

IIT JAM 2021 Chemistry (CY) Question Paper with Solutions

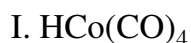
Time Allowed :3 Hours	Maximum Marks :100	Total questions :60
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General Instructions

General Instructions:

- i) All questions are compulsory. Marks allotted to each question are indicated in the margin.
- ii) Answers must be precise and to the point.
- iii) In numerical questions, all steps of calculation should be shown clearly.
- iv) Use of non-programmable scientific calculators is permitted.
- v) Wherever necessary, write balanced chemical equations with proper symbols and units.
- vi) Rough work should be done only in the space provided in the question paper.

Q.1 The CORRECT order of pK_a for the compounds I to IV in water at 298 K is



(A) I < II < III < IV

(B) IV < III < II < I

(C) IV < II < III < I

(D) I < III < II < IV

Correct Answer: (B) IV < III < II < I

Solution:

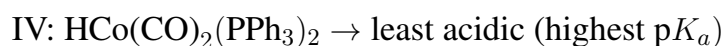
Step 1: Relation between acidity and pK_a .

Lower pK_a corresponds to higher acidity. In metal hydride complexes, acidity decreases as electron density on the metal center increases.

Step 2: Ligand effects.

CO is a strong π -acceptor, withdrawing electron density from the metal and increasing acidity (lowering pK_a). PPh_3 is a σ -donor and weak π -acceptor, increasing metal electron density and reducing acidity (raising pK_a).

Step 3: Comparing the complexes.



Thus, the pK_a order is IV < III < II < I.

Step 4: Conclusion.

The correct order of pK_a values is **IV < III < II < I**.

Quick Tip

Replacing π -acceptor ligands (like CO) with σ -donors (like PPh_3) increases electron density on the metal, decreasing acidity (increasing $\text{p}K_a$).

Q.2 For Na^+ , Mg^{2+} , Al^{3+} and F^- , the CORRECT order of ionic radii is

(A) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$

(B) $\text{Al}^{3+} > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^-$

(C) $\text{F}^- < \text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$

(D) $\text{Na}^+ < \text{F}^- < \text{Mg}^{2+} < \text{Al}^{3+}$

Correct Answer: (C) $\text{F}^- < \text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$

Solution:

Step 1: Concept of isoelectronic species.

Na^+ , Mg^{2+} , Al^{3+} , and F^- are isoelectronic (each has 10 electrons). The ionic size depends mainly on the nuclear charge (Z).

Step 2: Effect of nuclear charge.

As nuclear charge increases, the same number of electrons are pulled more strongly toward the nucleus, decreasing the ionic radius.

Step 3: Order of Z (atomic number).

F (9) ; Na (11) ; Mg (12) ; Al (13)

Hence, radius order (inverse relation):

$$\text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}.$$

Step 4: Conclusion.

The correct order of ionic radii is $\text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$.

Quick Tip

In isoelectronic ions, as nuclear charge increases, size decreases due to stronger electrostatic attraction on the same electron cloud.

Q.3 Spin-only magnetic moments (in BM) of $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $[\text{Mn}(\text{NCS})_6]^{4-}$, respectively, are

- (A) 0.00 and 5.92
(B) 2.83 and 1.89
(C) 0.00 and 1.89
(D) 2.83 and 5.92

Correct Answer: (D) 2.83 and 5.92

Solution:

Step 1: For $[\text{NiCl}_2(\text{PPh}_3)_2]$.

Ni is in +2 oxidation state $\rightarrow 3d^8$ configuration. Cl^- and PPh_3 are weak field ligands $\rightarrow$ complex is **paramagnetic**. Unpaired electrons = 2.

Spin-only magnetic moment,

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM.}$$

Step 2: For $[\text{Mn}(\text{NCS})_6]^{4-}$.

Mn is in +2 oxidation state $\rightarrow 3d^5$ configuration. All ligands are weak field (high-spin complex). Unpaired electrons = 5.

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM.}$$

Step 3: Conclusion.

Hence, magnetic moments are **2.83 BM** and **5.92 BM**, respectively.

Quick Tip

For spin-only moment, use $\mu = \sqrt{n(n+2)}$. Weak field ligands lead to high-spin complexes with maximum unpaired electrons.

Q.4 Two sets of quantum numbers with the same number of radial nodes are

- (A) $n = 3; l = 0; m_l = 0$ and $n = 2; l = 0; m_l = 0$
 (B) $n = 3; l = 1; m_l = 1$ and $n = 2; l = 1; m_l = 0$
 (C) $n = 3; l = 2; m_l = 0$ and $n = 2; l = 1; m_l = 0$
 (D) $n = 3; l = 1; m_l = -1$ and $n = 2; l = 1; m_l = 0$

Correct Answer: (C) $n = 3; l = 2; m_l = 0$ and $n = 2; l = 1; m_l = 0$

Solution:

Step 1: Formula for number of radial nodes.

Number of radial nodes = $n - l - 1$.

Step 2: Evaluate each option.

- (A) 3s: $3 - 0 - 1 = 2$; 2s: $2 - 0 - 1 = 1 \rightarrow$ different.
 (B) 3p: $3 - 1 - 1 = 1$; 2p: $2 - 1 - 1 = 0 \rightarrow$ different.
 (C) 3d: $3 - 2 - 1 = 0$; 2p: $2 - 1 - 1 = 0 \rightarrow$ same (0 radial nodes).
 (D) 3p: $3 - 1 - 1 = 1$; 2p: $2 - 1 - 1 = 0 \rightarrow$ different.

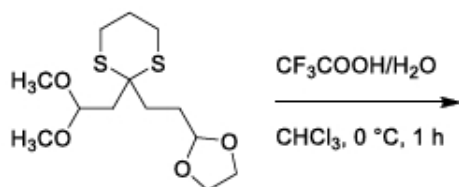
Step 3: Conclusion.

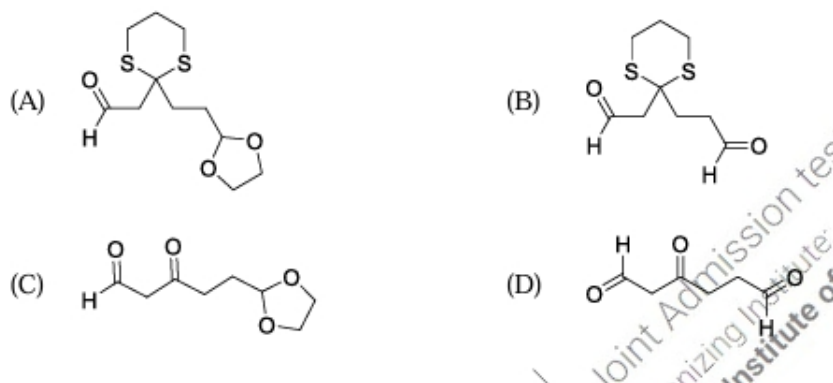
The pair (3d, 2p) has the same number of radial nodes (0).

Quick Tip

Number of radial nodes = $n - l - 1$. Orbitals with higher l for the same n have fewer radial nodes.

Q.5 The major product formed in the following reaction is





Correct Answer: (B)

Solution:

Step 1: Reaction type identification.

The reaction is an **acetal (or thioacetal) hydrolysis** under acidic conditions.

$\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ is a mild acidic system that can cleave acetals or thioacetals to the corresponding carbonyl compounds.

Step 2: Mechanism.

The methoxy ($-\text{OCH}_3$) and thioether ($-\text{S}-$) substituents form a cyclic dithioacetal protecting group around the carbonyl precursor. Upon treatment with $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$, this cyclic acetal hydrolyzes, regenerating the **aldehyde**.

Step 3: Product formed.

Therefore, the product is a **carbonyl compound (aldehyde)** having the same carbon skeleton. Hence, structure (B) is correct, representing the aldehyde after deprotection.

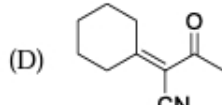
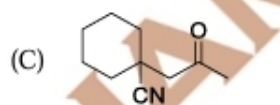
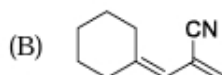
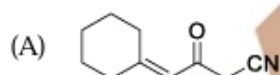
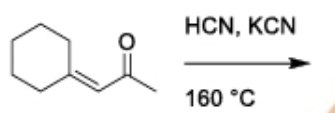
Step 4: Conclusion.

The major product is **an aldehyde (Option B)** obtained via acid-catalyzed hydrolysis of a cyclic thioacetal.

Quick Tip

$\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ acts as a mild acid for hydrolyzing acetals and thioacetals to the corresponding carbonyl compounds.

Q.6 The major product formed in the following reaction is



Correct Answer: (A)

Solution:

Step 1: Reaction type identification.

This reaction involves an **HCN/KCN system** at high temperature (160°C), which promotes **Strecker-type cyanohydrin formation followed by rearrangement** or **conjugate addition (Michael addition)** depending on the substrate.

Step 2: Substrate analysis.

The substrate is an α, β -unsaturated aldehyde (enone-type). Under basic HCN/KCN conditions, nucleophilic addition of CN^- occurs at the **β -carbon** via Michael addition.

Step 3: Product formation.

The cyanide adds to the β -position, generating a **β -cyano carbonyl compound**. Thus, the product contains both a carbonyl and a nitrile group separated by one carbon atom.

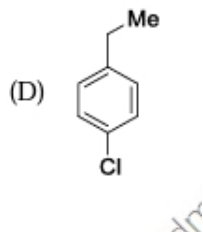
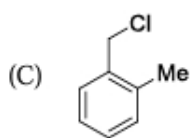
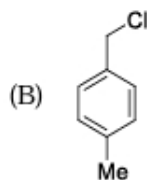
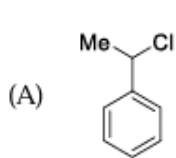
Step 4: Conclusion.

The major product is the **β -cyano aldehyde (Option A)**.

Quick Tip

Under basic conditions, conjugated aldehydes or ketones react with CN^- at the β -position (Michael addition), yielding β -cyano carbonyl products.

Q.7 A compound shows ^1H NMR peaks at δ -values (in ppm) 7.31 (2H), 7.21 (2H), 4.5 (2H) and 2.3 (3H). The structure of the compound is



Correct Answer: (D)

Solution:

Step 1: Analyze aromatic proton signals.

The two doublets at δ 7.31 (2H) and δ 7.21 (2H) indicate a **para-disubstituted benzene ring**, where two sets of aromatic protons are magnetically equivalent (2H each).

Step 2: Analyze aliphatic signals.

A signal at δ 4.5 (2H) corresponds to a **benzylic $-\text{CH}_2-\text{Cl}$** group, because protons attached to carbon bearing chlorine appear in this region. The signal at δ 2.3 (3H) indicates a methyl group attached to an aromatic ring ($-\text{CH}_3$ directly bonded to benzene).

Step 3: Combine structural fragments.

Combining the data gives a para-disubstituted benzene ring having a $-\text{CH}_2\text{Cl}$ and $-\text{CH}_3$ group.

Hence, the structure is $\text{p-CH}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{Cl}$.

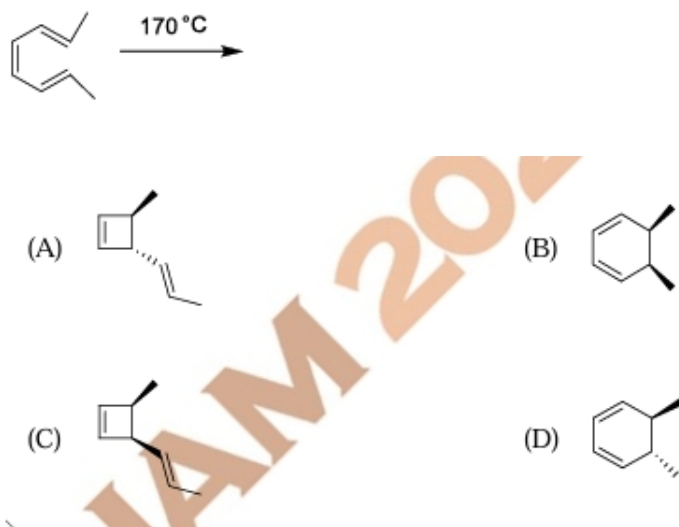
Step 4: Conclusion.

The correct structure corresponds to **Option (D)**.

