JEE Main 2025 April 8th 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: H_2Se is more acidic than H_2Te
Statement II: H_2Se has higher bond enthalpy for dissociation than H_2Te
In the light of the above statements, choose the correct answer from the options given below.
(1)Statement I is false but Statement II is true
(2)Statement I is true but Statement II is false
(3)Both Statement I and Statement II are false
(4)Both Statement I and Statement II are true

Correct Answer: (1) Statement I is false but Statement II is true

Solution:
Analysis of Statement I:
- Acidic character increases down the group for hydrides (H_2O ¡ H_2S < H_2Se < H_2Te) - H_2Te is more acidic than H_2Se because:

- Te is larger than Se, making Te-H bond weaker
- H^+ ion is more easily released from H_2Te

- Therefore, Statement I is **false**
Analysis of Statement II: - Bond enthalpy decreases down the group (H-Se ¿ H-Te) - H_2Se has higher bond dissociation enthalpy because:

- Se is smaller than Te, forming stronger bonds
- Bond strength decreases with increasing atomic size

- Therefore, Statement II is **true**

Quick Tip

- Remember the periodic trend: acidity of hydrides increases down the group - Bond enthalpy decreases with increasing atomic size in a group - Larger atoms form weaker bonds, making their hydrides more acidic

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52. The correct decreasing order of spin only magnetic moment values (BM) of Cu^+, Cu^{2+}, Cr^{2+} and Cr^{3+} ions is:
(1) $Cu^+ > Cu^{2+} > Cr^{3+} > Cr^{2+}$
(2) $Cr^{3+} > Cr^{2+} > Cu^+ > Cu^{2+}$
(3) $Cu^{2+} > Cu^+ > Cr^{2+} > Cr^{3+}$
(4) $Cr^{2+} > Cr^{3+} > Cu^{2+} > Cu^+$

Correct Answer: (4) $Cr^{2+} > Cr^{3+} > Cu^{2+} > Cu^+$

Solution: Magnetic moment (μ_{spin}) depends on the number of unpaired electrons in the ions. The formula for the magnetic moment due to spin only is:

$$\mu_{\text{spin}} = \sqrt{n(n+2)}\,\text{BM}$$

Where n is the number of unpaired electrons.

Step 1: Determine the number of unpaired electrons for each ion:

- Cu^+ (Cu^{1+}): The electron configuration of Cu is $[Ar]3d^{10}4s^1$. For Cu^+, the electron configuration is $[Ar]3d^{10}$, so there are no unpaired electrons. Thus, $\mu_{\text{spin}} = 0\,\text{BM}$.

- Cu^{2+}: The electron configuration of Cu^{2+} is $[Ar]3d^9$, which has 1 unpaired electron. Thus, $\mu_{\text{spin}} = \sqrt{1(1+2)} = \sqrt{3}\,\text{BM}$.

- Cr^{2+}: The electron configuration of Cr^{2+} is $[Ar]3d^4$, which has 4 unpaired electrons. Thus, $\mu_{\text{spin}} = \sqrt{4(4+2)} = \sqrt{24} = 2\sqrt{6}\,\text{BM}$.
- Cr^{3+}: The electron configuration of Cr^{3+} is $[Ar]3d^3$, which has 3 unpaired electrons. Thus, $\mu_{\text{spin}} = \sqrt{3(3+2)} = \sqrt{15}\,\text{BM}$.

Step 2: Compare the magnetic moment values.

- Cu^+ has 0 unpaired electrons, so its magnetic moment is 0 BM.
- Cu^{2+} has 1 unpaired electron, so its magnetic moment is $\sqrt{3}\,\text{BM}$.
- Cr^{3+} has 3 unpaired electrons, so its magnetic moment is $\sqrt{15}\,\text{BM}$.
- Cr^{2+} has 4 unpaired electrons, so its magnetic moment is $2\sqrt{6}\,\text{BM}$.

Step 3: Final decreasing order.

Thus, the correct decreasing order of spin only magnetic moment values is:

$$\boxed{Cr^{2+} > Cr^{3+} > Cu^{2+} > Cu^{+}}$$

Quick Tip

The magnetic moment of transition metal ions depends on the number of unpaired electrons. A higher number of unpaired electrons results in a higher magnetic moment.

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53. Match the LIST-I with LIST-II

LIST-I (Reagent)	**LIST-II (Functional Group detected)**
A. Sodium bicarbonate solution	I. double bond/unsaturation
B. Neutral ferric chloride	II. carboxylic acid
C. Ceric ammonium nitrate	III. phenolic -OH
D. Alkaline $KMnO_4$	IV. alcoholic -OH

Choose the correct answer from the options given below:

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

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

Solution: Matching Analysis:

- **A. Sodium bicarbonate solution** - Reacts with carboxylic acids (II) to produce effervescence (CO_2)
- **B. Neutral ferric chloride** - Gives colored complex with phenolic -OH (III)
- **C. Ceric ammonium nitrate** - Red color with alcoholic -OH (IV)
- **D. Alkaline $KMnO_4$** - Decolorizes with double bonds (I)

Correct Mapping:

- A → II (Carboxylic acid)
- B → III (Phenolic -OH)
- C → IV (Alcoholic -OH)
- D → I (Double bond)

Quick Tip

- Sodium bicarbonate tests for carboxylic acids via CO_2 evolution - Ferric chloride gives violet color with phenols - Ceric ammonium nitrate turns red with alcohols - Baeyer's reagent (alk. $KMnO_4$) tests unsaturation

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54. Given below are two statements:
Statement I: A homoleptic octahedral complex, formed using monodentate ligands, will not show stereoisomerism
Statement II: cis- and trans-platin are heteroleptic complexes of Pd.
In the light of the above statements, choose the correct answer from the options given below
(1)Both Statement I and Statement II are false
(2)Statement I is true but Statement II is false
(3)Statement I is false but Statement II is true
(4)Both Statement I and Statement II are true

