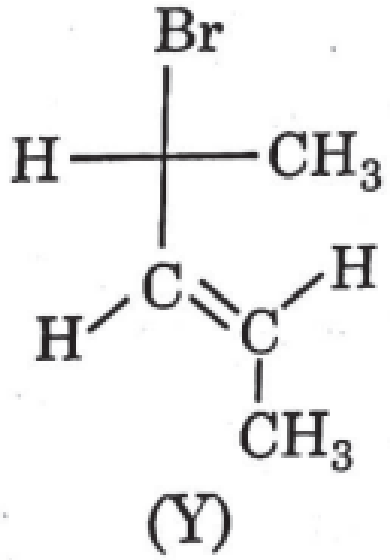
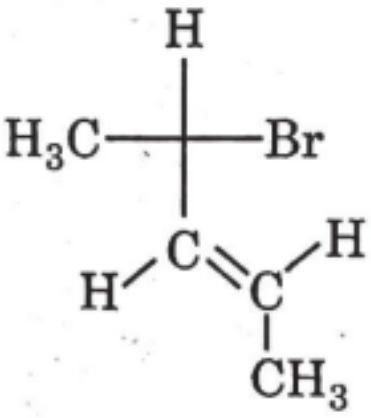
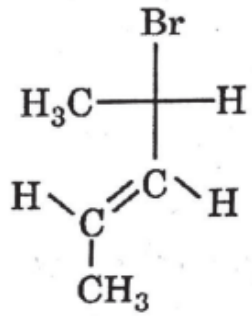
39. Which of the following represent(s) the enantiomer of Y?

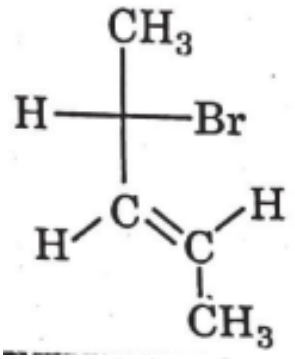


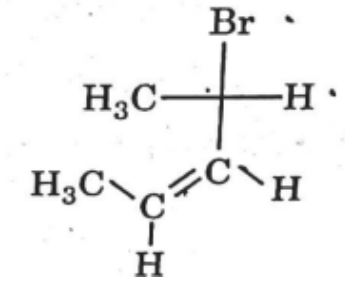
(Y)

Options:

1. 

2. 

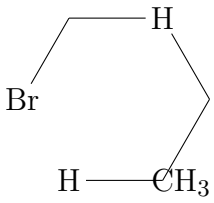
3. 

4. 

Correct Answer: 2. Image B, c **Solution:**

Given Compound (Y):

The structure of compound Y is represented as:



In this compound:

- The central carbon is a chiral center.
- The attached groups are Br, H, CH_3, and $CH(H)(CH_3)$.

To determine the enantiomer of Y, we need to identify the mirror images of Y that are non-superimposable.

Analysis of the Options:

- **Option (A):** This structure is not a mirror image of Y, as the positions of the substituents remain unchanged.
- **Option (B):** This compound represents the correct mirror image of Y. The relative positions of Br, H, CH_3, and the secondary group $CH(H)(CH_3)$ are inverted, making it an enantiomer of Y.
- **Option (C):** This structure also represents a mirror image of Y, with the correct spatial inversion of groups, making it another enantiomer of Y.
- **Option (D):** This compound is identical to Y, not an enantiomer.

Conclusion: Both (B) and (C) are enantiomers of Y. Therefore, the correct answer is:

$$\boxed{\text{(B), (C).}}$$

Quick Tip

To identify enantiomers, search for non-superimposable mirror images by analyzing the spatial arrangement of the substituent groups.

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40. Identify the correct statement(s):
Options:

(A) The oxidation number of Cr in CrO_5 is +6.
(B) $\Delta H > \Delta U$ for the reaction $N_2O_4(g) \rightarrow 2\ NO_2(g)$, provided both gases behave ideally.
(C) pH of 0.1 N H_2SO_4 is less than that of 0.1 N HCl at 25°C.
(D) RT/F = 0.0591 V at 25°C.

Correct Answer: (A), (B) **Solution:**

Analysis of Each Statement:

- **(A) The oxidation number of Cr in CrO_5 is +6.**
  CrO_5 (chromium pentoxide) is a peroxide compound with one Cr atom and five O atoms. To calculate the oxidation number of Cr:

  $$\text{Oxidation number of Cr} + 5(-2) = 0.$$

  Since four oxygen atoms are in peroxide bonds (with an oxidation state of -1 for each O), the equation becomes:

  $$\text{Oxidation number of Cr} + (-2 \times 4) + (-2) = 0.$$

  Solving for Cr gives:

  $$\text{Oxidation number of Cr} = +6.$$

  This statement is **correct**.

- **(B) $\Delta H > \Delta U$ for the reaction $N_2O_4(g) \rightarrow 2\ NO_2(g)$, provided both gases behave ideally.**
  For ideal gases:

  $$\Delta H = \Delta U + \Delta n_g RT,$$

  where Δn_g is the change in the number of moles of gas. In this reaction:

  $$N_2O_4(g) \rightarrow 2NO_2(g),$$

  $\Delta n_g = 2 - 1 = 1$. Therefore, $\Delta H > \Delta U$, making this statement **correct**.

- **(C) pH of 0.1 N H_2SO_4 is less than that of 0.1 N HCl at 25°C.**
  H_2SO_4 dissociates completely in water to form 2 H^+ ions per molecule. In a 0.1 N solution, the second ionization is suppressed due to the high concentration of H^+, resulting in a slightly higher concentration of H^+. In contrast, 0.1 N HCl dissociates completely to give 0.1 M H^+ ions. Therefore, the pH of 0.1 N H_2SO_4 is slightly higher (less acidic) than that of 0.1 N HCl. This statement is **incorrect**.

- **(D) RT/F = 0.0591 V at 25°C.**
  The value of RT/F at 25°C is:

$$\frac{RT}{F} = \frac{(8.314)(298)}{96485} \approx 0.0257\,\text{V}.$$

  The value 0.0591 V corresponds to $2.303 \times \frac{RT}{F}$, which is used in the Nernst equation for logarithmic terms. Thus, this statement is **incorrect**.

Conclusion: The correct statements are:

$$\boxed{(A), (B).}$$

Quick Tip

Use the equation $\Delta H = \Delta U + \Delta nRT$ to compare enthalpy and internal energy changes. For pH calculations, consider the dissociation behavior of acids.
