JEE Main 2023 25 Jan Shift 1 Chemistry Question Paper with Solutions

Time Allowed : 180 minutes	Maximum Marks : 300	Total questions : 90

General Instructions

Read the following instructions very carefully and strictly follow them:

(A) The test is of 3 hours duration.

(B) The question paper consists of 90 questions. The maximum marks are 300.

(C) There are three parts in the question paper consisting of Physics, Chemistry and Mathematics having 30 questions in each part of equal weightage.

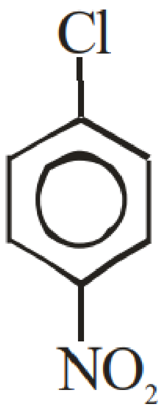
(D) Each part (subject) has two sections.

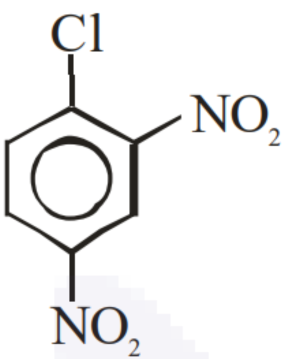
(i) Section-A: This section contains 20 multiple choice questions which have only one correct answer. Each question carries 4 marks for correct answer and –1 mark for wrong answer.

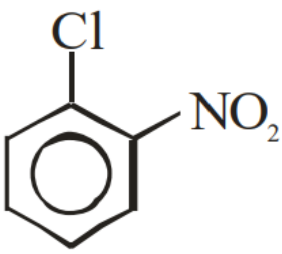
(ii) Section-B: This section contains 10 questions. In Section-B, attempt any five questions out of 10. The answer to each of the questions is a numerical value. Each question carries 4 marks for correct answer and –1 mark for wrong answer. For Section-B, the answer should be rounded off to the nearest integer.

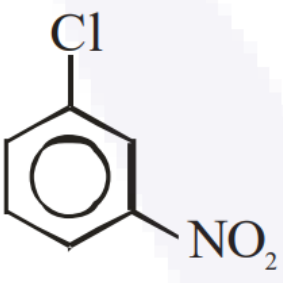
Section-A

1. The compound which will have the lowest rate towards nucleophilic aromatic substitution on treatment with OH^- is:

(1) 

(2) 

(3) 

(4) 

Correct Answer: (4)

Solution:

The rate of nucleophilic aromatic substitution (NAS) depends on the position of the electron-withdrawing group (**EWG**) relative to the leaving group. Electron-withdrawing

groups such as nitro ($\mathbf{NO_2}$) enhance the reactivity of the aromatic compound towards NAS by stabilizing the intermediate Meisenheimer complex. The stabilization is maximized when:
1. The **EWG** is in the ortho or para position relative to the leaving group. This allows strong resonance interactions that stabilize the negative charge on the intermediate complex.
2. The **EWG** at the meta position does not stabilize the intermediate effectively due to the lack of resonance alignment between the substituent and the site of nucleophilic attack.

Analysis of the Options:

- Compound (1): The nitro group is in the para position relative to the leaving chlorine atom (**Cl**), enhancing the rate of reaction due to resonance stabilization.
- Compound (2): The nitro group is in the ortho position, which also provides strong resonance stabilization, enhancing the rate of reaction.
- Compound (3): The nitro group is in the para position, similar to Compound (1), favoring the reaction.
- Compound (4): The nitro group is in the meta position relative to the chlorine atom. At this position, the nitro group cannot stabilize the negative charge developed during the reaction effectively, resulting in the **lowest rate** of nucleophilic aromatic substitution.

Electron-withdrawing groups enhance the reactivity of aromatic compounds towards nucleophilic substitution by stabilizing the intermediate negative charge. However, this effect is position-dependent. At the meta position, the inductive effect of the $\mathbf{NO_2}$ group contributes minimally to stabilization because resonance interactions are not possible. Consequently, compound (4), with $\mathbf{NO_2}$ at the meta position, shows the **lowest rate of reaction**.

Quick Tip

Electron-withdrawing groups at the ortho or para positions significantly stabilize the intermediate complex in nucleophilic aromatic substitution. The meta position is far less effective in this regard.

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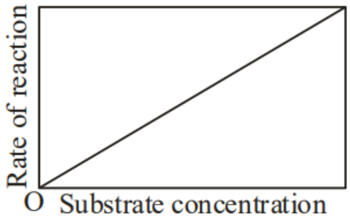
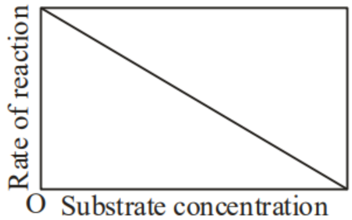
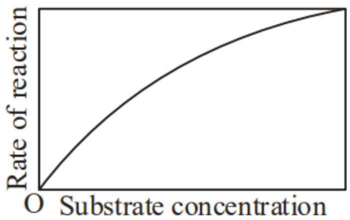
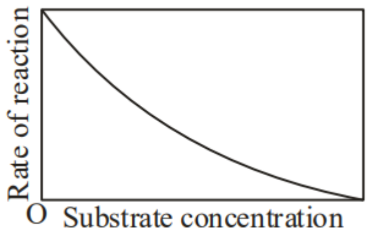
2. The variation of the rate of an enzyme-catalyzed reaction with substrate concentration is correctly represented by which graph?

(a) 

(b) 

(c) 

(d) 

Options:

1. a
2. b.
3. c.
4. d.

Correct Answer: (2)

Solution:

The graph representing the variation of the rate of an enzyme-catalyzed reaction with substrate concentration follows Michaelis-Menten kinetics. Initially, the rate of reaction increases linearly with substrate concentration as active sites on the enzyme are free and readily available. However, as the enzyme becomes saturated with substrate, the rate reaches a maximum (V_{max}) and remains constant, regardless of further increases in substrate concentration.

Graph (b) best represents this relationship as it shows:

- An initial linear phase where the reaction rate increases.
- A plateau phase where the reaction rate becomes constant due to enzyme saturation.