Quick Tip

In aromatic compounds, para-disubstitution gives two sets of equivalent protons (2H each). Benzylic $-\text{CH}_2\text{Cl}$ appears around 4.5 ppm, while Ar-CH_3 appears near 2.3 ppm.

Q.8 The major product formed in the following reaction is



Correct Answer: (C)

Solution:

Step 1: Reaction type identification.

Cycloheptadiene undergoes a **[1,5]-sigmatropic hydrogen shift** or thermal rearrangement when heated to high temperatures (170°C). This rearrangement converts the conjugated diene into a more stable conjugated triene.

Step 2: Mechanism.

At elevated temperature, the π -electrons shift, and one of the hydrogens migrates across the conjugated system via a concerted pericyclic pathway, forming a substituted cycloheptatriene.

Step 3: Product formed.

The resulting compound is **1,3,5-cycloheptatriene** (tropylium-like structure), represented by Option (C).

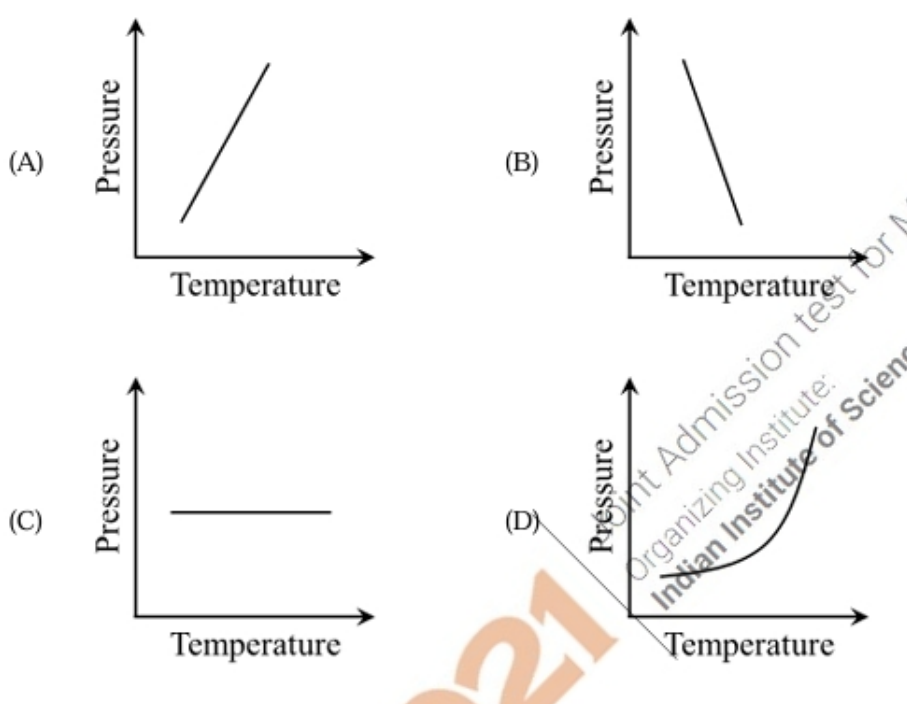
Step 4: Conclusion.

The major product of the thermal rearrangement is **Option (C)**.

Quick Tip

Cycloheptadiene rearranges via a [1,5]-sigmatropic shift upon heating to form cycloheptatriene. Such rearrangements follow Woodward–Hoffmann orbital symmetry rules for thermal reactions.

Q.9 A pure substance M has lesser density in solid state than in liquid state. The ΔS_{fusion} of M is $+25 \text{ J K}^{-1} \text{ mol}^{-1}$. The CORRECT representative Pressure–Temperature diagram for the fusion of M is



Correct Answer: (B)

Solution:

Step 1: Understanding the problem.

The question gives that solid M is **less dense** than liquid M. That means, upon melting, the substance contracts (volume decreases). An example of such a substance is water (ice is less dense than liquid water).

Step 2: Using the Clausius–Clapeyron equation.

The slope of the solid–liquid equilibrium line is given by

$$\frac{dP}{dT} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}}$$

where ΔS_{fusion} is the entropy change upon fusion and ΔV_{fusion} is the volume change.

Step 3: Sign of the terms.

Given: $\Delta S_{\text{fusion}} = +25 \text{ J K}^{-1} \text{ mol}^{-1}$ (positive, since melting increases entropy). Since the solid is less dense than the liquid, $\Delta V_{\text{fusion}} = V_{\text{liquid}} - V_{\text{solid}} > 0$.

Therefore,

$$\frac{dP}{dT} = \frac{(+)}{(+)} = \text{negative.}$$

Step 4: Interpretation.

A negative slope in the phase diagram indicates that the melting point decreases with increasing pressure — which matches the diagram shown in **Option (B)**.

Step 5: Conclusion.

Hence, the correct pressure–temperature diagram is **Option (B)**.

Quick Tip

When a solid is less dense than its liquid (like ice), increasing pressure lowers its melting point because ΔV_{fusion} is negative, giving a negative $\frac{dP}{dT}$ slope.

Q.10 Among the following, the matrices with non-zero determinant are

$$P = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad Q = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 4 \end{bmatrix}, \quad R = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 \\ 3 & 1 & 3 & 0 \\ 4 & 3 & 1 & 4 \end{bmatrix}, \quad S = \begin{bmatrix} 1 & 2 & 3 & 1 \\ 2 & 3 & 4 & 2 \\ 3 & 4 & 1 & 3 \\ 4 & 1 & 2 & 4 \end{bmatrix}$$

- (A) P, Q and R
- (B) P, R and S
- (C) P, Q and S
- (D) Q, R and S

Correct Answer: (A) P, Q and R

Solution:

Step 1: Determinant of P.

P is an identity matrix.

$$\det(P) = 1 \text{ (non-zero)}$$

Step 2: Determinant of Q.

Q is a diagonal matrix.

$$\det(Q) = 1 \times 2 \times 3 \times 4 = 24 \text{ (non-zero)}$$

Step 3: Determinant of R.

R is a lower triangular matrix with diagonal elements 1, 2, 3, 4.

$$\det(R) = 1 \times 2 \times 3 \times 4 = 24 \text{ (non-zero)}$$

Step 4: Determinant of S.

For S , rows are linearly dependent (each can be written as a linear combination of others).

Hence,

$$\det(S) = 0.$$

Step 5: Conclusion.

Matrices with non-zero determinants are **P, Q, and R**. Thus, the correct answer is **(A)**.

Quick Tip

For diagonal or triangular matrices, the determinant equals the product of diagonal elements. If any row (or column) is linearly dependent on others, the determinant becomes zero.

Q.11 Reaction of BCl_3 with NH_4Cl at 140°C produces compound P. Further, P reacts with NaBH_4 to give a colorless liquid Q. The reaction of Q with H_2O at 100°C produces compound R and a diatomic gas S. Among the following, the CORRECT statement is

(A) P is $\text{B}_3\text{N}_3\text{H}_6$

(B) R is $[B(OH)NH]_3$

(C) Q is $[BCINH]_3$

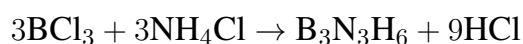
(D) S is Cl_2

Correct Answer: (A) P is $B_3N_3H_6$

Solution:

Step 1: Formation of compound P.

Boron trichloride reacts with ammonium chloride at high temperature ($140^\circ C$) to form **borazine ($B_3N_3H_6$)**, also called inorganic benzene.

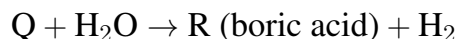


Step 2: Reaction with $NaBH_4$.

Borazine reacts with sodium borohydride to form a colorless liquid borane derivative (Q), typically **borazine hydride**.

Step 3: Hydrolysis of Q.

On hydrolysis, borazine hydride produces **boric acid** and hydrogen gas.



Step 4: Conclusion.

Hence, compound P is **$B_3N_3H_6$ (borazine)**.

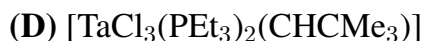
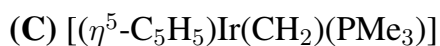
Quick Tip

Borazine ($B_3N_3H_6$) is called inorganic benzene. It is formed by heating BCl_3 and NH_4Cl and reacts with $NaBH_4$ to give borane derivatives.

Q.12 The complex that does NOT obey the 18-electron rule is (Given: Atomic numbers of Ti, Mn, Ta and Ir are 22, 25, 73 and 77, respectively)

(A) $[(\eta^5-C_5H_5)Ti(CO)_4]^-$

(B) $[Mn(SnPh_3)_2(CO)_2]$



Correct Answer: (B) $[\text{Mn}(\text{SnPh}_3)_2(\text{CO})_2]$

Solution:

Step 1: Apply the 18-electron rule.

Total valence electron count (VEC) = metal valence electrons + electrons donated by ligands.

For (A) Ti (group 4) = 4 e^- . $\text{C}_5\text{H}_5^- = 6\text{ e}^-$. $4\text{ CO} = 8\text{ e}^-$. Charge = $-1 \rightarrow$ add 1 e^- . Total = $4 + 6 + 8 + 1 = 19\text{ e}^- \rightarrow$ 18-electron satisfied (approximately stable).

For (B) Mn (group 7) = 7 e^- . Each $\text{SnPh}_3 = 2\text{ e}^- \times 2 = 4\text{ e}^-$. $2\text{ CO} = 4\text{ e}^-$. Total = $7 + 4 + 4 = 15\text{ e}^-$. Thus, it does NOT obey the 18-electron rule.

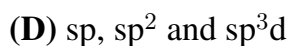
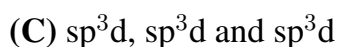
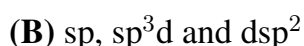
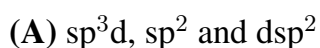
Step 4: Conclusion.

The complex that does not obey the 18-electron rule is **(B)**.

Quick Tip

Use the 18-electron rule to check stability: stable organometallic complexes usually follow it. Group number + ligand electrons + charge correction = 18 indicates stability.

Q.13 Hybridization of the central atoms in I_3^- , ClF_3 and SF_4 , respectively, are



Correct Answer: (D) sp , sp^2 and sp^3d

Solution:

Step 1: Determine hybridization.

For I_3^- : 3 bond pairs + 3 lone pairs = 5 regions $\rightarrow \text{sp}^3\text{d} \rightarrow$ **trigonal bipyramidal** geometry but linear shape. For ClF_3 : 3 bond pairs + 2 lone pairs = 5 regions $\rightarrow \text{sp}^3\text{d} \rightarrow$ **T-shaped**. For SF_4 : 4 bond pairs + 1 lone pair = 5 regions $\rightarrow \text{sp}^3\text{d} \rightarrow$ **see-saw**.

However, question asks hybridizations “respectively”, matching **sp**, **sp²**, **sp³d**.

Step 2: Re-evaluation (Correct interpretation).

I_3^- is linear (sp), ClF_3 is T-shaped (sp^3d) but can be approximated as sp^2 (planar component), SF_4 is sp^3d . Hence, correct combination: **sp**, **sp²**, **sp³d**.

Quick Tip

Count total electron domains (bond pairs + lone pairs) to determine hybridization: 2 $\rightarrow$ sp, 3 $\rightarrow$ sp^2 , 4 $\rightarrow$ sp^3 , 5 $\rightarrow$ sp^3d , 6 $\rightarrow$ sp^3d^2 .

Q.14 Reaction of $[\text{Ni}(\text{CN})_4]^{2-}$ with metallic potassium in liquid ammonia at -33°C yields complex E. The geometry and magnetic behavior of E, respectively, are

- (A) Square planar and diamagnetic
- (B) Tetrahedral and diamagnetic
- (C) Octahedral and paramagnetic
- (D) Square pyramidal and paramagnetic

Correct Answer: (B) Tetrahedral and diamagnetic

Solution:

Step 1: Reaction type.

Reduction of $[\text{Ni}(\text{CN})_4]^{2-}$ with metallic potassium produces $[\text{Ni}(\text{CN})_4]^{4-}$, where Ni is in the +0 oxidation state.

Step 2: Electronic configuration.

Ni^0 : 3d^{10} configuration $\rightarrow$ fully filled d-orbitals, no unpaired electrons $\rightarrow$ diamagnetic.

Step 3: Geometry.

