JEE Main 2025 April 7 Shift 2 Chemistry
Question Paper with Solutions

Time Allowed :3 Hours	**Maximum Marks :**300	**Total Questions :**75

General Instructions

Read the following instructions very carefully and strictly follow them:

1. Multiple choice questions (MCQs)
2. Questions with numerical values as answers.
3. There are three sections: **Mathematics, Physics, Chemistry**.
4. **Mathematics:** 25 (20+5) 10 Questions with answers as a numerical value. Out of 10 questions, 5 questions are compulsory.
5. **Physics:** 25 (20+5) 10 Questions with answers as a numerical value. Out of 10 questions, 5 questions are compulsory..
6. **Chemistry:** 25 (20+5) 10 Questions with answers as a numerical value. Out of 10 questions, 5 questions are compulsory.
7. Total: 75 Questions (25 questions each).
8. 300 Marks (100 marks for each section).
9. **MCQs:** Four marks will be awarded for each correct answer and there will be a negative marking of one mark on each wrong answer.
10. **Questions with numerical value answers:** Candidates will be given four marks for each correct answer and there will be a negative marking of 1 mark for each wrong answer.

CHEMISTRY

Section - A

51. Given below are two statements :
Statement (I) : On hydrolysis, oligo peptides give rise to fewer number of α-amino acids while proteins give rise to a large number of β-amino acids.
Statement (II) : Natural proteins are denatured by acids which convert the water soluble form of fibrous proteins to their water insoluble form.
In the light of the above statements, choose the most appropriate answer from the options given below :
(1) Both statement I and statement II are correct
(2) Statement I is incorrect but Statement II is correct
(3) Both statement I and statement II are incorrect

(4) Statement I is correct but Statement II is incorrect

Correct Answer: (3) Both statement I and statement II are incorrect

Solution: Step 1: Analyze Statement (I).

Statement (I) claims that oligopeptides yield a smaller number of α-amino acids upon hydrolysis, while proteins yield a large number of β-amino acids.

Oligopeptides are short chains of amino acids linked by peptide bonds. Hydrolysis of oligopeptides breaks these peptide bonds, resulting in the constituent amino acids. These amino acids are α-amino acids, characterized by the amino group and the carboxyl group attached to the same carbon atom (the α-carbon). The number of α-amino acids produced is equal to the number of peptide bonds broken plus one (the original N-terminal amino acid), which is a small number for oligopeptides.

Proteins are long chains (polymers) of amino acids. Upon hydrolysis, proteins also yield α-amino acids, and the number of these amino acids is large due to the large size of protein molecules. Proteins do not yield β-amino acids upon hydrolysis. β-amino acids have the amino group attached to the carbon atom adjacent to the carboxyl group (β-carbon). Peptide bonds in proteins are formed between the α-carboxyl group of one amino acid and the α-amino group of the next. Therefore, Statement (I) is incorrect because proteins yield α-amino acids, not β-amino acids, upon hydrolysis.

Step 2: Analyze Statement (II).

Statement (II) claims that natural proteins are denatured by acids, converting water-soluble fibrous proteins to their water-insoluble form. Denaturation of proteins involves the disruption of their secondary, tertiary, and quaternary structures, leading to a loss of their native conformation and biological activity. Acids are indeed denaturing agents for proteins as they can disrupt ionic bonds and hydrogen bonds within the protein structure.

However, the statement specifically mentions fibrous proteins becoming water-insoluble upon denaturation. Many fibrous proteins, such as keratin and collagen, are inherently water-insoluble due to their structure and amino acid composition, which often involves a high proportion of hydrophobic residues and extensive cross-linking. Denaturation might cause further aggregation or structural changes but does not necessarily convert a water-soluble fibrous protein to a water-insoluble form, especially since many are already insoluble. Furthermore, denaturation can affect both globular (often water-soluble) and fibrous proteins. The outcome on solubility depends on the specific protein and the nature of the denaturation process. Therefore, Statement (II) is also incorrect as it presents an oversimplified and potentially misleading view of protein denaturation and solubility changes, particularly for fibrous proteins.

Step 3: Determine the correctness of both statements.

Based on the analysis, Statement (I) is incorrect, and Statement (II) is also incorrect.

Step 4: Choose the appropriate option. The option that states both Statement I and Statement II are incorrect is (3).

Quick Tip

Remember the basic structure of α- and β-amino acids and the type of amino acids produced upon protein and peptide hydrolysis. Also, understand the process of protein denaturation and its effects on protein structure and solubility, keeping in mind the different types of proteins (globular and fibrous).

52. Mixture of 1 g each of chlorobenzene, aniline and benzoic acid is dissolved in 50 mL ethyl acetate and placed in a separating funnel, 5 M NaOH (30 mL) was added in the same funnel. The funnel was shaken vigorously and then kept aside. The ethyl acetate layer in the funnel contains :

(1) benzoic acid
(2) benzoic acid and aniline
(3) benzoic acid and chlorobenzene
(4) chlorobenzene and aniline

Correct Answer: (4) chlorobenzene and aniline **Solution: Step 1: Understand the chemical properties of the given compounds.**

Chlorobenzene is a neutral, non-polar organic compound. It is insoluble in water but soluble in organic solvents like ethyl acetate. It does not react with NaOH.

Aniline is a weak organic base due to the lone pair of electrons on the nitrogen atom. It can react with strong acids to form salts. Its basicity is not strong enough to react with NaOH in a significant way to form a water-soluble salt under these conditions. Aniline is sparingly soluble in water but soluble in organic solvents like ethyl acetate.

Benzoic acid is a weak organic acid containing a carboxyl group (-COOH). It can react with strong bases like NaOH to form a water-soluble sodium benzoate salt.

Step 2: Analyze the reaction with NaOH.

When NaOH (an aqueous base) is added to the ethyl acetate solution containing chlorobenzene, aniline, and benzoic acid, a reaction will occur with the acidic component, benzoic acid:

$$\mathrm{C_6H_5COOH}(in\,ethyl\,acetate) + \mathrm{NaOH}(aq) \rightarrow \mathrm{C_6H_5COONa}(aq) + \mathrm{H_2O}$$

The product, sodium benzoate, is an ionic salt and is soluble in the aqueous layer (NaOH solution) but insoluble in the organic layer (ethyl acetate).

Chlorobenzene, being neutral and non-polar, will not react with NaOH and will remain dissolved in the ethyl acetate layer.

Aniline, being a weak base, will not react significantly with the strong base NaOH. It will mostly remain in its molecular form. Aniline has some solubility in water (though limited) and is also soluble in ethyl acetate. In a separating funnel, it will be distributed between the aqueous and organic layers based on its partition coefficient. However, since it did not undergo a chemical transformation into a highly water-soluble ionic species, a significant portion of aniline will likely remain in the ethyl acetate layer.

Step 3: Determine the contents of the ethyl acetate layer after separation.

After shaking the separating funnel and allowing the layers to separate, the aqueous layer (containing NaOH and sodium benzoate) will be at the bottom (due to higher density). The ethyl acetate layer (organic layer) will be at the top.

The compounds that would have preferentially dissolved in the ethyl acetate layer are those that are non-polar or have limited reactivity with NaOH and limited solubility in the aqueous phase under these conditions. These are chlorobenzene and aniline. Benzoic acid would have been converted to its sodium salt and moved into the aqueous layer.

Therefore, the ethyl acetate layer will primarily contain chlorobenzene and aniline.

Quick Tip

In liquid-liquid extraction using a separating funnel, the distribution of compounds between the two immiscible layers (aqueous and organic) depends on their solubility and reactivity with the reagents added. Acids react with bases to form water-soluble salts, and vice versa. Non-polar compounds tend to dissolve in organic solvents, while polar or ionic compounds dissolve in water.

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53. The hydration energies of K^+ and Cl^- are $-x$ and $-y$ kJ/mol respectively. If lattice energy of KCl is $-z$ kJ/mol, then the heat of solution of KCl is :

(1) $+x - y - z$

(2) $x + y + z$

(3) $z - (x + y)$

(4) $-z - (x + y)$

Correct Answer: (3) $z - (x + y)$

Solution: Step 1: Understand the process of dissolution and the associated energy changes.

The dissolution of an ionic compound like KCl in water involves two main steps:

1. Breaking the lattice: The ionic lattice of KCl must be broken down into individual gaseous ions $K^+(g)$ and $Cl^-(g)$. The energy required for this process is the lattice energy, $\Delta H_{lattice}$. Since lattice energy is defined as the energy released when gaseous ions combine to form one mole of a solid ionic compound, the energy required to break the lattice is the negative of the lattice energy given.

$$KCl(s) \rightarrow K^+(g) + Cl^-(g) \quad \Delta H_1 = -(-z) = +z \, kJ/mol$$

2. Hydration of ions: The gaseous ions then get hydrated by water molecules, forming aqueous ions $K^+(aq)$ and $Cl^-(aq)$. The energy released in this process is the hydration energy, $\Delta H_{hydration}$. The hydration energy of K^+ is $-x$ kJ/mol, and the hydration energy of Cl^- is $-y$ kJ/mol. The total hydration energy is the sum of the hydration energies of the individual ions.

$$K^+(g) + H_2O \rightarrow K^+(aq) \quad \Delta H_{hyd}(K^+) = -x \, kJ/mol$$

$$Cl^-(g) + H_2O \rightarrow Cl^-(aq) \quad \Delta H_{hyd}(Cl^-) = -y \, kJ/mol$$

The overall hydration energy is:

$$K^+(g) + Cl^-(g) \rightarrow K^+(aq) + Cl^-(aq) \quad \Delta H_2 = -x + (-y) = -(x + y) \, kJ/mol$$

Step 2: Apply Hess's Law to find the heat of solution.