The reaction rate of an enzyme-catalyzed process depends on the concentration of substrate. At low substrate concentrations, the reaction rate is proportional to the substrate concentration. At high concentrations, the enzyme becomes saturated, and the reaction rate levels off at V_max, indicating that all enzyme active sites are occupied.

Quick Tip

Enzyme-catalyzed reactions follow a hyperbolic curve described by Michaelis-Menten kinetics. Remember, saturation occurs when the substrate concentration is very high.

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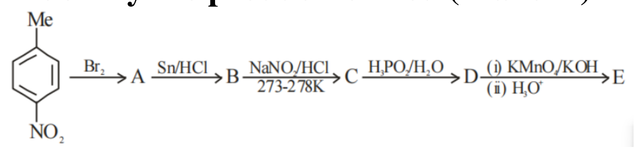
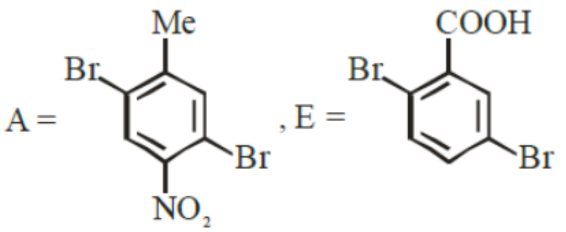
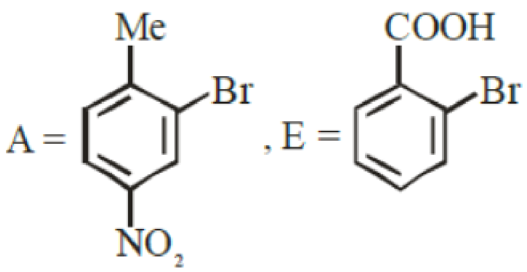
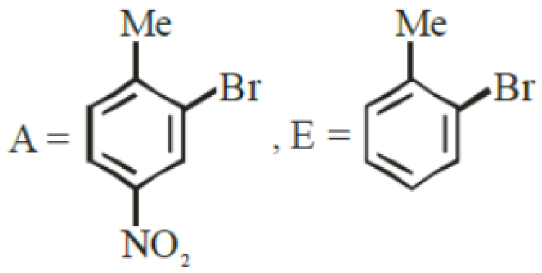
3. Identify the product formed (A and E) in the following reaction sequence:

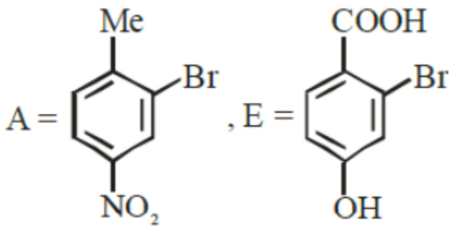


(A) 

(B) 



(C)



(D)

Correct Answer: (2)

Solution:

The reaction involves the following steps: 1. Step A: Bromination of the aromatic ring using Br_2 in the presence of Fe results in the selective addition of bromine to the meta position relative to the existing nitro group ($\mathbf{NO_2}$) due to its electron-withdrawing nature.

2. Step B: Diazonium salt formation occurs when the amine ($\mathbf{NH_2}$) group reacts with $NaNO_2$ and HCl under cold conditions.

3. Step C: Hydrolysis of the diazonium salt using H_3PO_4 replaces the diazo group ($\mathbf{-N_2^+}$) with a hydroxyl group (**-OH**).

4. Step D: Oxidation with $KMnO_4$ under basic conditions results in the conversion of the alkyl group (-Me) to a carboxylic acid (**-COOH**).

5. Step E: Reaction with dilute acid (H^+) ensures completion and stability of the carboxylic acid group.

The final products are as follows:

- **A:** 3-bromo-4-nitrobenzene

- **E:** 3-bromo-4-nitrobenzoic acid

The key to solving this question lies in understanding the regioselectivity of each step:

- Bromination occurs at the meta position relative to $\mathbf{NO_2}$ due to its electron-withdrawing nature.

- The diazonium salt intermediate facilitates substitution with a hydroxyl group.

- Oxidation converts the methyl group to a carboxylic acid, resulting in the final product.

Quick Tip

Electron-withdrawing groups like nitro (**NO_2**) direct electrophilic substitutions to the meta position. Use reaction mechanisms to predict intermediate and final products.

4. Match List I with List II and choose the correct answer from the options given below:

List I (Elements)	List II (Colour imparted to the flame)
K	Brick Red
Ca	Violet
Sr	Apple Green
Ba	Crimson Red

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

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

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

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

Correct Answer: (3)

Solution:

The flame test is used to identify elements based on the characteristic colors they emit when heated. The correct matching is:

- **K:** Violet
- **Ca:** Brick Red
- **Sr:** Crimson Red
- **Ba:** Apple Green

Thus, the correct matching corresponds to option (3).

Quick Tip

Flame tests are based on the excitation of electrons in the metal ions. When they return to their ground state, they emit light at characteristic wavelengths.

5. Reaction of thionyl chloride with white phosphorus forms a compound [A], which on hydrolysis gives [B], a dibasic acid. [A] and [B] are respectively:

(A) P_4O_6 and H_3PO_3

(B) PCl_3 and H_3PO_3

(C) PCl_5 and H_3PO_4

(D) $POCl_3$ and H_3PO_4

Correct Answer: (2)

Solution:

The reaction proceeds as follows: 1. Step 1: Reaction of white phosphorus ($\mathbf{P_4}$) with thionyl chloride ($\mathbf{SOCl_2}$) produces phosphorus trichloride ($\mathbf{PCl_3}$) and sulfur dioxide ($\mathbf{SO_2}$):

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

2. Step 2: Hydrolysis of $\mathbf{PCl_3}$ produces phosphorous acid ($\mathbf{H_3PO_3}$):

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Thus, **[A] = $\mathbf{PCl_3}$** and **[B] = $\mathbf{H_3PO_3}$**, corresponding to option (2).

Quick Tip

Phosphorus trichloride ($\mathbf{PCl_3}$) is a common reagent in chemical synthesis and reacts readily with water to form phosphorous acid ($\mathbf{H_3PO_3}$).

