WBJEE 2024 Chemistry Question Paper with Solutions

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

General Instructions

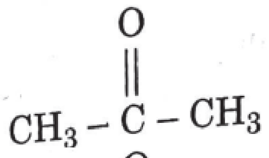
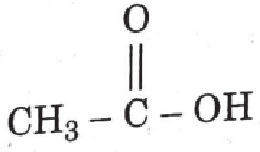
Read the following instructions very carefully and strictly follow them:

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. ½ 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.

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

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

Options:

1. $CH_3COCH_2COCH_3$
2. $CH_3COCH_2CO_2Et$
3. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
4. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

Correct Answer: 1. $CH_3COCH_2COCH_3$

Solution: The given reaction sequence involves the following steps: 1. Reaction with Grignard reagent: Compound M reacts with CH_3MgBr (a Grignard reagent) to form an intermediate compound N. In this step, the Grignard reagent adds to the carbonyl group of M, creating a new C–C bond and releasing CH_4 gas as a by-product. The reaction mechanism involves nucleophilic attack by CH_3^- on the carbonyl carbon.

2. Hydrolysis: The intermediate N undergoes acid hydrolysis. During this process, the intermediate is converted into $CH_3COCH_2COCH_3$, which is a β-diketone. Hydrolysis ensures the protonation and stabilization of the newly formed compound.

Key Structural Feature: $CH_3COCH_2COCH_3$ has a β-diketone structure, where two keto groups are separated by a CH_2 group. This confirms that compound M must also be a β-diketone precursor.

Among the options provided, only $CH_3COCH_2COCH_3$ matches the final product structure. Thus, the correct answer is Option 1.

Quick Tip

Grignard reagents react with carbonyl compounds to form alcohol intermediates, which can further undergo hydrolysis to yield ketones, β-diketones, or carboxylic acids depending on the reaction conditions.

42. 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 Gd (Gadolinium) is [Xe] $4f^7$ $5d^1$ $6s^2$. When Gd loses 3 electrons (one from the 6s orbital and two from the 5d orbital), it becomes Gd^{3+} with the electronic configuration [Xe] $4f^7$. This configuration does not match $4f^6$.

The electronic configuration of Sm (Samarium) is [Xe] $4f^6$ $6s^2$. When Sm loses 2 electrons from the 6s orbital, it becomes Sm^{2+} with the configuration [Xe] $4f^6$. This matches the given $4f^6$ configuration.

The configuration of Sm^{3+} is [Xe] $4f^5$, and that of Tb^{3+} (Terbium) is [Xe] $4f^8$. Neither of these matches the required configuration.

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

Quick Tip

Remember, the 4f configuration of lanthanides is determined by the number of electrons lost in forming their ions.

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43. 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: Conductivity in materials depends on the availability of free charge carriers and their mobility.

1. For metallic conductors: Conductivity decreases with an increase in temperature. This is because as temperature rises, the lattice vibrations in the metal increase, leading to more frequent collisions between electrons and the lattice ions. This reduces the mobility of electrons, thereby decreasing conductivity.
2. For semiconductors: Conductivity increases with an increase in temperature. In semiconductors, thermal energy excites more electrons from the valence band to the conduction band, increasing the number of free charge carriers (electrons and holes). This leads to higher conductivity at elevated temperatures.

Thus, the correct answer is that the conductivity of metals decreases while the conductivity of semiconductors increases when heated.

Quick Tip

Metal conductivity decreases with heat, while semiconductor conductivity increases because of electron excitation.

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44. 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 reaction involves:

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

Here, each molecule of $Na_2S_2O_3$ donates 1 electron, leading to a total of 2 electrons being transferred per molecule of I_2.

1. Oxidation states of sulfur: In $Na_2S_2O_3$, the average oxidation state of sulfur is +2. During the reaction, sulfur in $Na_2S_2O_3$ is partially oxidized to $Na_2S_4O_6$, where the average oxidation state becomes +2.5.

2. Definition of equivalent weight: The equivalent weight of a substance is given by:

$$\text{Equivalent Weight} = \frac{\text{Molecular Weight}}{n}$$

Here, n represents the number of electrons transferred per molecule in the reaction.

3. Calculation: For $Na_2S_2O_3$, $n = 1$, because each molecule transfers 1 electron. Therefore, the equivalent weight of $Na_2S_2O_3$ is equal to its molecular weight, M.

Thus, the equivalent weight of $Na_2S_2O_3$ in this reaction is M.

Quick Tip

Equivalent weight = Molecular weight divided by the number of electrons transferred.

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45. 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: The reactivity order towards an SN1 reaction is determined by the stability of the carbocation intermediate. Allyl chloride forms an allyl carbocation, which is resonance-stabilized, making it more stable. Ethyl chloride forms a primary carbocation, which is less stable than the allyl carbocation. Chlorobenzene, however, does not undergo SN1 reactions readily because the carbocation would be destabilized due to the aromatic ring. Thus, the reactivity order is I $>$ III $>$ II

Quick Tip

The stability of carbocations plays a crucial role in determining the rate of SN1 reactions.