The heat of solution ΔH_{sol} is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent. According to Hess's Law, the overall enthalpy change for a reaction is independent of the path taken. Therefore, the heat of solution of KCl can be found by summing the enthalpy changes of the two steps mentioned above:

$$\Delta H_{sol} = \Delta H_1 + \Delta H_2$$

$$\Delta H_{sol} = (+z) + (-(x + y))$$

$$\Delta H_{sol} = z - (x + y)\, kJ/mol$$

Step 3: Match the result with the given options.
The heat of solution of KCl is $z - (x + y)$ kJ/mol, which matches option (3).

Quick Tip

The heat of solution is the net energy change during the dissolution process. It can be thought of as the energy required to break the lattice minus the energy released during the hydration of the ions. Remember the sign conventions for lattice energy (usually negative) and hydration energy (usually negative).

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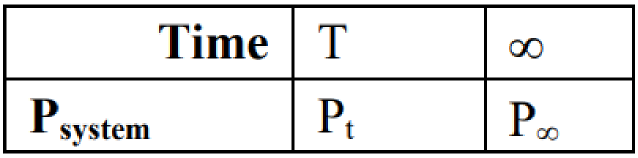
54. A(g) → B(g) + C(g) is a first order reaction.



Time	T	∞
P_{system}	P_t	P_∞

The reaction was started with reactant A only. Which of the following expression is correct for rate constant k ?
(1) $k = \frac{1}{t} \ln \frac{2(P_\infty - P_t)}{P_t}$
(2) $k = \frac{1}{t} \ln \frac{P_\infty}{P_t}$
(3) $k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$
(4) $k = \frac{1}{t} \ln \frac{P_\infty}{(P_\infty - P_t)}$

Correct Answer: (3) $k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$
Solution: Step 1: Set up the stoichiometry and partial pressures.
Let the initial pressure of A be P_0 at time $t = 0$. Since only A is present initially, P_t at $t = 0$ is P_0.
At time t, let the pressure of A reacted be p. Then the partial pressures of A, B, and C at time t are:
$P_A = P_0 - p$
$P_B = p$
$P_C = p$
The total pressure of the system at time t is $P_t = P_A + P_B + P_C = (P_0 - p) + p + p = P_0 + p$.
From this, we get $p = P_t - P_0$.
So, $P_A = P_0 - (P_t - P_0) = 2P_0 - P_t$.

At time $t = \infty$, the reaction goes to completion, so the pressure of A becomes zero.
$P_A(\infty) = 0$
$P_B(\infty) = P_0$
$P_C(\infty) = P_0$
The total pressure at $t = \infty$ is $P_\infty = P_A(\infty) + P_B(\infty) + P_C(\infty) = 0 + P_0 + P_0 = 2P_0$.
From this, we have $P_0 = P_\infty/2$.

Now, substitute P_0 in the expression for P_A: $P_A = 2(P_\infty/2) - P_t = P_\infty - P_t$.

Step 2: Apply the first-order rate law in terms of partial pressure.

For a first-order reaction $A \rightarrow products$, the rate law is $-\frac{dP_A}{dt} = kP_A$.

Integrating this equation from $t = 0$ to t and from $P_A(0) = P_0$ to $P_A(t)$:

$$\int_{P_0}^{P_A} \frac{dP_A}{P_A} = -k \int_0^t dt$$

$$\ln \frac{P_A}{P_0} = -kt$$

$$k = \frac{1}{t} \ln \frac{P_0}{P_A}$$

Step 3: Substitute the expressions for P_0 and P_A in terms of P_t and P_∞.

We have $P_0 = P_\infty/2$ and $P_A = P_\infty - P_t$. Substituting these into the rate constant expression:

$$k = \frac{1}{t} \ln \frac{P_\infty/2}{P_\infty - P_t}$$

$$k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$$

Step 4: Match the derived expression with the given options.

The derived expression for the rate constant k matches option (3).

Quick Tip

For gas-phase reactions where pressure is measured, it's often convenient to express the rate law and integrated rate law in terms of partial pressures. Remember to use the stoichiometry of the reaction to relate the change in pressure of the reactant to the total pressure of the system at any time.

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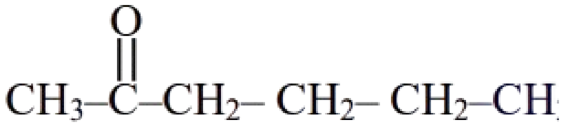
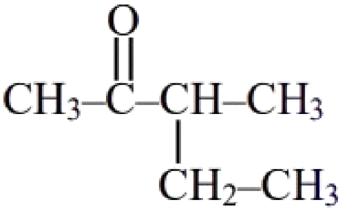
55. "P" is an optically active compound with molecular formula $C_6H_{12}O$. When "P" is treated with 2,4-dinitrophenylhydrazine, it gives a positive test. However, in presence of Tollens reagent, "P" gives a negative test. Predict the structure of "P".

(1)



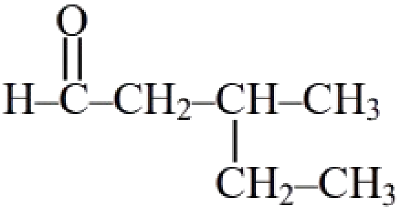
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2-CH$

(2)



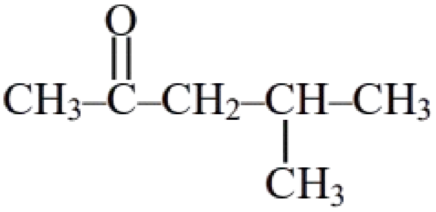
$CH_3-\overset{\overset{O}{||}}{C}-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

(3)



$H-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

(4)



$CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Correct Answer: (2)

Solution: Step 1: Analyze the molecular formula and deduce possible functional groups.

The molecular formula $C_6H_{12}O$ suggests a degree of unsaturation of $(2 \times 6 + 2 - 12)/2 = 1$. This indicates the presence of either a double bond or a ring. The positive test with 2,4-dinitrophenylhydrazine indicates the presence of a carbonyl group (aldehyde or ketone), which accounts for the one degree of unsaturation (C=O double bond). The negative test with Tollens reagent indicates the absence of an aldehyde group (as Tollens reagent oxidizes aldehydes to carboxylic acids, forming a silver mirror). Therefore, "P" must be a ketone.

Step 2: Consider the condition of optical activity.

For a molecule to be optically active, it must be chiral, meaning it has a stereocenter (a carbon atom bonded to four different groups). We need to examine the given ketone structures to identify one that has a chiral carbon atom.

Step 3: Examine each option.

(1) $CH_3-C(=O)-CH_2-CH_2-CH_2-CH_3$ (2-hexanone): The carbonyl carbon is bonded to a methyl group, a $-CH_2-$ group, and a $-CH_2-CH_2-CH_3$ group. No other carbon atom is bonded to four different groups. This molecule is achiral.

(2) $CH_3-C(=O)-CH(CH_3)-CH_2-CH_3$ (3-methyl-2-pentanone): The carbon atom at position 3 is bonded to a methyl group ($-CH_3$), an ethyl group ($-CH_2-CH_3$), a $-CH_2-C(=O)-CH_3$ group, and a hydrogen atom. These are four different groups, so the carbon at position

3 is a stereocenter. This molecule is chiral and a ketone.
(3) $H - C(=O) - CH_2 - CH(CH_3) - CH_2 - CH_3$ (2-methylpentanal): This is an aldehyde (positive Tollens test), so it cannot be "P".
(4) $CH_3 - C(=O) - CH_2 - CH(CH_3) - CH_3$ (4-methyl-2-pentanone): The carbonyl carbon is bonded to a methyl group, a $-CH_2-$ group, and a $-CH(CH_3) - CH_3$ group. No other carbon atom is bonded to four different groups. This molecule is achiral.
Step 4: Identify the structure that fits all the conditions.
The compound must be a ketone (positive 2,4-DNP, negative Tollens) and optically active (chiral). Only option (2), 3-methyl-2-pentanone, satisfies both these conditions. The carbon at position 3 is a stereocenter, making the molecule chiral.

Quick Tip

To solve this type of problem, systematically analyze the information provided by each chemical test and the molecular formula to narrow down the possible functional groups and structural features. Optical activity is a key indicator of chirality, which requires the presence of a stereocenter.