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6. A cubic solid is made up of two elements X and Y. Atoms of X are present on every alternate corner and one at the center of the cube. Y is at $\frac{1}{4}$ of the total faces. The empirical formula of the compound is:

(A) $X_2Y_{1.5}$

(B) $X_{2.5}Y$

(C) $XY_{2.5}$

(D) $X_{1.5}Y_2$

Correct Answer: (2)

Solution:

1. Atoms of X: - X is present on alternate corners of the cube, which means it occupies 4 out of the 8 corners. - Each corner contributes $\frac{1}{8}$ to the unit cell.

$$\text{Contribution from corners} = 4 \times \frac{1}{8} = \frac{1}{2}.$$

- Additionally, there is one X atom at the center of the cube, contributing 1 atom.

$$\text{Total contribution from X} = \frac{1}{2} + 1 = 1.5 \text{ atoms.}$$

2. Atoms of Y: - Y atoms are present at $\frac{1}{4}$ of the 6 faces of the cube. - Each face contributes $\frac{1}{2}$ atom to the unit cell.

$$\text{Contribution from faces} = 6 \times \frac{1}{4} \times \frac{1}{2} = \frac{3}{2} \text{ atoms.}$$

3. Empirical Formula: - The ratio of atoms of X to Y is:

$$\text{X : Y} = 1.5 : 1.5 = 1 : 1.$$

- However, the empirical formula accounts for their fractional contributions, giving:

$$\text{Empirical formula} = X_{2.5}Y.$$

1. Atoms at corners contribute $\frac{1}{8}$ to the unit cell, while atoms at the center contribute fully.
2. Atoms at faces contribute $\frac{1}{2}$ of their count to the unit cell.
3. By calculating individual contributions of X and Y, the correct empirical formula is derived as $X_{2.5}Y$.

Quick Tip

Always account for the fractional contributions of atoms in unit cells based on their positions (corner, center, face) to calculate the empirical formula.

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7. The radius of the 2nd orbit of Li^{2+} is x. The expected radius of the 3rd orbit of Be^{3+} is:

(A) $\frac{9}{4}x$

(B) $\frac{4}{9}x$

(C) $\frac{27}{16}x$

(D) $\frac{16}{27}x$

Correct Answer: (3)

Solution:

Using the formula for the radius of the nth orbit:

$$r_n = k \cdot \frac{n^2}{Z}$$

For Li^{2+} ($Z = 3$, $n = 2$):

$$r_2 = k \cdot \frac{2^2}{3} = \frac{4k}{3}$$

For Be^{3+} ($Z = 4$, $n = 3$):

$$r_3 = k \cdot \frac{3^2}{4} = \frac{9k}{4}$$

The ratio of radii:

$$\frac{r_3}{r_2} = \frac{\frac{9k}{4}}{\frac{4k}{3}} = \frac{27}{16}$$

Thus, the radius of the 3^{rd} orbit of Be^{3+} is $\frac{27}{16}x$.

Quick Tip

The radius of an orbit in a hydrogen-like atom is proportional to $\frac{n^2}{Z}$. Higher orbits have larger radii.

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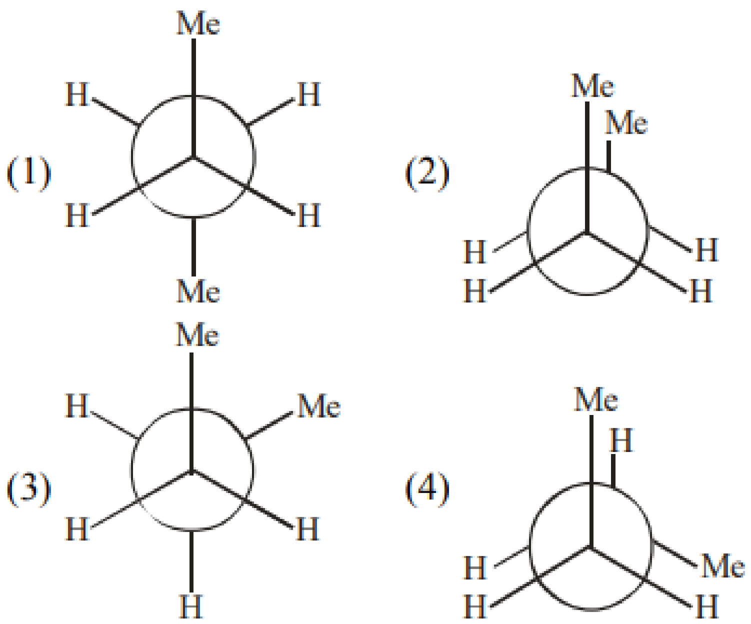
8. Which of the following conformations will be the most stable?



(A) (1)

(B) (2)

(C) (3)

(D) (4)

Correct Answer: (1)

Solution:

In the chair conformation of cyclohexane, bulky groups prefer the equatorial position to minimize steric hindrance and achieve greater stability.

In conformation (1), both methyl (**Me**) groups are in equatorial positions, resulting in the lowest steric hindrance and highest stability.

Quick Tip

Always place bulkier groups in the equatorial position of cyclohexane to maximize stability in chair conformations.

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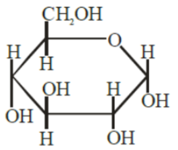
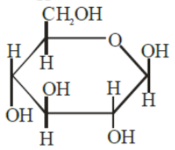
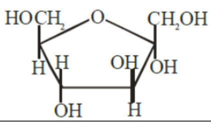
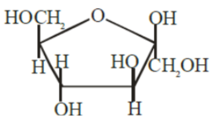
9. Match items of Row I with those of Row II:

Row I:

(P) 

(Q) 

(R) 

(S) 

Row II:

(A) [(i)] α-D-(-)-Fructofuranose

(B) [(ii)] β-D-(-)-Fructofuranose

(C) [(iii)] α-D-(+)-Glucopyranose

(D) [(iv)] β-D-(+)-Glucopyranose

Correct Match:

(A) (1) P $\rightarrow$ iv, Q $\rightarrow$ iii, R $\rightarrow$ i, S $\rightarrow$ ii

(B) (2) P $\rightarrow$ i, Q $\rightarrow$ ii, R $\rightarrow$ iii, S $\rightarrow$ iv

(C) (3) P $\rightarrow$ iii, Q $\rightarrow$ iv, R $\rightarrow$ ii, S $\rightarrow$ i

(D) (4) P $\rightarrow$ iii, Q $\rightarrow$ iv, R $\rightarrow$ i, S $\rightarrow$ ii

Correct Answer: (4)

Solution:

- (P): α-D-(+)-Glucopyranose (iii): This structure has the -OH group at C1 in the α-position (below the plane) in the six-membered pyranose ring.
- (Q): β-D-(+)-Glucopyranose (iv): This structure has the -OH group at C1 in the β-position (above the plane) in the six-membered pyranose ring.
- (R): α-D-(-)-Fructofuranose (i): This structure is a five-membered fructofuranose ring with the α-configuration (OH group at C2 below the plane).
- (S): β-D-(-)-Fructofuranose (ii): This structure is a five-membered fructofuranose ring with the β-configuration (OH group at C2 above the plane).