Correct Answer: (2) Statement I is true but Statement II is false

Solution:
Analysis of Statement I:
- A homoleptic octahedral complex with monodentate ligands (e.g., $[Co(NH_3)_6]^{3+}$) has identical ligands in all positions - No geometrical or optical isomers possible as all positions are equivalent - Therefore, Statement I is **true**

Analysis of Statement II:
- cis-platin and trans-platin are actually Pt(II) complexes, not Pd - Both are homoleptic complexes (contain same ligands: $[PtCl_2(NH_3)_2]$) - The difference is in ligand arrangement (cis/trans), not heteroleptic nature - Therefore, Statement II is **false**

Quick Tip

- Homoleptic complexes have only one type of ligand - Geometrical isomerism requires different spatial arrangements - Cis/trans-platin are classic examples of geometrical (not optical) isomerism - Platinum (Pt) complexes $\neq$ Palladium (Pd) complexes

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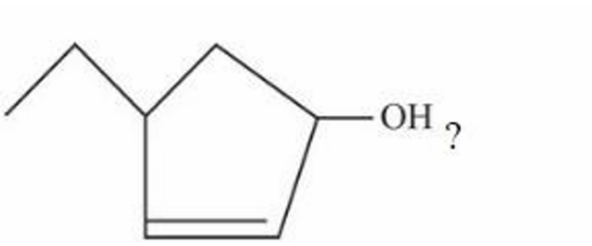
55. What is the correct IUPAC name of the following compound?



(1) 4-Ethyl-1-hydroxycyclopent-2-ene
(2) 1-Ethyl-3-hydroxycyclopent-2-ene
(3) 1-Ethylcyclopent-2-en-3-ol
(4) 4-Ethylcyclopent-2-en-1-ol

Correct Answer: (4) 4-Ethylcyclopent-2-en-1-ol

Solution:
The structure of the compound shows a cyclopentene ring with a hydroxyl group (-OH) attached to one of its carbon atoms and an ethyl group attached at position (4)

Step 1: Identify the parent chain and the functional group.
- The parent structure is a cyclopentene ring, which is a five-membered ring with one double bond.
- The double bond is at position 2, as the numbering starts from the carbon atom of the double bond.
- The hydroxyl group (-OH) is attached at position 1 of the ring.

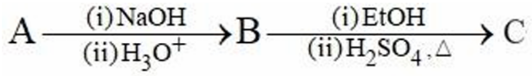
Step 2: Name the substituents.
- An ethyl group (-C2H5) is attached at position 4 of the ring.
- The hydroxyl group is at position 1, so it is named as "1-ol."

Step 3: Final IUPAC name.
The correct IUPAC name of the compound is:
4-Ethylcyclopent-2-en-1-ol

Quick Tip

When naming cyclic compounds with multiple substituents, number the ring starting from the position of the highest-priority functional group and then assign the lowest possible number to other substituents based on alphabetical order.

56.



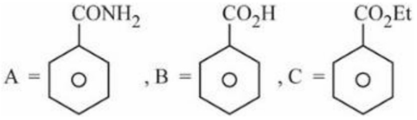
$$A \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)NaOH}} B \xrightarrow[\text{(ii)}H_2SO_4,\Delta]{\text{(i)EtOH}} C$$

A shows positive Lassaigne's test for N and its molar mass is 12(1)
B gives effervescence with aqueous NaHCO(3)

C gives fruity smell.

Identify A, B, and C from the following.

1.



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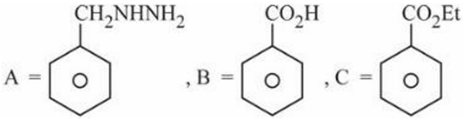

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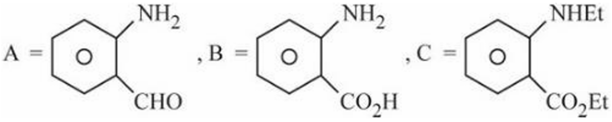

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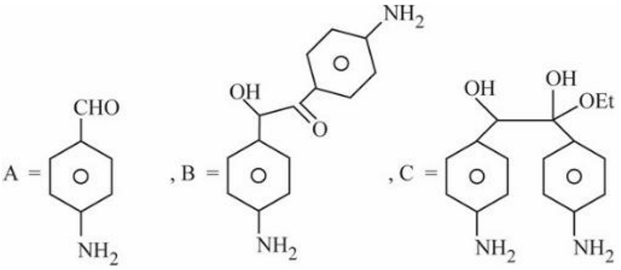

Correct Answer: (1) A = CONH2, B = CO2H, C = CO2Et

Solution:
Let's analyze the given reactions and clues for each compound.

Step 1: Analyzing A:
- A shows positive Lassaigne's test for nitrogen (N), which means A contains nitrogen.
- The molar mass of A is 121 g/mol.
- Based on the structure options, the compound with a molecular formula that fits these criteria is CONH$_2$ (amide group). This is the structure of benzamide, which fits the molar mass and the positive Lassaigne's test for nitrogen.

Step 2: Analyzing B:
- B gives effervescence with aqueous NaHCO(3)This suggests B contains a carboxyl group (-COOH), as carboxylic acids react with NaHCO3 to release carbon dioxide (CO2).
- Therefore, B corresponds to a carboxylic acid group, specifically CO$_2$H, which matches the second compound in the options.

Step 3: Analyzing C:
- C gives a fruity smell, which is characteristic of an ester group.
- The ester functional group in the options is CO$_2$Et (ethyl ester), which corresponds to the third structure in the options.