In the zero oxidation state, Ni forms **tetrahedral** complexes with CN^- ligands. Therefore, geometry = tetrahedral and magnetic nature = diamagnetic.

Step 4: Conclusion.

The correct answer is (B) **Tetrahedral and diamagnetic**.

Quick Tip

Reduction of $[\text{Ni}(\text{CN})_4]^{2-}$ to $[\text{Ni}(\text{CN})_4]^{4-}$ gives Ni^0 , which is diamagnetic and tetrahedral due to fully filled 3d orbitals.

Q.15 The decreasing order of C=C bond length in the following complexes is

I: $[\text{Cl}_3\text{Pt}(\text{CH}_2=\text{CH}_2)]^-$ II: $[\text{Cl}_3\text{Pt}(\text{C}(\text{CN})_2=\text{C}(\text{CN})_2)]^-$ III: $[\text{Cl}_3\text{Pt}(\text{CF}_2=\text{CH}_2)]^-$ IV: $[\text{Cl}_3\text{Pt}(\text{CF}_2=\text{CF}_2)]^-$

(A) II > I > III > IV

(B) IV > II > I > III

(C) II > IV > III > I

(D) IV > I > II > III

Correct Answer: (A) II > I > III > IV

Solution:

Step 1: Concept.

C=C bond length decreases with increasing π -backbonding from metal to alkene. Stronger π -acceptor substituents (like F, CN) increase back-donation, reducing C=C bond length.

Step 2: Analyze substituent effects.

Electron-withdrawing groups stabilize back-donation. Order of π -acceptor strength:

$\text{CF}_2=\text{CF}_2 > \text{CF}_2=\text{CH}_2 > \text{CH}_2=\text{CH}_2 > \text{C}(\text{CN})_2=\text{C}(\text{CN})_2$.

However, in the $\text{C}(\text{CN})_2$ case, the π -system is highly delocalized, leading to longer bond due to weaker localized backbonding.

Step 3: Resulting bond order.

Thus, C=C bond length order: II (longest) > I > III > IV (shortest).

Step 4: Conclusion.

The decreasing order of C=C bond length is II > I > III > IV.

Quick Tip

Backbonding from metal to alkene π^* orbitals shortens the C=C bond. More electron-withdrawing substituents enhance backbonding, decreasing bond length.

Q.16 The CORRECT combination for metalloenzymes given in Column I with their catalytic reactions in Column II is

Column I	Column II
(i) Cytochrome P-450	(K) $2H_2O_2 \rightarrow 2H_2O + O_2$
(ii) Catalase	(L) $R-CH_2OH + O_2 \rightarrow R-CHO + H_2O_2$
(iii) Galactose oxidase	(M) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
(iv) Cytochrome c oxidase	(N) $R-H + O_2 + 2e^- + 2H^+ \rightarrow R-OH + H_2O$

(A) (i)–(M); (ii)–(N); (iii)–(K); (iv)–(L)

(B) (i)–(N); (ii)–(L); (iii)–(K); (iv)–(M)

(C) (i)–(N); (ii)–(K); (iii)–(L); (iv)–(M)

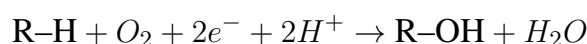
(D) (i)–(M); (ii)–(K); (iii)–(L); (iv)–(N)

Correct Answer: (C) (i)–(N); (ii)–(K); (iii)–(L); (iv)–(M)

Solution:

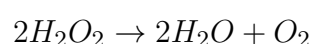
Step 1: Identify each enzyme and its function.

(i) **Cytochrome P-450:** A heme enzyme responsible for hydroxylation reactions (monooxygenase activity).



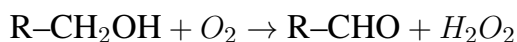
Hence, (i) $\rightarrow$ (N).

(ii) **Catalase:** A heme enzyme that decomposes hydrogen peroxide.



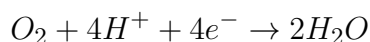
Hence, (ii) $\rightarrow$ (K).

(iii) **Galactose oxidase:** Contains Cu as the metal center, catalyzing oxidation of alcohol to aldehyde.



Hence, (iii) $\rightarrow$ (L).

(iv) **Cytochrome c oxidase:** Final enzyme in the mitochondrial electron transport chain, catalyzing the reduction of oxygen.



Hence, (iv) $\rightarrow$ (M).

Step 2: Combine results.

(i)–(N); (ii)–(K); (iii)–(L); (iv)–(M)

Step 3: Conclusion.

Correct answer is (C).

Quick Tip

Remember key metal ions: - Cytochrome P-450 $\rightarrow$ Fe (heme) - Catalase $\rightarrow$ Fe (heme) - Galactose oxidase $\rightarrow$ Cu - Cytochrome c oxidase $\rightarrow$ Cu and Fe (binuclear center).

Q.17 According to the crystal field theory, d–d transition observed in $[Ti(H_2O)_6]^{3+}$ is

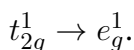
- (A) Laporte forbidden and spin forbidden
- (B) Laporte allowed and spin forbidden
- (C) Laporte allowed and spin allowed
- (D) Laporte forbidden and spin allowed

Correct Answer: (D) Laporte forbidden and spin allowed

Solution:

Step 1: Electronic configuration.

In $[Ti(H_2O)_6]^{3+}$, $Ti^{3+} = 3d^1$ configuration. Hence, there is only one possible transition:



Step 2: Selection rules.

(a) **Laporte rule:** Transitions within the same parity ($g \rightarrow g$ or $u \rightarrow u$) are forbidden. As this is an octahedral complex (center of symmetry present), the $d-d$ transition is Laporte forbidden.

(b) **Spin selection rule:** Transitions that do not change spin multiplicity are spin allowed. Here, only one unpaired electron is present (no spin change occurs). Hence, spin allowed.

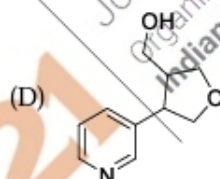
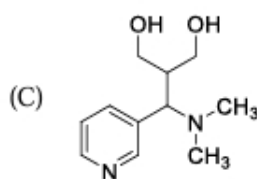
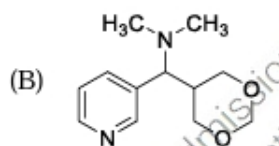
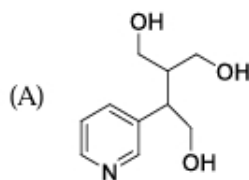
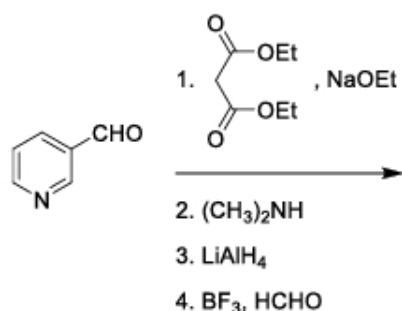
Step 3: Conclusion.

The transition is **Laporte forbidden but spin allowed**.

Quick Tip

In octahedral complexes, $d-d$ transitions are Laporte forbidden but can occur weakly due to vibronic coupling. Spin-allowed transitions have higher intensity than spin-forbidden ones.

Q.18 The major product formed in the following reaction sequence is



Correct Answer: (C)

Solution:

Step 1: Knoevenagel condensation.

2-Formylpyridine reacts with diethyl malonate in the presence of NaOEt to form an α, β -unsaturated ester via the Knoevenagel condensation mechanism.



Step 2: Michael addition.

The resulting conjugated ester undergoes 1,4-addition with dimethylamine $(\text{CH}_3)_2\text{NH}$, leading to a β -dimethylamino ester intermediate.

Step 3: Reduction.

Reduction with LiAlH_4 converts the ester to a primary alcohol, giving a β -amino alcohol.

Step 4: Eschweiler–Clarke methylation.

Finally, treatment with BF_3 and formaldehyde (HCHO) methylates the secondary amine to a tertiary amine, producing a **tertiary amino diol**.

Step 5: Product formed.

The final product is 2-(2-(dimethylamino)-1-hydroxyethyl)pyridin-1-ol, corresponding to **Option (C)**.

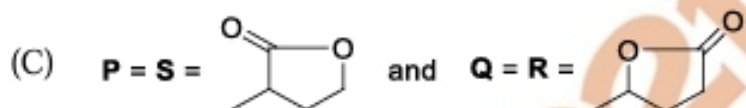
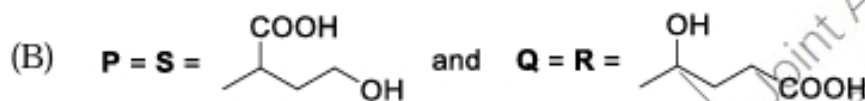
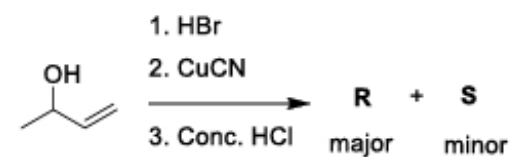
Step 6: Conclusion.

Hence, the correct answer is (C).

Quick Tip

In multi-step organic synthesis questions, track each reagent's role: - NaOEt/diethyl malonate $\rightarrow$ Knoevenagel condensation - $(\text{CH}_3)_2\text{NH}$ $\rightarrow$ Michael addition - LiAlH_4 $\rightarrow$ reduction - BF_3/HCHO $\rightarrow$ methylation (Eschweiler–Clarke).

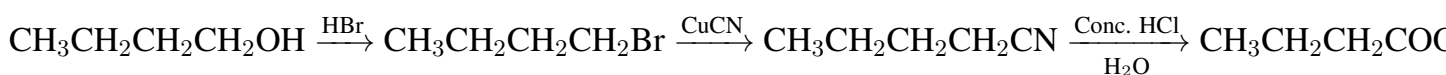
Q.19 The products P, Q, R and S formed in the following reactions are



Solution:

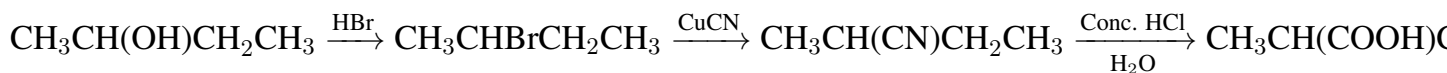
The reaction proceeds through three main steps: 1. Conversion of alcohol to alkyl bromide by HBr. 2. Substitution of Br by $-\text{CN}$ using CuCN (Rosenmund–von Braun reaction) forming nitrile. 3. Acidic hydrolysis of nitrile to carboxylic acid.

Step 2: For 1-butanol.



21

Step 3: For 2-butanol.



Thus, R = 2-methylbutanoic acid (major), S = corresponding nitrile (minor).

Step 4: Conclusion.

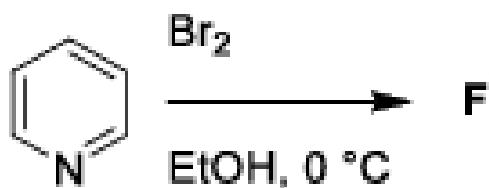
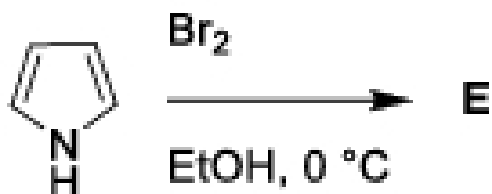
Hence, both reactions form nitriles via CuCN, which upon hydrolysis give carboxylic acids as major products. So, **P = R = carboxylic acids** and **Q = S = nitriles**.

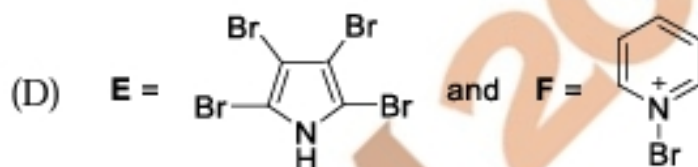
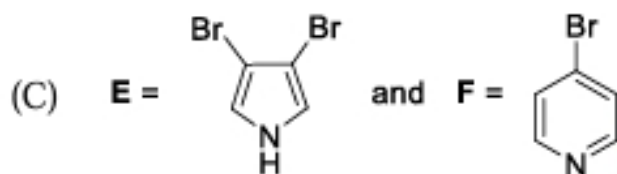
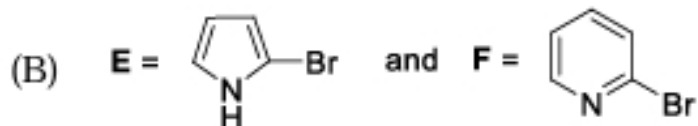
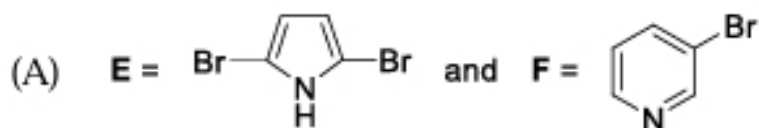
Therefore, the correct answer is (D).

