IIT JAM 2022 Chemistry (CY) Question Paper with Solutions

Time Allowed :3 Hours	**Maximum Marks :**100	**Total questions :**60

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.

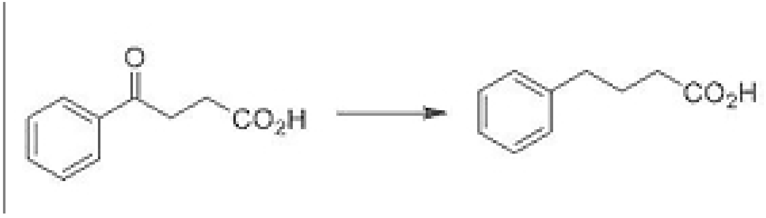
iii) In numerical questions, all steps of calculation should be shown clearly.

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.

1. The reagent required for the following transformation



(A) $NaBH_4$

(B) $LiAlH_4$

(C) $H_3B\cdot THF$

(D) Zn(Hg)/HCl

Correct Answer: (C) $H_3B\cdot THF$

Solution:

Step 1: Understanding the Reaction.

The transformation shown is the reduction of a carboxylic acid group to an aldehyde. The selective reduction of carboxylic acids typically requires a mild reducing agent. $H_3B\cdot THF$ is a well-known reagent that reduces carboxylic acids to aldehydes without reducing other functional groups.

Step 2: Analyzing the options.

(A) $NaBH_4$: This is a weaker reducing agent and typically reduces aldehydes and ketones, but it cannot reduce carboxylic acids to aldehydes.

(B) $LiAlH_4$: This is a strong reducing agent and reduces carboxylic acids to alcohols, not aldehydes.

(C) $H_3B\cdot THF$: This is the correct choice, as it selectively reduces carboxylic acids to aldehydes.

(D) Zn(Hg)/HCl: This reagent, known as the Clemmensen reduction, reduces carbonyl groups (such as aldehydes and ketones) but does not affect carboxylic acids.

Step 3: Conclusion.

The correct reagent for reducing the carboxylic acid to an aldehyde is **$H_3B\cdot THF$** (option C).

Quick Tip

$H_3B\cdot THF$ is specifically used for the selective reduction of carboxylic acids to aldehydes.

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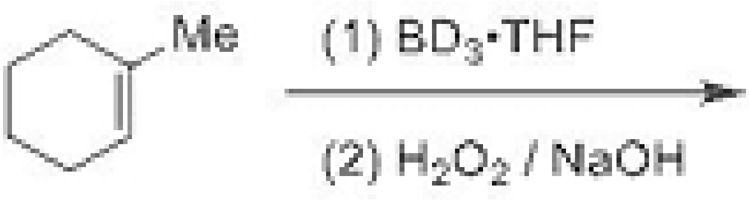
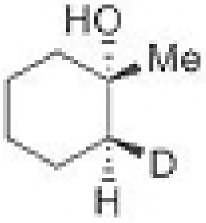
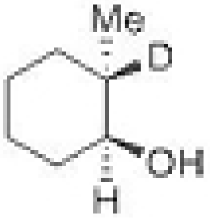
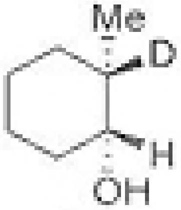
2. The major product formed in the following reaction



(A)	 (±)
(B)	 (±)
(C)	 (±)
(D)	 (±)

Correct Answer: (D)

Solution:

Step 1: Understanding the Reaction.

The reaction involves the use of diborane (BD_3) followed by hydrogen peroxide and sodium hydroxide, which is a hydroboration-oxidation reaction. This reaction converts alkenes to alcohols with anti-Markovnikov regioselectivity.

Step 2: Analyzing the options.

(A) HO-CH_2-Me: This is incorrect because the reaction does not produce a hydroxyl group on the terminal carbon.

(B) Me-CH_2-OH: This is also incorrect because it suggests a different reaction product.

(C) Me-OH: This product is not consistent with the hydroboration-oxidation mechanism.

(D) Me-CH_2-OH: Correct — The reaction leads to the formation of an alcohol at the less substituted carbon (anti-Markovnikov product), which is Me-CH_2-OH.

Step 3: Conclusion.

The correct product is **Me-CH_2-OH** (option D).

Quick Tip

In hydroboration-oxidation reactions, the addition of water across the double bond occurs with anti-Markovnikov selectivity.

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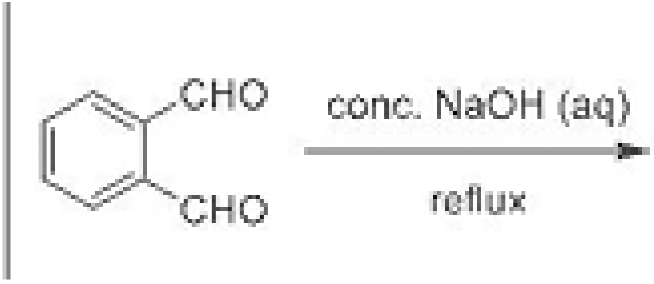
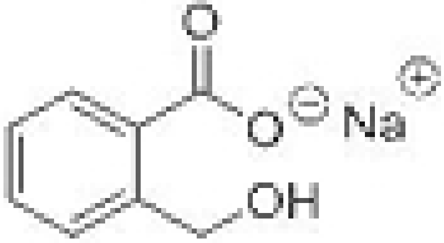
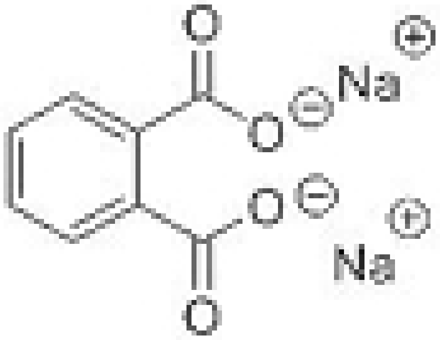
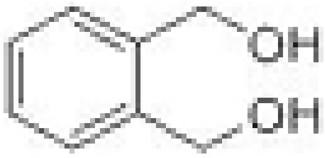
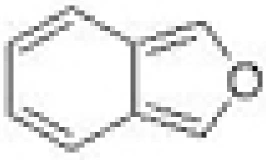
3. The major product formed in the following reaction



(A)	
(B)	
(C)	
(D)	

Correct Answer: (C) $C_6H_4OHCOOH$

Solution:

Step 1: Understanding the Reaction.

This is an aldol condensation reaction. The reaction involves a benzaldehyde being treated with concentrated sodium hydroxide in a reflux condition. This leads to the formation of a product in which two aldehyde groups are condensed into a -hydroxy aldehyde or -hydroxy carboxylic acid.

Step 2: Analyzing the options.

(A) $C_6H_4COO^-Na^+$: This product is incorrect as it represents a sodium salt of the product which does not fit the reaction mechanism.

(B) $C_6H_4COO^-Na^+$: Same as option (A), incorrect.

(C) $C_6H_4OHCOOH$: Correct — this is the product of the aldol condensation, forming a hydroxy acid.

(D) $C_6H_4COOHCOOH$: This is incorrect as the reaction forms a hydroxy acid, not a dicarboxylic acid.

Step 3: Conclusion.

The major product is $C_6H_4OHCOOH$ (option C).

Quick Tip

In aldol condensation reactions, the presence of sodium hydroxide under reflux conditions typically leads to the formation of -hydroxy aldehydes or -hydroxy carboxylic acids.

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4. The major product formed in the following reaction

$K + O_2$

(A) K_2O
(B) K_2O_2
(C) KO_2
(D) K_2O_3

Correct Answer: (B) K_2O_2

Solution:

Step 1: Understanding the Reaction.

This is the reaction of potassium with oxygen. Potassium reacts with oxygen to form various potassium oxides. In this case, the reaction yields potassium peroxide (K_2O_2) as the major product.

Step 2: Analyzing the options.

(A) K_2O: This represents potassium oxide, which can form under different conditions, but in this case, potassium peroxide is the major product.

(B) K_2O_2: Correct — this is the product formed when potassium reacts with excess oxygen.

(C) KO_2: This is potassium superoxide, which forms under different conditions (excess oxygen and specific reaction conditions), but K_2O_2 is the main product in this case.

(D) K_2O_3: This is not a common product for potassium-oxygen reactions.

Step 3: Conclusion.

The correct product is K_2O_2 (option B).

Quick Tip

When potassium reacts with oxygen, the major product is typically potassium peroxide (K_2O_2). Potassium oxide (K_2O) can form under different conditions but is less common in this reaction.

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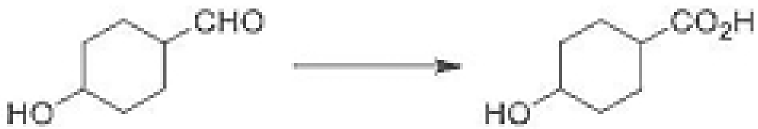
5. Which one of the following options is best suited for effecting the transformation?



(A) MnO_2

(B) DMSO, $(COCl)_2$, Et_3N

(C) $Al(Oi\text{-}Pr)_3$

(D) Ag_2O/NH_4OH

Correct Answer: (A) MnO_2

Solution:

Step 1: Understanding the Reaction.

This transformation involves the oxidation of a primary alcohol (HO-CHO) to a carboxylic acid (COOH) group. The appropriate reagent for this transformation should be capable of oxidizing the primary alcohol to the carboxyl group.

Step 2: Analyzing the options.

(A) MnO_2: This is manganese dioxide, which is a mild oxidizer that is commonly used to oxidize primary alcohols to carboxylic acids. This is the correct choice.

(B) DMSO, $(COCl)_2$, Et_3N: This is a reagent combination used for the conversion of alcohols to aldehydes, not carboxylic acids.

(C) $Al(Oi\text{-}Pr)_3$: This is an aluminum alkoxide, typically used in specific types of reactions but not for the oxidation of alcohols to carboxylic acids.

(D) Ag_2O/NH_4OH: This combination is used for other types of reactions, such as silver mirror formation, not for oxidizing alcohols to acids.

Step 3: Conclusion.

The best reagent for this transformation is MnO_2 (option A).

Quick Tip

Manganese dioxide (MnO_2) is a selective oxidizer for primary alcohols to carboxylic acids, making it ideal for this type of transformation.

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6. The structure of $[XeF_8]^{2-}$ is

(A) cubic

(B) hexagonal bipyramid

(C) square antiprism

(D) octagonal

Correct Answer: (B) hexagonal bipyramid

Solution:

Step 1: Understanding the structure of $[XeF_8]^{2-}$.

The structure of $[XeF_8]^{2-}$ is determined by the octet rule and the number of fluorine atoms bonded to the xenon atom. Xenon in this compound has 8 fluorine atoms surrounding it, leading to a coordination number of 8, which corresponds to a hexagonal bipyramid geometry.

Step 2: Analyzing the options.

(A) cubic: This structure is not suitable for $[XeF_8]^{2-}$ because a cubic arrangement is less stable for this molecule.

(B) hexagonal bipyramid: Correct — The structure of $[XeF_8]^{2-}$ is a hexagonal bipyramid, with the fluorine atoms arranged around the xenon atom in this geometry.

(C) square antiprism: This structure is not appropriate for an 8-coordinate xenon complex.

(D) octagonal: This is not a common molecular geometry for this compound.

Step 3: Conclusion.

The correct structure of $[XeF_8]^{2-}$ is hexagonal bipyramid (option B).

Quick Tip

For molecules with a coordination number of 8, the most common geometry is a hexagonal bipyramid, such as in $[XeF_8]^{2-}$.

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7. Among the following, the compound that forms the strongest hydrogen bond is

(A) HF

(B) HCl

(C) HBr

(D) HI

Correct Answer: (A) HF

Solution:

Step 1: Understanding Hydrogen Bonding.

Hydrogen bonding occurs when hydrogen is bonded to a highly electronegative atom, typically fluorine (F), oxygen (O), or nitrogen (N). The strength of the hydrogen bond increases with the electronegativity of the atom bonded to hydrogen.

Step 2: Analyzing the options.

(A) HF: Hydrogen fluoride (HF) has the strongest hydrogen bond due to the high electronegativity of fluorine, making the hydrogen bond more significant.

(B) HCl: While HCl also has hydrogen bonding, chlorine is less electronegative than fluorine, so the hydrogen bond is weaker.

(C) HBr: Bromine is even less electronegative than chlorine, leading to a weaker hydrogen bond.

(D) HI: Iodine is the least electronegative among the halogens, resulting in the weakest hydrogen bonding.

Step 3: Conclusion.

The strongest hydrogen bond is formed by HF (option A).

Quick Tip

Fluorine (F) is the most electronegative element, which results in the strongest hydrogen bonding when bonded to hydrogen.

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8. Among the following, the biomolecule with a direct metal-carbon bond is

(A) coenzyme B_{12}

(B) nitrogenase

(C) chlorophyll

(D) hemoglobin

Correct Answer: (A) coenzyme B_{12}

Solution:

Step 1: Understanding Metal-Carbon Bonds.