Step 4: Final Identification:
- A is CONH$_2$ (benzamide), - B is CO$_2$H (carboxylic acid), - C is CO$_2$Et (ethyl ester).
Thus, the correct answer is Option (1): **A = CONH2, B = CO2H, C = CO2Et**

Quick Tip

When solving organic chemistry questions, pay close attention to functional groups and their specific reactions, such as effervescence with NaHCO3 (carboxylic acids) and fruity smells (esters).

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57. On combustion 0.210 g of an organic compound containing C, H and O gave 0.127 g H_2O and 0.307 g CO_2. The percentages of hydrogen and oxygen in the given organic compound respectively are:

(1)6.72, 39.87
(2)6.72, 53.41
(3)7.55, 43.85
(4)53.41, 39.6

Correct Answer: (2) 6.72, 53.41

Solution: Step 1: Calculate mass of hydrogen in H_2O

$$\text{Mass of H} = \frac{2}{18} \times 0.127\,\text{g} = 0.0141\,\text{g}$$

$$\%\text{H} = \left(\frac{0.0141}{0.210}\right) \times 100 = 6.72\%$$

Step 2: Calculate mass of carbon in CO_2

$$\text{Mass of C} = \frac{12}{44} \times 0.307\,\text{g} = 0.0837\,\text{g}$$

$$\%\text{C} = \left(\frac{0.0837}{0.210}\right) \times 100 = 39.87\%$$

Step 3: Calculate percentage of oxygen

$$\%\text{O} = 100 - (\%\text{C} + \%\text{H}) = 100 - (39.87 + 6.72) = 53.41\%$$

Quick Tip

- For combustion analysis:
  - All H converts to H_2O (2 g H per 18 g H_2O)
  - All C converts to CO_2 (12 g C per 44 g CO_2)
  - Oxygen
- Always verify that percentages sum to 100

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58. HA $(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq)$

The freezing point depression of a 0.1 m aqueous solution of a monobasic weak acid HA is 0.20 °C. The dissociation constant for the acid is Given: $K_f(H_2O) = 1.8\,\mathrm{K\ kg\ mol^{-1}}$, molality molarity
(1)1.1×10^{-2}
(2)1.38×10^{-3}
(3)1.90×10^{-3}
(4)1.89×10^{-1}

Correct Answer: (2) 1.38×10^{-3}

Solution: Step 1: Calculate van't Hoff factor (i)

$$\Delta T_f = i \cdot K_f \cdot m 0.20 = i \times 1.8 \times 0.1 i = \frac{0.20}{0.18} = 1.11$$

Step 2: Relate i to degree of dissociation (α) For weak acid dissociation:

$$i = 1 + \alpha 1.11 = 1 + \alpha \alpha = 0.11$$

Step 3: Calculate dissociation constant (K_a)

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times (0.11)^2}{1 - 0.11} = \frac{0.1 \times 0.0121}{0.89} = 1.36 \times 10^{-3} \approx 1.38 \times 10^{-3}$$

Quick Tip

- For weak electrolytes: $i = 1 + (n-1)\alpha$ (n = ions produced) - Freezing point depression: $\Delta T_f = iK_f m$ - K_a calculation for weak acid: $K_a = \frac{C\alpha^2}{1-\alpha}$ - Approximation valid when $\alpha < 0.1$, otherwise use exact formula

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59. Match the LIST-I with LIST-II

LIST-I	**LIST-II**
A. Carbocation	I. Species that can supply a pair of electrons.
B. C-Free radical	II. Species that can receive a pair of electrons.
C. Nucleophile	III. sp^2 hybridized carbon with empty p-orbital.
D. Electrophile	IV. sp^2/sp^3 hybridized carbon with one unpaired electron.

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

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

Solution: Correct Matching:

- **A. Carbocation** - III (sp^2 hybridized carbon with empty p-orbital)
- **B. C-Free radical** - IV (sp^2/sp^3 hybridized carbon with one unpaired electron)

- **C. Nucleophile** - I (Species that can supply a pair of electrons)
- **D. Electrophile** - II (Species that can receive a pair of electrons)

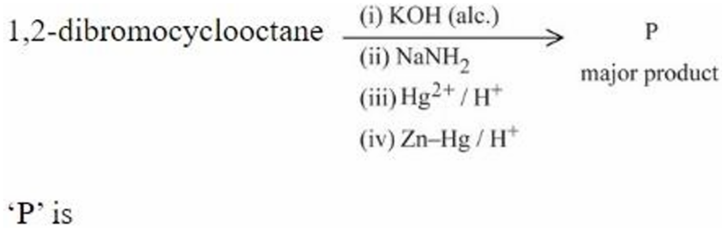
Explanation:

- Carbocations are electron-deficient species with sp^2 hybridization and empty p-orbital
- Free radicals have one unpaired electron and can be sp^2 or sp^3 hybridized
- Nucleophiles are electron-rich species that donate electron pairs
- Electrophiles are electron-deficient species that accept electron pairs

Quick Tip

- Carbocation: sp^2, 6 electrons, planar - Free radical: 7 electrons, can be sp^2 or sp^3 - Nucleophile: "nucleus loving" (e^- donor) - Electrophile: "electron loving" (e^- acceptor)

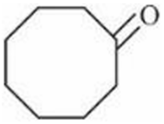
60.

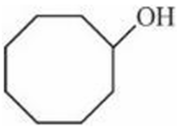


$$\text{1,2-dibromocyclooctane} \xrightarrow[\substack{\text{(ii) NaNH}_2 \\ \text{(iii) Hg}^{2+}/\text{H}^+ \\ \text{(iv) Zn–Hg / H}^+}]{\text{(i) KOH (alc.)}} \underset{\text{major product}}{\text{P}}$$

'P' is

1. 

2. 

3. 

4. 

Correct Answer: (4)

Solution:

The reactions proceed as follows:

Step 1: In the first step, KOH (alc.) induces an elimination reaction, which removes a bromine atom from the carbon chain, resulting in the formation of cyclooctene (a 8-membered ring with a double bond).