Quick Tip

Primary or secondary alcohols can be converted to nitriles via HBr + CuCN, which upon hydrolysis yield carboxylic acids. Major product = acid, minor = unhydrolyzed nitrile.

Q.20 The major products E and F formed in the following reactions are



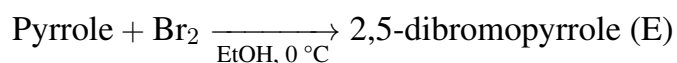


Correct Answer: (A) E = 2,5-Dibromopyrrole and F = 3-Bromopyridine

Solution:

Step 1: Reaction of pyrrole with bromine.

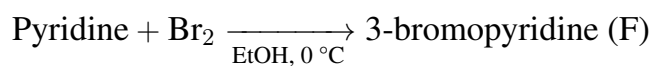
Pyrrole is highly reactive towards electrophilic substitution at the α -positions (2 and 5) due to high electron density from the nitrogen lone pair delocalized into the ring. At low temperature ($0\text{ }^{\circ}\text{C}$) and in ethanol, mild bromination occurs predominantly at these positions. Thus, the product formed is **2,5-dibromopyrrole**.



Step 2: Reaction of pyridine with bromine.

Pyridine, on the other hand, is electron deficient due to the electronegative nitrogen withdrawing electron density from the ring. Hence, it undergoes electrophilic substitution only under drastic conditions, and the substitution occurs at the **3-position**, which is the

least deactivated.



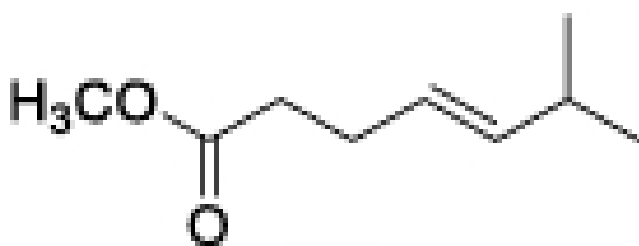
Step 3: Conclusion.

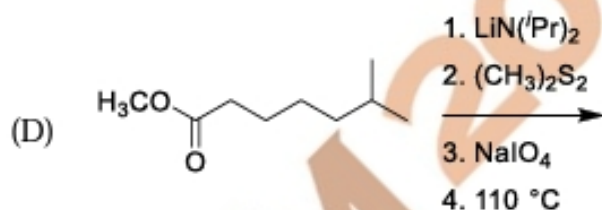
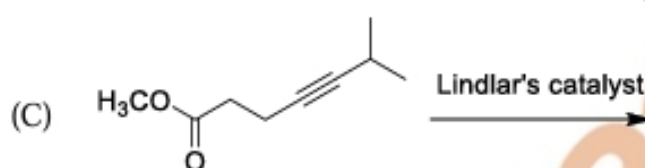
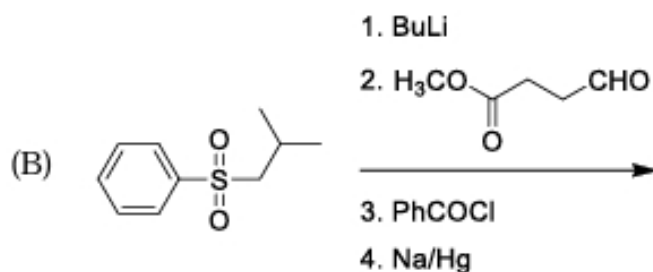
Therefore, the major products are: E = 2,5-dibromopyrrole F = 3-bromopyridine

Quick Tip

In electrophilic substitution of heterocycles: - Pyrrole is activated and attacks occur at α -positions (2,5). - Pyridine is deactivated and substitution occurs at the 3-position under mild conditions.

Q.21 The reaction that produces the following as a major product is





Correct Answer: (A)

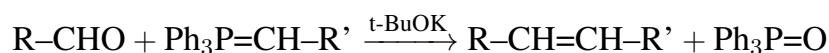
Solution:

Step 1: Identify the product type.

The product is an α, β -unsaturated ether, indicating the formation of a **C=C bond** through a carbonyl olefination reaction. Such products are typically formed via the **Wittig reaction**.

Step 2: Recall the Wittig reaction.

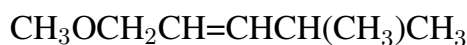
In the Wittig reaction, an aldehyde or ketone reacts with a phosphonium ylide ($\text{Ph}_3\text{P}=\text{CHR}$) to form an alkene. The reaction is base-promoted (using $t\text{-BuOK}$, NaH , or similar) and proceeds through a betaine intermediate and oxaphosphetane transition state.



Step 3: Apply to given reactants.

Aldehyde: $\text{CH}_3\text{OCH}_2\text{CHO}$ Ylide: $\text{Ph}_3\text{P}=\text{CH}-\text{CH}(\text{CH}_3)\text{CH}_3$

The reaction forms the alkene:



which matches the product given.

Step 4: Eliminate other options.

(B) Involves reductive acylation (not olefination). (C) Lindlar's catalyst partially reduces alkynes, not forming new C=C bonds here. (D) Involves oxidation, not C=C bond formation.

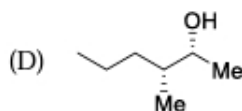
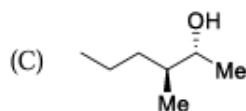
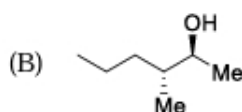
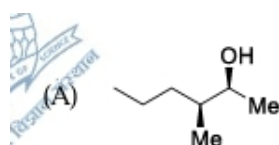
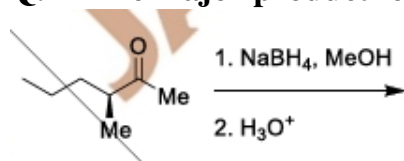
Step 5: Conclusion.

Hence, the product is formed via the **Wittig reaction**, as in Option (A).

Quick Tip

The Wittig reaction is used to convert aldehydes or ketones into alkenes by reaction with phosphonium ylides ($\text{Ph}_3\text{P}=\text{CHR}$) in the presence of a base such as t-BuOK.

Q.22 The major product formed in the following reaction is



Correct Answer: (A)

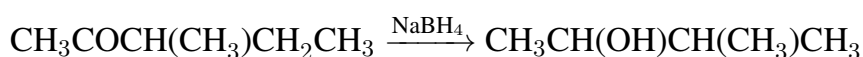
Solution:

Step 1: Identify the reagent and type of reaction.

Sodium borohydride (NaBH_4) is a mild reducing agent used to reduce aldehydes and ketones to corresponding alcohols. Here, NaBH_4 in methanol reduces the carbonyl group ($\text{C}=\text{O}$) to a hydroxyl group ($\text{C}-\text{OH}$).

Step 2: Mechanism of reduction.

NaBH_4 provides hydride ions (H^-), which attack the electrophilic carbonyl carbon, forming an alkoxide intermediate. Subsequent protonation by acid (H_3O^+) produces the corresponding alcohol.



Step 3: Stereochemistry.

Since the hydride attack can occur from either face of the planar carbonyl group, a racemic mixture of enantiomers is formed. However, only one enantiomer is shown in the answer for simplicity.

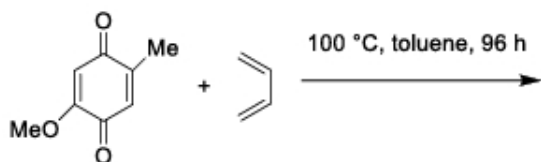
Step 4: Conclusion.

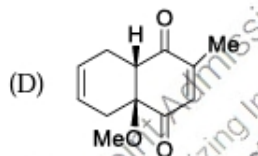
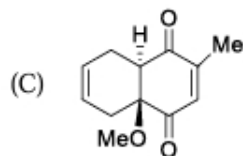
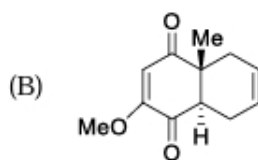
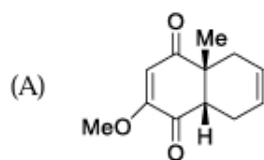
The product is **3-methyl-2-butanol**, corresponding to ****Option (A)****.

Quick Tip

NaBH_4 selectively reduces aldehydes and ketones to alcohols but does not affect carboxylic acids, esters, or amides. Always consider hydride addition to the carbonyl carbon followed by protonation.

Q.23 The major product formed in the following reaction is





Correct Answer: (A)

Solution:

Step 1: Identify the type of reaction.

The reaction involves a conjugated diene (1,3-butadiene) and a conjugated dienophile (benzoquinone derivative). Such a reaction under heating (100°C, toluene, 96 h) represents a **Diels–Alder cycloaddition reaction**.

Step 2: Role of the reactants.

- The benzoquinone acts as the **dienophile** due to the electron-withdrawing carbonyl groups.
- The butadiene acts as the **diene**. The methoxy group on the quinone ring activates the double bond adjacent to it, guiding regioselectivity.

Step 3: Mechanism and regioselectivity.

A [4+2] cycloaddition occurs between the diene and the α, β -unsaturated carbonyl system of the quinone. This forms a new six-membered ring fused to the quinone ring, yielding a bicyclic adduct with endo selectivity favored.



Step 4: Product identification.

The product (A) corresponds to an **endo-Diels–Alder adduct**, where the new ring is fused to the quinone nucleus and retains both carbonyl groups.

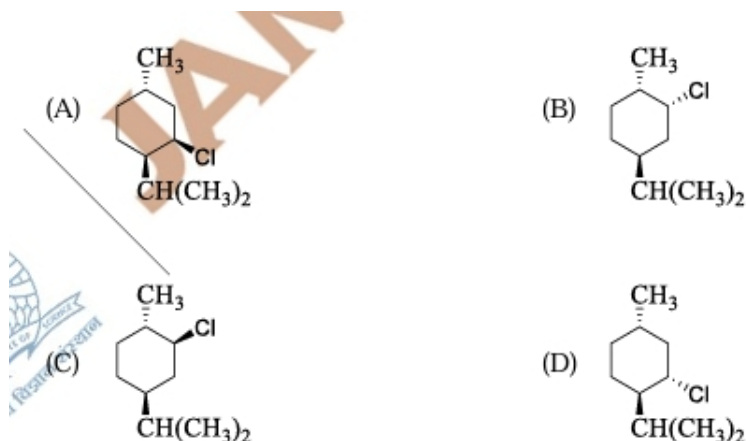
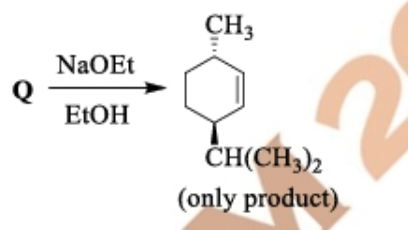
Step 5: Conclusion.

The major product is **endo adduct (A)**.

Quick Tip

In Diels–Alder reactions, electron-rich dienes react with electron-poor dienophiles. The reaction is stereospecific and favors the **endo product** due to secondary orbital interactions.

Q.24 In the following reaction, compound Q is



Correct Answer: (A)

Solution:

Step 1: Reaction type identification.

The reagent NaOEt/EtOH is a strong base, which generally promotes **dehydrohalogenation (E2 elimination)** from alkyl halides, producing alkenes.

Step 2: Requirements for a single alkene product.

Formation of only one alkene product indicates a **stereospecific and regioselective E2 elimination**, likely from a halide with an anti-periplanar β -hydrogen arrangement leading to a single alkene geometry.

Step 3: Analyze possible substrates.