A direct metal-carbon bond is a type of coordination bond between a metal ion and a carbon atom in a ligand. This is commonly seen in organometallic compounds.

Step 2: Analyzing the options.

(A) coenzyme B_{12}: Coenzyme B_{12}, also known as cobalamin, has a direct metal-carbon bond as the central metal ion (cobalt) is directly bonded to the carbon atom in the coenzyme.

(B) nitrogenase: Nitrogenase is an enzyme that contains iron, but it does not have a direct metal-carbon bond in the same sense as coenzyme B_{12}.

(C) chlorophyll: Chlorophyll contains a magnesium ion, but the metal is coordinated to nitrogen atoms, not carbon atoms.

(D) hemoglobin: Hemoglobin contains iron, but it does not form direct metal-carbon bonds; instead, iron coordinates with nitrogen in the heme group.

Step 3: Conclusion.

The biomolecule with a direct metal-carbon bond is coenzyme B_{12} (option A).

Quick Tip

Coenzyme B_{12} is a classic example of a biomolecule that contains a direct metal-carbon bond, with cobalt bonded directly to carbon in its structure.

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9. For the reaction

$H_2PO_4^-$ (aq) + OH^- (aq) $\rightarrow$ HPO_4^{2-} (aq) + H_2 (g)

the rate expression is $k[H_2PO_4^-][OH^-]$**. If the concentration of** $H_2PO_4^-$ **is doubled, the rate is**

(A) tripled

(B) halved

(C) doubled

(D) unchanged

Correct Answer: (C) doubled

Solution:

Step 1: Understanding the Rate Law.

The rate law for this reaction is given as Rate $= k[H_2PO_4^-][OH^-]$, meaning the rate is directly proportional to the concentrations of $H_2PO_4^-$ and OH^-.

Step 2: Analyzing the Effect of Doubling $H_2PO_4^-$.

If the concentration of $H_2PO_4^-$ is doubled, the rate will also double because the rate is directly proportional to this concentration. The concentration of OH^- remains unchanged, so the rate will be doubled.

Step 3: Conclusion.

The rate will be doubled if the concentration of $H_2PO_4^-$ is doubled (option C).

Quick Tip

For reactions where the rate is directly proportional to the concentration of a reactant, doubling that concentration will double the rate.

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10. The nature of interaction involved at the gas-solid interface in physisorption is

(A) ionic
(B) van der Waals
(C) hydrogen bonding
(D) covalent

Correct Answer: (B) van der Waals

Solution:

Step 1: Understanding Physisorption.

Physisorption is a type of adsorption where the interaction between the adsorbate and the adsorbent is weak, typically involving van der Waals forces. This interaction is much weaker compared to chemisorption, where chemical bonds are formed.

Step 2: Analyzing the options.

(A) ionic: Ionic interactions are typically seen in chemisorption, not in physisorption.

(B) van der Waals: Correct — Physisorption involves weak van der Waals forces, which are the primary type of interaction at the gas-solid interface.

(C) hydrogen bonding: This is not the main interaction in physisorption. Hydrogen bonding is seen in specific cases but not typically in physisorption.

(D) covalent: Covalent bonds are strong chemical bonds, which are characteristic of chemisorption, not physisorption.

Step 3: Conclusion.

The nature of the interaction in physisorption is van der Waals forces (option B).

Quick Tip

Physisorption is driven by weak van der Waals forces, unlike chemisorption, which involves stronger covalent or ionic bonds.

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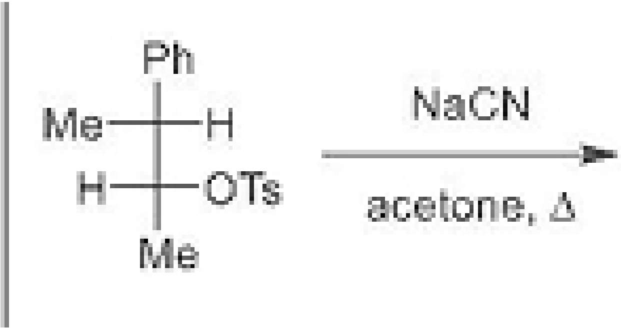
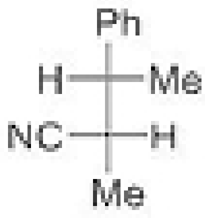
11. The major product formed in the following reaction



(A)



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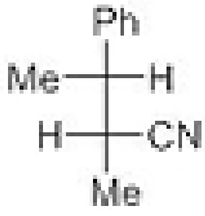
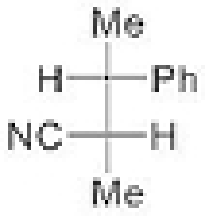
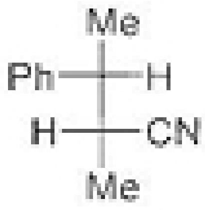


(C)



(D)



Correct Answer: (C) Me-CH$_2$Ph-NC-H

Solution:

Step 1: Understanding the Reaction.

The reaction shown involves the displacement of the tosyl group (OTs) by a cyanide ion (CN$^-$) in the presence of acetone and heat, indicating a nucleophilic substitution mechanism.

The reaction will replace the leaving group (OTs) with CN, forming a nitrile product.

Step 2: Analyzing the options.

(A) Ph-CH_2CH_2NC-H: This is incorrect because the product does not match the expected nitrile structure.

(B) Ph-CH_2CH_2CN: This is not the correct product; it lacks the proper structure.

(C) Me-CH_2Ph-NC-H: Correct — this is the expected product, with the cyanide group replacing the leaving group (OTs) on the carbon atom.

(D) Me-CH_2Ph-CN: This is incorrect because it does not account for the proper positioning of the groups.

Step 3: Conclusion.

The correct product formed in this reaction is Me-CH_2Ph-NC-H (option C).

Quick Tip

In nucleophilic substitution reactions, cyanide (CN^-) replaces a leaving group such as tosyl (OTs) to form a nitrile group.

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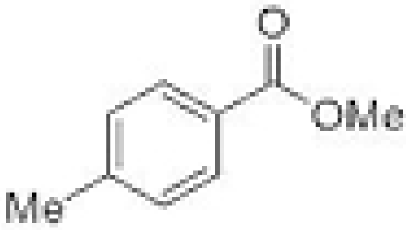
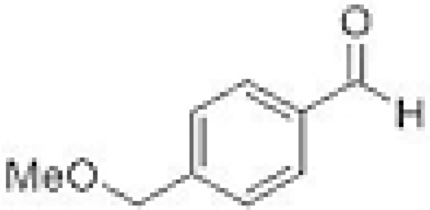
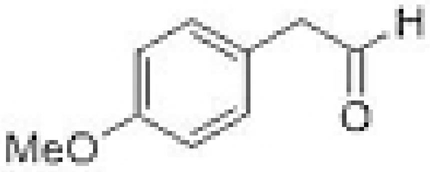
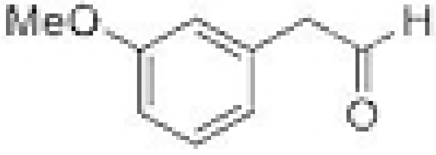
12. An organic compound having molecular formula $C_9H_{10}O_2$ exhibits the following spectral characteristics:

$^1HNMR : \delta 9.72$ **(t, 1H),** $\delta 7.1$ **(d, 2H),** $\delta 6.7$ **(d, 2H),** $\delta 3.8$ **(s, 3H),** $\delta 3.6$ **(d, 2H)**

IR: 1720 cm$^-1$

The most probable structure of the compound is

(A)	
(B)	
(C)	
(D)	

Correct Answer: (A) Ph-COOCH$_3$

Solution:

Step 1: Analyzing the NMR Spectrum.

The NMR spectrum shows a triplet at $\delta 9.72$, which suggests the presence of a methyl group adjacent to an ester or carboxyl group. The doublets at $\delta 7.1$ and $\delta 6.7$ indicate a

para-substituted benzene ring (indicating aromatic protons). The singlet at $\delta 3.8$ indicates the presence of a methyl ester group (-OCH$_3$) attached to the aromatic ring. The doublet at $\delta 3.6$ suggests the presence of another methyl group on the ring. The IR absorption at 1720 cm$^-1$ is characteristic of a carbonyl group (C=O), confirming the presence of an ester or carboxyl group.

Step 2: Analyzing the options.

(A) Ph-COOCH$_3$: Correct — The structure of methyl ester fits the NMR and IR data perfectly, with the ester group (-COOCH$_3$) and the typical aromatic proton signals.

(B) Ph-OCH$_3$: This would result in a different NMR spectrum, and the IR would not show a strong carbonyl stretch.

(C) Ph-CHO: This would not match the NMR or IR data because an aldehyde group would show different proton chemical shifts.

(D) Ph-COOH: This would also not fit the data since carboxylic acids would have a different NMR spectrum.

Step 3: Conclusion.

The most probable structure of the compound is Ph-COOCH$_3$ (option A).

Quick Tip

The presence of a methyl ester group $(-OCH_3)$ can be inferred from the NMR spectrum showing a singlet at $\delta 3.8$ and a triplet at $\delta 9.72$, along with an IR absorption at 1720 cm$^-1$.

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13. The major product formed in the reaction of (2S,3R)-2-chloro-3-phenylbutane with NaOEt in EtOH is

(A) (E)-2-phenyl-but-2-ene
(B) (Z)-2-phenyl-but-2-ene
(C) 3-phenyl-but-1-ene
(D) (2R,3R)-2-ethoxy-3-phenylbutane

Correct Answer: (A) (E)-2-phenyl-but-2-ene

Solution:

Step 1: Understanding the Reaction.

This is a typical elimination reaction involving a halogenated alkane and a base (NaOEt). The base will remove a proton adjacent to the carbon bearing the leaving group (Cl) via an E2 mechanism, leading to the formation of an alkene.

Step 2: Analyzing the options.

(A) (E)-2-phenyl-but-2-ene: Correct — The elimination leads to the formation of the trans (E) alkene. The stereochemistry of the starting compound allows for this product.

(B) (Z)-2-phenyl-but-2-ene: This is the incorrect product, as the base would favor the trans (E) product in this case.

(C) 3-phenyl-but-1-ene: This product does not result from the reaction, as it would require a different elimination site.

(D) (2R,3R)-2-ethoxy-3-phenylbutane: This is not the expected product as it does not match the elimination mechanism.

Step 3: Conclusion.

The correct product is (E)-2-phenyl-but-2-ene (option A).

Quick Tip

In E2 elimination reactions, the product typically follows the trans (E) stereochemistry due to the anti-periplanar arrangement of the hydrogen and the leaving group.

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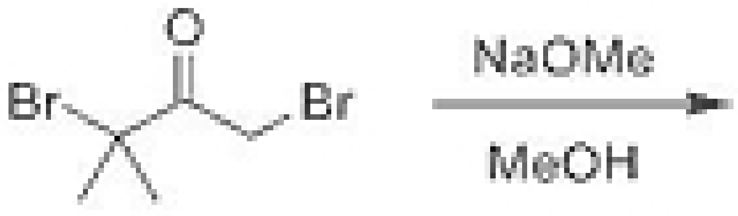
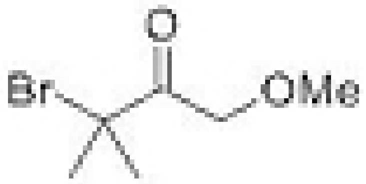
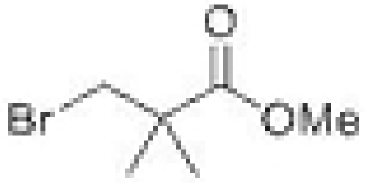
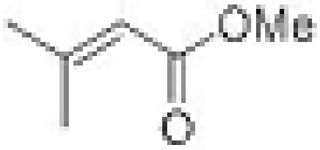
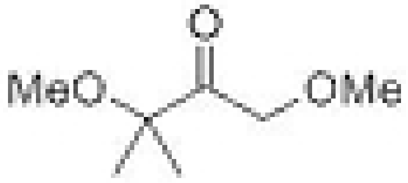
14. The major product formed in the following reaction



(A)	
(B)	
(C)	
(D)	

Correct Answer: (C) $CH_3C(OMe)_2$

Solution:

Step 1: Understanding the Reaction.

This is a nucleophilic substitution reaction where the methoxide ion ($NaOCH_3$) will act as a nucleophile and displace the bromide ion (Br^-) from the alkyl halide. The reaction occurs in methanol (MeOH), which will also participate in the substitution.

Step 2: Analyzing the options.

(A) $BrCH_2OCH_3$: This product does not match the expected reaction outcome.

(B) $BrCH_2OCH_3$: Same as option A.

(C) $CH_3C(OMe)_2$: Correct — This is the expected product, where the methoxide ion substitutes the bromine, forming an ester-like product.