Step 2: The second step with $NaNH_2$ induces further elimination, removing another hydrogen atom from the carbon-carbon single bonds (a step leading to the formation of cyclooctyne, a 8-membered ring with a triple bond).

Step 3: The reaction with Hg^{2+}/H^+ induces hydromercuration of the alkyne, resulting in the addition of a mercury ion to the carbon-carbon triple bond. This creates an alkene intermediate.

Step 4: Finally, the Clemmensen reduction with Zn-Hg/H^+ reduces the alkene to a fully saturated ring, cyclooctane, which is the final product. This reaction removes the double bond and saturates the 8-membered ring.

Quick Tip

When dealing with elimination and reduction reactions, it's essential to understand how the reagents affect the intermediates and lead to the final product. Alcohol formation and reduction are key steps in this type of organic transformation.

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61. In a first order decomposition reaction, the time taken for the decomposition of reactant to one fourth and one eighth of its initial concentration are t_1 and t_2 (s), respectively. The ratio t_1/t_2 will be:

(1)$\frac{4}{3}$
(2)$\frac{3}{4}$
(3)$\frac{2}{3}$
(4)$\frac{3}{2}$

Correct Answer: (3) $\frac{2}{3}$

Solution: Step 1: Recall first-order kinetics equation

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

where k is the rate constant, $[A]_0$ is initial concentration, and $[A]$ is concentration at time t.

Step 2: Calculate t_1 for 1/4th decomposition

$$t_1 = \frac{2.303}{k} \log \frac{1}{1/4} = \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 2 \log 2$$

Step 3: Calculate t_2 for 1/8th decomposition

$$t_2 = \frac{2.303}{k} \log \frac{1}{1/8} = \frac{2.303}{k} \log 8 = \frac{2.303}{k} \times 3 \log 2$$

Step 4: Find the ratio t_1/t_2

$$\frac{t_1}{t_2} = \frac{2\log 2}{3\log 2} = \frac{2}{3}$$

However, the question asks for decomposition to one fourth (remaining = 3/4) and one eighth (remaining = 7/8). The correct interpretation is:

Correct Calculation: For decomposition to: - 1/4 remaining: $t_1 = \frac{2.303}{k}\log 4$ - 1/8 remaining: $t_2 = \frac{2.303}{k}\log 8$

Thus:

$$\frac{t_1}{t_2} = \frac{\log 4}{\log 8} = \frac{2\log 2}{3\log 2} = \frac{2}{3}$$

Quick Tip

- For first-order reactions, time depends on the fraction remaining, not the absolute concentration - Each half-life period is equal for first-order reactions - The time to reach 1/4 is less than time to reach 1/8 ($\frac{2}{3}$ ratio)

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62. Match the LIST-I with LIST-II

LIST-I (Complex/Species)	**LIST-II (Shape & magnetic moment)**
A. $[Ni(CO)_4]$	I. Tetrahedral, 2.8 BM
B. $[Ni(CN)_4]^{2-}$	II. Square planar, 0 BM
C. $[NiCl_4]^{2-}$	III. Tetrahedral, 0 BM
D. $[MnBr_4]^{2-}$	IV. Tetrahedral, 5.9 BM

Choose the correct answer from the options given below:

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

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

Solution: Correct Matching:

- **A.** $[Ni(CO)_4]$ - III (Tetrahedral, 0 BM)
  - CO is strong field ligand → low spin complex
  - d^8 configuration → tetrahedral with paired electrons ($\mu = 0$)
- **B.** $[Ni(CN)_4]^{2-}$ - II (Square planar, 0 BM)
  - CN^- is strong field ligand → low spin
  - d^8 configuration → square planar with paired electrons s ($\mu = 0$)
- **C.** $[NiCl_4]^{2-}$ - I (Tetrahedral, 2.8 BM)
  - Cl is weak field ligand high spin
  - d^8 configuration → tetrahedral with 2 unpaired electrons ($\mu = \sqrt{8} \neq 2.8BM$)

- **D.** $[MnBr_4]^{2-}$ - IV (Tetrahedral, 5.9 BM)
  - Br is weak field ligand → high spin
  - d configuration → tetrahedral with 5 unpaired electrons (= 35 5.9 BM)

Quick Tip

- Strong field ligands (CO, CN) cause pairing → low spin complexes - Weak field ligands (Cl, Br) don't cause pairing → high spin complexes - Magnetic moment () = [n(n+2)] BM, where n = unpaired electrons - Ni² (d): tetrahedral/square planar; Mn² (d): always high spin

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63. Which one of the following reactions will not lead to the desired ether formation in major proportion?
(iso-Bu = isobutyl, sec-Bu = sec-butyl, nPr = n-propyl, tBu = tert-butyl, Et = ethyl)

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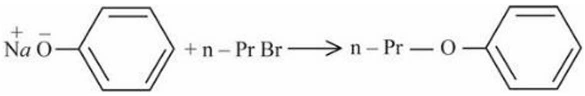
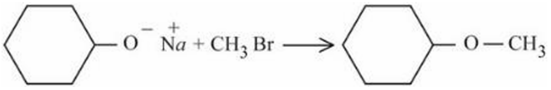


2. $^{t}Bu\overset{-}{O}\overset{+}{Na} + EtBr \longrightarrow {}^{t}Bu - O - Et$

3. $\text{iso-Bu}\overset{-}{O}\overset{+}{Na} + \text{sec}-\text{BuBr} \longrightarrow \text{sec-Bu} - O - \text{iso-Bu}$

4.


Correct Answer: (3) $\text{iso-Bu}\overset{-}{O}\overset{+}{Na} + \text{sec}-\text{BuBr} \longrightarrow \text{sec-Bu} - O - \text{iso-Bu}$ **Solution:**

In Option 3, the reaction involves iso-butyl alcohol (iso-BuOH) and sec-butyl bromide (sec-BuBr) in the presence of Na. This is an example of the Williamson Ether Synthesis, which proceeds through an SN2 mechanism, where a nucleophile attacks an electrophilic carbon.