Thus, the correct matching is:

$$P \rightarrow iii, Q \rightarrow iv, R \rightarrow i, S \rightarrow ii.$$

1. Glucose exists in both pyranose (six-membered) and furanose (five-membered) forms. Pyranose forms are more stable.
2. α and β forms differ in the configuration of the hydroxyl group at the anomeric carbon (C1 for glucose and C2 for fructose).
3. Fructose predominantly forms five-membered furanose rings due to its keto group.

Quick Tip

Remember: In α-anomers, the hydroxyl group on the anomeric carbon is trans to the CH_2OH group, while in β-anomers, it is cis.

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10. Given below are two statements: one is labelled as Assertion A and the other is labelled as Reason R:

Assertion A: Acetal/Ketal is stable in basic medium.

Reason R: The high leaving tendency of alkoxide ion gives the stability to acetal/ketal in basic medium.

In the light of the above statements, choose the correct answer from the options given below:

(A) Both A and R are true and R is the correct explanation of A

(B) Both A and R are true but R is NOT the correct explanation of A

(C) A is true but R is false

(D) A is false but R is true

Correct Answer: (1)

Solution:

- Assertion A: Acetals and ketals are stable in a basic medium because the basic conditions do not hydrolyze them, unlike acidic conditions where they undergo breakdown.
- Reason R: Alkoxide ions ($\mathbf{RO^-}$) are strong bases but not good leaving groups in a basic medium. This stability supports the structure of acetals and ketals.

Thus, both Assertion A and Reason R are correct, and R is the correct explanation of A. Acetals and ketals are commonly used as protecting groups in organic synthesis because they are stable in basic conditions but hydrolyze in acidic media. Alkoxide ions, being poor leaving groups, contribute to this stability.

Quick Tip

Acetals and ketals are stable in bases but break down in acids. Always analyze the role of leaving groups in reaction stability.

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11. Inert gases have positive electron gain enthalpy. Its correct order is:

(A) Xe $<$ Kr $<$ Ne $<$ He

(B) He $<$ Ne $<$ Kr $<$ Xe

(C) He $<$ Xe $<$ Kr $<$ Ne

(D) He $<$ Kr $<$ Xe $<$ Ne

Correct Answer: (3)

Solution:

- Electron gain enthalpy refers to the energy change when an atom gains an electron.
- Inert gases have closed electronic configurations, making electron addition unfavorable.
- Among the inert gases:

- He has the highest positive electron gain enthalpy due to its small size.

- Xe has the lowest due to its larger size and lower repulsion for incoming electrons.

Thus, the correct order is **He** $<$ **Xe** $<$ **Kr** $<$ **Ne**.

Electron gain enthalpy becomes less positive (or more favorable) as atomic size increases, as larger atoms experience less electron-electron repulsion. Hence, Xe has the least positive electron gain enthalpy among inert gases.

Quick Tip

Electron gain enthalpy in inert gases is positive due to their stable electronic configurations. Larger atoms like Xe have less positive values.

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12. Which one of the following reactions does not occur during the extraction of copper?

(A) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(B) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

(C) $CaO + SiO_2 \rightarrow CaSiO_3$

(D) $FeO + SiO_2 \rightarrow FeSiO_3$

Correct Answer: (3)

Solution:

In the extraction of copper from chalcopyrite ($CuFeS_2$), the key steps involve: 1. Partial roasting of chalcopyrite in the presence of oxygen to form Cu_2S, FeS, and SO_2.

$$2CuFeS_2 + 4O_2 \rightarrow Cu_2S + 2FeS + 3SO_2$$

2. Further oxidation of Cu_2S to form Cu_2O:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

3. FeO reacts with SiO_2 to form $FeSiO_3$:

$$FeO + SiO_2 \rightarrow FeSiO_3$$

This step removes iron as slag.

The reaction $CaO + SiO_2 \rightarrow CaSiO_3$ does not occur during copper extraction, as CaO is not used in this process. It is a reaction commonly observed in steel production.

The extraction of copper involves partial roasting of $CuFeS_2$, followed by oxidation and slag formation. Iron impurities are removed as $FeSiO_3$ (slag) by reaction with SiO_2. Calcium silicate ($CaSiO_3$) formation is not part of this process.

Quick Tip

Remember, FeO reacts with SiO_2 during copper extraction to form slag ($FeSiO_3$), while CaO is typically used in steel-making processes.

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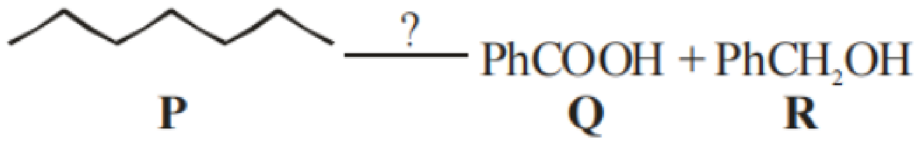
13. The correct sequence of reagents for the preparation of Q and R is:



(A) (i) CrO_3, 770 K, 20 atm; (ii) CrO_2Cl_2, H^+; (iii) NaOH; (iv) H_3O^+

(B) (i) CrO_2Cl_2, H_3O^+; (ii) CrO_3, 770 K, 20 atm; (iii) NaOH; (iv) H_3O^+

(C) (i) $KMnO_4$, OH^{--}; (ii) MoO_3, Δ; (iii) NaOH; (iv) H_3O^+

(D) (i) MoO_3, Δ; (ii) CrO_2Cl_2, H_3O^+; (iii) NaOH; (iv) H_3O^+

Correct Answer: (1)

Solution:

The reaction sequence involves:

1. Step 1: Oxidation of benzene to benzoquinone using CrO_3 at 770 K and 20 atm.
2. Step 2: Formation of phenol by further oxidation with CrO_2Cl_2 in acidic medium.
3. Step 3: Neutralization with NaOH to form phenoxide ion.
4. Step 4: Acidification with H_3O^+ to yield phenol.