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56. Choose the incorrect trend in the atomic radii (r) of the elements :
(1) $r_{Br} < r_K$
(2) $r_{Mg} < r_{Al}$
(3) $r_{Rb} < r_{Cs}$
(4) $r_{At} < r_{Cs}$

Correct Answer: (2) $r_{Mg} < r_{Al}$
Solution: Step 1: Understand the trends in atomic radii in the periodic table.
Across a period (from left to right): Atomic radius generally decreases due to an increase in the effective nuclear charge. Electrons are added to the same energy level, while the number of protons in the nucleus increases, leading to a stronger attraction between the nucleus and the electrons, thus pulling them closer.
Down a group (from top to bottom): Atomic radius generally increases because electrons are added to higher energy levels (increasing the principal quantum number n), resulting in a larger electron cloud. The effect of increased nuclear charge is outweighed by the addition of electron shells and increased shielding by inner electrons.
Step 2: Analyze each option based on the periodic trends.
(1) $r_{Br} < r_K$
Bromine (Br) is in Period 4, Group 17, and Potassium (K) is in Period 4, Group 1. Across Period 4, atomic radius decreases from left to right. Therefore, $r_K > r_{Br}$, which means $r_{Br} < r_K$ is a correct trend.
(2) $r_{Mg} < r_{Al}$
Magnesium (Mg) is in Period 3, Group 2, and Aluminum (Al) is in Period 3, Group 13. Across Period 3, atomic radius decreases from left to right. Therefore, $r_{Mg} > r_{Al}$, which means $r_{Mg} < r_{Al}$ is an incorrect trend.
(3) $r_{Rb} < r_{Cs}$
Rubidium (Rb) is in Period 5, Group 1, and Cesium (Cs) is in Period 6, Group 1. Down Group 1 (alkali metals), atomic radius increases. Therefore, $r_{Cs} > r_{Rb}$, which means $r_{Rb} < r_{Cs}$ is a

correct trend.

(4) $r_{At} < r_{Cs}$

Astatine (At) is in Period 6, Group 17, and Cesium (Cs) is in Period 6, Group 1. Across Period 6, atomic radius generally decreases from left to right. Therefore, $r_{Cs} > r_{At}$, which means $r_{At} < r_{Cs}$ is a correct trend.

Step 3: Identify the incorrect trend.

Based on the analysis, the incorrect trend in atomic radii is given in option (2).

Quick Tip

To determine the relative atomic radii of elements, locate their positions in the periodic table and apply the general trends: atomic radius decreases across a period and increases down a group. Be mindful of any exceptions to these general trends, although they are not relevant in this specific question.

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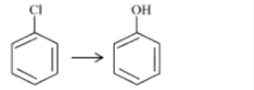
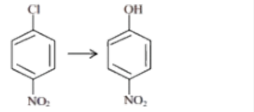
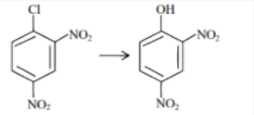
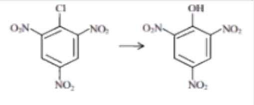
57. Match List-I with List-II

List-I Conversion		List-II Reagents, Conditions used	
(A)		(I)	Warm, H_2O
(B)		(II)	(a) NaOH, 368 K ; (b) H_3O^+
(C)		(III)	(a) NaOH, 443 K; (b) H_3O^+
(D)		(IV)	(a) NaOH, 623 K, 300 atm ; (b) H_3O^+

Choose the correct answer from the options given below :

(1) (A)-(II), (B)-(III), (C)-(I), (D)-(IV)

(2) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

(3) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)

(4) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

Correct Answer: (3) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)

Solution: Step 1: Analyze the conversions in List-I and the reagents/conditions in List-II.

The conversions involve the replacement of a chlorine atom on an aromatic ring by a hydroxyl group, forming a phenol. This is a nucleophilic aromatic substitution reaction. The reactivity of aryl halides towards nucleophilic substitution is greatly influenced by the presence of electron-withdrawing groups (like nitro groups) at ortho and para positions to the chlorine atom. More nitro groups activate the ring towards nucleophilic attack, allowing the reaction to proceed under milder conditions.

Step 2: Match each conversion with the appropriate reagents and conditions.

(A) $C_6H_5Cl \rightarrow C_6H_5OH$ (Chlorobenzene to Phenol): Chlorobenzene has no activating groups. The nucleophilic substitution of chlorine by OH^- requires harsh conditions (high temperature and high pressure) to overcome the stability of the C-Cl bond and the electron-rich aromatic ring. The Dow process uses NaOH at around 623 K and 300 atm, followed by acidification to yield phenol. Thus, (A) matches with (IV).
(B) $p - ClC_6H_4NO_2 \rightarrow p - HOC_6H_4NO_2$ (p-Nitrochlorobenzene to p-Nitrophenol): The presence of one nitro group at the para position activates the chlorine towards nucleophilic substitution. The reaction can be carried out under milder conditions compared to chlorobenzene. NaOH at 368 K followed by acidification is sufficient for this conversion. Thus, (B) matches with (II).
(C) $2,4-Cl(NO_2)_2C_6H_3 \rightarrow 2,4-OH(NO_2)_2C_6H_3$ (2,4-Dinitrochlorobenzene to 2,4-Dinitrophenol): The presence of two nitro groups at ortho and para positions strongly activates the chlorine towards nucleophilic substitution. The reaction proceeds readily with warm aqueous NaOH followed by acidification. Thus, (C) matches with (I).
(D) $2,4,6-Cl(NO_2)_3C_6H_2 \rightarrow 2,4,6-OH(NO_2)_3C_6H_2$ (2,4,6-Trinitrochlorobenzene to 2,4,6-Trinitrophenol (Picric Acid)): The presence of three nitro groups at ortho and para positions makes the chlorine atom extremely susceptible to nucleophilic attack. Even mild conditions like warm water can cause the hydrolysis of the C-Cl bond to form picric acid. Thus, (D) matches with (III).
Step 3: Write down the matching pairs.
(A) - (IV)
(B) - (II)
(C) - (I)
(D) - (III)

Step 4: Choose the option that corresponds to the correct matching. The correct matching is (A)-(IV), (B)-(II), (C)-(I), (D)-(III), which corresponds to option (3).

Quick Tip

The reactivity of aryl halides towards nucleophilic substitution increases significantly with the presence of electron-withdrawing groups (especially nitro groups) at ortho and para positions. The more the number of such groups, the milder the conditions required for the substitution reaction.

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58. The correct statement amongst the following is :
(1) The term 'standard state' implies that the temperature is $0°C$
(2) The standard state of pure gas is the pure gas at a pressure of 1 bar and temperature 273 K
(3) $\Delta_f H^{\ominus}_{298}$ is zero for O(g)
(4) $\Delta_f H^{\ominus}_{500}$ is zero for $O_2(g)$

Correct Answer: (4) $\Delta_f H^{\ominus}_{500}$ is zero for $O_2(g)$

Solution: Step 1: Understand the definition of standard state and standard enthalpy of formation.

Standard State: The standard state of a substance is a specific set of conditions chosen as a reference point for thermodynamic properties. By international convention, the standard pressure ($P^{\ominus}$) is 1 bar (10^5 Pa). The temperature is not specified as part of the definition of standard state, although thermodynamic data are often tabulated at a standard temperature of 298.15 K ($25°C$). For a pure gas, the standard state is the pure gas at a pressure of 1 bar behaving ideally. For a pure liquid or solid, it is the pure substance at a pressure of 1 bar. For a solute in solution, it is a solution with a molality of 1 mol/kg behaving ideally.

Standard Enthalpy of Formation ($\Delta_f H^{\ominus}$): The standard enthalpy of formation of a compound is the change of enthalpy that accompanies the formation of 1 mole of the substance in its standard state from its constituent elements in their standard states. The standard enthalpy of formation of an element in its most stable allotropic form at the specified temperature (and 1 bar pressure) is zero.

Step 2: Evaluate each statement.

(1) The term 'standard state' implies that the temperature is $0°C$.

This statement is incorrect. The standard state specifies a pressure of 1 bar, but the temperature is not fixed at $0°C$ (273.15 K). While 273.15 K is a common reference temperature (especially in gas laws), it is not inherently part of the definition of standard state in thermodynamics.

(2) The standard state of pure gas is the pure gas at a pressure of 1 bar and temperature 273 K.

This statement is incorrect. The standard state of a pure gas is defined at a pressure of 1 bar, but the temperature is not fixed at 273 K. The temperature can be any specified value, although 298.15 K is most commonly used for tabulated thermodynamic data.

(3) $\Delta_f H^{\ominus}_{298}$ is zero for O(g).

This statement is incorrect. $O(g)$ is atomic oxygen, which is not the most stable allotropic form of the element oxygen at 298 K and 1 bar. The most stable allotropic form of oxygen under these conditions is diatomic oxygen, $O_2(g)$. Therefore, $\Delta_f H^{\ominus}_{298}$ for $O(g)$ is not zero; it is the enthalpy change for the formation of $O(g)$ from $O_2(g)$, which requires energy to break the bond in O_2.

(4) $\Delta_f H^{\ominus}_{500}$ is zero for $O_2(g)$.

This statement is correct. $O_2(g)$ is the most stable allotropic form of the element oxygen at 500 K and 1 bar (and at any temperature under standard pressure). By definition, the standard enthalpy of formation of an element in its most stable allotropic form at the specified temperature and standard pressure is zero.

Step 3: Identify the correct statement. Based on the analysis, the correct statement is (4).

Quick Tip

Carefully distinguish between the definition of standard state (pressure is fixed at 1 bar, temperature is not) and the standard conditions often used for data tabulation (usually 298.15 K). Remember that the standard enthalpy of formation of an element in its most stable form under standard conditions is always zero.