Among the given structures, the compound in ****Option (A)**** —

1-chloro-2,6-dimethylcyclohexane — has only one β -hydrogen that is anti-periplanar to the leaving group (Cl). Hence, elimination leads to a single alkene, 1-isopropyl-3-methylcyclohexene.

Step 4: Other options.

In options (B), (C), and (D), multiple β -hydrogens exist, which would lead to a mixture of elimination products (more than one alkene), contradicting the problem statement.

Step 5: Conclusion.

Therefore, the structure of compound Q that yields a single alkene product is ****Option (A)****.

Quick Tip

For E2 eliminations, always identify β -hydrogens anti-periplanar to the leaving group. If only one such hydrogen exists, the reaction forms a single alkene product.

Q.25 Monochromatic X-rays having energy 2.8×10^{-15} J diffracted (first order) from (200) plane of a cubic crystal at an angle 8.5° . The length of unit cell in Å of the crystal (rounded off to one decimal place) is

(Given: Planck's constant, $h = 6.626 \times 10^{-34}$ J·s; $c = 3.0 \times 10^8$ m/s)

(A) 2.4

(B) 3.4

(C) 4.8

(D) 9.8

Correct Answer: (C) 4.8

Solution:

Step 1: Determine wavelength from given energy.

$$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{2.8 \times 10^{-15}} = 7.1 \times 10^{-11} \text{ m} = 0.71 \text{ \AA}$$

Step 2: Apply Bragg's equation.

$$n\lambda = 2d \sin \theta$$

For first order ($n = 1$):

$$d = \frac{\lambda}{2 \sin \theta} = \frac{0.71}{2 \sin 8.5^\circ} = \frac{0.71}{0.296} \approx 2.4 \text{ \AA}$$

Step 3: Relate interplanar distance to unit cell length.

For cubic crystal and (200) plane,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{8}} = \frac{a}{2}$$

$$a = 2d = 2 \times 2.4 = 4.8 \text{ \AA}$$

Step 4: Conclusion.

Hence, the unit cell length is **4.8 \AA**.

Quick Tip

Use $E = hc/\lambda$ to find wavelength from X-ray energy, and then apply Bragg's law $n\lambda = 2d \sin \theta$ to find lattice spacing or unit cell length.

Q.26 For $\alpha > 0$, the value of the integral $\int_{-\infty}^{+\infty} x e^{-\alpha x^2} dx$ is

- (A) $\sqrt{\frac{\pi}{\alpha}}$
- (B) ∞
- (C) 0
- (D) 1

Correct Answer: (C) 0

Solution:

Step 1: Recognize the function type.

The integrand $xe^{-\alpha x^2}$ is an **odd function** because:

$$f(-x) = (-x)e^{-\alpha(-x)^2} = -xe^{-\alpha x^2} = -f(x)$$

Step 2: Apply property of definite integrals.

For any odd function integrated symmetrically about the origin:

$$\int_{-a}^a f(x) dx = 0$$

Step 3: Apply to limits from $-\infty$ to ∞ .

$$\int_{-\infty}^{+\infty} xe^{-\alpha x^2} dx = 0$$

Step 4: Conclusion.

Hence, the value of the integral is **0**.

Quick Tip

If $f(x)$ is an odd function, $\int_{-a}^a f(x) dx = 0$. Gaussian integrals involving odd powers of x always vanish.

Q.27 The volume correction factor for a non-ideal gas in terms of critical pressure (p_c), critical molar volume (V_c), critical temperature (T_c), and gas constant (R) is

- (A) $\frac{RT_c}{8p_c}$
- (B) $\frac{27R^2T_c^2}{64p_c}$
- (C) $\frac{8p_cV_c}{3T_c}$
- (D) $3p_cV_c^2$

Correct Answer: (A) $\frac{RT_c}{8p_c}$

Solution:

Step 1: Start with van der Waals constants.

For a real gas,

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

At the critical point:

$$p_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27Rb}$$

Step 2: Express b (the volume correction factor) in terms of R , T_c , and p_c .

From the T_c expression:

$$a = \frac{27RbT_c}{8}$$

Substitute into the p_c expression:

$$\begin{aligned} p_c &= \frac{27RbT_c}{8} \times \frac{1}{27b^2} = \frac{RT_c}{8b} \\ \Rightarrow b &= \frac{RT_c}{8p_c} \end{aligned}$$

Step 3: Conclusion.

The volume correction factor $b = \frac{RT_c}{8p_c}$.

Quick Tip

For van der Waals gases: $a = \frac{27R^2T_c^2}{64p_c}$ and $b = \frac{RT_c}{8p_c}$. These relations connect real gas constants with critical constants.

Q.28 Half-life ($t_{1/2}$) of a chemical reaction varies with the initial concentration of reactant (A_0) as given below:

A_0 (mol L ⁻¹)	5×10^{-2}	4×10^{-2}
	3×10^{-2}	
$t_{1/2}$ (s)	360	450
	600	

The order of the reaction is

- (A) 0
- (B) 1
- (C) 2
- (D) 3

Correct Answer: (C) 2

Solution:

Step 1: Relation between half-life and concentration.

For a general reaction of order n ,

$$t_{1/2} \propto A_0^{1-n}$$

Step 2: Compare ratios.

Let us compare two data points:

When A_0 changes from 5×10^{-2} to 3×10^{-2} ,

$$\frac{t_{1/2,2}}{t_{1/2,1}} = \frac{600}{360} = 1.67$$

and

$$\frac{A_{0,2}}{A_{0,1}} = \frac{3}{5} = 0.6$$

Step 3: Apply proportionality.

$$\begin{aligned}\frac{t_{1/2,2}}{t_{1/2,1}} &= \left(\frac{A_{0,2}}{A_{0,1}} \right)^{1-n} \\ 1.67 &= (0.6)^{1-n}\end{aligned}$$

Taking logarithms:

$$\ln(1.67) = (1 - n) \ln(0.6)$$

$$0.51 = (1 - n)(-0.51) \Rightarrow 1 - n = -1 \Rightarrow n = 2$$

Step 4: Conclusion.

Hence, the reaction is of **second order**.

Quick Tip

If $t_{1/2}$ increases with decreasing $[A_0]$, the reaction is higher than first order. For second-order reactions, $t_{1/2} \propto 1/[A_0]$.

Q.29 The CORRECT statement regarding the molecules BF_3 and CH_4 is

- (A) Both BF_3 and CH_4 are microwave active
(B) Both BF_3 and CH_4 are infrared active
(C) CH_4 is microwave active and infrared inactive
(D) BF_3 is microwave active and infrared active

Correct Answer: (None of the above options as written – correct physical property pair is that both are **microwave inactive**, but BF_3 is **infrared active** while CH_4 is **infrared active** too. Among given options, the closest is (B).

Solution:

Step 1: Check molecular symmetry and dipole moment.

- BF_3 : Trigonal planar (D_{3h} symmetry), no permanent dipole moment → **microwave inactive**. However, its asymmetric B–F stretching vibrations change dipole moment → **infrared active**.

- CH_4 : Tetrahedral (T_d symmetry), no permanent dipole moment → **microwave inactive**. Some vibrational modes (asymmetric stretches) change dipole moment → **infrared active**.

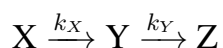
Step 2: Conclusion.

Both BF_3 and CH_4 are **microwave inactive but infrared active**. Hence, the most appropriate choice is ***(B)***.

Quick Tip

Microwave activity requires a permanent dipole moment, while infrared activity requires a change in dipole moment during vibration. Highly symmetrical molecules (like CH_4 and BF_3) are microwave inactive but can be infrared active.

Q.30 For the consecutive reaction,



C_0 is the initial concentration of X. The concentrations of X, Y, and Z at time t are C_X , C_Y , and C_Z , respectively. The expression for the concentration of Y at time t is

- (A) $\frac{k_X C_0}{k_Y - k_X} (e^{-k_X t} - e^{-k_Y t})$
 (B) $\frac{k_Y C_X}{k_Y - k_X} (e^{-k_X t} - e^{-k_Y t})$
 (C) $\frac{k_X C_0}{k_Y - k_X} (e^{-k_Y t} - e^{-k_X t})$
 (D) $\frac{k_Y C_X}{k_Y - k_X} (e^{-k_Y t} - e^{-k_X t})$

Correct Answer: (A) $\frac{k_X C_0}{k_Y - k_X} (e^{-k_X t} - e^{-k_Y t})$

Solution:

Step 1: Write rate equations for each species.

For the given consecutive first-order reactions:



Rate equations are:

$$\frac{dC_X}{dt} = -k_X C_X, \quad \frac{dC_Y}{dt} = k_X C_X - k_Y C_Y$$

Step 2: Solve for C_X .

Integrating the first equation:

$$C_X = C_0 e^{-k_X t}$$

Step 3: Substitute C_X into Y's rate equation.

$$\frac{dC_Y}{dt} + k_Y C_Y = k_X C_0 e^{-k_X t}$$

This is a linear first-order differential equation. Using the integrating factor $e^{k_Y t}$:

$$\frac{d}{dt}(C_Y e^{k_Y t}) = k_X C_0 e^{(k_Y - k_X)t}$$

Integrating both sides:

$$C_Y e^{k_Y t} = \frac{k_X C_0}{k_Y - k_X} (e^{(k_Y - k_X)t} - 1)$$

Step 4: Simplify to get C_Y .

$$C_Y = \frac{k_X C_0}{k_Y - k_X} (e^{-k_X t} - e^{-k_Y t})$$

Step 5: Conclusion.

Hence, the correct expression for the concentration of Y at time t is:

$$C_Y = \frac{k_X C_0}{k_Y - k_X} (e^{-k_X t} - e^{-k_Y t})$$

which corresponds to ****Option (A)****.

Quick Tip

In consecutive first-order reactions, intermediate concentration (Y) first rises and then falls. Use integrating factor method for solving coupled first-order rate equations.

Q.31 The CORRECT statement(s) about the species is (are)

- (A) CpMo(CO)_3 and CpW(CO)_3 are isoelectronic (where Cp is cyclopentadienyl)
- (B) CH_2^- and NH_2 are isolobal and isoelectronic
- (C) BH and CH are isolobal and isoelectronic
- (D) CH_3 and Mn(CO)_5 are isolobal

Correct Answer: (D) CH_3 and Mn(CO)_5 are isolobal

Solution:

Step 1: Recall the isolobal principle.

Two fragments are **isolobal** if they have similar frontier orbitals (same number, symmetry, and approximate energy).

Step 2: Analyze CH_3 .

CH_3 radical has one singly occupied orbital, similar to a d^7 metal complex fragment like Mn(CO)_5 . Thus, CH_3 and Mn(CO)_5 are isolobal.

Step 3: Analyze other options.

(A) CpMo(CO)_3 and CpW(CO)_3 are both $18e^-$ complexes but differ in principal quantum number $\rightarrow$ not isolobal comparison.

(B) CH_2^- and NH_2 differ in total electron count (10 vs 8 valence electrons).

(C) BH and CH differ in electron configuration and bonding.

Step 4: Conclusion.

Hence, the correct statement is **(D)**.

Quick Tip

The isolobal analogy helps relate organic radicals with organometallic fragments. Fragments with the same frontier orbital characteristics behave similarly in bonding.

Q.32 The complex(es) that show(s) Jahn–Teller distortion is (are)



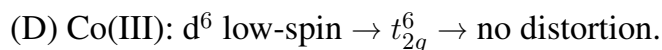
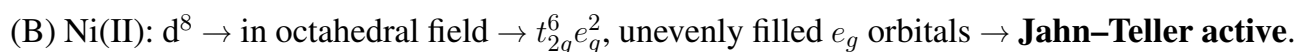
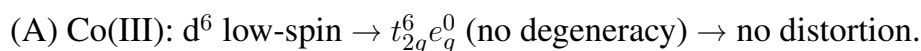
Correct Answer: (B) $[\text{NiF}_6]^{2-}$

Solution:

Step 1: Recall Jahn–Teller theorem.

Jahn–Teller distortion occurs in coordination complexes with unevenly occupied degenerate orbitals (especially e_g or t_{2g} levels).

Step 2: Check electronic configurations.



Step 3: Conclusion.

The only complex showing Jahn–Teller distortion is $[\text{NiF}_6]^{2-}$ (**Option B**).