(D) $MeOCH_2OCH_3$: This is an incorrect product as it does not align with the nucleophilic substitution mechanism.

Step 3: Conclusion.

The correct product is $CH_3C(OMe)_2$ (option C).

Quick Tip

In nucleophilic substitution reactions, methoxide ion (MeO^-) can replace a halide ion to form an ester or ether product.

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15. The reactivity of the enol derivatives towards benzaldehyde follows the order

I

II

III

(A) I ¿ II ¿ III

(B) III ¿ II ¿ I

(C) II ¿ I ¿ III

(D) I ¿ III ¿ II

Correct Answer: (A) I ¿ II ¿ III

Solution:

Step 1: Understanding the Reactivity.

Enol derivatives show different reactivity based on the electron-donating and electron-withdrawing groups attached to the enol. The reactivity towards electrophiles

like benzaldehyde will depend on the electron density around the enol.

Step 2: Analyzing the options.

(A) I ¿ II ¿ III: Correct — The reactivity follows this order, with I being the most reactive due to the lithium group, followed by II (the silyl group) and III (the bromide group).

(B) III ¿ II ¿ I: This is incorrect as the bromide group is the least reactive.

(C) II ¿ I ¿ III: This is incorrect. The lithium group in I is more reactive than the silyl group in II.

(D) I ¿ III ¿ II: Incorrect, as III has the least reactivity.

Step 3: Conclusion.

The correct order is I ¿ II ¿ III (option A).

Quick Tip

When considering reactivity towards electrophiles, electron-donating groups increase the nucleophilicity of the enol, while electron-withdrawing groups decrease it.

---

16. All possible lattice types are observed in the

(A) cubic crystal system

(B) monoclinic crystal system

(C) tetragonal crystal system

(D) orthorhombic crystal system

Correct Answer: (D) orthorhombic crystal system

Solution:

Step 1: Understanding the Crystal Systems.

In crystallography, different crystal systems correspond to different symmetries in the unit cell. The orthorhombic crystal system has three axes of unequal length, and all angles are 90 degrees. This system allows for all possible lattice types to occur.

Step 2: Analyzing the options.

(A) cubic crystal system: This system has equal-length axes and 90-degree angles, but it does not accommodate all lattice types.

(B) monoclinic crystal system: This system has unequal axes and an angle other than 90 degrees, but it doesn't accommodate all lattice types.

(C) tetragonal crystal system: This system has two axes of equal length, but it also doesn't accommodate all lattice types.

(D) orthorhombic crystal system: Correct — The orthorhombic system allows for all lattice types, with three axes of unequal length and 90-degree angles.

Step 3: Conclusion.

The correct answer is the orthorhombic crystal system (option D).

Quick Tip

The orthorhombic crystal system has three unequal axes, allowing for all possible lattice types.

---

17. The structure types of $B_{10}H_{10}^{2-}$ and $B_{10}H_{14}$, respectively, are

(A) closo and nido

(B) nido and arachno

(C) nido and closo

(D) closo and arachno

Correct Answer: (D) closo and arachno

Solution:

Step 1: Understanding Boron Hydride Structure Types.

In boron hydride chemistry, the terms closo, nido, and arachno describe different types of polyhedral structures that boron clusters can adopt. Closo refers to a closed polyhedron, nido to a partially closed structure, and arachno to an open structure.

Step 2: Analyzing the options.

(A) closo and nido: Incorrect — $B_{10}H_{10}^{2-}$ adopts a closo structure, but $B_{10}H_{14}$ does not adopt a nido structure.

(B) nido and arachno: Incorrect, as both $B_{10}H_{10}^{2-}$ and $B_{10}H_{14}$ do not adopt these structures.

(C) nido and closo: Incorrect — the $B_{10}H_{10}^{2-}$ species adopts a closo structure.

(D) closo and arachno: Correct — $B_{10}H_{10}^{2-}$ adopts a closo structure, and $B_{10}H_{14}$ adopts an arachno structure.

Step 3: Conclusion.

The correct answer is closo and arachno (option D).

Quick Tip

The closo structure is fully closed, while the arachno structure has an open arrangement, often found in larger boron clusters.

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18. The ground state and the maximum number of spin-allowed electronic transitions possible in a Co^{2+} tetrahedral complex, respectively, are

(A) $^4A_2$ and 3

(B) $^4T_1$ and 2

(C) $^4A_2$ and 2

(D) $^4T_1$ and 3

Correct Answer: (D) $^4T_1$ and 3

Solution:

Step 1: Understanding Spin-Allowed Transitions.

In a Co^{2+} tetrahedral complex, the electronic transitions can be determined by the d-orbital configuration. The ground state and the number of spin-allowed transitions depend on the electronic configuration and the symmetry of the complex.

Step 2: Analyzing the options.

(A) $^4A_2$ and 3: This is incorrect because the $^4A_2$ state is not the ground state for Co^{2+}.

(B) $^4T_1$ and 2: Incorrect — Co^{2+} has a higher number of spin-allowed transitions.

(C) $^4A_2$ and 2: Incorrect — again, the ground state is not $^4A_2$.

(D) $^4T_1$ and 3: Correct — Co^{2+} in a tetrahedral field has the $^4T_1$ ground state, and the maximum number of spin-allowed transitions is 3.

Step 3: Conclusion.

The correct answer is $^4T_1$ and 3 (option D).

Quick Tip

In transition metal complexes, the number of spin-allowed transitions is determined by the electronic configuration and the symmetry of the complex.

19. The correct statement about the geometries of BH_2^+ and NH_2^+ based on valence shell electron pair repulsion (VSEPR) theory is

(A) both BH_2^+ and NH_2^+ are trigonal planar

(B) BH_2^+ is linear and NH_2^+ is trigonal planar

(C) BH_2^+ is trigonal planar and NH_2^+ is linear

(D) both BH_2^+ and NH_2^+ are linear

Correct Answer: (A) both BH_2^+ and NH_2^+ are trigonal planar

Solution:

Step 1: Understanding the VSEPR Theory.

According to the VSEPR theory, the geometry of a molecule depends on the number of bonding electron pairs around the central atom. Both BH_2^+ and NH_2^+ have two bonding electron pairs and no lone pairs, so both adopt a trigonal planar geometry.

Step 2: Analyzing the options.

(A) both BH_2^+ and NH_2^+ are trigonal planar: Correct — Both species have a trigonal planar geometry.

(B) BH_2^+ is linear and NH_2^+ is trigonal planar: This is incorrect because both species have trigonal planar geometry.

(C) BH_2^+ is trigonal planar and NH_2^+ is linear: This is incorrect because NH_2^+ also has a trigonal planar geometry.

(D) both BH_2^+ and NH_2^+ are linear: This is incorrect because the geometry is trigonal planar, not linear.

Step 3: Conclusion.

The correct answer is (A) both BH_2^+ and NH_2^+ are trigonal planar.

Quick Tip

Both BH_2^+ and NH_2^+ have two bonding pairs and no lone pairs, leading to trigonal planar geometry.

---

20. The order of increasing CO stretching frequencies in $[Co(CO)_4]^+$, $[Cu(CO)_4]^+$, $[Fe(CO)_4]^{2-}$ and $[Ni(CO)_4]$ is

(A) $[Cu(CO)_4]^+$ ¡ $[Ni(CO)_4]$ ¡ $[Co(CO)_4]^+$ ¡ $[Fe(CO)_4]^{2-}$

(B) $[Fe(CO)_4]^{2-}$ ¡ $[Co(CO)_4]^+$ ¡ $[Ni(CO)_4]$ ¡ $[Cu(CO)_4]^+$

(C) $[Co(CO)_4]^+$ ¡ $[Fe(CO)_4]^{2-}$ ¡ $[Cu(CO)_4]^+$ ¡ $[Ni(CO)_4]$

(D) $[Ni(CO)_4]$ ¡ $[Cu(CO)_4]^+$ ¡ $[Fe(CO)_4]^{2-}$ ¡ $[Co(CO)_4]^+$

Correct Answer: (A) $[Cu(CO)_4]^+$ ¡ $[Ni(CO)_4]$ ¡ $[Co(CO)_4]^+$ ¡ $[Fe(CO)_4]^{2-}$

Solution:

Step 1: Understanding the Effect of Metal Oxidation State on CO Stretching.

In metal carbonyl complexes, the CO stretching frequency is influenced by the metal's oxidation state. Higher oxidation states lead to stronger electron withdrawal from CO ligands, which in turn lowers the CO stretching frequency.

Step 2: Analyzing the options.

(A) $[Cu(CO)_4]^+$ ¡ $[Ni(CO)_4]$ ¡ $[Co(CO)_4]^+$ ¡ $[Fe(CO)_4]^{2-}$: Correct — This order reflects the increasing oxidation state of the metal, which leads to increasing electron withdrawal and thus increasing CO stretching frequencies.

(B) $[Fe(CO)_4]^{2-}$ ¡ $[Co(CO)_4]^+$ ¡ $[Ni(CO)_4]$ ¡ $[Cu(CO)_4]^+$: Incorrect — the order is reversed, as oxidation state plays a key role.

(C) $[\mathrm{Co(CO)_4}]^+$ ¡ $[\mathrm{Fe(CO)_4}]^{2-}$ ¡ $[\mathrm{Cu(CO)_4}]^+$ ¡ $[\mathrm{Ni(CO)_4}]$: Incorrect — the order does not match with the expected oxidation states.

(D) $[\mathrm{Ni(CO)_4}]$ ¡ $[\mathrm{Cu(CO)_4}]^+$ ¡ $[\mathrm{Fe(CO)_4}]^{2-}$ ¡ $[\mathrm{Co(CO)_4}]^+$: Incorrect — the order of CO stretching frequencies is wrong based on oxidation states.

Step 3: Conclusion.

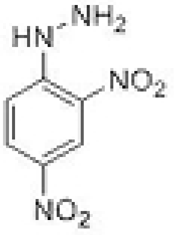
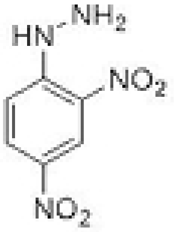
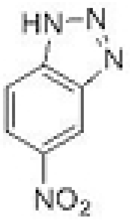
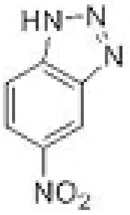
The correct order of CO stretching frequencies is (A) $[\mathrm{Cu(CO)_4}]^+$ ¡ $[\mathrm{Ni(CO)_4}]$ ¡ $[\mathrm{Co(CO)_4}]^+$ ¡ $[\mathrm{Fe(CO)_4}]^{2-}$.

Quick Tip

The CO stretching frequency increases with the oxidation state of the metal due to increased electron withdrawal.

---

21. The reaction of 2,4-dinitrofluorobenzene with hydrazine produces a yellow-orange solid X used for the identification of an organic functional group G. X and G, respectively, are

(A)		and	carboxylic acid
(B)		and	aldehyde
(C)		and	aldehyde
(D)		and	carboxylic acid

Correct Answer: (A) HN-NH_2 and carboxylic acid

Solution:

Step 1: Understanding the Reaction.

The reaction between 2,4-dinitrofluorobenzene and hydrazine typically leads to the formation of a hydrazone compound, which is a yellow-orange solid. This product can be used to identify functional groups like carboxylic acids.

Step 2: Analyzing the options.

(A) $HN\text{-}NH_2$ and carboxylic acid: Correct — the reaction produces hydrazone ($HN\text{-}NH_2$) and can identify the carboxylic acid functional group.

(B) $HN\text{-}NH_2$ and aldehyde: Incorrect, as the reaction forms a carboxylic acid, not an aldehyde.

(C) $HN\text{-}NH_2$ and aldehyde: Same as option B, incorrect.

(D) $HN\text{-}NH_2$ and carboxylic acid: Same as option A, correct.

Step 3: Conclusion.

The correct answer is (A) $HN\text{-}NH_2$ and carboxylic acid.

Quick Tip

Hydrazone formation with hydrazine and aromatic compounds like 2,4-dinitrofluorobenzene is a common reaction for identifying carboxylic acids.

---

22. The stability of adducts $H_3B\text{-}PF_3$, $H_3B\text{-}NMe_3$, $H_3B\text{-}CO$, $H_3B\text{-}OMe_2$ follows the order

(A) $H_3B\text{-}OMe_2$ ¡ $H_3B\text{-}CO$ ¡ $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}NMe_3$

(B) $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}CO$ ¡ $H_3B\text{-}NMe_3$ ¡ $H_3B\text{-}OMe_2$

(C) $H_3B\text{-}CO$ ¡ $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}NMe_3$ ¡ $H_3B\text{-}OMe_2$

(D) $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}CO$ ¡ $H_3B\text{-}OMe_2$ ¡ $H_3B\text{-}NMe_3$

Correct Answer: (A) $H_3B\text{-}OMe_2$ ¡ $H_3B\text{-}CO$ ¡ $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}NMe_3$

Solution:

Step 1: Understanding the Stability of Adducts.