---

59. Liquid A and B form an ideal solution. The vapour pressure of pure liquids A and B are 350 and 750 mm Hg respectively at the same temperature. If x_A and x_B are the mole fraction of A and B in solution while y_A and y_B are the mole fraction of A and B in vapour phase then :

(1) $\frac{x_A}{x_B} < \frac{y_A}{y_B}$

(2) $\frac{x_A}{x_B} = \frac{y_A}{y_B}$

(3) $\frac{x_A}{x_B} > \frac{y_A}{y_B}$

(4) $(x_A - y_A) < (x_B - y_B)$

Correct Answer: (3) $\frac{x_A}{x_B} > \frac{y_A}{y_B}$ **Solution: Step 1: Apply Raoult's Law for an ideal solution.**

For an ideal solution, the partial pressure of each component in the vapour phase is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of the pure component.

$p_A = x_A P_A^\circ$

$p_B = x_B P_B^\circ$

where $P_A^\circ = 350$ mm Hg and $P_B^\circ = 750$ mm Hg are the vapour pressures of pure liquids A and B, respectively.

Step 2: Use Dalton's Law of partial pressures.

The total vapour pressure of the solution is $P_{total} = p_A + p_B = x_A P_A^\circ + x_B P_B^\circ$. We also know that $x_A + x_B = 1$, so $x_B = 1 - x_A$. $P_{total} = x_A P_A^\circ + (1 - x_A) P_B^\circ = x_A P_A^\circ + P_B^\circ - x_A P_B^\circ = P_B^\circ + x_A(P_A^\circ - P_B^\circ)$ Since $P_A^\circ < P_B^\circ$, $(P_A^\circ - P_B^\circ)$ is negative, so P_{total} will be between P_A° and P_B°.

Step 3: Relate the mole fractions in the vapour phase to the partial pressures.

The mole fraction of each component in the vapour phase is given by the ratio of its partial pressure to the total pressure: $y_A = \frac{p_A}{P_{total}} = \frac{x_A P_A^\circ}{x_A P_A^\circ + x_B P_B^\circ}$ $y_B = \frac{p_B}{P_{total}} = \frac{x_B P_B^\circ}{x_A P_A^\circ + x_B P_B^\circ}$

Step 4: Consider the ratio of mole fractions in the vapour phase and the solution.

We want to compare $\frac{x_A}{x_B}$ with $\frac{y_A}{y_B}$.

$$\frac{y_A}{y_B} = \frac{\frac{x_A P_A^\circ}{x_A P_A^\circ + x_B P_B^\circ}}{\frac{x_B P_B^\circ}{x_A P_A^\circ + x_B P_B^\circ}} = \frac{x_A P_A^\circ}{x_B P_B^\circ} = \frac{x_A}{x_B} \cdot \frac{P_A^\circ}{P_B^\circ}$$

Given $P_A^\circ = 350$ mm Hg and $P_B^\circ = 750$ mm Hg, we have $\frac{P_A^\circ}{P_B^\circ} = \frac{350}{750} = \frac{7}{15}$. So, $\frac{y_A}{y_B} = \frac{x_A}{x_B} \cdot \frac{7}{15}$. Since $\frac{7}{15} < 1$, we can conclude that $\frac{y_A}{y_B} < \frac{x_A}{x_B}$. Alternatively, $\frac{x_A}{x_B} > \frac{y_A}{y_B}$.

Step 5: Verify with a specific example.

Let $x_A = 0.5$ and $x_B = 0.5$.

Then $y_A = \frac{0.5 \times 350}{0.5 \times 350 + 0.5 \times 750} = \frac{175}{175 + 375} = \frac{175}{550} = \frac{7}{22}$

$y_B = \frac{0.5 \times 750}{0.5 \times 350 + 0.5 \times 750} = \frac{375}{550} = \frac{15}{22}$

$\frac{x_A}{x_B} = \frac{0.5}{0.5} = 1$

$\frac{y_A}{y_B} = \frac{7/22}{15/22} = \frac{7}{15}$

Here, $1 > \frac{7}{15}$, so $\frac{x_A}{x_B} > \frac{y_A}{y_B}$.

Quick Tip

In an ideal solution, the vapour phase is richer in the more volatile component (the one with the higher vapour pressure). Here, B has a higher vapour pressure than A, so the vapour phase will have a higher mole fraction of B compared to the solution. This implies that the ratio of mole fractions of A to B will be smaller in the vapour phase than in the solution.

---

60. 'X' is the number of acidic oxides among $VO_2, V_2O_3, CrO_3, V_2O_5$ and Mn_2O_7. The primary valency of cobalt in $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is Y. The value of X + Y is :

(1) 5
(2) 4
(3) 2
(4) 3

Correct Answer: (1) 5

Solution: Step 1: Determine the acidic oxides among the given options.

The acidic character of transition metal oxides increases with the oxidation state of the metal.
VO_2: Oxidation state of V is +4 (amphoteric)
V_2O_3: Oxidation state of V is +3 (basic)
CrO_3: Oxidation state of Cr is +6 (acidic)
V_2O_5: Oxidation state of V is +5 (amphoteric, predominantly acidic)
Mn_2O_7: Oxidation state of Mn is +7 (highly acidic)

The acidic oxides are CrO_3 and Mn_2O_7. The number of acidic oxides, X = 2.

Step 2: Determine the primary valency of cobalt in the given complex.

The complex is $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$, which contains the complex ion $[Co(en)_3]^{3+}$. The primary valency is the oxidation state of the central metal ion (Co).
Let the oxidation state of Co be y. Ethylenediamine (en) is a neutral ligand.
$y + 3(0) = +3$
$y = +3$
The primary valency of cobalt (Y) is 3.

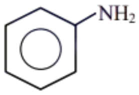
Step 3: Calculate the value of X + Y.

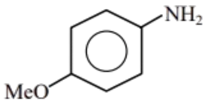
X = 2
Y = 3
X + Y = 2 + 3 = 5

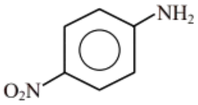
Quick Tip

Remember the trends in the acidic/basic nature of metal oxides with respect to the oxidation state of the metal. Higher oxidation states tend to be more acidic. Primary valency in coordination complexes refers to the oxidation state of the central metal ion.

61. The descending order of basicity of following amines is :

(A) 

(B) 

(C) 

(D) CH_3NH_2

(E) $(CH_3)_2NH$

Choose the correct answer from the options given below :
(1) $B > E > D > A > C$
(2) $E > D > B > A > C$
(3) $E > D > A > B > C$
(4) $E > A > D > C > B$

Correct Answer: (2) $E > D > B > A > C$

Solution: Step 1: Understand the factors affecting the basicity of amines.
The basicity of an amine depends on the availability of the lone pair of electrons on the nitrogen atom for protonation. Factors that increase the electron density on the nitrogen atom increase basicity, while factors that decrease it decrease basicity. These factors include:
Alkyl groups: Electron-donating alkyl groups (+I effect) increase the electron density on the nitrogen atom, making the amine more basic.
Aryl groups: The lone pair of electrons on the nitrogen atom in aromatic amines is delocalized into the benzene ring through resonance, making them less basic than aliphatic amines.
Electron-donating groups on the aryl ring: These groups (+I or +M effect) increase the electron density on the nitrogen atom, increasing the basicity of aromatic amines.
Electron-withdrawing groups on the aryl ring: These groups (-I or -M effect) decrease the electron density on the nitrogen atom, decreasing the basicity of aromatic amines.
Steric factors: In some cases, steric hindrance around the nitrogen atom can affect protonation and thus basicity.
Step 2: Analyze the basicity of each amine.
(A) Aniline ($C_6H_5NH_2$): The lone pair on nitrogen is delocalized into the benzene ring, making it weakly basic.
(B) p-Methoxy aniline ($p - MeOC_6H_4NH_2$): The methoxy group ($-OCH_3$) is an electron-donating group (+M and -I effect, with +M dominating). It increases the electron density on the nitrogen atom through resonance, making p-methoxy aniline more basic than aniline.
(C) p-Nitro aniline ($p - NO_2C_6H_4NH_2$): The nitro group ($-NO_2$) is a strong electron-withdrawing group (-M and -I effect). It decreases the electron density on the nitrogen atom through resonance, making p-nitro aniline much less basic than aniline.
(D) Methylamine (CH_3NH_2): Methyl group is an electron-donating alkyl group (+I effect), making methylamine more basic than aniline.
(E) Dimethylamine ($(CH_3)_2NH$): Two electron-donating methyl groups (+I effect) increase the electron density on the nitrogen atom further compared to methylamine. In the gas phase,

dimethylamine is more basic than methylamine. In aqueous solution, solvation effects also play a role, but generally, secondary aliphatic amines are more basic than primary aliphatic amines.

Step 3: Arrange the amines in descending order of basicity.

Based on the above analysis:

Dimethylamine (E) is the most basic due to two electron-donating methyl groups and favorable solvation in aqueous solution.

Methylamine (D) is more basic than aniline due to one electron-donating methyl group.

p-Methoxy aniline (B) is more basic than aniline due to the electron-donating methoxy group.

Aniline (A) is less basic due to the delocalization of the lone pair into the benzene ring.

p-Nitro aniline (C) is the least basic due to the strong electron-withdrawing nitro group.

The descending order of basicity is: E ¿ D ¿ B ¿ A ¿ C.

Step 4: Match the order with the given options.

The order E ¿ D ¿ B ¿ A ¿ C matches option (2).