In the preparation of phenol from benzene, the use of CrO_3 and CrO_2Cl_2 ensures selective oxidation steps. Acidic and basic conditions aid in subsequent transformations.

Quick Tip

Use of CrO_3 and CrO_2Cl_2 is crucial for oxidation reactions. Remember, NaOH neutralizes phenol derivatives.

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14. The correct order in aqueous medium of basic strength in case of

methyl-substituted amines is:

(A) $Me_2NH > MeNH_2 > Me_3N > NH_3$

(B) $Me_2N > Me_3NH > MeNH_2 > NH_3$

(C) $NH_3 > Me_3N > MeNH_2 > Me_2NH$

(D) $Me_3N > Me_2NH > MeNH_2 > NH_3$

Correct Answer: (1)

Solution:

In aqueous medium, the basic strength of amines depends on:

1. Electron density on the nitrogen atom (due to inductive effect of methyl groups).

2. Solvation effect, which stabilizes the conjugate acid after accepting a proton.

- **Dimethylamine (Me_2NH):** The best combination of inductive effect and solvation, making it the most basic.
- **Methylamine ($MeNH_2$):** Slightly less basic due to less inductive effect but better solvation.
- **Trimethylamine (Me_3N):** Weaker basicity because bulky groups hinder solvation.
- **Ammonia (NH_3):** Lowest basicity due to the absence of inductive effect.

Thus, the basic strength order is $\mathbf{Me_2NH} > \mathbf{MeNH_2} > \mathbf{Me_3N} > \mathbf{NH_3}$.

Basicity in aqueous medium is influenced by both inductive effects and solvation. Dimethylamine balances these effects best, while trimethylamine suffers from steric hindrance.

Quick Tip

In aqueous medium, bulky substituents reduce basicity due to poor solvation of the conjugate acid.

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15. 25-volume hydrogen peroxide means:

(A) 1 L marketed solution contains 250 g of H_2O_2

(B) 1 L marketed solution contains 75 g of H_2O_2

(C) 1 L marketed solution contains 25 g of H_2O_2

(D) 1 L marketed solution contains 25 g of H_2O

Correct Answer: (2)

Solution:

1. The term ”25-volume” means that 1 L of H_2O_2 solution can release 25 L of oxygen gas upon decomposition:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

2. To calculate the strength of H_2O_2 solution:

$$\text{Strength (g/L)} = \frac{\text{Molar mass} \times \text{Volume of O}_2}{11.35} = \frac{25 \times 34}{11.35} = 74.889\,\text{g/L}.$$

Thus, the solution contains approximately 75 g of H_2O_2 in 1 L.

”Volume strength” refers to the amount of oxygen gas released by a given volume of H_2O_2. A 25-volume solution releases 75 L of O_2 per liter.

Quick Tip

To find the strength of H_2O_2, use the formula: Strength (g/L) $= \frac{\text{Volume strength} \times \text{Molar mass}}{11.35}$.

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16. Which of the following statements is incorrect for antibiotics?

(A) An antibiotic must be a product of metabolism.

(B) An antibiotic is a synthetic substance produced as a structural analogue of naturally occurring antibiotic.

(C) An antibiotic should promote the survival of microorganisms.

(D) An antibiotic should be effective in low concentrations.

Correct Answer: (3)

Solution:

1. (1): Correct. Antibiotics are often products of microbial metabolism (e.g., penicillin from Penicillium species).

2. (2): Correct. Many antibiotics are synthetic analogues (e.g., sulfonamides).

3. (3): Incorrect. Antibiotics inhibit the growth or kill microorganisms; they do not promote their survival.

4. (4): Correct. Antibiotics are effective at low concentrations due to their high specificity.

Antibiotics are agents that inhibit the growth of or kill microorganisms. They do not promote survival and are effective at low concentrations.

Quick Tip

Antibiotics act as inhibitors of microbial growth and are used in small doses due to their high potency.

---

17. Compound A reacts with NH_3Cl and forms B and C. Compound B reacts with H_2O and CO_2 to form C. The compounds A, B, and C are:

(A) $CaCl_2$, NH_3, NH_4HCO_3

(B) $CaCl_2$, NH_4^+, $(NH_4)_2CO_3$

(C) $Ca(OH)_2$, NH_3, NH_4HCO_3

(D) $Ca(OH)_2$, NH_4^+, $(NH_4)_2CO_3$

Correct Answer: (3)

Solution:

1. Reaction 1: $Ca(OH)_2$ reacts with NH_3Cl to form NH_3, $CaCl_2$, and H_2O.

2. Reaction 2: NH_3 reacts with H_2O and CO_2 to form NH_4HCO_3.

Thus, **A = $Ca(OH)_2$**, **B = NH_3**, and **C = NH_4HCO_3**.

Ammonium bicarbonate (**NH_4HCO_3**) is formed when ammonia reacts with water and carbon dioxide, a key step in the Solvay process.

Quick Tip

The reaction of NH_3 with CO_2 and water forms NH_4HCO_3, commonly used in the Solvay process.

---

18. Some reactions of NO_2 relevant to photochemical smog formation are:

Identify A, B, X, and Y:

(A) X = O, Y = NO, A = O_2, B = O_3

(B) $X = N_2O$, $Y = O$, $A = O_3$, $B = NO$

(C) $X = \frac{1}{2}O_2$, $Y = NO_2$, $A = O_3$, $B = O_2$

(D) $X = NO$, $Y = O$, $A = O_2$, $B = N_2O_3$

Correct Answer: (1)

Solution:

1. NO_2 dissociates in sunlight:

$$NO_2 \xrightarrow{\text{sunlight}} NO + O.$$

2. O reacts with O_2 to form ozone:

$$O + O_2 \rightarrow O_3.$$

Thus, **X = O**, **Y = NO**, **A = O_2**, and **B = O_3**.