The stability of adducts involving boron (B) is influenced by the electron-withdrawing or electron-donating ability of the ligands. Strong electron-withdrawing ligands like PF_3 increase the stability, while electron-donating groups like Me_3 and OMe_2 tend to decrease stability.

Step 2: Analyzing the options.

(A) $H_3B\text{-}OMe_2$ ¡ $H_3B\text{-}CO$ ¡ $H_3B\text{-}PF_3$ ¡ $H_3B\text{-}NMe_3$: Correct — The order reflects the

increasing electron-withdrawing ability of the ligands, which increases the stability of the adducts.

(B) H_3B-PF$_3$ ¡ H_3B-CO ¡ H_3B-NMe$_3$ ¡ H_3B-OMe$_2$: Incorrect, the order is reversed.

(C) H_3B-CO ¡ H_3B-PF$_3$ ¡ H_3B-NMe$_3$ ¡ H_3B-OMe$_2$: Incorrect, as PF$_3$ should be more stable than CO.

(D) H_3B-PF$_3$ ¡ H_3B-CO ¡ H_3B-OMe$_2$ ¡ H_3B-NMe$_3$: Incorrect, as the order of stability is not correct.

Step 3: Conclusion.

The correct order is (A) H_3B-OMe$_2$ ¡ H_3B-CO ¡ H_3B-PF$_3$ ¡ H_3B-NMe$_3$.

Quick Tip

Electron-withdrawing groups like PF$_3$ enhance the stability of boron adducts, while electron-donating groups like OMe$_2$ decrease stability.

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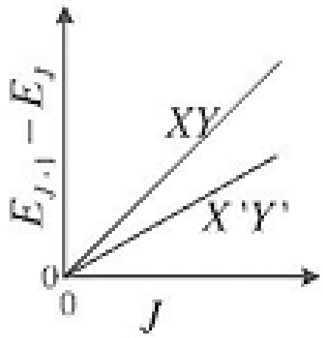
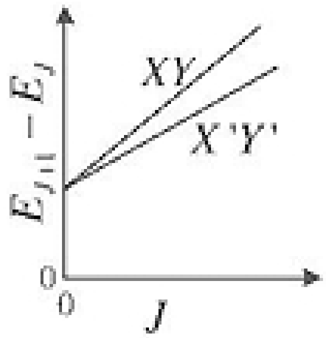
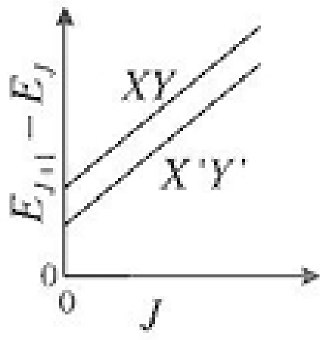
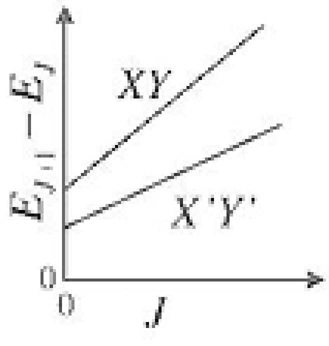
23. The spacing between successive rotational energy levels of a diatomic molecule XY and its heavier isotopic analogue X'Y' varies with the rotational quantum number, J, as

(A)	
(B)	
(C)	
(D)	

Correct Answer: (C) X'Y' shows a steeper slope than XY.

Solution:

Step 1: Understanding Rotational Energy Levels.

For diatomic molecules, the rotational energy levels are quantized and are described by the equation $E_J = BJ(J+1)$, where B is the rotational constant and J is the rotational quantum number. The spacing between successive energy levels depends on B. A heavier isotopic analogue will have a smaller B, resulting in a smaller slope for the $E_J - E_0$ vs. J plot.

Step 2: Analyzing the options.

(A) XY and X'Y' both show the same slope for $E_J - E_0$ vs. J, with X'Y' having a steeper slope: Incorrect — the slope for the heavier isotope (X'Y') should be less steep.

(B) XY shows a steeper slope than X'Y': Incorrect, as the lighter molecule (XY) should have a steeper slope than the heavier one.

(C) X'Y' shows a steeper slope than XY: Correct — X'Y' has a smaller rotational constant, leading to a steeper slope.

(D) XY and X'Y' show the same slope: Incorrect — the slopes differ due to different moment of inertia for the isotopes.

Step 3: Conclusion.

The correct answer is (C) X'Y' shows a steeper slope than XY.

Quick Tip

Heavier isotopes have a smaller rotational constant, leading to a less steep slope in the $E_J - E_0$ vs. J plot.

---

24. The ratio of the 2p $\rightarrow$ 1s transition energy in He$^+$ to that in the H atom is closest to

(A) 1

(B) 2

(C) 4

(D) 8

Correct Answer: (C) 4

Solution:

Step 1: Understanding the Transition Energies.

The energy of a transition in a hydrogen-like atom is given by the formula:

$$E = -13.6\,\frac{Z^2}{n^2}\ \textbf{eV}$$

where Z is the atomic number, and n is the principal quantum number. For He$^+$, $Z = 2$, and for H, $Z = 1$. The ratio of transition energies is the square of the ratio of their atomic numbers.

Step 2: Calculation.

For the 2p $\rightarrow$ 1s transition: - For He$^+$, the energy is $E_{\textbf{He}} = -13.6 \times \frac{2^2}{2^2} = -13.6$ eV. - For H, the energy is $E_{\textbf{H}} = -13.6 \times \frac{1^2}{2^2} = -3.4$ eV.

Thus, the ratio of energies is:

$$\frac{E_{\textbf{He}}}{E_{\textbf{H}}} = \frac{4}{1} = 4$$

Step 3: Conclusion.

The correct ratio of transition energies is 4 (option C).

Quick Tip

In hydrogen-like atoms, the transition energy scales with the square of the atomic number (Z).

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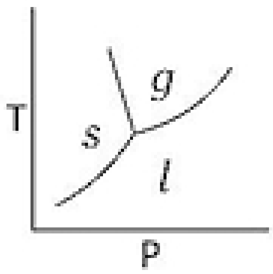
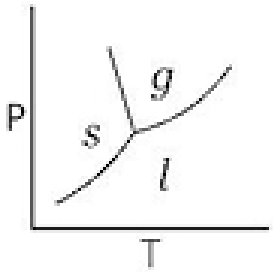
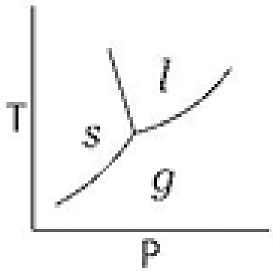
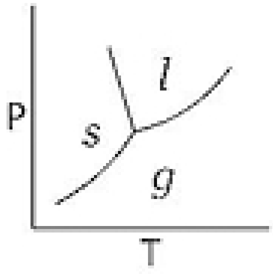
25. The phase diagram of water is best represented by

(A)	
(B)	
(C)	
(D)	

Correct Answer: (B) P vs T with gas (g), solid (s), and liquid (l) phases in the usual configuration

Solution:

Step 1: Understanding the Phase Diagram of Water.

A phase diagram shows the equilibrium states of a substance as a function of temperature and pressure. For water, the typical configuration has a gas (g) phase at high temperatures and low pressures, a liquid (l) phase at moderate temperatures and pressures, and a solid (s) phase at low temperatures and high pressures.

Step 2: Analyzing the options.

(A) T vs P with solid (s), liquid (l), and gas (g) phases in the usual configuration: Incorrect — the axes should be pressure (P) on the y-axis, not temperature.

(B) P vs T with gas (g), solid (s), and liquid (l) phases in the usual configuration: Correct — this is the typical phase diagram for water.

(C) T vs P with solid (s), liquid (l), and gas (g) phases in the usual configuration: Incorrect — it incorrectly places temperature on the vertical axis.

(D) P vs T with liquid (l), gas (g), and solid (s) phases in the usual configuration: Incorrect — the order of the phases is incorrect in the diagram.

Step 3: Conclusion.

The correct answer is (B) P vs T with gas (g), solid (s), and liquid (l) phases in the usual configuration.

Quick Tip

In a phase diagram, the solid, liquid, and gas phases are typically arranged according to pressure and temperature conditions, with gas at low pressure and high temperature.

---

26. Capillary W contains water and capillary M contains mercury. The contact angles between the capillary wall and the edge of the meniscus at the air-liquid interface in W and M are θ_w and θ_m, respectively. The contact angles satisfy the conditions

(A) $\theta_w > 90^\circ$ **and** $\theta_m > 90^\circ$

(B) $\theta_w > 90^\circ$ **and** $\theta_m < 90^\circ$

(C) $\theta_w < 90^\circ$ **and** $\theta_m > 90^\circ$

(D) $\theta_w < 90^\circ$ **and** $\theta_m < 90^\circ$

Correct Answer: (C) $\theta_w < 90^\circ$ **and** $\theta_m > 90^\circ$

Solution:

Step 1: Understanding Contact Angles.

Contact angles are determined by the interaction between the liquid and the surface. For water, the contact angle (θ_w) is typically less than 90° because water wets most surfaces. For mercury, the contact angle (θ_m) is greater than 90° because mercury does not wet most surfaces, leading to a high contact angle.

Step 2: Analyzing the options.

(A) $\theta_w > 90^\circ$ **and** $\theta_m > 90^\circ$**: Incorrect — the contact angle for water is typically less than 90°.**

(B) $\theta_w > 90^\circ$ **and** $\theta_m < 90^\circ$**: Incorrect — water's contact angle is typically less than 90°.**

(C) $\theta_w < 90^\circ$ **and** $\theta_m > 90^\circ$**: Correct — water has a contact angle less than 90°, while mercury has a contact angle greater than 90°.**

(D) $\theta_w < 90^\circ$ **and** $\theta_m < 90^\circ$**: Incorrect — mercury has a contact angle greater than 90°.**

Step 3: Conclusion.

The correct answer is (C) $\theta_w < 90^\circ$ **and** $\theta_m > 90^\circ$**.**

Quick Tip

Water typically has a contact angle less than 90° on most surfaces, while mercury has a contact angle greater than 90° due to its non-wetting nature.

---

27. The Maxwell-Boltzmann distribution $f(v_x)$ of one-dimensional velocities v_x at temperature T is

[Given: A is a normalization constant such that $\int_{-\infty}^{\infty} f(v_x)\,dv_x = 1$, and k_b is the Boltzmann constant]

(A) $A \exp\left(-\frac{mv_x^2}{2k_bT}\right)$

(B) $A \exp\left(-\frac{mv_x^2}{k_bT}\right)$

(C) $Av_x^2 \exp\left(-\frac{mv_x^2}{2k_bT}\right)$
(D) $Av_x^2 \exp\left(-\frac{mv_x^2}{k_bT}\right)$

Correct Answer: (C) $Av_x^2 \exp\left(-\frac{mv_x^2}{2k_bT}\right)$

Solution:

Step 1: Understanding the Maxwell-Boltzmann Distribution.

The Maxwell-Boltzmann distribution describes the distribution of velocities for particles in a gas. The distribution is given by:

$$f(v_x) = Av_x^2 \exp\left(-\frac{mv_x^2}{2k_bT}\right)$$

where A **is the normalization constant,** m **is the mass of the particle, and** k_b **is the Boltzmann constant.**

Step 2: Analyzing the options.

(A) $A \exp\left(-\frac{mv_x^2}{2k_bT}\right)$**: Incorrect — this form lacks the** v_x^2 **factor, which is required by the Maxwell-Boltzmann distribution.**

(B) $A \exp\left(-\frac{mv_x^2}{k_bT}\right)$**: Incorrect — this form has a factor of 1 in the exponent instead of** $2k_bT$**.**

(C) $Av_x^2 \exp\left(-\frac{mv_x^2}{2k_bT}\right)$**: Correct — this is the correct form of the Maxwell-Boltzmann distribution in one dimension.**

(D) $Av_x^2 \exp\left(-\frac{mv_x^2}{k_bT}\right)$**: Incorrect — this form has a factor of 1 in the exponent instead of** $2k_bT$**.**

Step 3: Conclusion.

The correct form of the Maxwell-Boltzmann distribution is given by option (C).

Quick Tip

The Maxwell-Boltzmann distribution includes a v_x^2 **factor and an exponential decay term with** $\frac{mv_x^2}{2k_bT}$ **in the exponent.**

---

28. The potential for a particle in a one-dimensional box is given as:

$V(x) = 0$ for $0 \leq x \leq L$, and $V(x) = \infty$ elsewhere.

The locations of the internal nodes of the eigenfunctions $\psi_n(x)$, $n \geq 2$, are

[Given: m is an integer such that $0 < m < n$]

(A) $x = \frac{m+\frac{1}{2}}{n}L$

(B) $x = \frac{m}{n}L$

(C) $x = \frac{m}{n+1}L$

(D) $x = \frac{m+1}{n+1}L$

Correct Answer: (C) $x = \frac{m}{n+1}L$

Solution:

Step 1: Understanding the Quantum Well Problem.