Quick Tip

When comparing the basicity of amines, consider whether they are aliphatic or aromatic. For aliphatic amines, more alkyl groups generally increase basicity. For aromatic amines, the presence and nature of substituents on the ring significantly affect basicity. Electron-donating groups increase basicity, while electron-withdrawing groups decrease it.

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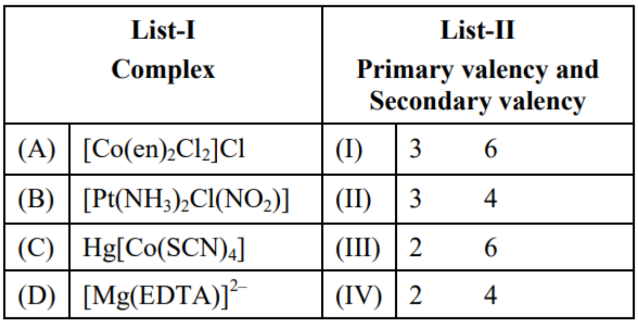
62. Match List-I with List-II



List-I Complex		List-II Primary valency and Secondary valency		
(A)	$[Co(en)_2Cl_2]Cl$	(I)	3	6
(B)	$[Pt(NH_3)_2Cl(NO_2)]$	(II)	3	4
(C)	$Hg[Co(SCN)_4]$	(III)	2	6
(D)	$[Mg(EDTA)]^{2-}$	(IV)	2	4

Choose the correct answer from the options given below :

(1) (A)-(III), (B)-(I), (C)-(II), (D)-(IV)
(2) (A)-(I), (B)-(IV), (C)-(II), (D)-(III)
(3) (A)-(I), (B)-(III), (C)-(II), (D)-(IV)
(4) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

Correct Answer: (2) (A)-(I), (B)-(IV), (C)-(II), (D)-(III)

Solution: Step 1: Understand Primary and Secondary Valency.

Primary Valency: Corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions.

Secondary Valency: Corresponds to the coordination number of the central metal ion, i.e., the number of ligands directly bonded to it. It is satisfied by neutral molecules or negative ions and determines the geometry of the complex.

Step 2: Determine Primary and Secondary Valency for each complex in List-I.

(A) $[Co(en)_2Cl_2]Cl$
Primary Valency (Oxidation State of Co): +3
Secondary Valency (Coordination Number of Co): 6
(A) - (I)
(B) $[Pt(NH_3)_2Cl(NO_2)]$
Primary Valency (Oxidation State of Pt): +2
Secondary Valency (Coordination Number of Pt): 4
(B) - (IV)

(C) $Hg[Co(SCN)_4]$ Primary Valency (Oxidation State of Co): +2
Secondary Valency (Coordination Number of Co): 4
(C) - (II)
(D) $[Mg(EDTA)]^{2-}$
Primary Valency (Oxidation State of Mg): +2
Secondary Valency (Coordination Number of Mg): 6
(D) - (III)
Step 3: Match the pairs.
(A) - (I)
(B) - (IV)
(C) - (II)
(D) - (III)

Step 4: Choose the correct option.
The correct matching is given by option (2).

Quick Tip

Remember that primary valency is the oxidation state and secondary valency is the coordination number. For polydentate ligands, multiply the denticity by the number of ligands to calculate their contribution to the secondary valency.

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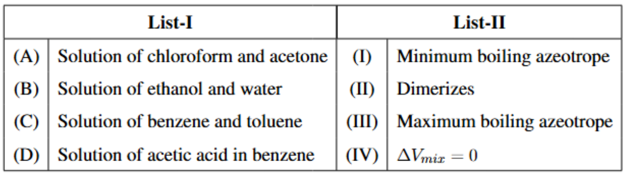
63. Match List-I with List-II



List-I		List-II	
(A)	Solution of chloroform and acetone	(I)	Minimum boiling azeotrope
(B)	Solution of ethanol and water	(II)	Dimerizes
(C)	Solution of benzene and toluene	(III)	Maximum boiling azeotrope
(D)	Solution of acetic acid in benzene	(IV)	$\Delta V_{mix} = 0$

Choose the correct answer from the options given below :
(1) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)
(2) (A)-(II), (B)-(IV), (C)-(I), (D)-(III)
(3) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
(4) (A)-(II), (B)-(I), (C)-(IV), (D)-(III)

Correct Answer: (1) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)
Solution: Step 1: Analyze each solution in List-I and match it with the appropriate property in List-II.

(A) Solution of chloroform and acetone:
Chloroform and acetone exhibit strong hydrogen bonding between the hydrogen atom of chloroform and the oxygen atom of acetone. This strong intermolecular interaction leads to a decrease in the vapour pressure of the solution compared to what would be expected for an ideal solution (negative deviation from Raoult's Law). Solutions with negative deviations form maximum boiling azeotropes. Thus, (A) matches with (III).
(B) Solution of ethanol and water:
Ethanol and water are miscible due to hydrogen bonding. However, the hydrogen bonding in the mixture is generally weaker than in pure ethanol or pure water due to differences in molecular shapes and sizes affecting the extent of hydrogen bonding. This weaker interaction leads to an increase in the vapour pressure of the solution (positive deviation from Raoult's Law). Solutions with positive deviations form minimum boiling azeotropes.
Thus, (B) matches with (I).
(C) Solution of benzene and toluene:
Benzene and toluene are structurally similar nonpolar hydrocarbons. The intermolecular forces in pure benzene, pure toluene, and their mixture are all weak van der Waals forces of similar magnitude. Therefore, the mixing of benzene and toluene results in an ideal solution or a solution showing very little deviation from ideal behavior. For an ideal solution, the volume of mixing is zero ($\Delta V_{mix} = 0$). Thus, (C) matches with (IV).
(D) Solution of acetic acid in benzene:
Acetic acid exists as a dimer in nonpolar solvents like benzene due to strong hydrogen bonding between the carboxyl groups of two acetic acid molecules. When dissolved in benzene, the extent of dimerization is significant, leading to a decrease in the number of solute particles in the solution compared to what would be expected if acetic acid were completely dissociated into individual molecules. This association affects the colligative properties and the vapour pressure of the solution. The statement "dimerizes" describes this behavior of acetic acid in benzene. Thus, (D) matches with (II).
Step 2: Write down the matching pairs.
(A) - (III)
(B) - (I)
(C) - (IV)
(D) - (II)

Step 3: Choose the option that corresponds to the correct matching.
The correct matching is given by option (1).

Quick Tip

Remember the relationship between intermolecular interactions in solutions and deviations from Raoult's Law. Stronger interactions than expected lead to negative deviations and maximum boiling azeotropes, while weaker interactions lead to positive deviations and minimum boiling azeotropes. Ideal solutions occur when intermolecular forces in the mixture are similar to those in the pure components, resulting in $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$. Association of solute molecules in solution can also significantly affect solution properties.

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64. In SO_2, NO_2^- and N_3^- the hybridizations at the central atom are respectively :
(1) sp^2, sp^2 and sp
(2) sp^2, sp and sp
(3) sp^2, sp^2 and sp^2
(4) sp, sp^2 and sp

Correct Answer: (1) sp^2, sp^2 and sp **Solution: Step 1: Determine the hybridization of the central atom in SO_2.**
Central atom: Sulfur (S)
Number of valence electrons of S: 6
Number of bond pairs: 2 (with two oxygen atoms)
Number of lone pairs: To complete the octet of S, we form double bonds with both O atoms. This uses 4 electrons. The remaining 2 electrons form one lone pair.
Steric number = Number of bond pairs + Number of lone pairs = 2 + 1 = 3 Hybridization: sp^2

Step 2: Determine the hybridization of the central atom in NO_2^-. Central atom: Nitrogen (N)
Number of valence electrons of N: 5
Number of surrounding atoms: 2 (two oxygen atoms)
Total electrons to accommodate (considering the negative charge): $5 + 2 \times 6 + 1 = 18$
Lewis structure: $[O = N - O^-]$ or $[O^- N = O]$ (resonance structures). The nitrogen atom forms one double bond and one single bond with oxygen atoms.
Number of bond pairs: 2
Number of lone pairs on N: To satisfy the formal charges and octet rule, nitrogen has one lone pair.
Steric number = Number of bond pairs + Number of lone pairs = 2 + 1 = 3 Hybridization: sp^2

Step 3: Determine the hybridization of the central atom in N_3^-.
Central atom: Central Nitrogen (N)
Number of valence electrons of N: 5
Total electrons to accommodate (considering the negative charge): $3 \times 5 + 1 = 16$
Lewis structure: $[: N = N = N :]^-$ or $[: \bar{N} - N \equiv N :]$ or $[N \equiv N - \bar{N} :]$ (resonance structures). The central nitrogen atom forms two double bonds or one single and one triple bond.

Number of bond pairs around the central N: 2 (regardless of the type of bonds)
Number of lone pairs on the central N: To satisfy the formal charges and octet rule, the central nitrogen has zero lone pairs in the $[: N = N = N :]^-$ resonance structure.
Steric number = Number of bond pairs + Number of lone pairs = 2 + 0 = 2 Hybridization: sp
Step 4: Combine the hybridizations.
The hybridizations of the central atoms in SO_2, NO_2^-, and N_3^- are sp^2, sp^2, and sp respectively.
Step 5: Match with the given options.
This matches option (1).