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46. 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: At 25°C, nitration of toluene with a mixture of nitric acid and sulfuric acid (mixed acid) predominantly gives ortho- and para-nitrotoluene as the products. The para isomer is the major product due to steric and electronic factors. The methyl group on toluene is an activating group, which directs the nitro group to the ortho and para positions.

Quick Tip

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

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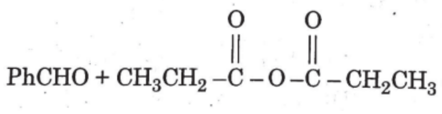
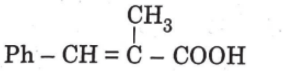
47. The product 'P' in the above reaction is:

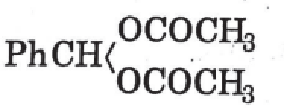


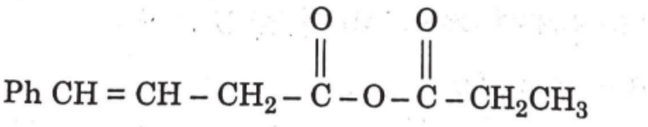
$$\text{PhCHO} + CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3 \xrightarrow{CH_3CH_2C(O)ONa\ \text{(anhydrous)}} P$$

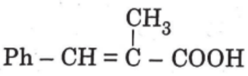
Options:

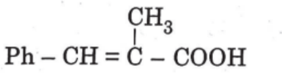
1. Ph CH = $CHCH_2COOH$
2. 

$$Ph-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOH$$

3.  $PhCH(OCOCH_3)_2$

4.  $Ph\,CH = CH - CH_2 - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_2CH_3$

Correct Answer: 2.  $Ph - CH = \overset{CH_3}{\overset{|}{C}} - COOH$

Solution: This reaction is a Perkin condensation reaction. Benzaldehyde (PhCHO) reacts with acetic anhydride in the presence of a base (sodium ethoxide) to produce cinnamic acid  $Ph - CH = \overset{CH_3}{\overset{|}{C}} - COOH$. The reaction proceeds through the formation of an enolate ion, followed by aldol-like condensation and dehydration to yield the α, β-unsaturated carboxylic acid product.

Quick Tip

Perkin condensation is typically used to synthesize α, β-unsaturated carboxylic acids by reacting an aromatic aldehyde with an anhydride in the presence of a base.

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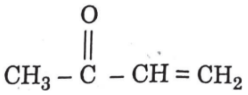
48. The decreasing order of reactivity of the following alkenes towards HBr addition is:

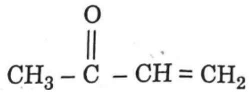
CH_3–CH=CH_2 (I), CF_3–CH=CH_2 (II), MeOCH=CH_2 (III),  $CH_3 - \overset{O}{\overset{\|}{C}} - CH = CH_2$ (IV)

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: The reactivity of alkenes towards HBr addition depends on the stability of the carbocation intermediate formed during the reaction:

- $MeOCH=CH_2$ (III) forms a resonance-stabilized carbocation due to the electron-donating methoxy group, making it the most reactive.
- $CH_3–CH=CH_2$ (I) forms a secondary carbocation, which is moderately stable.
- $CF_3–CH=CH_2$ (II) forms a destabilized carbocation due to the electron-withdrawing CF_3 group.
-  $CH_3-\overset{\overset{O}{\|}}{C}-CH=CH_2$ (IV) forms a sterically hindered carbocation, making it the least reactive. Thus, the order of reactivity is III > I > II > IV.

Quick Tip

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

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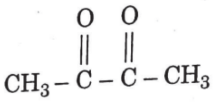
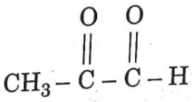
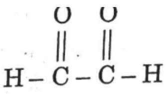
49. Ozonolysis of o-xylene produces:


$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

I


$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

II


$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

III

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: Ozonolysis of o-xylene involves the cleavage of the double bonds in the aromatic ring, leading to the formation of three carbonyl compounds:
- Compound I: $CH_3–C(O)–C(O)–CH_3$ (produced once),
- Compound II: $CH_3–C(O)–C(O)–H$ (produced twice),
- Compound III: $H–C(O)–C(O)–H$ (produced thrice).

The ratios of the products formed depend on the symmetry of the molecule and the distribution of substituents around the aromatic ring. In the case of o-xylene, the ratio of the products is I:II:III = 1:2:3.

Quick Tip

Ozonolysis of substituted aromatic compounds leads to products based on the cleavage of double bonds, with product ratios determined by the symmetry and substituents of the starting compound.