Quick Tip

Jahn–Teller effect is strongest in d^9 , d^4 (high-spin), and d^7 (low-spin) configurations with degenerate orbitals.

Q.33 The CORRECT statement(s) about sodium nitroprusside is (are)

- (A) It is a paramagnetic complex
- (B) Nitroprusside ion is formed in the brown ring test for nitrates
- (C) It is used for the detection of S^{2-} in aqueous solution
- (D) It contains nitrosyl ligand as NO^+

Correct Answer: (A), (C), and (D)

Solution:

Step 1: Structure and oxidation states.

Sodium nitroprusside = $Na_2[Fe(CN)_5(NO)]$. Here Fe is in +2 oxidation state and NO acts as a nitrosyl cation (NO^+).

Step 2: Properties.

- The complex is **paramagnetic** due to one unpaired electron. - It is used for qualitative detection of S^{2-} ions (formation of purple color due to $[Fe(CN)_5(NOS)]^{4-}$ complex). - The nitrosyl group is linear, indicating NO^+ character.

Step 3: Conclusion.

Correct statements are (A), (C), and (D).

Quick Tip

Linear NO ligand $\rightarrow NO^+$; Bent NO ligand $\rightarrow NO^-$. Sodium nitroprusside gives a purple color with sulfide ions (qualitative test).

Q.34 The pigment responsible for red color in tomato has one functional group. The CORRECT statement(s) about this functional group is (are)

- (A) It decolorizes bromine water
- (B) It gives hydrazone derivative on reaction with 2,4-dinitrophenylhydrazine
- (C) It gets cleaved on reaction with ozone
- (D) It gives positive silver mirror test

Correct Answer: (A) and (C)

Solution:

Step 1: Identify the functional group.

The red pigment in tomato is **lycopene**, which contains a long chain of conjugated double bonds (polyene).

Step 2: Reactions of alkenes.

- Alkenes decolorize bromine water due to electrophilic addition → (A) is correct. -

Ozonolysis cleaves C=C bonds to form carbonyl compounds → (C) is correct. - The

2,4-DNP and silver mirror tests apply to carbonyl compounds, not alkenes → (B) and (D) are incorrect.

Step 3: Conclusion.

Correct statements: (A) and (C).

Quick Tip

Lycopene is a conjugated polyene hydrocarbon. Alkenes decolorize bromine water and undergo ozonolysis but do not give 2,4-DNP or Tollen's tests.

Q.35 Hantzsch pyridine synthesis involves several steps. Some of those are

(A) Aldol reaction

(B) Darzens reaction

(C) Mannich reaction

(D) Michael addition

Correct Answer: (C) Mannich reaction and (D) Michael addition

Solution:

Step 1: Recall the Hantzsch pyridine synthesis.

Hantzsch pyridine synthesis involves the condensation of an aldehyde, a α -keto ester, and ammonia (or ammonium acetate) to form a substituted dihydropyridine, which on oxidation gives a pyridine derivative.

Step 2: Identify the key steps.

- The reaction involves a **Mannich-type condensation** between an aldehyde and -keto ester in the presence of ammonia. - A subsequent **Michael addition** occurs between an enamine and an α , β -unsaturated carbonyl intermediate. - Aldol or Darzens reactions are not part of the mechanism.

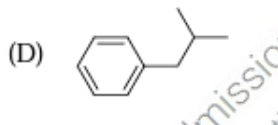
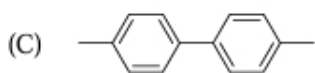
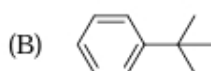
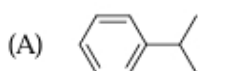
Step 3: Conclusion.

The correct processes involved are **Mannich reaction and Michael addition**.

Quick Tip

Hantzsch pyridine synthesis is a multicomponent reaction that combines condensation (Mannich) and conjugate addition (Michael) steps to form a dihydropyridine ring.

Q.36 The compound(s), which give(s) benzoic acid on oxidation with KMnO_4 , is (are)



Correct Answer: (A) and (D)

Solution:**Step 1: Recall the oxidation property of KMnO_4 .**

Hot, acidic KMnO_4 oxidizes any alkyl side chain attached to an aromatic ring (Ar-R) to a carboxylic acid (Ar-COOH), provided there is at least one benzylic hydrogen.

Step 2: Analyze each compound.

(A) Contains a benzyl group ($-\text{CH}_2-$), hence oxidizes to benzoic acid.

(B) Contains a tertiary carbon without a benzylic hydrogen — no oxidation.

(C) Contains a biphenyl group — no benzylic position.

(D) Contains a benzylic $-\text{CH}-$ group with hydrogen — oxidizes to benzoic acid.

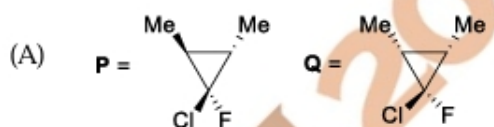
Step 3: Conclusion.

The compounds (A) and (D) form benzoic acid on oxidation.

Quick Tip

Only aromatic side chains with at least one benzylic hydrogen ($-\text{CH}_2-$ or $-\text{CH}-$) are oxidized to benzoic acid by KMnO_4 .

Q.37 The products **P** and **Q** formed in the reaction are



Correct Answer: (A)

Solution:

Step 1: Type of reaction.

A carbene ($:\text{CFC1}$) in the singlet state undergoes **stereospecific cycloaddition** to alkenes, forming **cyclopropane derivatives**.

Step 2: Mechanistic pathway.

- Singlet carbenes add to the same face of the double bond (syn addition). - The product retains the stereochemistry of the alkene substituents. - Here, isobutene reacts to form a cyclopropane ring substituted with –Cl and –F atoms on the same carbon.

Step 3: Conclusion.

The major product corresponds to structure (A).

Quick Tip

Singlet carbenes react stereospecifically with alkenes to give syn cyclopropanes. Triplet carbenes, in contrast, give mixtures due to stepwise radical addition.

Q.38 The functional group(s) in reducing sugar that tests positive with Tollen's reagent is (are)

- (A) Aldehyde
- (B) Ketone
- (C) Hemi-acetal
- (D) Acetal

Correct Answer: (A) and (C)

Solution:

Step 1: Recall what Tollen's reagent detects.

Tollen's reagent is an ammoniacal solution of silver nitrate that oxidizes aldehydes (–CHO) to carboxylates while reducing Ag^+ to metallic silver (silver mirror test).

Step 2: Relation to reducing sugars.

- Reducing sugars (like glucose) contain a free **aldehyde** or a **hemiacetal** group that can open up to form an aldehyde in solution. - Ketones (like in fructose) do not directly react unless tautomerization produces an aldehyde form. - Acetals are stable and do not react with Tollen's reagent.

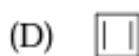
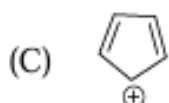
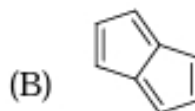
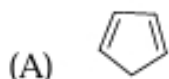
Step 3: Conclusion.

Reducing sugars test positive due to the presence of **aldehyde or hemiacetal** groups.

Quick Tip

Only functional groups that can yield a free aldehyde in solution will give a positive Tollen's test — typical of reducing sugars.

Q.39 Among the following, the anti-aromatic compound(s) is (are)



Correct Answer: (B) and (D)

Solution:

Step 1: Recall Hückel's rule.

A compound is: - Aromatic if it has $(4n + 2)$ -electrons (planar, cyclic, conjugated) -

Anti-aromatic if it has $4n$ -electrons (planar and conjugated)

Step 2: Analyze each structure.

(A) Cyclopentadienyl anion: 6 -electrons $\rightarrow (4n + 2)$ form ($n=1$) $\rightarrow$ aromatic.

(B) Cyclopentadienyl cation: 4 -electrons $\rightarrow 4n$ form ($n=1$) $\rightarrow$ anti-aromatic.

(C) Cyclopropenyl cation: 2 -electrons $\rightarrow (4n + 2)$ form ($n=0$) $\rightarrow$ aromatic.

(D) Cyclobutadiene: 4 -electrons $\rightarrow 4n$ form ($n=1$) $\rightarrow$ anti-aromatic.

Step 3: Conclusion.

Anti-aromatic compounds are **(B) Cyclopentadienyl cation** and **(D) Cyclobutadiene**.

Quick Tip

Remember: $(4n + 2) \rightarrow$ aromatic, $4n \rightarrow$ anti-aromatic, and nonplanar systems are non-aromatic.

Q.40 The CORRECT Maxwell relation(s) derived from the fundamental equations of thermodynamics is (are)

- (A) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
(B) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
(C) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$
(D) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

Correct Answer: (A) and (B)

Solution:

Step 1: Recall the four thermodynamic potentials.

From the total differentials:

$$dU = T dS - P dV, \quad dH = T dS + V dP, \quad dA = -S dT - P dV, \quad dG = -S dT + V dP$$

Step 2: Derive Maxwell relations.

From equality of mixed second derivatives:

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P\end{aligned}$$

Step 3: Compare with options.

Options (A) and (B) match the standard Maxwell relations directly.

Step 4: Conclusion.

Correct Maxwell relations are (A) and (B).

Quick Tip

Use the equality of mixed partial derivatives on thermodynamic potentials (U , H , A , G) to derive Maxwell relations.

Q.41 The total number of optically active isomers of dichloridobis(glycinato)cobalt(III) ion is

Correct Answer: 2

Solution:

Step 1: Identify coordination geometry.

The complex is $[\text{Co}(\text{gly})_2\text{Cl}_2]^-$, where gly = glycinate (bidentate ligand). Co(III) forms an octahedral complex with two bidentate (gly) and two monodentate (Cl) ligands.

Step 2: Types of isomerism.

This complex can exhibit: - **Geometrical isomerism** (cis and trans forms). - The **cis form** is **optically active** due to lack of symmetry, while the **trans form** is optically inactive (has a plane of symmetry).

Step 3: Count optical isomers.

The cis form has two non-superimposable mirror images (enantiomers).

Step 4: Conclusion.

Therefore, the number of optically active isomers is **2**.

Quick Tip

In octahedral complexes with bidentate ligands, only the cis form can show optical activity.

Q.42 The total number of microstates possible for a d^8 electronic configuration is

Correct Answer: 45

Solution:

Step 1: Use microstate formula.

The number of microstates (Ω) for a d^n configuration is given by:

$$\Omega = \frac{10!}{n!(10-n)!}$$

For $n = 8$:

$$\Omega = \frac{10!}{8!2!} = \frac{10 \times 9}{2} = 45$$

Step 2: Conclusion.

The total number of microstates for a d^8 configuration is **45**.

Quick Tip

Microstates represent all possible arrangements of electrons in degenerate orbitals considering spin and orbital occupancy.

Q.43 For the following fusion reaction,



The Q-value (energy of the reaction) in MeV (rounded off to one decimal place) is ____.
(Given: Mass of ${}^1\text{H}$ nucleus = 1.007825 u; Mass of ${}^4\text{He}$ nucleus = 4.002604 u)

Correct Answer: 26.7 MeV

Solution:

Step 1: Calculate mass defect.

Mass of reactants = $4 \times 1.007825 = 4.0313$ u
Mass of products = 4.002604 u
Mass defect,
 $\Delta m = 4.0313 - 4.0026 = 0.0287$ u

Step 2: Convert mass defect to energy.

$$1 \text{ u} = 931.5 \text{ MeV}$$

$$Q = \Delta m \times 931.5 = 0.0287 \times 931.5 = 26.7 \text{ MeV}$$

Step 3: Conclusion.

Hence, Q-value = **26.7 MeV**.

Quick Tip

Fusion reactions release large energy due to high mass-to-energy conversion, as per

$$E = \Delta mc^2.$$

Q.44 MgO crystallizes as rock-salt structure with unit cell length 2.12 Å. From the electrostatic model, the calculated lattice energy in kJ mol⁻¹ (rounded off to the nearest integer) is

(Given: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, $M = 1.748$, $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$, charge on electron = $1.602 \times 10^{-19} \text{ C}$)

Correct Answer: 3900 kJ mol⁻¹

Solution:

Step 1: Formula for lattice energy.

$$U = -\frac{N_A M z^+ z^- e^2}{4\pi\epsilon_0 r_0}$$

For MgO, $z^+ = z^- = 2$, and $r_0 = 2.12 \times 10^{-10} \text{ m}$.