For a particle in a one-dimensional box, the eigenfunctions $\psi_n(x)$ are sinusoids with nodes at the walls of the box. The internal nodes occur at positions where the sine function is zero, except at the endpoints. The locations of the nodes depend on the quantum number n.

Step 2: Analyzing the options.

(A) $x = \frac{m+\frac{1}{2}}{n}L$**: Incorrect — the position of the nodes does not include this form.**

(B) $x = \frac{m}{n}L$**: Incorrect — this is the incorrect formula for the position of nodes.**

(C) $x = \frac{m}{n+1}L$**: Correct — the nodes for $\psi_n(x)$ are located at this position.**

(D) $x = \frac{m+1}{n+1}L$**: Incorrect — the nodes follow the formula in option (C).**

Step 3: Conclusion.

The correct position of the nodes is given by option (C).

Quick Tip

The locations of the internal nodes for a particle in a box are given by $x = \frac{m}{n+1}L$, where m is an integer and n is the quantum number.

---

29. The number of CO stretching bands in the infrared spectrum of Fe(CO)$_5$ is

(A) 1

(B) 2

(C) 3

(D) 4

Correct Answer: (B) 2

Solution:

Step 1: Understanding the Infrared Spectrum of Fe(CO)$_5$.

Fe(CO)$_5$ is a metal carbonyl complex. The infrared spectrum of this molecule typically shows two CO stretching bands due to the different symmetries of the CO ligands in the complex.

Step 2: Analyzing the options.

(A) 1: Incorrect — there are typically two stretching bands in the IR spectrum for Fe(CO)$_5$.

(B) 2: Correct — the Fe(CO)$_5$ complex has two CO stretching bands.

(C) 3: Incorrect — three CO stretching bands are not observed for this complex.

(D) 4: Incorrect — four CO stretching bands are not observed for this complex.

Step 3: Conclusion.

The correct number of CO stretching bands is (B) 2.

Quick Tip

The IR spectrum of Fe(CO)$_5$ typically shows two CO stretching bands due to the symmetry of the complex.

---

30. The standard Gibbs free energy change for the reaction

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

at 2500 K is $+118$ kJ mol^{-1}. The equilibrium constant for the reaction is

[Given: $R = 8.314$ J K^{-1}mol^{-1}]

(A) 0.994

(B) 1.006

(C) 3.42×10^{-3}

(D) 292.12

Correct Answer: (C) 3.42×10^{-3}

Solution:

Step 1: The Relationship Between Gibbs Free Energy and Equilibrium Constant.

The equilibrium constant K is related to the Gibbs free energy change ΔG° by the equation:

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

where R is the gas constant, T is the temperature, and K is the equilibrium constant. Rearranging, we get:

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

Substituting the given values, we calculate K.

Step 2: Calculations.

$$\Delta G^\circ = 118\,\textbf{kJ mol}^{-1} = 118000\,\textbf{J mol}^{-1}$$

$$K = \exp\left(\frac{-118000}{8.314 \times 2500}\right) = 3.42 \times 10^{-3}$$

Step 3: Conclusion.

The equilibrium constant is 3.42×10^{-3}, so the correct answer is (C).

Quick Tip

The equilibrium constant is related to the Gibbs free energy change by the equation $K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$.

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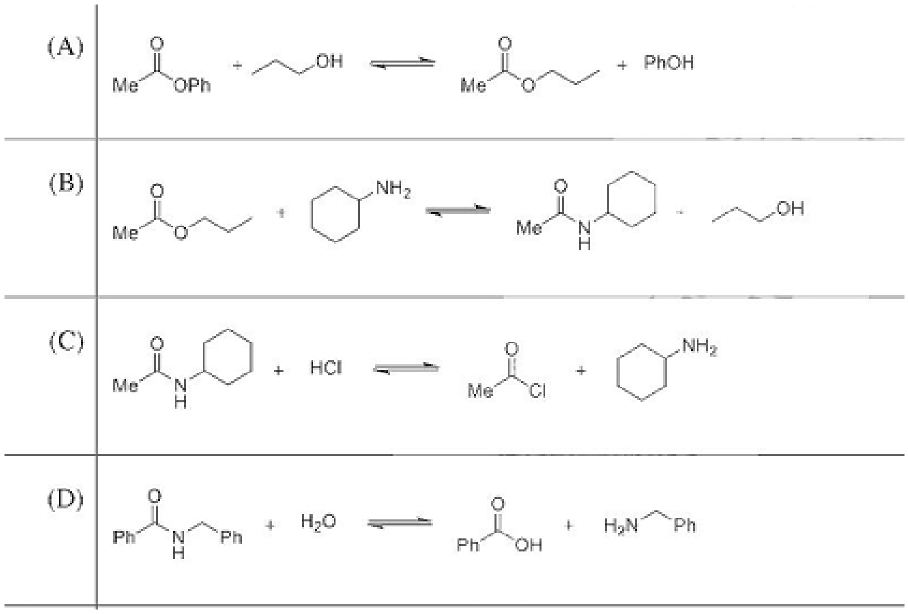
31. Among the following, the reaction(s) that favor(s) the formation of the products at 25°C is/are



Correct Answer: (A) $\mathbf{Me-OPh + OH \rightarrow MeO + PhOH}$

Solution:

Step 1: Understanding the Reactions.

This question asks us to identify the reaction that favors the formation of products at 25°C. To determine this, we consider factors such as the reaction conditions, equilibrium, and whether the reaction is likely to be exothermic or endothermic at the given temperature.

Step 2: Analysis of the reactions.

- **(A) $\mathbf{Me-OPh + OH \rightarrow MeO + PhOH}$** :

$Thisisanucleophilicsubstitutionwhereahydroxideionreplacesthephenylgroup.Thisreactionfavorsthefor$

- **(B) $\mathbf{Me-CH_2 + NH_2 \rightarrow MeNH_2 + C_6H_{10}OH}$** :

$Thisreactionislesslikelytoproceedat25Cbecausetheadditionofammoniaislessfavorable.Theproductionof$

- **(C) $\mathbf{Me-CH_2} + HCl \rightarrow \mathbf{MeCl + C_6H_5NH_2}$** :

$Thisreactionisnotlikelyat25Cbecauseitinvolvestheformationofachloromethylgroup,whichrequiresspec$

- **(D) $\mathbf{MeOPh + H_2O} \leftrightarrow MeOH + PhOH$** :

$Thereactionisahydrolysis.Itisinequilibrium,butthisreactiondoesnotfavorproductformationat25C.Wate$

Step 3: Conclusion.

The reaction in (A) is most likely to proceed at 25°C, as it involves a simple nucleophilic substitution that easily favors the product formation.

Quick Tip

In nucleophilic substitution reactions, strong nucleophiles like hydroxide ions promote the reaction at room temperature.

32. Among the following, the correct statement(s) is/are:

(A) The first pK_a of malonic acid is lower than the pK_a of acetic acid while its second pK_a is higher than the pK_a of acetic acid.
(B) The first pK_a of malonic acid is higher than the pK_a of acetic acid while its second pK_a is lower than the pK_a of acetic acid.
(C) Both the first and the second pK_a's of malonic acid are lower than the pK_a of acetic acid.
(D) Both the first and the second pK_a's of malonic acid are higher than the pK_a of acetic acid.

Correct Answer: (A) The first pK_a of malonic acid is lower than the pK_a of acetic acid while its second pK_a is higher than the pK_a of acetic acid.

Solution:
Step 1: Understanding pK_a Values.
The pK_a value is a measure of the acidity of a molecule. A lower pK_a indicates a stronger acid. Malonic acid has two carboxylic acid groups, whereas acetic acid has only one. The first proton of malonic acid is more easily released than the proton from acetic acid, making the first pK_a of malonic acid lower. However, the second pK_a of malonic acid is higher because the second deprotonation is less favorable.
Step 2: Analyzing the options.
- **(A) The first pK_a of malonic acid is lower than the pK_a of acetic acid while its second pK_a is higher than the pK_a of acetic acid:** Correct — this statement correctly describes the pK_a values of malonic acid and acetic acid.
- **(B) The first pK_a of malonic acid is higher than the pK_a of acetic acid while its second pK_a is lower than the pK_a of acetic acid:** Incorrect — the first pK_a of malonic acid is lower, not higher.

- **(C) Both the first and the second pK_a's of malonic acid are lower than the pK_a of acetic acid:** Incorrect — the second pK_a of malonic acid is higher.
- **(D) Both the first and the second pK_a's of malonic acid are higher than the pK_a of acetic acid:** Incorrect — the first pK_a of malonic acid is lower.

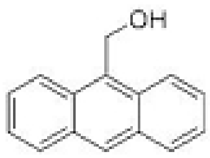
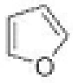
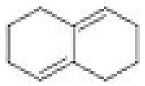
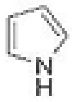
Step 3: Conclusion.

The correct statement is (A), as it accurately reflects the pK_a values for malonic acid and acetic acid.

> **Quick Tip**
>
> The second pK_a value of malonic acid is higher due to the decreased ease of proton removal after the first deprotonation.

---

33. The compound(s) that participate(s) in the Diels-Alder reaction with maleic anhydride is/are

(A)	
(B)	
(C)	
(D)	

Correct Answer: (C)

Solution:

Step 1: Understanding the Diels-Alder Reaction.

The Diels-Alder reaction is a cycloaddition reaction between a conjugated diene and a dienophile, typically resulting in a six-membered ring. The reaction requires a diene (which is typically electron-rich) and a dienophile (which is electron-deficient). Maleic anhydride is a classic dienophile due to its electron-deficient nature.

Step 2: Analyzing the options.

- **(A) Compound A:** This compound has a hydroxyl group attached to an aromatic ring. While it can undergo certain reactions, it is not likely to undergo the Diels-Alder reaction with maleic anhydride.
- **(B) Compound B:** This compound has an oxygen atom attached to a benzene ring. It is unlikely to act as a diene in a Diels-Alder reaction due to the electron-withdrawing nature of the oxygen, making it a poor candidate.
- **(C) Compound C:** This compound is an aromatic diene, which is an excellent candidate for the Diels-Alder reaction. The electron-rich nature of the diene will easily react with the electron-deficient maleic anhydride.
- **(D) Compound D:** This compound is an amine, which does not readily undergo a Diels-Alder reaction with maleic anhydride.

Step 3: Conclusion.

Compound (C) is the most likely participant in the Diels-Alder reaction with maleic anhydride.

Quick Tip

In Diels-Alder reactions, the diene must be electron-rich and the dienophile electron-deficient. Maleic anhydride is a common dienophile.

---

34. Among the following, the suitable route(s) for the conversion of benzaldehyde to acetophenone is/are

(A) CH_3COCl, anhydrous $AlCl_3$

(B) (i)HS(CH$_2$)$_3$SH, F$_3$B-OEt$_2$, $(ii)n$-BuLi, (iii)MeI, (iv)HgCl$_2$, CdCO$_3$, H$_2$O

(C) NaNH$_2$, MeI

(D) (i)MeMgBr, (ii)aq. acid, (iii)pyridinium chlorochromate (PCC)

Correct Answer: (A) CH$_3$COCl, anhydrous AlCl$_3$

Solution:

Step 1: Understanding the Reaction.

To convert benzaldehyde to acetophenone, we need to introduce a methyl group (-CH) onto the aromatic ring at the position adjacent to the carbonyl group. This is a Friedel-Crafts acylation reaction where acetyl chloride (CH$_3$COCl) reacts with the benzaldehyde in the presence of a Lewis acid such as anhydrous aluminum chloride (AlCl$_3$) to form acetophenone.

Step 2: Analyzing the options.

- **(A) CH$_3$COCl, anhydrous AlCl$_3$:** Correct — This is the standard Friedel-Crafts acylation reaction, which successfully converts benzaldehyde to acetophenone.
- **(B)** (i)**HS(CH$_2$)$_3$SH, F$_3$B-OEt$_2$**, $(ii)n$**-BuLi**, (iii)**MeI**, (iv)**HgCl$_2$, CdCO$_3$, H$_2$O:** Incorrect — This sequence is not a conventional route for the conversion of benzaldehyde to acetophenone. The reagents here are not suited for the required transformation.
- **(C) NaNH$_2$, MeI:** Incorrect — This reaction sequence involves the generation of a nucleophilic methyl anion, but it does not involve a suitable pathway for acylation to form acetophenone.
- **(D)** (i)**MeMgBr**, (ii)**aq. acid**, (iii)**pyridinium chlorochromate (PCC):** Incorrect — This sequence is not applicable for the conversion from benzaldehyde to acetophenone, as it suggests different types of reactions like nucleophilic substitution and oxidation rather than acylation.

Step 3: Conclusion.

The correct route is option (A), where acetylation occurs using acetyl chloride and aluminum chloride as a catalyst.