In photochemical smog formation, NO_2 dissociates into NO and O under sunlight. Atomic oxygen reacts with O_2 to form O_3 (ozone).

Quick Tip

Photochemical smog involves NO_2 photolysis to produce NO and O, which leads to ozone formation.

---

19. Match the List-I with List-II:

Cations (List-I)	Group Reaction (List-II)
$P \rightarrow Pb^{2+}, Cu^{2+}$	(i) H_2S gas in presence of dilute HCl
$Q \rightarrow Al^{3+}, Fe^{3+}$	(ii) $(NH_4)_2CO_3$ in presence of NH_4OH
$R \rightarrow Co^{2+}, Ni^{2+}$	(iii) NH_4OH in presence of NH_4Cl
$S \rightarrow Ba^{2+}, Ca^{2+}$	(iv) H_2S in presence of NH_4OH

(1) P→ i, Q→ iii, R→ ii, S→ iv

(2) P→ iv, Q→ ii, R→ iii, S→ i

(3) P→ iii, Q→ i, R→ iv, S→ ii

(4) P→ i, Q→ iii, R→ iv, S→ ii

Correct Answer: (4)

Solution:

- P (Pb^{2+}, Cu^{2+}): Group I cations are precipitated as sulfides in the presence of H_2S and dilute HCl.

- Q (Al^{3+}, Fe^{3+}): Group III cations form hydroxides in the presence of NH_4Cl and NH_4OH.
- R (Co^{2+}, Ni^{2+}): Group IV cations form sulfides in the presence of H_2S and NH_4OH.
- S (Ba^{2+}, Ca^{2+}): Group V cations form carbonates with $(NH_4)_2CO_3$ in the presence of NH_4OH.

Qualitative analysis involves group-wise separation of cations based on selective precipitation using reagents like H_2S, NH_4OH, and $(NH_4)_2CO_3$.

Quick Tip

Memorize group reagents and their corresponding cations for qualitative inorganic analysis.

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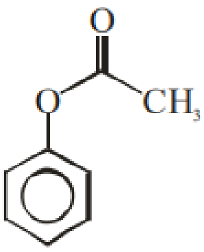
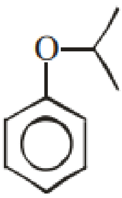
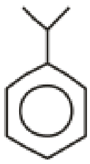
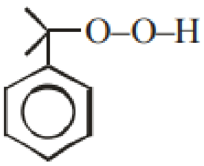
20. In the cumene to phenol preparation in the presence of air, the intermediate is:

(1) 

(2) 

(3) 

(4) 

Correct Answer: (4)

Solution: a In the cumene to phenol process: 1. Cumene is oxidized in the presence of air to form cumene hydroperoxide:

$$\text{Cumene} + O_2 \rightarrow \text{Cumene hydroperoxide.}$$

2. Cumene hydroperoxide undergoes acid-catalyzed cleavage to yield phenol and acetone. The correct intermediate is cumene hydroperoxide.
Cumene hydroperoxide is a key intermediate in phenol production, formed by air oxidation of cumene.

Quick Tip

The cumene process produces both phenol and acetone as valuable co-products.

Section B

21. An athlete is given 100 g of glucose ($C_6H_12O_6$) for energy, which is equivalent to 1800 kJ of energy. If 50% of this energy is utilized for activities, the weight of extra water needed to perspire is ____ g. (Nearest integer)

Given: Enthalpy of evaporation of water = 45 kJ/mol; molar masses: C = 12 g/mol, H = 1 g/mol, O = 16 g/mol.

Correct Answer: 360

Solution:

1. Energy to be dissipated = 50% of 1800 kJ:

$$\text{Energy} = \frac{50}{100} \times 1800 = 900\,\text{kJ}.$$

2. Moles of water required for evaporation:

$$\text{Moles of water} = \frac{\text{Energy}}{\Delta H_{\text{vap}}} = \frac{900}{45} = 20\,\text{mol}.$$

3. Mass of water required:

$$\text{Mass} = \text{Moles} \times \text{Molar mass of water} = 20 \times 18 = 360\,\text{g}.$$

Half of the energy must be dissipated through perspiration. Using the enthalpy of vaporization of water, the mass required to evaporate this energy is calculated.

Quick Tip

The energy required for evaporation is directly proportional to the moles of water vaporized.

---

22. A litre of buffer solution contains 0.1 mole of each NH_3 and NH_4Cl. On addition of 0.02 mole of HCl, the pH of the solution is found to be ______ $\times 10^{-3}$ (Nearest integer).

Given: $pK_b(NH_3) = 4.745$; $\log 2 = 0.301$; $\log 3 = 0.477$; T = 298 K.

Correct Answer: (9079)

Solution:

1. Buffer equation:

$$\text{pH} = 14 - \text{pK}_b + \log \frac{[\text{Base}]}{[\text{Acid}]}.$$

2. After HCl addition:

$$[\text{Base}] = 0.1 - 0.02 = 0.08\,\text{mol}, \quad [\text{Acid}] = 0.1 + 0.02 = 0.12\,\text{mol}.$$

3. pH calculation:

$$\text{pH} = 14 - 4.745 + \log \frac{0.08}{0.12} = 14 - 4.745 + \log \frac{2}{3}.$$