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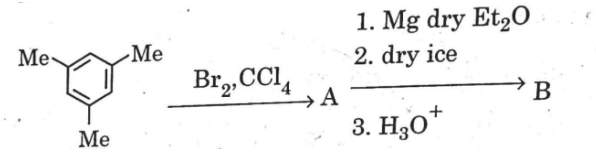
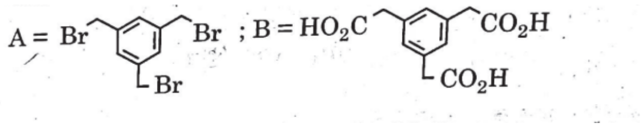
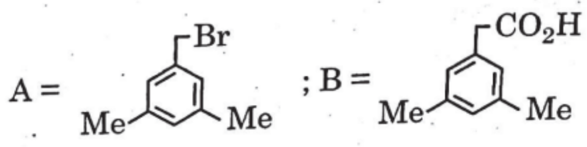
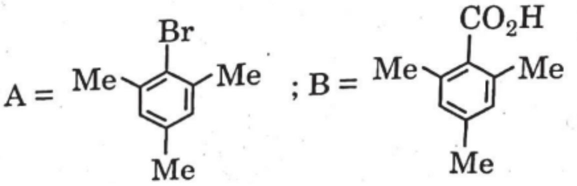
50. The compounds A and B are respectively:

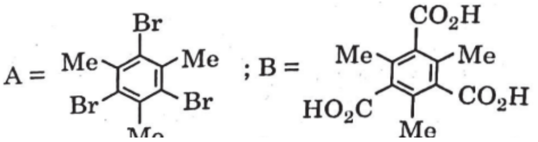


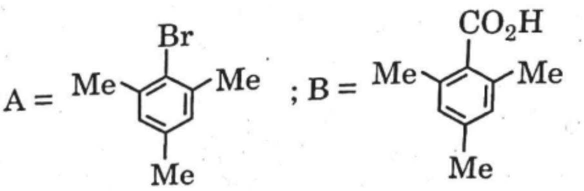
Options:

1. 

2. 

3. 

4. 

Correct Answer: 3. 

Solution: The reaction sequence involves the formation of a Grignard reagent from Me Br and Mg in dry ether. The Grignard reagent reacts with CO_2 (from dry ice) to form a carboxylate, which upon protonation with H_3O^+ gives a carboxylic acid. The correct structures of A and B are shown in option (3).

Quick Tip

Grignard reagents are versatile in forming alcohols or acids depending on the electrophile used.

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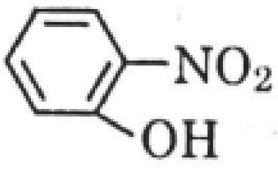
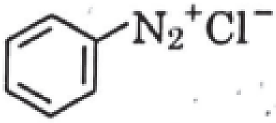
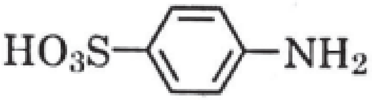
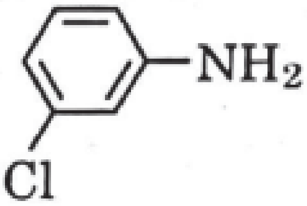
51. The compound that does not give a positive test for nitrogen in Lassaigne's test is:

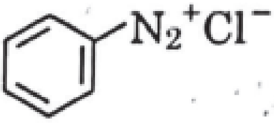
Options:

1. 

2. 

3. 

4. 

Correct Answer: 2. 

Solution:

In Lassaigne's test, compounds containing nitrogen form a characteristic blue or purple color with sodium fusion extract when treated with sodium picrate or other reagents. The compound that does not give a positive test for nitrogen is the one that does not contain nitrogen in its structure.

The given compounds are:

- (A) Nitro phenol ($C_6H_4NO_2OH$) contains nitrogen and will give a positive test.
- (B) Chlorobenzene (C_6H_5Cl) does not contain nitrogen, and thus does not give a positive test for nitrogen in Lassaigne's test.
- (C) Aniline ($C_6H_4NH_2$) contains nitrogen and will give a positive test.
- (D) Aminobenzene ($C_6H_4NH_2$) contains nitrogen and will give a positive test.

Thus, the compound that does not give a positive test for nitrogen is **(B) Chlorobenzene**.

Quick Tip

For Lassaigne's test, nitrogen must be directly bonded to carbon in the organic compound for a positive test.

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52. 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:

Phenol is acidic due to the resonance stabilization of the phenoxide ion. The introduction of an electron-withdrawing group such as -CHO increases acidity by stabilizing the negative charge on the oxygen atom.
- 4-Hydroxybenzaldehyde (II): The -CHO group at the para position exerts the maximum electron-withdrawing effect due to resonance and inductive effects, making II the most acidic. - 3-Hydroxybenzaldehyde (III): The -CHO group at the meta position provides a

lesser electron-withdrawing effect compared to the para position, making III less acidic than II but more acidic than I. - Phenol (I): Without any substituents, phenol has the lowest acidity among the three compounds.