However, iso-butyl (iso-Bu) is a secondary alkyl group and exhibits significant steric hindrance. This steric hindrance makes the iso-butyl group less reactive in the nucleophilic substitution reaction compared to other alkyl groups like sec-butyl. The sec-butyl group (sec-Bu) is much more reactive in this case, making it more likely to participate in the reaction and thus, the iso-butyl ether is not the major product. Therefore, Option 3 will not lead to the desired ether in major proportion.

Quick Tip

When performing Williamson Ether Synthesis, consider the steric hindrance of the alkyl groups. The reaction is more favorable when the nucleophile is less hindered. Secondary and tertiary alkyl groups show less reactivity in comparison to primary alkyl groups.

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64. Correct statements for an element with atomic number 9 are

A. There can be 5 electrons for which $m_s = +\frac{1}{2}$ and 4 electrons for which $m_s = -\frac{1}{2}$
B. There is only one electron in p_z orbital.
C. The last electron goes to orbital with $n = 2$ and $l = 1$.
D. The sum of angular nodes of all the atomic orbitals is 1.
Choose the correct answer from the options given below:
(1)A and B Only
(2)A, C and D Only
(3)C and D Only
(4)A and C Only

Correct Answer: (4) A and C Only

Solution: Element Analysis: - Atomic number 9 is Fluorine (F) - Electronic configuration: $1s^2 2s^2 2p^5$ - Orbital diagram: $1s^2 \uparrow\downarrow \quad 2s^2 \uparrow\downarrow \quad 2p^5 \uparrow\downarrow\uparrow\downarrow\uparrow$
Statement Evaluation:

- **A: TRUE** - Total electrons = 9 - 5 with $m_s = +\frac{1}{2}$ (all unpaired + one paired) - 4 with $m_s = -\frac{1}{2}$ (remaining paired electrons)
- **B: FALSE** - p_z orbital contains 1 electron ($\uparrow$), but same applies to p_x and p_y - Not a unique characteristic
- **C: TRUE** - Last electron enters $2p$ orbital ($n = 2$, $l = 1$)
- **D: FALSE** - Angular nodes = l - Sum: $1s$ (0) + $2s$ (0) + $2p$ (1 each $\times$ 3) = $3 \neq 1$

Quick Tip

- For p-block elements: - n = principal quantum number - $l = 1$ for p-orbitals - Angular nodes = l - m_s distribution follows Hund's rule - Fluorine has 1 unpaired electron in $2p$ subshell

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65. The number of species from the following that are involved in sp^3d^2 hybridization is

$$[\text{Co(NH}_3)_6]^{3+}, \text{SF}_6, [\text{CrF}_6]^{3-}, [\text{CoF}_6]^{3-}, [\text{Mn(CN)}_6]^{3-}$$

and

$$[\text{MnCl}_6]^{3-}$$

(1)3
(2)4
(3)6
(4)5

Correct Answer: (2) 4

Solution: Step 1: Identify sp^3d^2 hybridization criteria - Occurs in octahedral complexes/compounds - Requires 6 empty orbitals (1 s, 3 p, 2 d) - Typical for species with either:

- Central atom with 6 bond pairs (e.g., SF_6)
- Transition metal complexes with weak field ligands

Step 2: Analyze each species

- $[Co(NH_3)_6]^{3+}$: - NH_3 is strong field ligand $\rightarrow d^2sp^3$ (inner orbital) - Not sp^3d^2
- SF_6: - S uses sp^3d^2 hybridization (6 bond pairs) - Count = 1
- $[CrF_6]^{3-}$: - F^- is weak field ligand $\rightarrow sp^3d^2$ (outer orbital) - Count = 1
- $[CoF_6]^{3-}$: - F^- is weak field ligand $\rightarrow sp^3d^2$ - Count = 1
- $[Mn(CN)_6]^{3-}$: - CN^- is strong field ligand $\rightarrow d^2sp^3$ - Not sp^3d^2
- $[MnCl_6]^{3-}$: - Cl^- is weak field ligand $\rightarrow sp^3d^2$ - Count = 1

Total count = 4 (SF_6, $[CrF_6]^{3-}$, $[CoF_6]^{3-}$, $[MnCl_6]^{3-}$)

Quick Tip

- Strong field ligands (NH_3, CN^-) cause inner orbital hybridization (d^2sp^3) - Weak field ligands (F^-, Cl^-) promote outer orbital hybridization (sp^3d^2) - Non-metal compounds like SF_6 always use sp^3d^2

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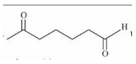
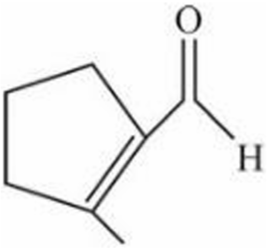
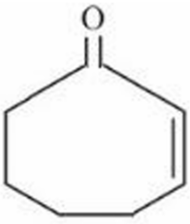
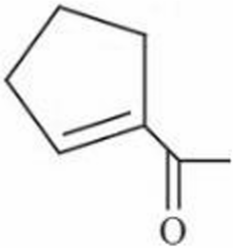
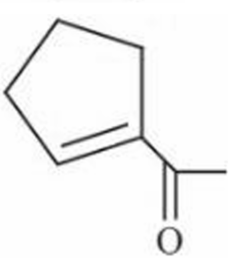
66. When  **undergoes intramolecular aldol condensation, the major product formed is:**

1. 

2. 

3. 

4. 