4. Using logarithms:

$$\log \frac{2}{3} = \log 2 - \log 3 = 0.301 - 0.477 = -0.176.$$

$$\text{pH} = 14 - 4.745 - 0.176 = 9.079 \times 10^{-3}.$$

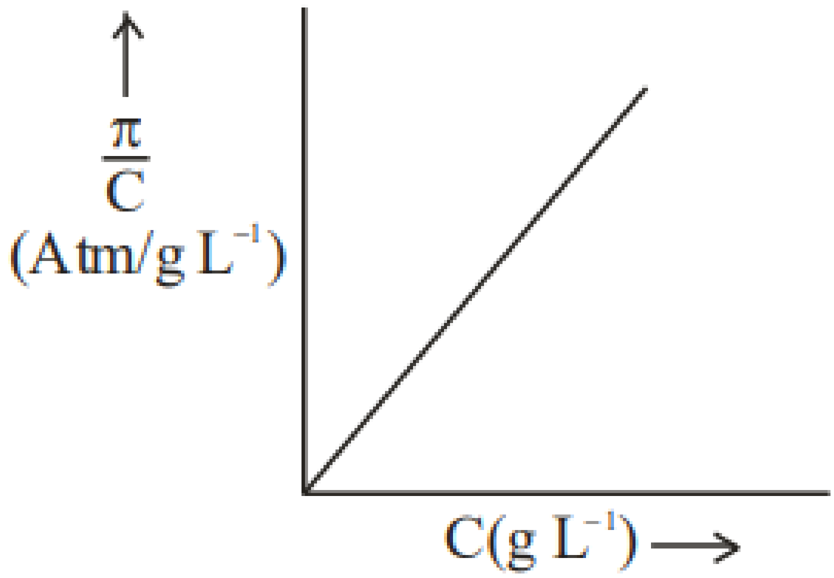
Buffer solutions resist changes in pH. The pH is calculated using the Henderson-Hasselbalch equation for weak bases.

Quick Tip

Use $\text{pH} = 14 - \text{pK}_b + \log \frac{[\text{Base}]}{[\text{Acid}]}$ for weak base buffers.

---

23. The osmotic pressure of solutions of PVC in cyclohexanone at 300 K are plotted on the graph. The molar mass of PVC is ______ g mol^{-1} (Nearest integer).



Given: R = 0.083 L atm K^{-1} mol^{-1}

Correct Answer: 41500

Solution:

The van 't Hoff equation for osmotic pressure (π) is:

$$\pi = CRT$$

Dividing both sides by concentration (C):

$$\frac{\pi}{C} = RT \times \frac{1}{M}$$

From the graph, the slope ($\frac{\pi}{C}$) is determined to be 6.0 atm L g^{-1}.

Using the relation:

$$M = \frac{RT}{\text{slope}}$$

Substituting the values:

$$M = \frac{0.083 \times 300}{6.0} = 41500\,\text{g mol}^{-1}.$$

Thus, the molar mass of PVC is **41500 g mol^{-1}**.

The molar mass of a polymer like PVC can be calculated from osmotic pressure data using the van 't Hoff equation. The slope of the π/C graph provides critical information for this calculation.

Quick Tip

Osmotic pressure is inversely proportional to molar mass. Larger molecules like polymers exhibit lower osmotic pressures for the same concentration.

---

24. How many of the following metal ions have a similar value of spin-only magnetic moment in the gaseous state?

$$V^{3+}, Cr^{3+}, Fe^{2+}, Ni^{3+}$$

Given: Atomic numbers: V = 23, Cr = 24, Fe = 26, Ni = 28.

Correct Answer: (2)

Solution:

The spin-only magnetic moment (μ) is given by:

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

where n is the number of unpaired electrons.

1. V^{3+}:

- Electronic configuration: [Ar] $3d^2$

- Number of unpaired electrons (n) = 2.

- $\mu = \sqrt{2(2+2)} = \sqrt{8}\,\text{BM}$.

2. Cr^{3+}:

- Electronic configuration: [Ar] $3d^3$

- Number of unpaired electrons (n) = 3.

- $\mu = \sqrt{3(3+2)} = \sqrt{15}\,\text{BM}$.

3. Fe^{2+}:

- Electronic configuration: [Ar] $3d^6$

- Number of unpaired electrons (n) = 4.

- $\mu = \sqrt{4(4+2)} = \sqrt{24}\,\text{BM}$.

4. Ni^{3+}:

- Electronic configuration: [Ar] $3d^7$

- Number of unpaired electrons (n) = 3.

- $\mu = \sqrt{3(3+2)} = \sqrt{15}\,\text{BM}$.

Result:

Cr^{3+} and Ni^{3+} have the same magnetic moment ($\sqrt{15}\,\text{BM}$).

The spin-only magnetic moment depends on the number of unpaired electrons (n). Cr^{3+} and Ni^{3+} have identical magnetic moments because they have the same number of unpaired electrons.

> **Quick Tip**
>
> To determine magnetic moments, calculate the number of unpaired electrons from the electronic configuration of the ion.

---

25. The density of a monobasic strong acid (Molar mass 24.2 g mol^{-1}) is 1.21 kg L^{-1}. The volume of its solution required for the complete neutralization of 25 mL of 0.24 M NaOH is ______ $\times 10^{-3}$ mL (Nearest integer).

Correct Answer: (12)

Solution:

1. Calculate millimoles of NaOH:

$$\text{Millimoles of NaOH} = 0.24 \times 25 = 6\,\text{mmol}.$$

2. Since the acid is monobasic, millimoles of acid required = millimoles of NaOH = 6 mmol.

3. Mass of acid required:

$$\text{Mass of acid} = 6 \times 24.2 = 145.2\,\text{mg}.$$

4. Volume of acid solution:

Using Volume $= \frac{\text{mass}}{\text{density}}$,

$$V = \frac{145.2}{1.21 \times 10^3} = 0.12\,\text{mL}.$$

5. Convert to 10^{-3}:

$$V = 12 \times 10^{-3}\,\text{mL}.$$

Thus, the volume required is **12** $\times 10^{-3}$ **mL**.

Neutralization of a monobasic acid requires equal millimoles of acid and base. Use the density of the acid solution to calculate the required volume.

Quick Tip

For neutralization reactions, always equate the milliequivalents of acid and base for stoichiometric calculations.

---

26. For the first-order reaction $A \to B$, the half-life is 30 min. The time taken for 75% completion of the reaction is ______ min (Nearest integer).

Correct Answer: (60)

Solution:

1. For a first-order reaction, the time required for completion is given by:

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

2. For 75% completion, $[A] = \frac{1}{4}[A]_0$. Substituting:

$$t = \frac{2.303}{k} \log \frac{[A]_0}{\frac{1}{4}[A]_0} = \frac{2.303}{k} \log 4.$$

3. Use the relation between half-life and rate constant:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}.$$

4. Substituting k and $\log 4 = 0.602$:

$$t = \frac{2.303 \times 0.602}{0.693/30} = 60\,\text{min}.$$

Thus, the time taken is **60 min**.