Therefore, the acidity order is I < III < II.

Quick Tip

Electron-withdrawing groups stabilize the phenoxide ion and increase acidity. Their effect depends on their position relative to the hydroxyl group.

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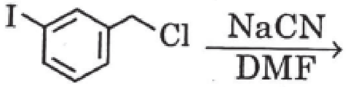
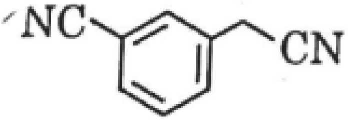
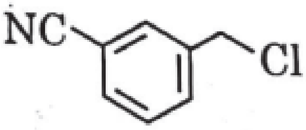
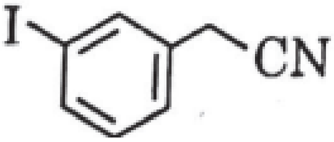
53. The major product of the following reaction is:

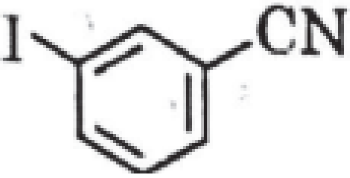


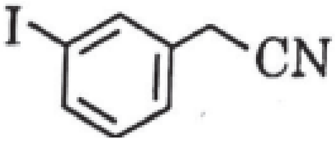
Options:

1. 

2. 

3. 

4. 

Correct Answer: 3. 

Solution:

The given reaction involves a nucleophilic substitution (S_N2) where sodium cyanide (NaCN) is used as the nucleophile and DMF is the solvent. In this reaction, the cyanide ion (CN^-) will attack the electrophilic carbon attached to the halide group (Cl or I) and replace it.

The structure of the reactant is:

$$C_6H_4ClI$$

When NaCN is added, the cyanide ion (CN^-) will substitute for the halide group, leading to the formation of a nitrile group (CN).

The major product of this reaction will be:

$$C_6H_4CN$$

Thus, the major product is the compound **(C) Iodobenzene with one CN group attached to the benzene ring**.

Quick Tip

Nucleophilic aromatic substitution reactions favor positions that stabilize the intermediate through resonance or inductive effects.

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54. 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:

The spontaneity of a chemical reaction, including polymerization, is determined by the Gibbs free energy change (ΔG). For a reaction to be spontaneous, ΔG must be negative:

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

where ΔH is the enthalpy change, ΔS is the entropy change, and T is the temperature in Kelvin.
In the case of spontaneous polymerization:

- $\Delta H < 0$: The process is exothermic, releasing energy as bonds are formed between monomers.
- $\Delta S < 0$: Polymerization involves the formation of a more ordered structure from monomers, leading to a decrease in entropy.

Even though ΔS is negative, the large negative ΔH ensures that ΔG remains negative, satisfying the condition for spontaneity. Thus, the correct answer is:

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

Quick Tip

For spontaneity, focus on the balance of ΔH, ΔS, and T in the ΔG equation.

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55. 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 relationship between Gibbs Free Energy change (ΔG°) and the equilibrium constant (K) is given by:

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

Here: - $K = 10^{-14}$ (ionic product of water), - $R = 1.987$ cal mol^{-1} K^{-1} (universal gas constant), - $T = 298$ K (temperature in Kelvin).

Substituting these values:

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

Since $\ln(10^{-14}) = -14 \ln(10)$ and $\ln(10) \approx 2.303$:

$$\Delta G^\circ = -1.987 \times 298 \times (-14 \times 2.303) = 19100 \, \text{cal mol}^{-1}$$

Converting to kcal mol^{-1}:

$$\Delta G^\circ = 19.1 \, \text{kcal mol}^{-1}$$

Thus, the free energy change is approximately 19.1 kcal mol^{-1}.

Quick Tip

Always use $\Delta G^\circ = -RT \ln K$ for equilibrium constant-related problems. Remember to convert units as needed.

---

56. 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:

The velocity of an electron in a Bohr orbit is inversely proportional to the principal quantum number (n):

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

For the first Bohr orbit ($n = 1$), the velocity is v_1. For the third Bohr orbit ($n = 3$), the velocity is v_3. Using the proportionality:

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

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

Quick Tip

For Bohr model calculations, remember that velocity is inversely proportional to the principal quantum number ($v \propto 1/n$).

---

57. 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:

The compressibility factor (Z) is defined as:

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

For a van der Waals gas, the equation of state is:

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

At high pressures, the volume V decreases, making the term b (excluded volume) significant. The term involving a (intermolecular attraction) becomes negligible. Simplifying for high pressure:

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

Thus, the compressibility factor is approximately $1 + \frac{Pb}{RT}$ under high-pressure conditions.