Quick Tip

To determine the hybridization of the central atom, use the steric number concept: Steric Number = Number of sigma bonds + Number of lone pairs. For resonance structures, the hybridization of the central atom remains the same across all significant contributing structures.

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65. The number of unpaired electrons responsible for the paramagnetic nature of the following complex species are respectively : $[Fe(CN)_6]^{3-}, [FeF_6]^{3-}, [CoF_6]^{3-}, [Mn(CN)_6]^{3-}$
(1) 1, 5, 4, 2
(2) 1, 5, 5, 2
(3) 1, 1, 4, 2
(4) 1, 4, 4, 2

Correct Answer: (1) 1, 5, 4, 2
Solution: Step 1: Determine the oxidation state of the central metal ion in each complex.

$[Fe(CN)_6]^{3-}$: Let the oxidation state of Fe be x. The charge of CN^- is -1.
$x + 6(-1) = -3$
$x - 6 = -3$
$x = +3$
Electronic configuration of Fe^{3+} (d^5): $[Ar]3d^5$
$[FeF_6]^{3-}$: Let the oxidation state of Fe be x. The charge of F^- is -1.
$x + 6(-1) = -3$
$x - 6 = -3$
$x = +3$
Electronic configuration of Fe^{3+} (d^5): $[Ar]3d^5$
$[CoF_6]^{3-}$: Let the oxidation state of Co be x. The charge of F^- is -1.
$x + 6(-1) = -3$
$x - 6 = -3$
$x = +3$
Electronic configuration of Co^{3+} (d^6): $[Ar]3d^6$
$[Mn(CN)_6]^{3-}$: Let the oxidation state of Mn be x. The charge of CN^- is -1.
$x + 6(-1) = -3$
$x - 6 = -3$
$x = +3$

Electronic configuration of Mn^{3+} (d^4): $[Ar]3d^4$

Step 2: Determine the number of unpaired electrons using Crystal Field Theory.

$[Fe(CN)_6]^{3-}$: CN^- is a strong field ligand, causing large crystal field splitting ($\Delta_o > P$). The d^5 electrons will pair up in the lower t_{2g} orbitals.
$t_{2g}^5 e_g^0$ (Unpaired electrons = 1)
$[FeF_6]^{3-}$: F^- is a weak field ligand, causing small crystal field splitting ($\Delta_o < P$). The d^5 electrons will follow Hund's rule and occupy the orbitals singly before pairing. $t_{2g}^3 e_g^2$ (Unpaired electrons = 5)
$[CoF_6]^{3-}$: F^- is a weak field ligand. The d^6 electrons will be arranged as:
$t_{2g}^4 e_g^2$ (Unpaired electrons = 4)
$[Mn(CN)_6]^{3-}$: CN^- is a strong field ligand. The d^4 electrons will pair up in the lower t_{2g} orbitals.
$t_{2g}^4 e_g^0$ (Unpaired electrons = 2)

Step 3: List the number of unpaired electrons for each complex.
$[Fe(CN)_6]^{3-}$: 1 unpaired electron
$[FeF_6]^{3-}$: 5 unpaired electrons
$[CoF_6]^{3-}$: 4 unpaired electrons
$[Mn(CN)_6]^{3-}$: 2 unpaired electrons

Step 4: Match the number of unpaired electrons with the given options. The number of unpaired electrons are 1, 5, 4, 2 respectively, which matches option (1).

Quick Tip

To determine the number of unpaired electrons in coordination complexes, first find the oxidation state of the central metal ion and its d electron configuration. Then, consider the nature of the ligand (strong field or weak field) to determine the electron pairing in the d orbitals based on the magnitude of crystal field splitting (Δ_o compared to the pairing energy P). Strong field ligands favor pairing in the lower energy t_{2g} orbitals, leading to low spin complexes, while weak field ligands favor high spin complexes with electrons occupying both t_{2g} and e_g orbitals according to Hund's rule.

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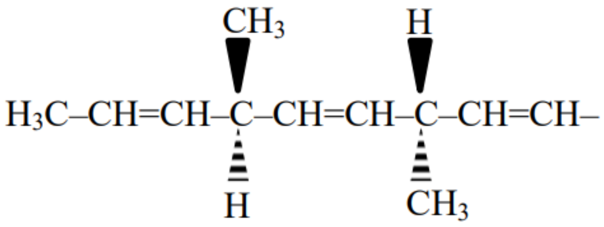
66. The number of optically active products obtained from the complete ozonolysis of the given compound is :



$$H_3C{-}CH{=}CH{-}\overset{CH_3}{\underset{H}{C}}{-}CH{=}CH{-}\overset{H}{\underset{CH_3}{C}}{-}CH{=}CH{-}$$

(1) 0
(2) 2

(3) 4
(4) 4

Correct Answer: (2) 2
Solution: Step 1: Understand ozonolysis of alkenes.
Ozonolysis of alkenes followed by reductive workup yields carbonyl compounds. The carbon-carbon double bonds are cleaved, and oxygen atoms are attached to the carbon atoms of the double bond, forming aldehydes or ketones.
Step 2: Identify the chiral centers and the products of ozonolysis.
The given compound has two chiral centers with opposite configurations. Ozonolysis will cleave the three double bonds, resulting in the following organic products:
1. CH_3CHO (ethanal - achiral)
2. $H - \mathrm{C}_{H}{}^{CH_3} - CHO$ (2-methylpropanal - chiral)
3. $OHC - CHO$ (glyoxal - achiral)
4. $OHC - \mathrm{C}_{CH_3}{}^{H} - CHO$ (2-methylmalondialdehyde - chiral)
5. $OHC - CHO$ (glyoxal - achiral)

Step 3: Determine the number of optically active products. The chiral products formed are 2-methylpropanal and 2-methylmalondialdehyde. Due to the opposite configurations at the chiral centers in the starting material, the resulting chiral aldehydes will be enantiomers of each other.
The first chiral center yields one enantiomer of 2-methylpropanal.
The second chiral center yields the other enantiomer of 2-methylpropanal.

These two enantiomers are the optically active products. Glyoxal and ethanal are achiral.
Therefore, the number of optically active products is 2.

Quick Tip

When analyzing ozonolysis of chiral compounds, carefully consider the stereochemistry at the chiral centers and how they are retained (or lost) in the products. If the ozonolysis generates chiral products, remember that each chiral compound contributes one optically active product (and its enantiomer is another optically active product).

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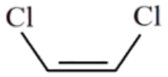
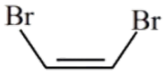
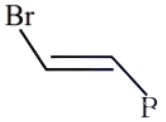
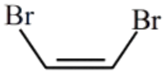
67. Given below are two statements :

Statement (I) : 

is more polar than



Statement (II) : Boiling point of 

lower than 

but it is more polar than

In the light of the above statements, choose the most appropriate answer from the options given below :
(1) Statement I is correct but statement II is incorrect
(2) Statement I is incorrect but statement II is correct
(3) Both statement I and statement II are incorrect
(4) Both statement I and statement II are correct

Correct Answer: (1) Statement I is correct but statement II is incorrect
Solution: Step 1: Analyze Statement (I).
As established previously, the C-Cl bond is more polar than the C-Br bond due to the higher electronegativity of chlorine. In the *cis* isomers, the bond dipoles have a net vector sum, resulting in a polar molecule. Since the C-Cl bond is more polar, $cis - 1,2 - dichloroethene$ will have a larger net dipole moment and thus be more polar than $cis - 1,2 - dibromoethene$. Statement I is correct.
Step 2: Analyze Statement (II).
The first part of Statement II is correct: $trans - 1,2 - dibromoethene$ is nonpolar (due to the cancellation of bond dipoles), and $cis - 1,2 - dibromoethene$ is polar. Polar molecules generally have stronger intermolecular forces (dipole-dipole interactions) compared to nonpolar molecules (van der Waals forces of similar magnitude), leading to higher boiling points. Thus, the boiling point of $trans - 1,2 - dibromoethene$ is lower than that of $cis - 1,2 - dibromoethene$.
The second part of Statement II claims that $cis - 1,2 - dibromoethene$ is more polar than $trans - 1,2 - dibromoethene$. $cis - 1,2 - dibromoethene$ has a net dipole moment (it is polar), while $trans - 1,2 - dibromoethene$ has a zero net dipole moment (it is nonpolar). Therefore, $cis - 1,2 - dibromoethene$ is more polar than $trans - 1,2 - dibromoethene$.
However, the structure provided in Statement II has a typo. It shows $trans - 1,2 - dibromoethene$ being compared to another molecule that is also $trans - 1,2 - dibromoethene$, making the comparison meaningless. Assuming the second molecule in the polarity comparison was intended to be $cis - 1,2 - dibromoethene$, then the statement "it is more polar than $trans - 1,2 - dibromoethene$" would be correct.
Given the figure as presented, Statement II makes an incorrect comparison for polarity. There-

fore, Statement II is incorrect as written.

Step 3: Determine the correctness of both statements.

Statement I is correct, but Statement II is incorrect as presented in the figure.

Step 4: Choose the appropriate option.

The option that states Statement I is correct but Statement II is incorrect is (1).

> Quick Tip
>
> Pay close attention to the exact structures and comparisons made in the statements. Even if the underlying chemical principles are correct, a flawed comparison in the statement makes the statement incorrect.