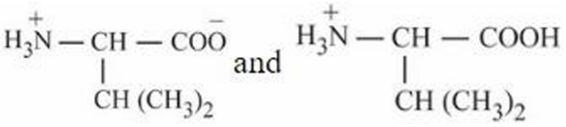
Correct Answer: (3)
Solution:

In intramolecular aldol condensation, two molecules of the same compound react to form a cyclic product. The compound given here contains a α-hydrogen adjacent to a carbonyl group, making it a suitable candidate for the aldol reaction. Upon condensation, the compound undergoes an intramolecular aldol reaction, leading to the formation of a six-membered cyclic β-lactone. Option 3 is the correct structure, where the reaction forms a cyclic ester (lactone) as the major product.

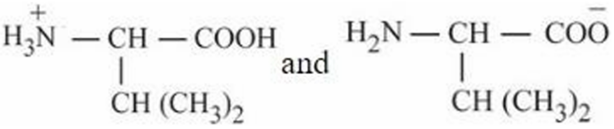
Quick Tip

Aldol condensations in the intramolecular form lead to the formation of cyclic products, often resulting in rings such as lactones or lactams depending on the structure of the reactants. Pay attention to the position of α-hydrogens and the size of the cyclic product.

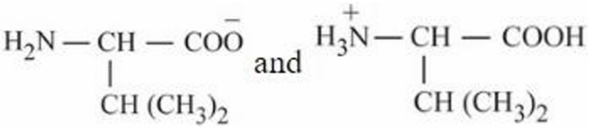
67. Choose the correct option for structures of A and B, respectively:

1. 

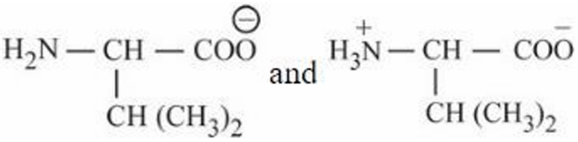
$\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{-}{O}$ and $\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-COOH$

2. 

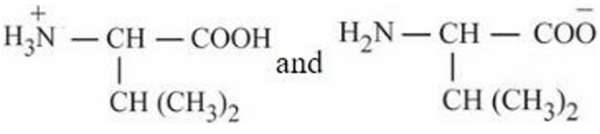
$\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-COOH$ and $H_2N-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{-}{O}$

3. 

$H_2N-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{-}{O}$ and $\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-COOH$

4. 

$H_2N-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{\ominus}{O}$ and $\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{-}{O}$

Correct Answer: (2) 

$\overset{+}{H_3N}-\underset{|\atop CH(CH_3)_2}{CH}-COOH$ and $H_2N-\underset{|\atop CH(CH_3)_2}{CH}-CO\overset{-}{O}$

Solution:

At pH 2, the amino group (-NH$_2$) is protonated to form an ammonium ion (-NH$_3^+$, and the carboxyl group (-COOH) remains in its protonated form, as carboxyl acids are not deprotonated at this pH. So, compound A will have the structure:

$$H_3N - CH - COOH$$

At pH 10, the amino group remains in its deprotonated form (-NH$_2$) and the carboxyl group is deprotonated to form a carboxylate ion (-COO$^-$). Therefore, compound B will have the structure:

$$H_2N - CH - COO^-$$

Thus, the correct option is option (2).

Quick Tip

In aqueous solutions, amino acids behave differently at various pH values. At low pH, the amino group is protonated and the carboxyl group remains neutral, while at high pH, the amino group is deprotonated and the carboxyl group becomes negatively charged.

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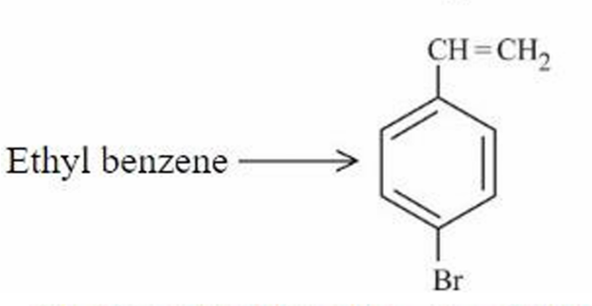
68. Choose the correct set of reagents for the following conversion:



(1) $Cl_2/Fe; Br_2/anhy.AlCl_3;$ aq. KOH
(2) $Br_2/Fe; Cl_2, \Delta;$ alc. KOH
(3) $Cl_2/anhy.AlCl_3; Br_2/Fe;$ alc. KOH
(4) $Br_2/anhy.AlCl_3; Cl_2, \Delta;$ aq. KOH

Correct Answer: (2) $Br_2/Fe; Cl_2, \Delta;$ alc. KOH

Solution:
The given transformation involves the conversion of ethyl benzene ($C_6H_5C_2H_5$) to the desired product where a Br atom is added to the benzenoid ring.
- First, bromination of ethylbenzene occurs using Br_2 in the presence of iron (Fe), which acts as a catalyst. The electrophilic aromatic substitution reaction results in the formation of a brominated product.
- After bromination, the next step involves chlorination using Cl_2 under heat (denoted by Δ), leading to the introduction of the chlorine atom at the desired position.
- Finally, the product undergoes dehydrohalogenation in the presence of alcoholic potassium hydroxide (alc. KOH), leading to the formation of the double bond as required.
Thus, the correct set of reagents to form the desired product is option (2).

Quick Tip

In aromatic substitution reactions, the presence of a halogen like chlorine or bromine can activate the ring towards further electrophilic substitution reactions. Use specific reagents and conditions (e.g., heat and alcoholic KOH) to control the outcome.