Quick Tip

The Friedel-Crafts acylation reaction is commonly used to introduce an acyl group (-COCH) onto an aromatic ring. Anhydrous AlCl is an effective Lewis acid catalyst for this reaction.

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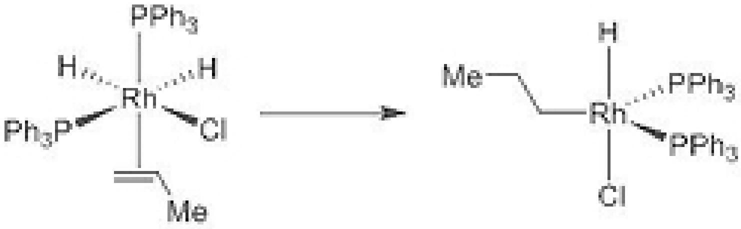
35. The reaction involves(s)



(A) migratory insertion

(B) change in electron count of Rh from 18 to 16

(C) oxidative addition

(D) change in electron count of Rh from 16 to 18

Correct Answer: (B) change in electron count of Rh from 18 to 16

Solution:

Step 1: Understanding the Reaction.

This reaction shows a rhodium complex, where a C-H bond is cleaved in the presence of a rhodium catalyst, leading to a shift in the electron count of the rhodium center. The starting complex has an 18-electron configuration. The product shows that the electron count of rhodium has decreased, meaning the metal has lost electrons due to the reaction with the ligand (C-H bond cleavage). This kind of process is characteristic of oxidative addition.

Step 2: Analyzing the options.

- **(A) Migratory insertion:** Migratory insertion is a type of mechanism where a ligand (typically alkyl or hydride) migrates to the metal center, but this does not describe the observed process in this reaction.

- **(B) Change in electron count of Rh from 18 to 16:** Correct — The electron count of the rhodium center changes from 18 to 16, which occurs in reactions involving oxidative addition. The metal moves from a low oxidation state to a higher one.
- **(C) Oxidative addition:** While oxidative addition involves the increase in the oxidation state of the metal, the observed electron count in this case is decreasing, which does not match the description of oxidative addition. Therefore, this option is misleading in terms of electron count.
- **(D) Change in electron count of Rh from 16 to 18:** This is incorrect — we observe the opposite, a decrease from 18 to 16.

Step 3: Conclusion.

The reaction is best described by option (B), where the electron count of the rhodium changes from 18 to 16 due to the cleavage of a C-H bond. This is consistent with a typical catalysis mechanism.

Quick Tip

In catalysis, oxidative addition typically leads to an increase in the oxidation state of the metal, while reductive elimination results in a decrease in electron count at the metal.

---

36. The reason(s) for the lower stability of Si_2H_6 compared to C_2H_6 is/are

(A) silicon is more electronegative than hydrogen

(B) Si-Si bond is weaker than C-C bond

(C) Si-H bond is weaker than C-H bond

(D) the presence of low-lying d-orbitals in silicon

Correct Answer: (B) Si-Si bond is weaker than C-C bond

Solution:

Step 1: Understanding the Problem.

This question asks about the reasons for the lower stability of Si_2H_6 compared to C_2H_6. In comparing the two molecules, the key difference is that silicon atoms are larger than carbon atoms, leading to weaker bonding and lower stability.

Step 2: Analyzing the options.

- **(A) Silicon is more electronegative than hydrogen:** This is incorrect. Silicon is less electronegative than carbon, not hydrogen. The stability issue arises more from bond strengths rather than electronegativity.
- **(B) Si-Si bond is weaker than C-C bond:** Correct — The Si-Si bond is indeed weaker than the C-C bond due to the larger atomic radius of silicon, which results in a longer, weaker bond. This contributes to the lower stability of Si_2H_6.
- **(C) Si-H bond is weaker than C-H bond:** This is incorrect — The Si-H bond is not inherently weaker than the C-H bond. The instability of Si_2H_6 comes from the Si-Si bond rather than the Si-H bond.
- **(D) The presence of low-lying d-orbitals in silicon:** This is a plausible explanation in some contexts but not a dominant factor in the case of Si_2H_6 compared to C_2H_6. While d-orbitals can affect reactivity, the primary reason for the difference in stability is the Si-Si bond strength.

Step 3: Conclusion.

The correct explanation for the lower stability of Si_2H_6 is that the Si-Si bond is weaker than the C-C bond, leading to a less stable molecule.

Quick Tip

The weaker Si-Si bond in Si_2H_6 compared to the C-C bond in C_2H_6 leads to lower stability, making silicon compounds less stable than their carbon counterparts.

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37. For an N-atom nonlinear polyatomic gas, the constant volume molar heat capacity $C_{v,m}$ has the expected value of $3(N-1)R$, based on the principle of equipartition of energy. The correct statement(s) about the measured value of $C_{v,m}$ is/are

(A) The measured $C_{v,m}$ is independent of temperature.

(B) The measured $C_{v,m}$ is dependent on temperature.

(C) The measured $C_{v,m}$ is typically lower than the expected value.

(D) The measured $C_{v,m}$ is typically higher than the expected value.

Correct Answer: (C) The measured $C_{v,m}$ is typically lower than the expected value.

Solution:

Step 1: Understanding the Equipartition of Energy.

For a nonlinear polyatomic gas, the heat capacity at constant volume $C_{v,m}$ is expected to be $3(N-1)R$, based on the principle of equipartition of energy. This value assumes all the degrees of freedom (translational, rotational, and vibrational) are fully excited and contribute equally to the total energy.

Step 2: Analyzing the Options.

- **(A) The measured $C_{v,m}$ is independent of temperature:** This is incorrect. The specific heat capacity $C_{v,m}$ is dependent on temperature, especially at lower temperatures where some degrees of freedom may not be fully excited.

- **(B) The measured $C_{v,m}$ is dependent on temperature:** While it is true that $C_{v,m}$ depends on temperature, this option doesn't explain the fact that the measured value is typically lower than the expected value, as is seen experimentally.

- **(C) The measured $C_{v,m}$ is typically lower than the expected value:** Correct — In real systems, the heat capacity is often lower than the expected value due to incomplete excitation of some degrees of freedom (especially vibrational modes) at lower temperatures.

- **(D) The measured $C_{v,m}$ is typically higher than the expected value:** This is incorrect. Due to quantum effects, the actual measured heat capacity is usually lower, not higher, than the classical value.

Step 3: Conclusion.

The correct answer is (C), as the measured heat capacity is typically lower than the expected value due to temperature-dependent excitation of molecular degrees of freedom.

Quick Tip

In polyatomic gases, the heat capacity at constant volume often appears lower than the classical expected value at low temperatures due to incomplete excitation of molecular modes.

38. Zinc containing enzyme(s) is/are

(A) carboxypeptidase

(B) hydrolase

(C) carbonic anhydrase

(D) urease

Correct Answer: (C) carbonic anhydrase

Solution:

Step 1: Identifying Zinc-Containing Enzymes.

Zinc is a crucial cofactor for many enzymes, and some enzymes require zinc for their catalytic activity. These enzymes are referred to as zinc-dependent enzymes. Carbonic anhydrase is a well-known zinc-dependent enzyme that plays a role in the conversion of carbon dioxide to bicarbonate.

Step 2: Analyzing the Options.

- **(A) Carboxypeptidase:** While carboxypeptidase is a metalloprotein, it does not require zinc for its activity. Instead, it typically uses a different metal ion such as copper.
- **(B) Hydrolase:** Hydrolases are a broad class of enzymes and do not necessarily contain zinc. While some hydrolases may require zinc, this option is too general.
- **(C) Carbonic anhydrase:** Correct — Carbonic anhydrase is a zinc-dependent enzyme involved in the hydration of carbon dioxide to bicarbonate. Zinc is essential for its enzymatic function.
- **(D) Urease:** Urease does require a metal cofactor, but it is nickel, not zinc, that is the essential metal in this enzyme.

Step 3: Conclusion.

The correct answer is (C), as carbonic anhydrase is a well-known zinc-dependent enzyme.

Quick Tip

Zinc is a critical cofactor in several enzymes, such as carbonic anhydrase, which catalyzes the conversion of carbon dioxide to bicarbonate.

39. The conversion of ICl to ICl$^+$ involves(s)

(A) the removal of an electron from a π^* molecular orbital of ICl

(B) an increase in the bond order from 1 in ICl to 1.5 in ICl$^+$

(C) the formation of a paramagnetic species

(D) the removal of an electron from a molecular orbital localized predominantly on Cl

Correct Answer: (A) the removal of an electron from a π^* molecular orbital of ICl

Solution:

Step 1: Understanding the Reaction.

The conversion of ICl to ICl$^+$ involves electron removal. In this case, the electron is typically removed from the π^* molecular orbital, which is the lowest unoccupied molecular orbital (LUMO) in ICl. The removal of an electron from this orbital results in the formation of ICl$^+$, a positively charged species.

Step 2: Analyzing the Options.

- **(A) The removal of an electron from a π^* molecular orbital of ICl:** Correct — The electron removed during the ionization process comes from the π^* molecular orbital of ICl. This leads to the formation of ICl$^+$.
- **(B) An increase in the bond order from 1 in ICl to 1.5 in ICl$^+$:** This is incorrect. The ionization of ICl does not result in a significant change in bond order from 1 to 1.5. The main change is in the charge of the molecule.
- **(C) The formation of a paramagnetic species:** This is incorrect. ICl$^+$ is not paramagnetic; it does not have any unpaired electrons after the ionization.
- **(D) The removal of an electron from a molecular orbital localized predominantly on Cl:** This is incorrect. The electron is not localized on Cl but is in the π^* orbital, which is a combination of I and Cl's orbitals.

Step 3: Conclusion.

The correct answer is (A), as the electron removed comes from the π^* molecular orbital.

Quick Tip

The removal of an electron from a π^* orbital is common in the ionization of diatomic molecules, leading to a positively charged species.

---

40. The common point defect(s) in a solid is/are

(A) Wadsley defect
(B) Schottky defect
(C) Suzuki defect
(D) Frenkel defect

Correct Answer: (B) Schottky defect

Solution:

Step 1: Understanding Point Defects.

Point defects are irregularities or deviations from the ideal atomic arrangement in a crystalline solid. The common types of point defects include Schottky defects and Frenkel defects. A Schottky defect occurs when both a cation and an anion are missing from the lattice, maintaining charge neutrality. A Frenkel defect, on the other hand, occurs when an atom or ion is displaced from its normal position to an interstitial site.

Step 2: Analyzing the Options.

- **(A) Wadsley defect:** This is a type of defect related to interstitial atoms in certain materials but is not a commonly discussed point defect.
- **(B) Schottky defect:** Correct — A Schottky defect involves the simultaneous vacancy of both cations and anions, maintaining charge neutrality. It is one of the most common types of point defects in ionic solids.
- **(C) Suzuki defect:** This is not a recognized point defect in materials science.
- **(D) Frenkel defect:** Although Frenkel defects are a common point defect, this question asks about the ”common point defects,” and Schottky defects are more prevalent in many ionic solids.

Step 3: Conclusion.

The correct answer is (B), as Schottky defects are common point defects found in ionic crystals.

Quick Tip

In ionic crystals, Schottky defects involve the missing of both cations and anions, while Frenkel defects involve the displacement of ions to interstitial sites.

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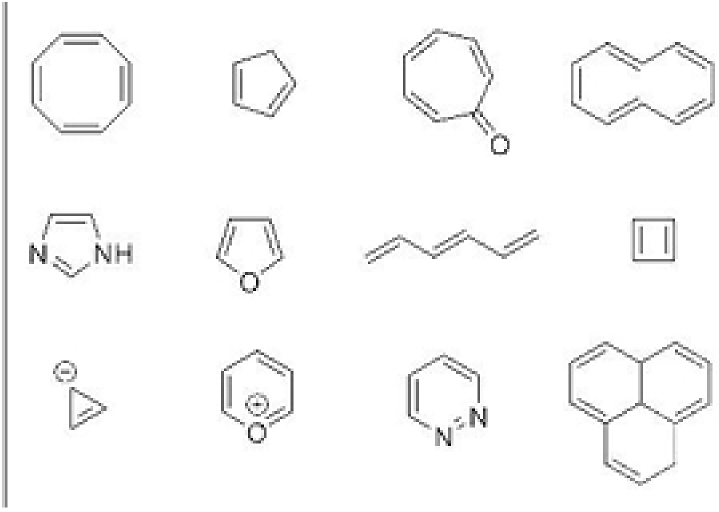
41. Among the following, the number of aromatic compounds is



Solution:

Step 1: Understanding Aromatic Compounds.

Aromatic compounds follow Huckel's rule, which states that a molecule is aromatic if it has a cyclic structure, is planar, and follows the $4n + 2$ rule for the number of π-electrons, where n is a non-negative integer.

Step 2: Analyzing the Structures.