Quick Tip

At high pressures, focus on the excluded volume effect in the van der Waals equation. The attraction term (a) becomes less significant.

---

58. 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:

For a spontaneous process at constant temperature and pressure:

- Gibbs Free Energy (ΔG) must be negative: $(\Delta G_{\text{system}})_{T,P} < 0$.
- The total entropy change (system + surroundings) must be positive: $(\Delta S_{\text{system}}) + (\Delta S_{\text{surroundings}}) > 0$.
- Internal energy change (ΔU) can vary depending on the process but is typically negative under adiabatic conditions.

Option 3, which states $(\Delta G_{\text{system}})_{T,P} > 0$, is incorrect because a positive ΔG implies a non-spontaneous process.

Quick Tip

For spontaneity, ΔG¡0 and total entropy must increase. Always check for contradictions in given statements.

---

59. 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:

- Option 1: Correct. Viscosity decreases with an increase in temperature because the intermolecular forces are weakened, allowing liquid molecules to flow more easily.
- Option 2: Correct. Surface tension decreases with temperature due to reduced cohesive forces at the liquid surface.
- Option 3: InCorrect. Impurities increase viscosity by disrupting the liquid's intermolecular interactions, making it harder for molecules to flow.
- Option 4: correct. The effect of impurities on surface tension depends on the type of impurity. Impurities can either increase or decrease surface tension. For example, surfactants lower surface tension, while some other impurities might increase it.

Therefore, option 3 is incorrect.

Quick Tip

Impurities have variable effects on surface tension depending on their nature. For viscosity, impurities always increase resistance to flow.

---

60. 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:

- The rate constant (k) is governed by the Arrhenius equation:

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

Here, A is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the temperature. As T increases, the exponential term increases, and hence, k always increases.

- The equilibrium constant (K) depends on the reaction's enthalpy change (ΔH):

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

For exothermic reactions (ΔH¡0), K decreases with temperature. For endothermic reactions (ΔH¿0), K increases with temperature.

Thus, the equilibrium constant can either increase or decrease depending on the reaction's nature, but the rate constant always increases with temperature.

Quick Tip

The rate constant always increases with temperature due to the Arrhenius equation. The equilibrium constant's behavior depends on the reaction's enthalpy change.

61. 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:

The atomic number of $^{214}_{83}Bi$ is 83, and the mass number is 214. 1. Emission of a β-particle: A β-particle emission increases the atomic number by 1 (83 $\rightarrow$ 84) but keeps the mass number unchanged (214). 2. Emission of an α-particle: An α-particle emission decreases the atomic number by 2 (84 $\rightarrow$ 82) and the mass number by 4 (214 $\rightarrow$ 210).

The number of neutrons is calculated as:

$$\text{Number of neutrons} = \text{Mass number} - \text{Atomic number} = 210 - 82 = 128$$

Quick Tip

Remember that β-emission increases the atomic number, while α-emission decreases both atomic number and mass number.

---

62. Which hydrogen-like species will have the same radius as the 1st 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:

The radius of the nth Bohr orbit for a hydrogen-like species is given by:

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

where n is the principal quantum number, a_0 is the Bohr radius for hydrogen, and Z is the atomic number. For the 1st Bohr orbit of hydrogen ($n = 1$, $Z = 1$), $r = a_0$.

We need to find a species where $r = a_0$. Let us check the options: - Option 1: $n = 2$, Li^{2+} ($Z = 3$):

$$r = \frac{2^2 a_0}{3} = \frac{4}{3} a_0$$

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

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

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

$$r = \frac{2^2 a_0}{2} = 2a_0$$

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

$$r = \frac{3^2 a_0}{3} = 3a_0$$

Only option 2 gives the same radius as the 1st Bohr orbit of hydrogen.

Quick Tip

The radius of a hydrogen-like species depends on n^2/Z. To match the radius of hydrogen's 1st Bohr orbit, r must equal a_0.

---

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

Options:

1. $k/2.303$
2. k
3. $-k/2.303$
4. $-k$

Correct Answer: 3. $-k/2.303$

Solution:

For a first-order reaction, the integrated rate law is:

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

where $[A]$ is the concentration at time t, k is the rate constant, and $[A]_0$ is the initial concentration. Taking the logarithm to base 10:

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

This equation is of the form $y = mx + c$, where: - $y = \log[A]$, - $x = t$, - $m = -\frac{k}{2.303}$ (slope), - $c = \log[A]_0$.

Thus, the slope of the plot of log(reactant concentration) against time is $-\frac{k}{2.303}$.

Quick Tip

For first-order reactions, remember that the slope of the log(concentration) vs. time plot is always $-k/2.303$.