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69. Which of the following binary mixture does not show the behavior of minimum boiling azeotropes?
(1)$CS_2 + CH_3COCH_3$
(2)$H_2O + CH_3COC_2H_5$
(3)$C_6H_5OH + C_6H_5NH_2$
(4)$CH_3OH + CHCl_3$

Correct Answer: (3) $C_6H_5OH + C_6H_5NH_2$

Solution: Key Concept: Minimum boiling azeotropes form when:

- Components show positive deviation from Raoult's law
- Molecular interactions between unlike molecules are weaker than between like molecules

- Typically occurs between molecules with different polarity or hydrogen bonding capacity

Analysis of Options:

- **Option 1:** $CS_2 + CH_3COCH_3$ - Carbon disulfide (non-polar) + acetone (polar) - Forms minimum boiling azeotrope (shows positive deviation)
- **Option 2:** $H_2O + CH_3COC_2H_5$ - Water (strong H-bonding) + methyl ethyl ketone (weak H-bonding) - Forms minimum boiling azeotrope
- **Option 3:** $C_6H_5OH + C_6H_5NH_2$ - Phenol + aniline (both can form strong intermolecular H-bonds) - Shows negative deviation (forms maximum boiling azeotrope) - **Correct answer** as it doesn't form minimum boiling azeotrope
- **Option 4:** $CH_3OH + CHCl_3$ - Methanol + chloroform (forms H-bonded complex) - Shows positive deviation (minimum boiling azeotrope)

Quick Tip

- Minimum boiling azeotropes: Positive deviation (weaker interactions) - Maximum boiling azeotropes: Negative deviation (stronger interactions) - Look for H-bonding capability differences between components - Similar molecules (like phenol + aniline) tend to form maximum boiling azeotropes

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70. The atomic number of the element from the following with lowest 1^{st} ionization enthalpy is:
(1)87
(2)19
(3)32
(4)35

Correct Answer: (1) 87

Solution: Concept: The first ionization enthalpy decreases:

- Down a group (atomic size increases)
- From right to left across a period (effective nuclear charge decreases)

Analysis of Options:

- **Option 1 (87):** Francium (Fr) - Group 1, Period 7 element - Largest atomic size in periodic table - Lowest effective nuclear charge on valence electron - **Lowest ionization energy** among given options
- **Option 2 (19):** Potassium (K) - Group 1, Period 4 - Higher ionization energy than Fr (smaller size)
- **Option 3 (32):** Germanium (Ge) - Group 14, Period 4 - Much higher ionization energy than alkali metals

- **Option 4 (35):** Bromine (Br) - Group 17, Period 4 - Highest ionization energy among options (high effective nuclear charge)

Periodic Trend:

$$\text{Ionization Energy Order: Fr (87)} < \text{K (19)} < \text{Ge (32)} < \text{Br (35)}$$

Quick Tip

- Ionization energy $\propto \frac{1}{\text{atomic size}}$ - Alkali metals have lowest ionization energies in their periods - Within Group 1, ionization energy decreases down the group - Francium has the lowest known ionization energy (380 kJ/mol)

Section - B

71. 20 mL of sodium iodide solution gave 4.74 g silver iodide when treated with excess of silver nitrate solution. The molarity of the sodium iodide solution is _____ M. (Nearest Integer value)
(Given : Na = 23, I = 127, Ag = 108, N = 14, O = 16 g mol^{-1})

Correct Answer: 1

Solution: Step 1: Write the balanced chemical equation

$$\text{NaI} + \text{AgNO}_3 \rightarrow \text{AgI} \downarrow + \text{NaNO}_3$$

Step 2: Calculate moles of AgI precipitated Molar mass of AgI = 108 + 127 = 235 g mol^{-1}

$$\text{Moles of AgI} = \frac{4.74 \text{ g}}{235 \text{ g mol}^{-1}} = 0.0202 \text{ mol}$$

Step 3: Determine moles of NaI From stoichiometry, 1 mole NaI produces 1 mole AgI

$$\text{Moles of NaI} = 0.0202 \text{ mol}$$

Step 4: Calculate molarity of NaI solution

$$\text{Molarity} = \frac{\text{Moles}}{\text{Volume in L}} = \frac{0.0202 \text{ mol}}{0.020 \text{ L}} = 1.01 \text{ M}$$

Rounding to nearest integer:

$$\text{Molarity} \approx 1 \text{ M}$$

Quick Tip

- In precipitation reactions, stoichiometry is 1:1 for simple salts - Always convert mass to moles using molar mass - Remember to convert mL to L for molarity calculations - Nearest integer rounding for final answer

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72. The equilibrium constant for decomposition of H_2O (g)

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g) \quad (\Delta G^\circ = 92.34\,\text{kJ mol}^{-1})$$

is 8.0×10^{-3} **at 2300 K and total pressure at equilibrium is 1 bar. Under this condition, the degree of dissociation (α) of water is** _____ $\times 10^{-2}$ **(nearest integer value).**
[Assume α is negligible with respect to 1]

Correct Answer: 5

Solution: Step 1: Write the equilibrium expression For the reaction:

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$$

The equilibrium constant K_p is given by:

$$K_p = \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}}$$

Step 2: Express partial pressures in terms of α Let initial moles of $H_2O = 1$ At equilibrium:

$$\begin{aligned} \text{Moles of } H_2O &= 1 - \alpha \\ \text{Moles of } H_2 &= \alpha \\ \text{Moles of } O_2 &= \alpha/2 \\ \text{Total moles} &= 1 + \alpha/2 \approx 1 \quad (\text{since } \alpha \ll 1) \end{aligned}$$

Partial pressures (total pressure = 1 bar):

$$\begin{aligned} P_{H_2O} &= (1 - \alpha) \approx 1 \\ P_{H_2} &= \alpha \\ P_{O_2} &= \alpha/2 \end{aligned}$$