- The first compound (benzene ring) is aromatic as it has 6 π-electrons.
- The second compound (pyrrole) is aromatic with 6 π-electrons in the ring.
- The third compound (pyridine) is aromatic, as it has 6 π-electrons.
- The fourth compound (cyclohexene) is not aromatic because it does not meet the criteria for aromaticity.
- The fifth compound (cycloheptatriene) is not aromatic as it does not follow Huckel's rule (it has 6 π-electrons, but is not fully conjugated).

- The sixth compound (aziridine) is not aromatic.

Step 3: Conclusion.

The number of aromatic compounds in the list is 3 (benzene, pyrrole, and pyridine).

Quick Tip

To determine whether a compound is aromatic, check if it is cyclic, planar, and follows the $4n + 2$ rule for π-electrons.

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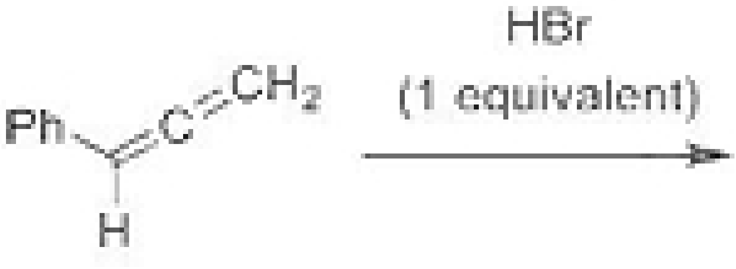
42. The number of stereoisomers possible for the major product formed in the reaction



is

Solution:

Step 1: Understanding the Reaction.

The given reaction involves an alkene and HBr. The reaction follows an electrophilic addition mechanism where the alkene reacts with HBr to form a bromoalkane. If the alkene has a chiral center after the addition of HBr, stereoisomers will be formed.

Step 2: Analyzing the Reaction.

The compound Ph-CH2CH2 is a propene molecule. After the addition of HBr, a chiral center is formed at the carbon that is attached to both the -CH2 group and the -Br group. This leads to the formation of two stereoisomers (R and S).

Step 3: Conclusion.

The reaction will produce two stereoisomers, one with R configuration and the other with S configuration. Hence, the number of stereoisomers possible is 2.

Quick Tip

When an electrophilic addition forms a chiral center, the reaction will produce two stereoisomers (R and S).

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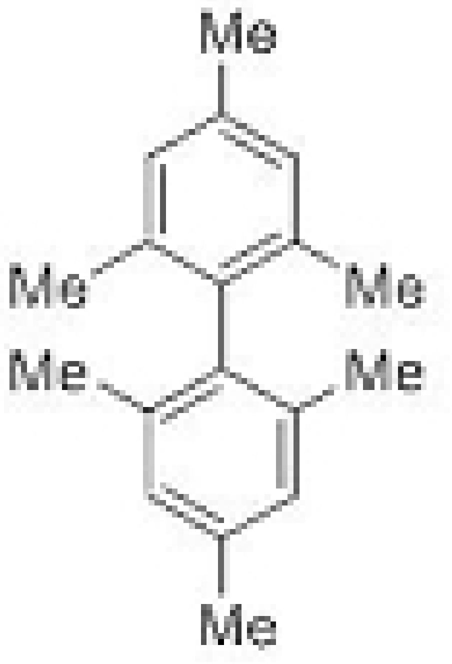
43. The number of signals observed in the 1H NMR spectrum of the compound



is

Solution:

Step 1: Understanding the Structure.

The given compound is a substituted benzene, where six methyl groups (Me) are attached to the benzene ring at different positions. This results in a highly symmetrical structure, where equivalent hydrogens are present.

Step 2: Identifying Equivalent Protons.

In the structure, all six methyl groups are symmetrically placed around the benzene ring. Due to this symmetry, the protons on each methyl group are equivalent to each other. Similarly, the six aromatic protons will also be equivalent because of the symmetry. Hence, we expect only one signal for the methyl protons and one signal for the aromatic protons.

Step 3: Conclusion.

The number of signals observed in the ^{1}H NMR spectrum will be 2: one for the methyl group protons and one for the aromatic protons.

Quick Tip

When the molecule has symmetry, equivalent protons give rise to the same signal in the ^{1}H NMR spectrum.

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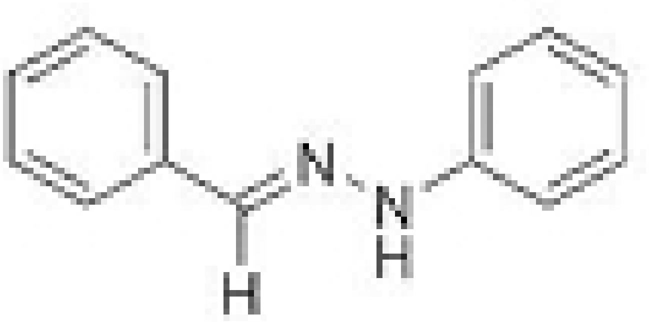
44. The reaction of 122 g of benzaldehyde with 108 g of phenylhydrazine gave 157 g of the product.



The yield of the product is ? (round off to the nearest integer)

Solution:

Step 1: Understanding the Reaction.

This reaction involves the condensation of benzaldehyde and phenylhydrazine to form the corresponding hydrazone. The yield is calculated using the formula:

$$\text{Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Step 2: Calculating the Moles of Benzaldehyde and Phenylhydrazine.

Molecular weight of benzaldehyde (C7H6O) = 106 g/mol Molecular weight of phenylhydrazine (C6H5NHNH2) = 93 g/mol

Moles of benzaldehyde = $\frac{122\,\text{g}}{106\,\text{g/mol}} = 1.15\,\text{mol}$ Moles of phenylhydrazine = $\frac{108\,\text{g}}{93\,\text{g/mol}} = 1.16\,\text{mol}$ Since both reactants are in a 1:1 molar ratio, the limiting reagent is benzaldehyde, which is present in 1.15 mol. Hence, the theoretical yield of the product will be based on 1.15 mol. The molecular weight of the hydrazone product is approximately 177 g/mol.

Theoretical yield = $1.15\,\text{mol} \times 177\,\text{g/mol} = 203.55\,\text{g}$

Step 3: Calculating the Yield.

The actual yield is given as 157 g. Now, the yield can be calculated:

$$\text{Yield} = \frac{157\,\text{g}}{203.55\,\text{g}} \times 100 = 77.1\%$$

Step 4: Conclusion.

The yield of the product is approximately 77

Quick Tip

To calculate the yield, determine the limiting reagent and calculate the theoretical yield, then use the formula for percentage yield.

---

45. The B-B bond order in B_2 is

Solution:

Step 1: Molecular Orbital Theory.

In the case of B_2, we use Molecular Orbital (MO) theory to determine the bond order. The bond order is given by the formula:

$$\text{Bond order} = \frac{1}{2}\,(\text{Number of bonding electrons} - \text{Number of anti-bonding electrons})$$

Step 2: Electronic Configuration for B_2.

The total number of valence electrons in each B atom is 3. Therefore, for B_2, the total number of electrons is 6. These electrons will fill the molecular orbitals in the following order: - $\sigma_{1s}^2, {\sigma_{1s}^*}^2, \sigma_{2s}^2, {\sigma_{2s}^*}^2, \pi_{2p_x}^1, \pi_{2p_y}^1$.

There are 2 electrons in the bonding π-orbitals and 0 in the anti-bonding orbitals for π-orbitals.

Step 3: Calculating the Bond Order.

$$\text{Bond order} = \frac{1}{2}(4-2) = 1$$

Step 4: Conclusion.

The B-B bond order in B_2 is 1.

Quick Tip

The bond order in a molecule can be found using the Molecular Orbital theory, where electrons are assigned to bonding and anti-bonding orbitals.

---

46. The number of unpaired electrons in $[\mathbf{Co(H_2O)_6}]^{2+}$ is

Solution:

Step 1: Understanding the Oxidation State of Co.

In $[\mathrm{Co(H_2O)_6}]^{2+}$, the oxidation state of Co is +2. Therefore, the electronic configuration of Co^{2+} is $[Ar]3d^7$.

Step 2: The Ligand Field.

The six water molecules act as ligands and will split the d-orbitals into two sets in an octahedral geometry: e_g and t_{2g}. For d^7 configuration: - The t_{2g} orbitals will be fully occupied with 6 electrons. - The e_g orbitals will have 1 electron, leaving it unpaired.

Step 3: Conclusion.

The number of unpaired electrons in $[\mathrm{Co(H_2O)_6}]^{2+}$ is 1.

Quick Tip

To find the number of unpaired electrons in a coordination complex, determine the electron configuration and the distribution of electrons in the metal's d-orbitals.

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47. The number of significant figures in 5.0820×10^2 is

Solution:

Step 1: Understanding Significant Figures.

Significant figures include all non-zero digits, zeros between non-zero digits, and trailing zeros in the decimal part. The number of significant figures is determined by counting these digits.

Step 2: Analyzing the Given Number.

The number 5.0820×10^2 has the digits $5, 0, 8, 2, 0$. All these digits are significant because the zero is after a decimal point and follows non-zero digits.

Step 3: Conclusion.

The number of significant figures in 5.0820×10^2 is 5.

Quick Tip

Remember, trailing zeros in a decimal number are significant. Leading zeros are not, and zeros in a whole number without a decimal are not counted as significant.

---

48. The d spacing for the first-order X-ray ($\lambda = 1.54\,\text{Å}$) diffraction event of metallic iron (fcc) at $2\theta = 20.2°$ is

(round off to three decimal places)

Solution:

Step 1: Using Bragg's Law.

Bragg's law for X-ray diffraction is given by:

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

For the first-order diffraction ($n = 1$), we substitute $\lambda = 1.54\,\text{Å}$ and $\theta = 20.2°$. The formula becomes:

$$1.54 = 2d\sin(20.2°)$$

Step 2: Solving for d.

Rearranging the equation:

$$d = \frac{1.54}{2\sin(20.2°)}$$

Now, calculate $\sin(20.2°)$:

$$\sin(20.2°) = 0.345$$

Substituting this into the equation:

$$d = \frac{1.54}{2 \times 0.345} = \frac{1.54}{0.69} \approx 2.23\,\text{Å}$$

Step 3: Conclusion.

The d spacing for the first-order X-ray diffraction is approximately $2.230\,\text{Å}$.

Quick Tip

For X-ray diffraction, use Bragg's law to relate the diffraction angle, wavelength, and the interplanar spacing in the crystal.

---

49. The volume fraction for an element in an fcc lattice is (round off to two decimal places)

Solution:

Step 1: Formula for Volume Fraction.

In an fcc lattice, there are 4 atoms per unit cell. The volume of the unit cell is given by a^3, where a is the lattice constant. The volume of a single atom is approximately $\frac{4}{3}\pi r^3$, where r is the atomic radius.

The volume fraction ϕ is given by:

$$\phi = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{4 \times \frac{4}{3}\pi r^3}{a^3}$$

Step 2: Relationship Between Atomic Radius and Lattice Constant.

For an fcc lattice, the relation between the lattice constant a and the atomic radius r is:

$$a = \sqrt{8}r$$

Step 3: Substituting in the Formula.

Substitute $a = \sqrt{8}r$ into the volume fraction formula:

$$\phi = \frac{4 \times \frac{4}{3}\pi r^3}{(\sqrt{8}r)^3}$$

Simplifying:

$$\phi = \frac{4 \times \frac{4}{3}\pi r^3}{8\sqrt{8}r^3} = \frac{16\pi}{8\sqrt{8}} \approx 0.74$$

Step 4: Conclusion.

The volume fraction for an element in an fcc lattice is approximately 0.74.

Quick Tip

For fcc lattices, the volume fraction is typically about 0.74 due to the efficient packing of atoms.

---

50. A steady current of 1.25 A is passed through an electrochemical cell for 1.5 h using a 12 V battery. The total charge, Q, drawn during this process is (round off to the nearest integer)

Solution:

Step 1: Formula for Charge.

The total charge Q is related to the current I and the time t by the formula:

$$Q = I \times t$$

Where: - $I = 1.25\,\text{A}$ - $t = 1.5\,\text{h} = 1.5 \times 3600\,\text{s} = 5400\,\text{s}$

Step 2: Calculating the Total Charge.

Substitute the given values into the formula:

$$Q = 1.25\,\text{A} \times 5400\,\text{s} = 6750\,\text{C}$$

Step 3: Conclusion.

The total charge drawn during this process is $6750\,\text{C}$.

Quick Tip

To calculate the total charge, simply multiply the current by the time the current flows.

---

51. The specific rotation of optically pure (R)-1-phenylethylamine is +40 (neat, 20°C). A synthetic sample of the same compound is shown to contain 4:1 mixture of (S)- and (R)-enantiomers. The specific rotation of the neat sample at 20°C is (round off to the nearest integer)

Solution:

Step 1: Understanding the Problem.