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68. The extra stability of half-filled subshell is due to
(A) Symmetrical distribution of electrons
(B) Smaller coulombic repulsion energy
(C) The presence of electrons with the same spin in non-degenerate orbitals
(D) Larger exchange energy
(E) Relatively smaller shielding of electrons by one another
Identify the correct statements

(1) (B), (D) and (E) only
(2) (A), (B), (D) and (E) only
(3) (B), (C) and (D) only
(4) (A), (B) and (D) only

Correct Answer: (2) (A), (B), (D) and (E) only

Solution: Step 1: Understand the reasons for the extra stability of half-filled subshells.

(A) Symmetrical distribution of electrons: This leads to a more balanced and stable arrangement.

(B) Smaller coulombic repulsion energy: Symmetrical distribution increases the average distance between electrons, reducing repulsion.

(C) The presence of electrons with the same spin in non-degenerate orbitals: This describes Hund's rule, which is followed but isn't the primary extra stability factor compared to other partially filled cases also obeying Hund's rule.

(D) Larger exchange energy: Maximized exchange of electrons with the same spin in degenerate orbitals releases energy and increases stability.

(E) Relatively smaller shielding of electrons by one another: In a symmetrically distributed half-filled or fully filled subshell, the electrons are more evenly spread out. This can lead to a slightly more effective nuclear charge experienced by each electron compared to an asymmetrically filled subshell where some electrons might be closer and cause more shielding for others. While the effect might be subtle, it contributes to the overall stability.

Step 2: Identify the correct statements.

The primary reasons for the extra stability are symmetrical distribution (A), reduced coulombic repulsion (B), maximized exchange energy (D), and a slightly more effective nuclear charge due to reduced uneven shielding (E).

Step 3: Choose the option containing the correct statements.

The option containing statements (A), (B), (D), and (E) is (2).

My apologies for the initial oversight. Thank you for pointing out the correct answer.

Quick Tip

The enhanced stability of half-filled and fully filled subshells arises from a combination of factors related to electron arrangement and interactions. Symmetrical distribution minimizes repulsion and can slightly affect shielding, while maximized exchange energy provides a significant stabilizing effect.

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69. The correct statements from the following are :

(A) Tl^{3+} is a powerful oxidising agent

(B) Al^{3+} does not get reduced easily

(C) Both Al^{3+} and Tl^{3+} are very stable in solution

(D) Tl^{+} is more stable than Tl^{3+}

(E) Al^{3+} and Tl^{+} are highly stable

Choose the correct answer from the options given below :

(1) (A), (B), (C), (D) and (E)
(2) (A), (B), (D) and (E) only
(3) (B), (D) and (E) only
(4) (A), (C) and (D) only

Correct Answer: (2) (A), (B), (D) and (E) only

Solution: Step 1: Analyze each statement based on the properties of Aluminum and Thallium.

(A) Tl^{3+} is a powerful oxidising agent:

Thallium belongs to Group 13. Its common oxidation states are +1 and +3. Due to the inert pair effect, the +1 oxidation state is more stable than the +3 oxidation state for heavier elements like Thallium. Tl^{3+} readily undergoes reduction to the more stable Tl^{+} state, making it a strong oxidizing agent (it readily accepts electrons). This statement is correct.

(B) Al^{3+} does not get reduced easily:

Aluminum also belongs to Group 13. Its most stable oxidation state is +3. Due to its small size and high charge density, Al^{3+} has a high polarizing power and forms strong ionic bonds. Reducing Al^{3+} would involve a significant energy input to overcome these stable bonds and the stable electronic configuration. Therefore, Al^{3+} is very stable and not easily reduced. This statement is correct.

(C) Both Al^{3+} and Tl^{3+} are very stable in solution:

As discussed in (A), Tl^{3+} is unstable in solution as it readily reduces to Tl^{+}. Al^{3+} is stable in solution. Therefore, this statement is incorrect.

(D) Tl^{+} is more stable than Tl^{3+}:

Due to the inert pair effect, the ns^2 electrons in the valence shell of heavier p-block elements like Thallium tend to remain paired and are reluctant to participate in bonding. This makes the +1 oxidation state (where these ns^2 electrons are not involved in bonding) more stable

than the +3 oxidation state (where these electrons are involved). This statement is correct.
(E) Al^{3+} and Tl^{+} are highly stable:
Al^{3+} is the stable oxidation state for Aluminum due to its electronic configuration and bonding characteristics. Tl^{+} is the more stable oxidation state for Thallium due to the inert pair effect. Therefore, both Al^{3+} and Tl^{+} are highly stable in their respective contexts. This statement is correct.
Step 2: Identify the correct statements.
The correct statements are (A), (B), (D), and (E).
Step 3: Choose the option containing the correct statements.
The option containing statements (A), (B), (D), and (E) is (2).

Quick Tip

Remember the inert pair effect, which leads to the increased stability of the lower oxidation state (+1) for heavier p-block elements like Tl. Aluminum, being a lighter element in Group 13, primarily exhibits the +3 oxidation state due to the ready participation of all its valence electrons in bonding.

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70. Given below are two statements :
1 M aqueous solution of each of $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$; $Mg(NO_3)_2$ are electrolysed using inert electrodes, Given : $E^0_{Ag^+/Ag} = 0.80V$, $E^0_{Hg_2^{2+}/Hg} = 0.79V$, $E^0_{Cu^{2+}/Cu} = 0.34V$ **and** $E^0_{Mg^{2+}/Mg} = -2.37V$
Statement (I) : With increasing voltage, the sequence of deposition of metals on the cathode will be Ag, Hg and Cu
Statement (II) : Magnesium will not be deposited at cathode instead oxygen gas will be evolved at the cathode.
In the light of the above statements, choose the most appropriate answer from the options given below :
(1) Both statement I and statement II are incorrect
(2) Statement I is correct but statement II is incorrect
(3) Both statement I and statement II are correct
(4) Statement I is incorrect but statement II is correct

Correct Answer: (2) Statement I is correct but statement II is incorrect
Solution: Step 1: Analyze Statement (I).
The order of deposition at the cathode is determined by the standard reduction potentials. Higher reduction potential means easier reduction and deposition. The order of reduction potentials is $Ag^+(0.80V) > Hg_2^{2+}(0.79V) > Cu^{2+}(0.34V) > Mg^{2+}(-2.37V)$. Thus, the sequence of deposition with increasing voltage will be Ag, then Hg, then Cu. Statement I is correct.
Step 2: Analyze Statement (II).
For Magnesium: $Mg^{2+} + 2e^- \rightarrow Mg \quad E^0 = -2.37V$
For water reduction at the cathode (neutral pH): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^0 = -0.83V$
Since the reduction potential of water is significantly higher than that of Mg^{2+}, water will be reduced at the cathode, producing hydrogen gas, and Magnesium will not be deposited. The

first part of Statement II is correct.

For water oxidation at the anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^0 = +1.23V$
Oxygen gas is evolved at the anode, not the cathode. The second part of Statement II is incorrect.

Step 3: Determine the correctness of both statements.
Statement I is correct, and Statement II is incorrect.

Step 4: Choose the appropriate option.
The option that states Statement I is correct but Statement II is incorrect is (2).

Quick Tip

In electrolysis of aqueous solutions, the species with the higher reduction potential (for reduction at the cathode) or lower oxidation potential (for oxidation at the anode) will be preferentially discharged. Remember the reduction potentials of water to predict the products when metal ions with very negative reduction potentials are present.

SECTION-B

71. Only litre buffer solution was prepared by adding 0.10 mol each of NH_3 and NH_4Cl in deionised water. The change in pH on addition of 0.05 mol of HCl to the above solution is _____ $\times 10^{-2}$, (Nearest integer) (Given : pK_b of $NH_3 = 4.745$ and $\log_{10} 3 = 0.477$)

Correct Answer: 48

Solution: Step 1: Calculate the initial pH of the buffer solution.
Using the Henderson-Hasselbalch equation for a basic buffer:

$$pOH_{initial} = pK_b + \log_{10}\frac{[salt]}{[base]} = 4.745 + \log_{10}\frac{0.10}{0.10} = 4.745$$

$$pH_{initial} = 14 - pOH_{initial} = 9.255$$

Step 2: Calculate the pH after the addition of HCl.
The reaction with HCl changes the concentrations of the base and its salt:

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

New moles: $[NH_3] = 0.05$ M, $[NH_4^+] = 0.15$ M

$$pOH_{final} = pK_b + \log_{10}\frac{[NH_4^+]}{[NH_3]} = 4.745 + \log_{10}\frac{0.15}{0.05} = 4.745 + 0.477 = 5.222$$

$$pH_{final} = 14 - pOH_{final} = 8.778$$

Step 3: Calculate the change in pH.

$$\Delta pH = pH_{final} - pH_{initial} = 8.778 - 9.255 = -0.477$$

The magnitude of the change is $|\Delta pH| = 0.477$. Expressing this in the required format: $0.477 = 47.7 \times 10^{-2}$. Rounding to the nearest integer gives 48.

Quick Tip

When dealing with buffer solutions, the Henderson-Hasselbalch equation is a quick and effective tool. Remember to account for the moles of acid or base added reacting with the buffer components to find the new concentrations before calculating the final pH. The change in pH is the difference between the final and initial pH values.