---

64. Equal volumes of aqueous solution 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:

- HCl is a monoprotic acid, so 0.1 M HCl provides 0.1 M H^+ ions. - H_2SO_4 is a diprotic acid, so 0.2 M H_2SO_4 provides $2 \times 0.2 = 0.4$ M H^+ ions.

When equal volumes of the two solutions are mixed, the total volume doubles, and the concentration of each acid is halved:

$$\text{New concentration of HCl} = \frac{0.1}{2} = 0.05\,\text{M H}^+$$

$$\text{New concentration of } H_2SO_4 = \frac{0.4}{2} = 0.2\,\text{M H}^+$$

The total H^+ concentration is:

$$0.05\,\text{M} + 0.2\,\text{M} = 0.25\,\text{M}$$

Quick Tip

When acids are mixed, calculate the new concentration of H^+ ions by considering dilution and the number of ionizable protons.

---

65. 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:

The boiling point elevation is a colligative property, which depends on the number of solute particles in the solution:

- KNO_3: Strong electrolyte, dissociates into 2 ions (K^+ and NO_3^-).
- NaCl: Strong electrolyte, dissociates into 2 ions (Na^+ and Cl^-).
- CH_3COOH: Weak electrolyte, partially dissociates into CH_3COO^- and H^+ ions.
- Sucrose: Non-electrolyte, does not dissociate.

Since strong electrolytes like KNO_3 and NaCl produce more particles in solution compared to weak electrolytes like CH_3COOH and non-electrolytes like sucrose, the order of boiling points is:

$$1\text{ N } KNO_3 = 1\text{ N NaCl}$$

¿1 N CH_3COOH¿1 N sucrose.

Quick Tip

Colligative properties depend on the number of solute particles. Strong electrolytes dissociate completely, producing more particles than weak electrolytes or non-electrolytes.

---

66. 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:

The solubility of silver halides in water decreases as the size of the halide ion increases. This is because:

- Larger halide ions (e.g., I^-) have lower lattice energy compared to smaller halide ions (e.g., F^-).

- The lattice energy dominates over the hydration energy, making the solubility lower for larger ions.

Therefore, the solubility order is:

$$\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}.$$

Quick Tip

The solubility of silver halides decreases as the size of the halide ion increases due to the balance of lattice energy and hydration energy.

---

67. 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:

Part (i): $CuSO_4$ added to saturated $(NH_4)_2SO_4$ solution

When $CuSO_4$ is added to a saturated solution of $(NH_4)_2SO_4$, it introduces Cu^{2+} ions into the solution. Cu^{2+} is a Lewis acid and reacts with water, increasing the concentration of H^+ ions. This reaction results in an increase in acidity:

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

Part (ii): SbF_5 added to anhydrous HF

SbF_5 is a strong Lewis acid and forms the superacid **HF-SbF_5** when mixed with HF. This combination greatly increases the acidity of the solution as it stabilizes the fluoride ion (F^-), shifting the equilibrium towards producing more H^+ ions:

$$\mathrm{HF} + \mathrm{SbF_5} \rightarrow \mathrm{HSbF_6} + \mathrm{H^+}$$

In both cases, the acidity of the system increases.

Conclusion: The correct answer is:

$$\boxed{\text{Increases, Increases.}}$$

Quick Tip

The effect of added compounds on acidity depends on whether the compound acts as a Lewis acid or base, or influences ion dissociation.

---

68. 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:

- ClO_3^-: Central Cl atom has 1 lone pair.
- XeF_4: Central Xe atom has 2 lone pairs.
- SF_4: Central S atom has 1 lone pair.
- I_3^-: Central I atom has 3 lone pairs.

Thus, I_3^- has the maximum number of lone pairs (3) on its central atom.

Quick Tip

To find the number of lone pairs on the central atom, calculate the total valence electrons, subtract bonding electrons, and divide the remainder by 2.

---

69. 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:

Mohr's salt, chemically known as ammonium iron(II) sulfate, has the formula $(NH_4)_2[Fe(SO_4)_2] \cdot 6H_2O$.

When dissolved in water, it dissociates completely as follows:

$$(NH_4)_2[Fe(SO_4)_2] \cdot 6H_2O \rightarrow 2\text{NH}_4^+ + \text{Fe}^{2+} + 2\text{SO}_4^{2-}$$

From this dissociation, the ions produced are:

- $2\,\text{NH}_4^+$ (ammonium ions),
- $1\,\text{Fe}^{2+}$ (iron(II) ion),
- $2\,\text{SO}_4^{2-}$ (sulfate ions).

Adding these, the total number of moles of ions produced from one mole of Mohr's salt is:

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

Conclusion: The correct answer is:

$$\boxed{5.}$$

Quick Tip

To calculate the number of ions, consider the complete dissociation of all components of the salt.