For first-order reactions, the time for completion depends logarithmically on the fraction of the reaction completed.

Quick Tip

Remember that 75% completion corresponds to $[A] = \frac{1}{4}[A]_0$ in first-order reactions.

---

27. The total number of lone pairs of electrons on oxygen atoms of ozone is _______.

Correct Answer: (6)

Solution:

1. The Lewis structure of ozone (O_3) is:

$$\text{O} = \text{O} - \text{O} \leftrightarrow \text{O} - \text{O} = \text{O}.$$

2. Each oxygen atom has 6 valence electrons. After bonding:

- One oxygen atom has 1 lone pair.

- The other two oxygen atoms have 2 lone pairs each.

3. Total number of lone pairs:

$$\text{Total lone pairs} = 1 + 2 + 2 = 6.$$

Thus, the total number of lone pairs is **6**.

The ozone molecule has a resonance structure, and the total number of lone pairs accounts for the bonding and nonbonding electrons on oxygen atoms.

Quick Tip

For resonance structures, calculate lone pairs for each contributing form and add them up.

---

28. In sulphur estimation, 0.471 g of an organic compound gave 1.4439 g of barium sulphate. The percentage of sulphur in the compound is ______ (Nearest Integer).

Given: Atomic masses: Ba = 137, S = 32, O = 16.

Correct Answer: (42)

Solution:

1. Molar mass of $BaSO_4$:

$$M = 137 + 32 + 64 = 233\,\text{g/mol}.$$

2. Mass of sulphur in $BaSO_4$:

$$\text{Mass of S} = \frac{32}{233} \times \text{mass of BaSO}_4.$$

3. Substituting the given mass of $BaSO_4$:

$$\text{Mass of S} = \frac{32}{233} \times 1.4439 = 0.1984\,\text{g}.$$

4. Percentage of sulphur:

$$\%\text{S} = \frac{\text{Mass of S}}{\text{Mass of compound}} \times 100 = \frac{0.1984}{0.471} \times 100 = 42.10\%.$$

Thus, the percentage of sulphur is **42%**.

In sulphur estimation, the amount of sulphur is directly calculated from the mass of $BaSO_4$ formed, using stoichiometric relations.

Quick Tip

Use the molar ratio of sulphur in $BaSO_4$ to find the mass of sulphur and calculate the percentage.

---

29. The number of paramagnetic species from the following is _______.

$$[\text{Ni(CN)}_4]^{2-}, [\text{Ni(CO)}_4], [\text{NiCl}_4]^{2-}, [\text{Fe(CN)}_6]^{3-}, [\text{Cu(NH}_3)_4]^{2+}, [\text{Fe(H}_2\text{O)}_6]^{2+}$$

Correct Answer: (4)

Solution:

1. Determine the electronic configuration and geometry for each species:

- $[Ni(CN)_4]^{2-}$:

Ni^{2+} $(3d^8)$ in a strong field ligand, forms a square planar complex. No unpaired electrons. (Diamagnetic)

- $[Ni(CO)_4]$:

Ni^0 $(3d^8 4s^2)$ in a strong field ligand, forms a tetrahedral complex. No unpaired electrons. (Diamagnetic)

- $[NiCl_4]^{2-}$:

Ni^{2+} $(3d^8)$ in a weak field ligand, forms a tetrahedral complex. 2 unpaired electrons. (Paramagnetic)

- $[Fe(CN)_6]^{3-}$:

Fe^{3+} $(3d^5)$ in a strong field ligand, forms a low-spin octahedral complex. 1 unpaired electron. (Paramagn

- $[Cu(NH_3)_4]^{2+}$: Cu^{2+} $(3d^9)$ 1 unpaired electron. (Paramagnetic)

- $[Fe(H_2O)_6]^{2+}$:

Fe^{2+} $(3d^6)$ in a weak field ligand, forms a high-spin octahedral complex. 4 unpaired electrons. (Paramagn

2. Count the paramagnetic species:

Paramagnetic species: $[NiCl_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^{2+}$, $[Fe(H_2O)_6]^{2+}$.

Total = 4 species.

Thus, the number of paramagnetic species is **4**.

Paramagnetic species have unpaired electrons, determined by ligand field strength and electron configurations. Strong field ligands like CN^- and CO lead to low-spin complexes, while weak field ligands like Cl^- and H_2O result in high-spin complexes.

Quick Tip

Use the ligand field strength to determine the spin state and identify paramagnetic species. Strong field ligands favor low spin, reducing unpaired electrons.

---

30. Consider the cell:

$$\text{Pt(s)—H}_2\text{(g)(1 atm)—H}^+\text{(aq,1 M)——Fe}^{3+}\text{(aq),Fe}^{2+}\text{(aq)—Pt(s)}$$

Given: $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771\,\text{V}$, $E^\circ_{H^+/H_2} = 0\,\text{V}$, $T = 298\,\text{K}$.

If the potential of the cell is 0.712 V, the ratio of concentration of Fe^{2+} to Fe^{3+} is ______ (Nearest integer).

Correct Answer: (10)

Solution:

1. Write the Nernst equation for the cell:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q,$$

where $Q = \frac{[Fe^{3+}]}{[Fe^{2+}]}$.

2. Determine E°_{cell}:

$$E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{H}^+/\text{H}_2} = 0.771 - 0 = 0.771\,\text{V}.$$

3. Rearrange the Nernst equation to find $\log Q$:

$$0.712 = 0.771 - \frac{0.0591}{1}\log Q.$$

$$\log Q = \frac{0.771 - 0.712}{0.0591} = \frac{0.059}{0.0591} \approx 1.$$

4. Calculate Q:

$$Q = 10^{\log Q} = 10^1 = 10.$$

5. Determine the ratio of concentrations:

$$Q = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \implies \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{1}{Q} = \frac{1}{10}.$$

Thus, the ratio is **10**.

The Nernst equation relates the cell potential to the ratio of reactant and product concentrations. Here, $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ is calculated from the measured cell potential.

Quick Tip

For electrochemical cells, use the Nernst equation to find concentration ratios when the cell potential is given.