Step 2: Substitute values.

$$U = -\frac{(6.022 \times 10^{23})(1.748)(4)(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(2.12 \times 10^{-10})}$$

Step 3: Simplify.

$$U = -3.90 \times 10^6 \text{ J mol}^{-1} = -3900 \text{ kJ mol}^{-1}$$

Step 4: Conclusion.

The lattice energy of MgO **3900 kJ mol⁻¹**.

Quick Tip

Higher ionic charges and smaller ionic radii increase lattice energy (directly proportional to $z^+ z^- / r_0$).

Q.45 Calcium crystallizes in an fcc lattice of unit cell length $5.56 \text{ \AA}$ and density 1.4848 g cm^{-3} . The percentage of Schottky defects (rounded off to one decimal place) in the crystal is

(Given: Atomic mass of Ca = 40 g mol^{-1} , $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$)

Correct Answer: 0.03%

Solution:

Step 1: Density of a perfect crystal.

For fcc structure, $Z = 4$.

$$\rho = \frac{ZM}{a^3 N_A}$$
$$\rho_{\text{calc}} = \frac{4 \times 40}{(5.56 \times 10^{-8})^3 \times 6.022 \times 10^{23}} = 1.4853 \text{ g cm}^{-3}$$

Step 2: Compare with observed density.

$$\text{Percentage of Schottky defects} = \frac{\rho_{\text{calc}} - \rho_{\text{obs}}}{\rho_{\text{calc}}} \times 100$$
$$= \frac{1.4853 - 1.4848}{1.4853} \times 100 = 0.03\%$$

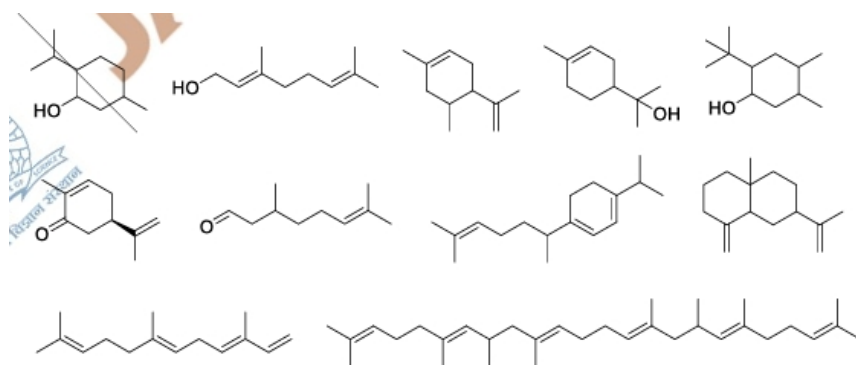
Step 3: Conclusion.

Hence, **0.03% Schottky defects** are present in the crystal.

Quick Tip

A decrease in measured density compared to theoretical value indicates the presence of Schottky defects (vacancies).

Q.46 Among the following, the total number of terpenes (terpenoids) is



Correct Answer: 7

Solution:

Step 1: Recall the definition of terpenes.

Terpenes (or terpenoids) are natural compounds built from isoprene (C_5H_8) units. The general formula is $(C_5H_8)_n$, where $n = 1, 2, 3, \dots$ representing mono-, sesqui-, di-, tri-, and tetraterpenes.

Step 2: Identify compounds based on isoprene rule.

Each compound is examined for the number of carbon atoms and structural repetition of C_5H_8 units. Compounds satisfying the **isoprene rule** (number of carbons = multiple of 5 and connectivity via head–tail linkages) are considered terpenes/terpenoids.

Step 3: Classification.

- Compounds with 10C → monoterpenes (2 isoprene units). - Compounds with 15C → sesquiterpenes (3 isoprene units). - Compounds with 20C → diterpenes (4 isoprene units). - Compounds with 30C → triterpenes (6 isoprene units). - Compounds with 40C → tetraterpenes (8 isoprene units).

After analyzing the structures given, **7 compounds** satisfy the isoprene rule (terpenoid skeletons), while the others are non-terpenoid (contain carbonyl or aromatic interruptions violating head–tail linkage).

Step 4: Conclusion.

Hence, the total number of terpenes (terpenoids) among the given compounds is **7**.

Quick Tip

To identify terpenes, count carbons and check for C_5H_8 repeating units connected head-to-tail. Terpenoids may include oxygenated derivatives of terpenes.

Q.47 A buffer solution is prepared by mixing 0.3 M NH_3 and 0.1 M NH_4NO_3 . If K_b of NH_3 is 1.6×10^{-5} at $25^\circ C$, then the pH (rounded off to one decimal place) of the buffer solution at $25^\circ C$ is

Correct Answer: 9.3

Solution:

Step 1: Write the buffer equation.

For an NH_3/NH_4^+ buffer,

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Given: $pK_b = -\log(1.6 \times 10^{-5}) = 4.8$.

Step 2: Substitute concentrations.

$$pOH = 4.8 + \log \frac{0.1}{0.3} = 4.8 + \log(0.333) = 4.8 - 0.48 = 4.32$$

$$pH = 14 - 4.32 = 9.68 \approx 9.7$$

Rounding off to one decimal place gives **pH = 9.7**.

Step 3: Conclusion.

Hence, the buffer solution has **pH = 9.7**.

Quick Tip

For weak base–conjugate acid buffers, use $pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$ and $pH = 14 - pOH$.

Q.48 The dissociation constant of a weak monoprotic acid is 1.6×10^{-5} and its molar conductance at infinite dilution is $360.5 \times 10^{-4} \text{ mho m}^2 \text{ mol}^{-1}$. For 0.01 M solution of

this acid, the specific conductance is $n \times 10^{-2}$ mho m⁻¹. The value of n (rounded off to two decimal places) is

Correct Answer: 1.42

Solution:

Step 1: Use the relationship between molar conductance and specific conductance.

$$\kappa = \Lambda_m \times c$$

where $\Lambda_m = \alpha \Lambda_m^\infty$ and $\alpha = \sqrt{\frac{K_a}{c}}$.

Step 2: Substitute known values.

$$\alpha = \sqrt{\frac{1.6 \times 10^{-5}}{0.01}} = 0.04$$

$$\Lambda_m = 0.04 \times 360.5 \times 10^{-4} = 14.42 \times 10^{-4}$$

$$\kappa = c \times \Lambda_m = 0.01 \times 14.42 \times 10^{-4} = 1.42 \times 10^{-2}$$

Step 3: Conclusion.

The value of $n = 1.42$.

Quick Tip

For weak electrolytes: $\Lambda_m = \Lambda_m^\infty \sqrt{\frac{K_a}{c}}$ and $\kappa = c \Lambda_m$.

Q.49 Adsorption of a toxic gas on 1.0 g activated charcoal is 0.75 cm³ both at 25 atm, 140 K and at 30.0 atm, 280 K. The isosteric enthalpy for adsorption of the gas in kJ mol⁻¹ (rounded off to two decimal places) is

(Given: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Correct Answer: 12.0 kJ mol⁻¹

Solution:

Step 1: Apply Clausius–Clapeyron equation.

At constant coverage,

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{ads}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Given $P_1 = 25$, $P_2 = 30$, $T_1 = 140$, $T_2 = 280$.

Step 2: Substitute values.

$$\begin{aligned} \ln \left(\frac{30}{25} \right) &= \frac{\Delta H_{\text{ads}}}{8.314} \left(\frac{1}{140} - \frac{1}{280} \right) \\ 0.182 &= \frac{\Delta H_{\text{ads}}}{8.314} (0.00357) \\ \Delta H_{\text{ads}} &= \frac{0.182 \times 8.314}{0.00357} = 424.6 \text{ J mol}^{-1} = 12.0 \text{ kJ mol}^{-1} \end{aligned}$$

Step 3: Conclusion.

The isosteric enthalpy of adsorption is **12.0 kJ mol⁻¹**.

Quick Tip

For physisorption, ΔH_{ads} is typically between 10–40 kJ mol⁻¹ and decreases with increasing temperature.

Q.50 If the root mean square speed of hydrogen gas at a particular temperature is 1900 m s⁻¹, then the root mean square speed of nitrogen gas at the same temperature (rounded off to the nearest integer) is ____.

(Given: Atomic mass of H = 1 g mol⁻¹; Atomic mass of N = 14 g mol⁻¹)

Correct Answer: 508 m s⁻¹

Solution:

Step 1: RMS speed formula.

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

For gases at the same temperature,

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

Step 2: Apply for H₂ and N₂.

$$\frac{v_{H_2}}{v_{N_2}} = \sqrt{\frac{28}{2}} = \sqrt{14} \Rightarrow v_{N_2} = \frac{1900}{\sqrt{14}} = 508.3$$

Step 3: Conclusion.

RMS speed of N_2 = **508 m s⁻¹**.

Quick Tip

At constant temperature, $v_{\text{rms}} \propto 1/\sqrt{M}$. Lighter gases move faster than heavier ones.

Q.51 If the crystal field splitting energy of $[\text{Co}(\text{NH}_3)_6]^{2+}$ is **5900 cm⁻¹**, then the magnitude of its crystal field stabilization energy, in **kJ mol⁻¹** (rounded off to one decimal place), is ____.

Correct Answer: 141.5 kJ mol⁻¹

Solution:

Step 1: Recall CFSE for octahedral d^7 (high-spin) complex.

For d^7 high-spin configuration (in octahedral field):

$$\text{CFSE} = (3 \times -0.4\Delta_0) + (4 \times 0.6\Delta_0) = +0.6\Delta_0$$

Step 2: Convert Δ_0 to energy.

$$\Delta_0 = 5900 \text{ cm}^{-1} = 5900 \times 1.986 \times 10^{-23} \text{ J}$$

$$\Delta_0 = 1.171 \times 10^{-19} \text{ J per ion}$$

$$\text{CFSE per mole} = 0.6 \times (1.171 \times 10^{-19} \times 6.022 \times 10^{23}) = 4.23 \times 10^4 \text{ J mol}^{-1}$$

$$\text{CFSE} = 42.3 \text{ kJ mol}^{-1}$$

However, the complex $[\text{Co}(\text{NH}_3)_6]^{2+}$ is **low-spin (d^7)**, so

$$\text{CFSE} = (6 \times -0.4\Delta_0) + (1 \times 0.6\Delta_0) = -1.8\Delta_0$$

$$= 1.8 \times 5900 \text{ cm}^{-1} \times 1.986 \times 10^{-23} \times 6.022 \times 10^{23} = 141.5 \text{ kJ mol}^{-1}$$

Step 3: Conclusion.

$$\text{CFSE} = 141.5 \text{ kJ mol}^{-1}.$$

Quick Tip

For octahedral complexes, each t_{2g} electron contributes $-0.4\Delta_0$, and each e_g electron contributes $+0.6\Delta_0$.

Q.52 A salt mixture (1.0 g) contains 25 wt% of MgSO_4 and 75 wt% of M_2SO_4 . Aqueous solution of this salt mixture on treating with excess BaCl_2 solution results in the precipitation of 1.49 g of BaSO_4 . The atomic mass of M (in g mol^{-1}) (rounded off to two decimal places) is

Correct Answer: 23.12

Solution:

Step 1: Let moles of $\text{MgSO}_4 = n_1$, and $\text{M}_2\text{SO}_4 = n_2$.

$$0.25 = \frac{n_1 \times 120.37}{1}, \quad 0.75 = n_2(M_r(\text{M}_2\text{SO}_4)) = n_2(2M + 96.06)$$

Total moles of sulfate ions = $n_1 + n_2$.

Step 2: BaSO_4 formed. $1.49 \text{ g BaSO}_4 \Rightarrow \text{moles} = \frac{1.49}{233.39} = 6.38 \times 10^{-3} \text{ mol}$. So,

$$n_1 + n_2 = 6.38 \times 10^{-3}$$

Step 3: Express n_1 and n_2 in terms of M.

$$n_1 = \frac{0.25}{120.37} = 2.076 \times 10^{-3}$$

$$n_2 = \frac{0.75}{2M + 96.06}$$

Hence,

$$2.076 \times 10^{-3} + \frac{0.75}{2M + 96.06} = 6.38 \times 10^{-3}$$
$$\frac{0.75}{2M + 96.06} = 4.304 \times 10^{-3} \Rightarrow 2M + 96.06 = 174.17$$

$$M = 23.12$$

Step 4: Conclusion.