---

70. Which of the following species exhibits both LMCT and paramagnetism?

Options:

1. MnO_4^-
2. MnO_4^{2-}
3. $\text{Cr}_2\text{O}_7^{2-}$
4. CrO_4^{2-}

Correct Answer: 2. MnO_4^{2-}

Solution:

To analyze the problem, we consider two properties:

- **Ligand-to-Metal Charge Transfer (LMCT):** LMCT occurs when there is a transfer of electrons from the ligand (oxygen) to the metal ion (Mn or Cr) due to a significant energy difference between the ligand and metal orbitals.
- **Paramagnetism:** Paramagnetic species have unpaired electrons in their electronic configuration.

Analysis of the given species:

- **MnO_4^- (Permanganate ion):** In MnO_4^-, Mn is in the +7 oxidation state with no unpaired electrons (electronic configuration: $3d^0$). This species shows LMCT but is diamagnetic.
- **MnO_4^{2-} (Manganate ion):** In MnO_4^{2-}, Mn is in the +6 oxidation state with one unpaired electron (electronic configuration: $3d^1$). This species exhibits both LMCT and paramagnetism.
- **$Cr_2O_7^{2-}$ (Dichromate ion):** In $Cr_2O_7^{2-}$, Cr is in the +6 oxidation state with no unpaired electrons (electronic configuration: $3d^0$). This species is diamagnetic and shows LMCT.
- **CrO_4^{2-} (Chromate ion):** In CrO_4^{2-}, Cr is also in the +6 oxidation state with no unpaired electrons. This species shows LMCT but is diamagnetic.

Conclusion: Among the given options, 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 correct answer is:

$$\boxed{2.\ MnO_4^{2-}}$$

Quick Tip

Paramagnetism arises from unpaired electrons, while LMCT involves electron transfer between ligand and metal.

---

71. 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:

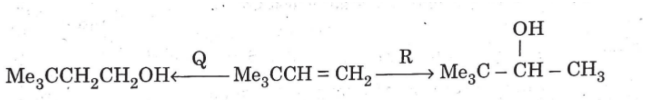
The structure of P_4O_{10} is based on four phosphorus atoms forming a tetrahedron with oxygen atoms bridging between them. There are six P–O–P linkages in the molecule.

Quick Tip

The number of P–O–P linkages in P_4O_{10} can be determined by analyzing its molecular structure. Each phosphorus atom is bonded to three oxygen atoms, with some forming bridges.

---

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



$$Me_3CCH_2CH_2OH \xleftarrow{Q} Me_3CCH=CH_2 \xrightarrow{R} Me_3C-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$$

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:

The reaction sequence involves:

1. Hydroboration-Oxidation: B_2H_6, H_2O_2/OH^- adds water across the double bond with anti-Markovnikov regioselectivity.

2. Acid-Catalyzed Hydration: H^+/H_2O adds water across the double bond with Markovnikov regioselectivity.

Quick Tip

Hydroboration-oxidation follows anti-Markovnikov addition, while acid-catalyzed hydration follows Markovnikov addition.

---

73. 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:

The concentration of HCl is 10^{-8} M. Since HCl is a strong acid, the $[H^+]$ from HCl is 10^{-8} M. However, the autoionization of water also contributes $[H^+] = 10^{-7}$ M. Therefore, the total $[H^+]$ is:

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

The pH is given by:

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

Thus, the pH is greater than 6 and less than 7.

Quick Tip

For very dilute strong acids, account for the autoionization of water when calculating pH.

---

74. 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:

Given: - $k = 1.65 \times 10^{-4}$ S cm^{-1}, - $C = 0.02$ M, - $\lambda^\circ_{\text{H}^+} = 349.1$ S cm^2 mol^{-1}, - $\lambda^\circ_{\text{CH}_3\text{COO}^-} = 40.9$ S cm^2 mol^{-1}.

1. Calculate Λ_m:

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

2. Calculate Λ°:

$$\Lambda^\circ = \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{CH}_3\text{COO}^-} = 349.1 + 40.9 = 390\,\text{S cm}^2\ \text{mol}^{-1}.$$

3. Calculate α:

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

Quick Tip

The degree of dissociation (α) is the ratio of the molar conductivity of the solution (Λ_m) to the limiting molar conductivity (Λ°).

---

75. 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: Contains two -OH groups and one H atom directly bonded to P.
- H_3PO_4: Contains three -OH groups and one P=O bond.

Quick Tip

The structure of oxyacids of phosphorus determines the number of -OH groups. Check for direct P-H bonds and P=O bonds.

76. 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 reaction characterized by:

- A single step where the nucleophile attacks the electrophilic carbon and the leaving group departs simultaneously.
- Statement 1: True. The reaction rate depends on the concentration of both the nucleophile and the substrate, and hence increases with increasing nucleophilicity.
- Statement 2: True. The ”2” in SN2 indicates that the reaction is second-order, dependent on two reactants.
- Statement 3: True. Tertiary substrates do not follow the SN2 mechanism due to steric hindrance.
- Statement 4: False. Optical rotation may change, but it is not guaranteed to shift from (+) to (-) or vice versa, as this depends on the specific nucleophile and substrate.