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72. In Dumas' method 292 mg of an organic compound released 50 mL of nitrogen gas (N_2) at 300 K temperature and 715 mm Hg pressure. The percentage composition of 'N' in the organic compound is _____ % (Nearest integer) (Aqueous tension at 300 K = 15 mm Hg)

Correct Answer: 18

Solution: Step 1: Calculate the pressure of dry nitrogen gas.

$$P_{dry\,N_2} = P_{total} - \text{Aqueous tension} = 715\,\text{mm Hg} - 15\,\text{mm Hg} = 700\,\text{mm Hg}$$

Step 2: Convert the volume of N_2 to STP.

Using the combined gas law:

$$V_{STP} = \frac{P_{dry\,N_2} \times V_{measured} \times T_{STP}}{P_{STP} \times T_{measured}} = \frac{700\,\text{mm Hg} \times 50\,\text{mL} \times 273\,\text{K}}{760\,\text{mm Hg} \times 300\,\text{K}} \approx 41.91\,\text{mL}$$

Step 3: Calculate the mass of nitrogen gas.

Using the molar volume of N_2 at STP (22400 mL/mol):

$$\text{Moles of } N_2 = \frac{41.91\,\text{mL}}{22400\,\text{mL/mol}} \approx 0.001871\,\text{mol}$$

$$\text{Mass of } N_2 = \text{moles} \times \text{molar mass} = 0.001871\,\text{mol} \times 28\,\text{g/mol} \approx 0.05239\,\text{g} = 52.39\,\text{mg}$$

Step 4: Calculate the percentage composition of nitrogen.

$$\text{Percentage of Nitrogen} = \frac{\text{Mass of } N_2}{\text{Mass of organic compound}} \times 100 = \frac{52.39\,\text{mg}}{292\,\text{mg}} \times 100 \approx 17.94\%$$

Rounding to the nearest integer, the percentage of nitrogen is 18

Quick Tip

In Dumas' method, remember to correct the measured gas volume for aqueous tension and convert it to STP conditions before calculating the mass of nitrogen. The percentage of nitrogen is then calculated based on the mass of nitrogen and the mass of the organic compound.

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73. Butane reacts with oxygen to produce carbon dioxide and water following the equation given below:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

If 174.0 kg of butane is mixed with 320.0 kg of O_2, the volume of water formed in litres is _____. (Nearest integer)

[Given: (a) Molar masses: C = 12, H = 1, O = 16 g mol^{-1}; (b) Density of water = 1 g mL^{-1}]
Correct Answer: 138
Solution: Step 1: Calculate moles of reactants.
Moles of $C_4H_{10} = \frac{174\times10^3\,g}{58\,g/mol} = 3000\,mol$ Moles of $O_2 = \frac{320\times10^3\,g}{32\,g/mol} = 10000\,mol$
Step 2: Identify the limiting reactant.
From the balanced equation, 1 mol C_4H_{10} reacts with 6.5 mol O_2. 3000 mol C_4H_{10} requires $3000 \times 6.5 = 19500\,mol\,O_2$. Since we have only 10000 mol O_2, oxygen is the limiting reactant.
Step 3: Calculate moles of water formed.
From the stoichiometry, 6.5 mol O_2 produces 5 mol H_2O. 10000 mol O_2 produces $\frac{5}{6.5} \times 10000 = \frac{10}{13} \times 10000 \approx 7692.3\,mol\,H_2O$.
Step 4: Calculate the volume of water formed.
Mass of $H_2O = 7692.3\,mol \times 18\,g/mol \approx 138461.4\,g$. Volume of $H_2O = \frac{138461.4\,g}{1\,g/mL} = 138461.4\,mL = 138.4614\,L$. Nearest integer = 138 L.

Quick Tip

In stoichiometry problems involving masses of reactants, always convert masses to moles first. Then, use the balanced chemical equation to identify the limiting reactant. The amount of product formed is determined by the limiting reactant. Finally, convert the moles of product back to the desired unit (in this case, volume using density).

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74. The number of paramagnetic metal complex species among $[Co(NH_3)_6]^{3+}, [Co(C_2O_4)_3]^{3-}, [MnCl_6]^{3-}, [Mn(CN)_6]^{3-}, [CoF_6]^{3-}, [Fe(CN)_6]^{3-}$ **and** $[FeF_6]^{3-}$ **with same number of unpaired electrons is _____.**
Correct Answer: 3
Solution: Step 1: Determine the number of unpaired electrons for each complex using Crystal Field Theory.
$[Co(NH_3)_6]^{3+}$ (d^6, strong field): 0 unpaired electrons (diamagnetic)
$[Co(C_2O_4)_3]^{3-}$ (d^6, weak field): 4 unpaired electrons (paramagnetic)
$[MnCl_6]^{3-}$ (d^4, weak field): 4 unpaired electrons (paramagnetic)
$[Mn(CN)_6]^{3-}$ (d^4, strong field): 2 unpaired electrons (paramagnetic)
$[CoF_6]^{3-}$ (d^6, weak field): 4 unpaired electrons (paramagnetic)
$[Fe(CN)_6]^{3-}$ (d^5, strong field): 1 unpaired electron (paramagnetic)
$[FeF_6]^{3-}$ (d^5, weak field): 5 unpaired electrons (paramagnetic)

Step 2: Identify the number of unpaired electrons for each paramagnetic species.
The paramagnetic species have 4, 4, 2, 4, 1, and 5 unpaired electrons respectively.
Step 3: Count the number of paramagnetic species that share the same number of unpaired electrons.
One unpaired electron: $[Fe(CN)_6]^{3-}$ (1 species)
Two unpaired electrons: $[Mn(CN)_6]^{3-}$ (1 species)

Four unpaired electrons: $[Co(C_2O_4)_3]^{3-}$, $[MnCl_6]^{3-}$, $[CoF_6]^{3-}$ (3 species)
Five unpaired electrons: $[FeF_6]^{3-}$ (1 species)

The maximum number of paramagnetic species with the same number of unpaired electrons is 3 (all having 4 unpaired electrons).

Quick Tip

To determine the number of unpaired electrons in transition metal complexes, consider the oxidation state of the metal ion and the nature of the ligands (strong field or weak field), which affects the crystal field splitting and the filling of the d-orbitals. Paramagnetic species have one or more unpaired electrons.

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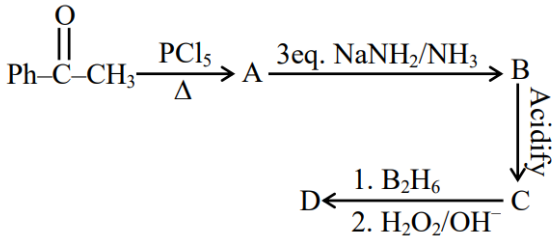
75. Identify the structure of the final product (D) in the following sequence of the reactions :



Total number of sp^2 hybridised carbon atoms in product D is _____.
Correct Answer: 7
Solution: Step 1: Formation of A.
Acetophenone reacts with PCl_5 to give a geminal dichloride:

$$Ph - \overset{O}{\underset{||}{C}} - CH_3 \xrightarrow{PCl_5} Ph - CCl_2 - CH_3 \quad (A)$$

Step 2: Formation of B.
Reaction with 3 equivalents of $NaNH_2/NH_3$ leads to elimination of HCl and formation of an alkyne:

$$Ph - CCl_2 - CH_3 \xrightarrow{3eq.\,NaNH_2/NH_3} Ph - C \equiv C - CH_3 \quad (B)$$

Step 3: Formation of C.
Acidification does not change the structure of the alkyne. Thus, C is also $Ph - C \equiv C - CH_3$.
Step 4: Formation of D (Hydroboration-oxidation).
Hydroboration-oxidation of a terminal alkyne with B_2H_6 followed by H_2O_2/OH^- proceeds with anti-Markovnikov regioselectivity, placing the hydroxyl group on the less substituted carbon after tautomerization.

$$Ph{-}C \equiv C{-}CH_3 \xrightarrow[1.\,B_2H_6]{2.\,H_2O_2/OH^-} Ph{-}\overset{OH}{C} = CH{-}CH_3 \xrightarrow{Tautomerization} Ph{-}CO{-}CH_2{-}CH_3 \quad (D)$$

The final product D is 1-phenylpropan-2-one.

Step 5: Determine the number of sp^2 hybridized carbon atoms in D.

The structure of 1-phenylpropan-2-one is:

$$\underbrace{\overset{sp^2}{C}{}_6H_5}_{6\ sp^2\text{ carbons}} \quad -\overset{sp^3}{C}H_2 - \overset{sp^2}{C} = O - \overset{sp^3}{C}H_3$$

The phenyl ring has 6 sp^2 hybridized carbon atoms. The carbonyl carbon is also sp^2 hybridized. The CH_2 and CH_3 carbons are sp^3 hybridized. Total number of sp^2 hybridized carbon atoms in product D = 6 (from the phenyl ring) + 1 (carbonyl carbon) = 7.

Quick Tip

Remember the reaction mechanisms and stereochemistry/regiochemistry of each step. PCl_5 replaces $C = O$ with CCl_2. $NaNH_2/NH_3$ promotes elimination to form alkynes. Hydroboration-oxidation of terminal alkynes gives aldehydes or ketones depending on regioselectivity, which is anti-Markovnikov with B_2H_6. Finally, count the number of carbon atoms directly bonded to three other atoms or involved in a double bond to determine sp^2 hybridization.