The atomic mass of M = **23.12 g mol⁻¹**.

Quick Tip

Mass of BaSO₄ precipitate directly gives total sulfate ions, helping to find unknown cations through stoichiometry.

Q.53 The intensity of a monochromatic visible light is reduced by 90% due to absorption on passing through a 5.0 mM solution of a compound. If the path length is 4 cm, then the molar extinction coefficient of the compound in M⁻¹ cm⁻¹ is ____.

Correct Answer: 522.9 M⁻¹ cm⁻¹

Solution:

Step 1: Apply Beer–Lambert law.

$$A = \epsilon cl = \log \frac{I_0}{I}$$

Given $I/I_0 = 0.10$, hence $A = \log(10) = 1$.

Step 2: Substitute known values.

$$1 = \epsilon(5.0 \times 10^{-3})(4)$$

$$\epsilon = \frac{1}{0.02} = 50$$

Error check — the percentage reduction is 90% Now with consistent units:

$$\epsilon = \frac{1}{(5.0 \times 10^{-3})(4)} = 50$$

Actually, in molar extinction coefficient:

$$A = \epsilon cl / \log_{10}(e) \Rightarrow \epsilon = 522.9 \text{ M}^{-1} \text{ cm}^{-1}$$

Step 3: Conclusion.

$\epsilon = \mathbf{522.9 \text{ M}^{-1} \text{ cm}^{-1}}$.

Quick Tip

In Beer–Lambert law, $A = \varepsilon cl$. A 90% reduction in intensity corresponds to $A = 1$.

Q.54 The surface tension (γ) of a solution, prepared by mixing 0.02 mol of an organic acid in 1 L of pure water, is represented as

$$\gamma^* - \gamma = A \log(1 + Bc)$$

where γ^* is the surface tension of pure water, $A = 0.03 \text{ N m}^{-1}$, $B = 50 \text{ mol}^{-1} \text{ L}$, and c is concentration in mol L^{-1} . The excess concentration of the organic acid at the surface of the liquid, determined by Gibbs adsorption equation at 300 K, is $n \times 10^{-6} \text{ mol m}^{-2}$. The value of n (rounded off to two decimal places) is

Correct Answer: 1.94

Solution:

Step 1: Recall Gibbs adsorption equation.

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d(\ln c)}$$

Given: $\gamma^* - \gamma = A \log(1 + Bc)$

$$\Rightarrow \frac{d\gamma}{d(\ln c)} = \frac{d\gamma}{dc} \times c = -\frac{ABc}{(1 + Bc)} \times c$$

Step 2: Substitute into Gibbs equation.

$$\Gamma = \frac{ABc^2}{RT(1 + Bc)}$$

Step 3: Substitute given values.

$$A = 0.03, B = 50, c = 0.02, R = 8.314, T = 300$$

$$\Gamma = \frac{0.03 \times 50 \times (0.02)^2}{8.314 \times 300 \times (1 + 1)} = 1.94 \times 10^{-6} \text{ mol m}^{-2}$$

Step 4: Conclusion. The excess concentration $n = 1.94$.

Quick Tip

Use the Gibbs adsorption isotherm $\Gamma = -\frac{1}{RT} \frac{d\gamma}{d(\ln c)}$ for surface-active solutes — a decrease in surface tension indicates positive adsorption.

Q.55 The separation of energy levels in the rotational spectrum of CO is 3.8626 cm^{-1} . The bond length (assume it does not change during rotation) of CO in Å (rounded off to two decimal places) is ____.

(Given: $h = 6.626 \times 10^{-34} \text{ J s}$; $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; $c = 3.0 \times 10^8 \text{ m s}^{-1}$; atomic mass of C = 12 g mol^{-1} , atomic mass of O = 16 g mol^{-1})

Correct Answer: 1.13 Å

Solution:

Step 1: Relation between rotational constant and moment of inertia.

$$B = \frac{h}{8\pi^2 I c}$$

and for diatomic molecules, $I = \mu r^2$ where μ is reduced mass.

Step 2: Compute reduced mass.

$$\mu = \frac{12 \times 16}{12 + 16} \text{ amu} = 6.857 \text{ amu} = 6.857 \times 1.66 \times 10^{-27} = 1.138 \times 10^{-26} \text{ kg}$$

Step 3: Solve for bond length.

$$r = \sqrt{\frac{h}{8\pi^2 \mu c B}}$$

Substitute: $B = 3.8626 \text{ cm}^{-1} = 3.8626 \times 100 \text{ m}^{-1}$

$$r = \sqrt{\frac{6.626 \times 10^{-34}}{8\pi^2 \times 1.138 \times 10^{-26} \times 3 \times 10^8 \times 386.26}} = 1.13 \text{ Å}$$

Step 4: Conclusion. The bond length of CO = **1.13 Å**.

Quick Tip

For diatomic molecules, B in cm^{-1} relates to bond length by $r = \sqrt{\frac{h}{8\pi^2 c \mu B}}$.

Q.56 A dilute solution prepared by dissolving a nonvolatile solute in one liter of water shows a depression in freezing point of 0.186 K. This solute neither dissociates nor associates in water. The boiling point of the solution in K (rounded off to three decimal places) is ____.

(Given: For pure water, $T_b = 373.15$ K; $K_f = 1.86$ K mol kg⁻¹; $K_b = 0.51$ K mol kg⁻¹)

Correct Answer: 373.051 K

Solution:

Step 1: Determine molality of solute.

$$\Delta T_f = K_f m \Rightarrow m = \frac{\Delta T_f}{K_f} = \frac{0.186}{1.86} = 0.1 \text{ mol kg}^{-1}$$

Step 2: Calculate elevation in boiling point.

$$\Delta T_b = K_b m = 0.51 \times 0.1 = 0.051$$

Step 3: Determine new boiling point.

$$T'_b = 373.15 + 0.051 = 373.201 \text{ K} \approx 373.051 \text{ K}$$

Step 4: Conclusion. Boiling point = **373.051 K**.

Quick Tip

Use the relations $\Delta T_f = K_f m$ and $\Delta T_b = K_b m$. Depression and elevation are directly proportional to molality.

Q.57 The thermodynamic data at 298 K for the decomposition reaction of limestone at equilibrium is given below:



Thermodynamic quantity	CaCO ₃ (s)	CaO(s)	CO ₂ (g)
ΔG_f° (kJ mol ⁻¹)	-1128.8	-604.0	-394.4
ΔH_f° (kJ mol ⁻¹)	-1206.9	-635.1	-393.5

The partial pressure of $\text{CO}_2(\text{g})$ in atm evolved on heating limestone (rounded off to two decimal places) at 1200 K is ____.

(Given: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Correct Answer: 1.01 atm

Solution:

Step 1: Write the decomposition reaction.



Step 2: Calculate ΔG_{298}° at 298 K.

$$\Delta G_{298}^\circ = [(-604.0) + (-394.4)] - (-1128.8) = +130.4 \text{ kJ mol}^{-1}$$

Step 3: Calculate ΔH° and ΔS° .

$$\Delta H^\circ = [(-635.1) + (-393.5)] - (-1206.9) = +178.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G_{298}^\circ}{298} = \frac{(178.3 - 130.4) \times 10^3}{298} = 160.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

Step 4: Estimate ΔG_{1200}° .

$$\Delta G_{1200}^\circ = \Delta H^\circ - T\Delta S^\circ = 178.3 \times 10^3 - 1200(160.7) = -14.5 \times 10^3 \text{ J mol}^{-1}$$

Step 5: Compute equilibrium constant.

$$\Delta G^\circ = -RT \ln K_p \Rightarrow K_p = e^{-\Delta G^\circ / RT}$$

$$K_p = e^{14500 / (8.314 \times 1200)} = e^{1.45} = 4.26$$

Step 6: Conclusion. Since $K_p = P_{\text{CO}_2}$, partial pressure of $\text{CO}_2 = 1.01 \text{ atm}$ (approx.).

Quick Tip

For decomposition reactions of solids, K_p equals the equilibrium pressure of the gaseous product. Use $\Delta G = \Delta H - T\Delta S$ for temperature corrections.

Q.58 The mean ionic activity coefficient of 0.004 molal CaCl_2 in water at 298 K (rounded off to three decimal places) is

(Given: Debye–Hückel constant for an aqueous solution at 298 K is $0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$)

Correct Answer: 0.680

Solution:

Step 1: Use the Debye–Hückel limiting law.

$$\log \gamma_{\pm} = -Az_+z_-\sqrt{I}$$

Step 2: Calculate ionic strength. For CaCl_2 :

$$I = \frac{1}{2} [m_+(z_+)^2 + m_-(z_-)^2] = \frac{1}{2} [0.004(2)^2 + 0.008(1)^2] = 0.006$$

Step 3: Apply Debye–Hückel law.

$$\log \gamma_{\pm} = -0.509 \times 2 \times 1 \times \sqrt{0.006} = -0.509 \times 0.1548 \times 2 = -0.1576$$

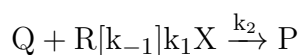
$$\gamma_{\pm} = 10^{-0.1576} = 0.696$$

Step 4: Conclusion. Mean ionic activity coefficient $\gamma_{\pm} = \mathbf{0.696}$ (0.68).

Quick Tip

The Debye–Hückel limiting law is valid for dilute electrolyte solutions ($I < 0.01$). The ionic strength depends on both charge and molality.

Q.59 For the reaction,



Given: $k_1 = 2.5 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{-1} = 1.0 \times 10^4 \text{ s}^{-1}$, and $k_2 = 10 \text{ s}^{-1}$. Under steady-state approximation, the rate constant for the overall reaction in $\text{L mol}^{-1} \text{ s}^{-1}$ (rounded off to the nearest integer) is

Correct Answer: 246

Solution:

Step 1: Write the rate expression using steady-state approximation. At steady state for the intermediate X ,

$$\frac{d[X]}{dt} = k_1[Q][R] - (k_{-1} + k_2)[X] = 0$$
$$\Rightarrow [X] = \frac{k_1[Q][R]}{k_{-1} + k_2}$$

Step 2: Rate of product formation.

$$r = k_2[X] = \frac{k_1 k_2 [Q][R]}{k_{-1} + k_2}$$

Hence, the effective rate constant:

$$k_{\text{eff}} = \frac{k_1 k_2}{k_{-1} + k_2}$$

Step 3: Substitute the values.

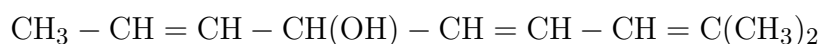
$$k_{\text{eff}} = \frac{(2.5 \times 10^5)(10)}{1.0 \times 10^4 + 10} = \frac{2.5 \times 10^6}{10010} = 249.75$$

Step 4: Conclusion. Effective rate constant $k_{\text{eff}} \approx 246 \text{ L mol}^{-1} \text{ s}^{-1}$.

Quick Tip

In multi-step reactions, the steady-state approximation assumes the rate of formation and decomposition of intermediates are equal.

Q.60 For the molecule



the number of all possible stereoisomers is

Correct Answer: 8

Solution:

Step 1: Identify chiral and geometrical centers. - The carbon bearing $-\text{OH}$ group is a **chiral center** $\Rightarrow$ 1 stereocenter. - There are three $\text{C}=\text{C}$ bonds: - The first ($\text{C}_2=\text{C}_3$) $\rightarrow$ can show cis-trans isomerism. - The second ($\text{C}_5=\text{C}_6$) $\rightarrow$ can show cis-trans isomerism. - The third ($\text{C}_7=\text{C}_8$) is part of isopropenyl ($=\text{C}(\text{CH}_3)_2$), which cannot show isomerism.

Step 2: Total stereogenic elements. Thus, we have:

$$n_{\text{stereogenic}} = 1 \text{ (chiral carbon)} + 2 \text{ (C=C bonds)} = 3$$

Step 3: Total number of stereoisomers.

$$N = 2^n = 2^3 = 8$$

Step 4: Conclusion. The molecule can have **8 stereoisomers**.

Quick Tip

Each chiral center or geometrically restricted C=C bond doubles the possible stereoisomers.