Quick Tip

SN2 reactions are stereospecific and result in inversion of configuration. Steric hindrance plays a critical role in determining the feasibility of the reaction.

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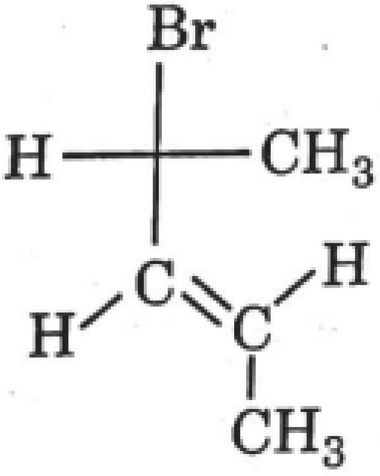
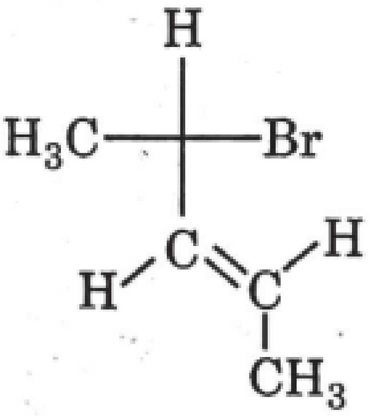
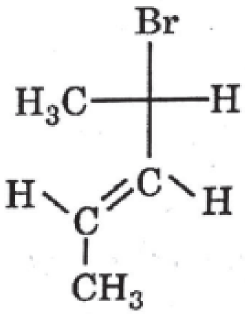
77. Which of the following represent(s) the enantiomer of Y?

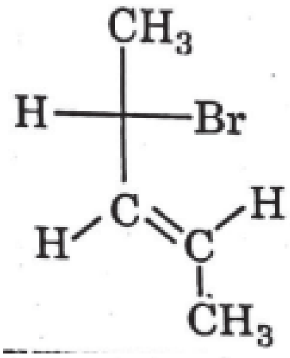


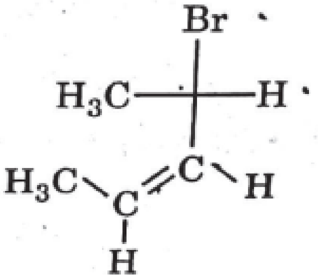
(Y)

Options:

1. 

2. 

3. 

4. 

Correct Answer: 2. Image B, c

Solution:

Given Compound (Y):

The structure of compound Y is as follows:

$$Br - [:: 60] - [:: -60]H - [:: -60] - [:: -60](CH_3) - [:: -60]H$$

In this compound:

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

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

Analysis of the Options:

- **Option (A):** This compound is not a mirror image of Y, as the positions of the groups are not flipped.
- **Option (B):** This structure matches the mirror image of Y. The relative positions of Br, H, CH_3, and the secondary group CH(H)(CH_3) are correctly inverted, making it an enantiomer.

- **Option (C):** This structure also matches a mirror image of Y with the correct spatial inversion of groups, making it another enantiomer of Y.
- **Option (D):** This structure is identical to Y, not its enantiomer.

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

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

Quick Tip

To identify enantiomers, look for non-superimposable mirror images by analyzing the relative positions of substituents.

---

78. 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 determine the oxidation number of Cr:

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

  Since 4 of the oxygen atoms form peroxide bonds (oxidation state of each O is -1), the calculation becomes:

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

Solving 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 an ideal gas:

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

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

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

  $\Delta n_g = 2 - 1 = 1$. Therefore, $\Delta H > \Delta U$. This statement is **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 into 2 H^+ ions and 1 SO_4^{2-} ion per molecule. However, in a 0.1 N solution, the second ionization of H_2SO_4 is suppressed due to high H^+ concentration, resulting in an effective contribution of slightly more than 0.1 M H^+. On the other hand, 0.1 N HCl contributes exactly 0.1 M H^+ ions. Thus, 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 relation 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 expressions. This statement is **incorrect**.

Conclusion: The correct statements are:

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

Quick Tip

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

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

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80. 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 is only slightly soluble in water.
- Statement 2: True. I_2 dissolves more in water in the presence of KI due to the formation of I_3^- complexes.
- Statement 3: True. I_2 is freely soluble in non-polar solvents like CCl_4.
- Statement 4: False. I_2 is freely soluble in hot water due to increased solubility at higher temperatures.

Quick Tip

The solubility of iodine depends on the solvent's polarity and temperature. Excess KI enhances solubility through complex formation.