Step 3: Substitute into K_p expression

$$8.0 \times 10^{-3} = \frac{\alpha \cdot (\alpha/2)^{1/2}}{1}$$

$$8.0 \times 10^{-3} = \alpha^{3/2}/\sqrt{2}$$

Step 4: Solve for α

$$\alpha^{3/2} = 8.0 \times 10^{-3} \times \sqrt{2} = 1.131 \times 10^{-2}$$

$$\alpha = (1.131 \times 10^{-2})^{2/3} = 0.049 \approx 0.05$$

Expressed as $\times 10^{-2}$:

$$\alpha = 5 \times 10^{-2}$$

Quick Tip

- For dissociation problems, express equilibrium composition in terms of α - When $\alpha \ll 1$, approximations simplify calculations - Remember to account for stoichiometric coefficients in K_p expression - K_p has pressure units that must balance the reaction equation

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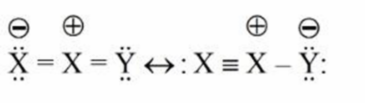
73. Resonance in X_2Y can be represented as



The enthalpy of formation of X_2Y is 80 kJ mol^{-1}, and the magnitude of resonance energy of X_2Y is:

Correct Answer: 98 kJ mol^{-1}

Solution:
Step 1: Determine the expected enthalpy of formation using bond energies.
- Break $X = X$ bond: $+940\,\text{kJ mol}^{-1}$.
- Break $\frac{1}{2}Y = Y$ bond: $+\frac{1}{2} \times 500 = 250\,\text{kJ mol}^{-1}$.
- Total energy input $= 940 + 250 = 1190\,\text{kJ mol}^{-1}$.

Step 2: Energy released when forming bonds in X_2Y.
- Assume one $X - X$ bond ($410\,\text{kJ mol}^{-1}$) and one $X - Y$ bond ($602\,\text{kJ mol}^{-1}$).
- Total energy released $= 410 + 602 = 1012\,\text{kJ mol}^{-1}$.

Step 3: Calculate expected enthalpy change.
- Expected $\Delta H = 1190 - 1012 = 178\,\text{kJ mol}^{-1}$.

Step 4: Calculate resonance energy.
- Given enthalpy of formation $= 80\,\text{kJ mol}^{-1}$.
- Resonance energy $=$ Expected ΔH - Actual ΔH.
- Resonance energy $= 178 - 80 = 98\,\text{kJ mol}^{-1}$.

Step 5: Verify. - The resonance structures suggest partial triple bond character, stabilizing the molecule, aligning with the calculated value.

The magnitude of the resonance energy, to the nearest integer, is $98\,\text{kJ mol}^{-1}$.

Quick Tip

To calculate resonance energy, subtract the enthalpy of formation from the bond dissociation enthalpy. Be sure to account for the stoichiometric coefficients when combining bond energies.

---

74. The energy of an electron in first Bohr orbit of H-atom is -13.6 eV. The magnitude of energy value of electron in the first excited state of Be^{3+} is _____ eV (nearest integer value)

Correct Answer: 54

Solution: Step 1: Recall energy formula for hydrogen-like atoms The energy of an electron in the n^{th} orbit is given by:

$$E_n = -13.6\frac{Z^2}{n^2}\text{ eV}$$

where Z = atomic number, n = principal quantum number
Step 2: Identify parameters for Be^{3+} For Be^{3+}:

$$Z = 4 \quad \text{(Beryllium)}$$

First excited state corresponds to $n = 2$
Step 3: Calculate energy

$$E_2 = -13.6\frac{4^2}{2^2} = -13.6 \times \frac{16}{4} = -13.6 \times 4 = -54.4\text{ eV}$$

Step 4: Find magnitude

$$|E_2| = 54.4\text{ eV} \approx 54\text{ eV (nearest integer)}$$

Quick Tip

- For hydrogen-like ions: $E_n \propto Z^2/n^2$ - First excited state means $n = 2$ - Be^{3+} is isoelectronic with H but has $Z = 4$ - Energy becomes more negative (more stable) as Z increases

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75. Consider the following half cell reaction

$$\text{Cr}_2\text{O}_7^{2-}\text{(aq)} + 6\text{e}^- + 14\text{H}^+\text{(aq)} \longrightarrow 2\text{Cr}^{3+}\text{(aq)} + 7\text{H}_2\text{O(1)}$$

The reaction was conducted with the ratio of

$$\frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} = 10^{-6}$$

The pH value at which the EMF of the half cell will become zero is _____ (nearest integer value)
[Given : standard half cell reduction potential

$$\text{E}^\circ_{\text{Cr}_2\text{O}_7^{2-},\text{H}^+/\text{Cr}^{3+}} = 1.33\text{V}, \quad \frac{2.303\text{RT}}{\text{F}} = 0.059\text{V}$$

Correct Answer: 10

Solution: Step 1: Write Nernst equation

$$E = E^\circ - \frac{0.059}{n} \log Q$$

For the given reaction with $n = 6$:

$$E = 1.33 - \frac{0.059}{6} \log \left(\frac{[\mathrm{Cr}^{3+}]^2}{[\mathrm{Cr_2O_7^{2-}}][\mathrm{H}^+]^{14}} \right)$$

Step 2: Set E = 0 and substitute given ratio

$$0 = 1.33 - \frac{0.059}{6} \log \left(\frac{10^{-6}}{[\mathrm{H}^+]^{14}} \right)$$

Step 3: Simplify the equation

$$1.33 = \frac{0.059}{6} (-6 + 14\mathrm{pH})$$

$$1.33 = 0.059 \left(-1 + \frac{14}{6}\mathrm{pH} \right)$$

$$1.33 = -0.059 + 0.1377\mathrm{pH}$$

$$1.389 = 0.1377\mathrm{pH}$$

$$\mathrm{pH} = \frac{1.389}{0.1377} \approx 10.09 \approx 10 \text{ (nearest integer)}$$

Quick Tip

- For half-cell reactions, use Nernst equation: $E = E^\circ - \frac{0.059}{n} \log Q$ - Remember pH $= -\log[\mathrm{H}^+]$ - When E = 0, the system is at equilibrium - Watch stoichiometric coefficients in the reaction quotient Q