The specific rotation of the pure enantiomer (R)-1-phenylethylamine is given as +40. When we mix (S)- and (R)-enantiomers in a 4:1 ratio, we need to calculate the specific rotation of the mixture.

Step 2: Calculating the specific rotation of the mixture.

For a mixture of enantiomers, the specific rotation $[\alpha]_{\text{mix}}$ can be calculated as the weighted average of the specific rotations of the individual enantiomers:

$$[\alpha]_{\text{mix}} = \frac{4}{5} \times (+40) + \frac{1}{5} \times (-40)$$

$$[\alpha]_{\text{mix}} = 32 - 8 = +24$$

Step 3: Conclusion.

The specific rotation of the neat sample is approximately +24.

Quick Tip

When calculating the specific rotation of a mixture, use the weighted average based on the relative amounts of each enantiomer.

---

52. The number of β particles emitted in the nuclear reaction

$$^{238}_{92}\text{U} \rightarrow ^{206}_{82}\text{Pb}$$

is

Solution:

Step 1: Understanding the Decay Process.

In the nuclear reaction given, Uranium-238 ($^{238}_{92}\mathrm{U}$) decays to lead-206 ($^{206}_{82}\mathrm{Pb}$) by emitting β particles. The number of β particles is determined by the change in atomic number.

Step 2: Calculating the Number of β Particles.

The atomic number decreases from 92 (Uranium) to 82 (Lead), indicating the emission of 10 β particles (each β-decay decreases the atomic number by 1).

$$\text{Number of } \beta \text{ particles} = 92 - 82 = 10$$

Step 3: Conclusion.

The number of β particles emitted is 10.

Quick Tip

In β-decay, the emission of a β particle reduces the atomic number by 1 while the mass number remains unchanged.

---

53. Iron is extracted from its ore via the reaction

$$\mathrm{Fe_2O_3} + 3\mathrm{CO} \rightarrow 2\mathrm{Fe} + 3\mathrm{CO_2}$$

The volume of CO (at STP) required to produce 1 kg of iron is **Solution:**

Step 1: Molar Mass of Iron.

The molar mass of iron (Fe) is 56 g/mol. To calculate the amount of CO needed to produce 1 kg (1000 g) of iron, we first find the moles of Fe:

$$\text{Moles of Fe} = \frac{1000\,\text{g}}{56\,\text{g/mol}} = 17.857\,\text{mol}$$

Step 2: Moles of CO Required.

From the balanced equation, we see that 3 moles of CO are required to produce 2 moles of Fe. Therefore, the moles of CO required for 17.857 moles of Fe are:

$$\text{Moles of CO} = \frac{3}{2} \times 17.857 = 26.786\,\text{mol}$$

Step 3: Volume of CO at STP.

At STP, 1 mole of any gas occupies 22.4 L. Therefore, the volume of CO required is:

$$\text{Volume of CO} = 26.786\,\text{mol} \times 22.4\,\text{L/mol} = 600.3\,\text{L}$$

Step 4: Conclusion.

The volume of CO required to produce 1 kg of iron is approximately 600 liters.

Quick Tip

At STP, 1 mole of gas occupies 22.4 L. Use stoichiometry to convert moles of the product to moles of the reactant and then find the volume.

---

54. Total degeneracy (number of microstates) for a Ti^{3+} ion in spherical symmetry is

Solution:

Step 1: Understanding the Concept.

The degeneracy for a spherical ion is given by the equation:

$$\text{Degeneracy} = 2l + 1$$

where l is the angular momentum quantum number for the ion.

Step 2: Applying the Formula.

For Ti^{3+}, the electronic configuration is $3d^1$. This corresponds to $l = 2$ (since d-orbitals have $l = 2$).

Step 3: Calculating the Degeneracy.

Using the formula:

$$\text{Degeneracy} = 2(2) + 1 = 5$$

Step 4: Conclusion.

The total degeneracy for Ti^{3+} in spherical symmetry is 5.

Quick Tip

For an ion in spherical symmetry, the degeneracy is given by $2l+1$, where l is the orbital quantum number of the electron.

---

55. A galvanic electrochemical cell made of Zn^{2+}/Zn and Cu^{2+}/Cu half-cells produces 1.10 V at 25°C. The ratio of [Zn^{2+}] to [Cu^{2+}] is maintained at 1.0. The ΔG° for the reaction when 1.0 mol of Zn gets dissolved is (round off to the nearest integer)

Solution:

Step 1: Understanding the Problem.

We are given the following information: - Cell potential, $E_{\text{cell}} = 1.10\,\text{V}$ - Temperature, $T = 298\,\text{K}$ - Faraday's constant, $F = 96485\,\text{C/mol}$ - The reaction involves the dissolution of 1 mole of Zn.

We need to find the Gibbs free energy change, ΔG°.

Step 2: Calculating ΔG°.

The relationship between Gibbs free energy change and cell potential is given by:

$$\Delta G^\circ = -nFE_{\text{cell}}$$

where n is the number of moles of electrons involved in the reaction. For the reaction involving the dissolution of Zn, $n = 2$ (since Zn^{2+} is formed).

$$\Delta G^\circ = -2 \times 96485 \times 1.10 = -212,867\,\text{J/mol} = -213\,\text{kJ/mol}$$

Step 3: Conclusion.

The ΔG° for the reaction when 1 mole of Zn gets dissolved is approximately $-213\,\text{kJ/mol}$.

Quick Tip

The Gibbs free energy change for an electrochemical reaction is related to the cell potential by the equation $\Delta G^\circ = -nFE_{\text{cell}}$, where n is the number of moles of electrons.

---

56. At constant volume, 1.0 kJ of heat is transferred to 2 moles of an ideal gas at 1 atm and 298 K. The final temperature of the ideal gas is (round off to one decimal place)

Solution:

Step 1: Applying the Heat Transfer Equation.

For an ideal gas, the relationship between heat transferred (Q), number of moles (n), and change in temperature (ΔT) at constant volume is given by:

$$Q = nC_V \Delta T$$

where C_V is the molar heat capacity at constant volume. For an ideal gas, $C_V = \frac{3}{2}R$, where $R = 8.314\,\text{J/mol·K}$.

Step 2: Rearranging to Find the Final Temperature.

$$Q = n \times \frac{3}{2}R \times \Delta T$$

$$\Delta T = \frac{Q}{n \times \frac{3}{2}R}$$

Substitute the known values:

$$\Delta T = \frac{1000}{2 \times \frac{3}{2} \times 8.314} = \frac{1000}{24.942} \approx 40.04\,\text{K}$$

Step 3: Calculating the Final Temperature.

The initial temperature is 298 K, so the final temperature is:

$$T_{\text{final}} = 298 + 40.04 = 338.0\,\text{K}$$

Step 4: Conclusion.

The final temperature of the ideal gas is approximately $338.0\,\text{K}$.

Quick Tip

To calculate the final temperature of an ideal gas when heat is added at constant volume, use the equation $Q = nC_V\Delta T$, where $C_V = \frac{3}{2}R$ for ideal gases.

---

57. Two close lying bands in a UV spectrum occur at 274 nm and 269 nm. The magnitude of the energy gap between the two bands is (round off to the nearest integer)

Solution:

Step 1: Understanding the Relationship Between Energy and Wavelength.

The energy of a photon is related to its wavelength λ by the equation:

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

where: - $h = 6.626 \times 10^{-34}$ J·s (Planck's constant), - $c = 3.0 \times 10^{8}$ m/s (speed of light), - λ is the wavelength in meters.

Step 2: Finding the Energy of Each Band.

For the band at 274 nm:

$$E_1 = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^{8}}{274 \times 10^{-9}} = 7.26 \times 10^{-19}\,\text{J}$$

For the band at 269 nm:

$$E_2 = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^{8}}{269 \times 10^{-9}} = 7.39 \times 10^{-19}\,\text{J}$$

Step 3: Calculating the Energy Gap.

The energy gap is:

$$\Delta E = E_2 - E_1 = 7.39 \times 10^{-19} - 7.26 \times 10^{-19} = 0.13 \times 10^{-19}\,\text{J}$$

Step 4: Conclusion.

The magnitude of the energy gap between the two bands is approximately 1.3×10^{-20} J.

Quick Tip

The energy of a photon is inversely proportional to its wavelength. Use the equation $E = \frac{hc}{\lambda}$ to calculate the energy for each band.

---

58. The pH of an aqueous buffer prepared using CH_3COOH and CH_3COO^- and Na^+ is 4.80. The quantity

$$\frac{[CH_3COO^-] - [CH_3COOH]}{[CH_3COOH]}$$

is (round off to three decimal places)

Solution:

Step 1: Use the Henderson-Hasselbalch equation.

The Henderson-Hasselbalch equation is given by:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

where $[A^-]$ is the concentration of the base (CH_3COO^-) and $[HA]$ is the concentration of the acid (CH_3COOH).

Step 2: Plug in the given values.

We are given: - pH = 4.80 - pK_a of CH_3COOH = 4.75

Substituting these values into the equation:

$$4.80 = 4.75 + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

Step 3: Solve for the ratio.

$$4.80 - 4.75 = \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$0.05 = \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

Taking the antilog of both sides:

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{0.05} \approx 1.122$$

Step 4: Conclusion.

The quantity

$$\frac{[CH_3COO^-] - [CH_3COOH]}{[CH_3COOH]}$$

is approximately 0.122.

Quick Tip

The Henderson-Hasselbalch equation relates pH, pK_a, and the ratio of the concentrations of the conjugate base and acid in a buffer solution.

---

59. At constant temperature, 6.40 g of a substance dissolved in 78 g of benzene decreases the vapor pressure of benzene from 0.125 atm to 0.119 atm. The molar mass of the substance is (round off to one decimal place)

Solution:

Step 1: Use Raoult's Law.

Raoult's law states that the change in vapor pressure (ΔP) is proportional to the mole fraction of the solute:

$$\Delta P = P_0 - P = X_{\text{solute}} P_0$$

where P_0 is the vapor pressure of the pure solvent, P is the vapor pressure of the solution, and X_{solute} is the mole fraction of the solute.

Step 2: Find the mole fraction of the solute.

$$\Delta P = P_0 - P = 0.125 - 0.119 = 0.006\,\text{atm}$$

The mole fraction of the solute is:

$$X_{\text{solute}} = \frac{\Delta P}{P_0} = \frac{0.006}{0.125} = 0.048$$

Step 3: Calculate the moles of solute.

The mole fraction of the solute is also given by:

$$X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

where n_{solute} is the moles of solute and n_{solvent} is the moles of solvent (benzene).

The moles of benzene are:

$$n_{\text{solvent}} = \frac{78}{78} = 1\,\text{mol}$$

Substitute this value into the equation:

$$0.048 = \frac{n_{\text{solute}}}{n_{\text{solute}} + 1}$$

Solving for n_{solute}:

$$0.048(n_{\text{solute}} + 1) = n_{\text{solute}}$$

$$0.048 n_{\text{solute}} + 0.048 = n_{\text{solute}}$$

$$0.952 n_{\text{solute}} = 0.048$$

$$n_{\text{solute}} = \frac{0.048}{0.952} \approx 0.0505\,\text{mol}$$

Step 4: Find the molar mass.

The molar mass is given by:

$$\text{Molar mass} = \frac{\text{Mass of solute}}{\text{Moles of solute}} = \frac{6.40}{0.0505} \approx 126.7\,\text{g/mol}$$

Step 5: Conclusion.

The molar mass of the substance is approximately $126.7\,\text{g/mol}$.

Quick Tip

Raoult's Law can be used to find the mole fraction of a solute from the change in vapor pressure and vice versa.

---

60. For a van der Waals gas, the critical temperature is 150 K and the critical pressure is 5×10^6 Pa. The volume occupied by each gas molecule is (round off to two decimal places)

Solution:

Step 1: Use the Van der Waals equation.

The volume occupied by each gas molecule is related to the critical temperature and pressure by the van der Waals equation. The volume per molecule at the critical point is given by:

$$V_c = \frac{RT_c}{P_c}$$

where V_c is the volume per molecule, $R = 8.314\,\text{J/mol·K}$ is the gas constant, $T_c = 150\,\text{K}$ is the critical temperature, and $P_c = 5 \times 10^6\,\text{Pa}$ is the critical pressure.

Step 2: Substituting the given values.

$$V_c = \frac{8.314 \times 150}{5 \times 10^6} = \frac{1247.1}{5 \times 10^6} = 2.494 \times 10^{-4}\,\text{m}^3$$

Step 3: Convert the volume to Å^3.

Since $1\ \text{m}^3 = 10^{30}\,\text{Å}^3$,

$$V_c = 2.494 \times 10^{-4} \times 10^{30} = 2.49 \times 10^{26}\,\text{Å}^3$$

Step 4: Conclusion.

The volume occupied by each gas molecule is approximately $2.49 \times 10^{26}\,\text{Å}^3$.

Quick Tip

The volume per molecule for a gas at critical conditions can be calculated using the equation $V_c = \frac{RT_c}{P_c}$.