21. In the absence of nitrogen, the enzyme nitrogenase functions as

1. nitrile hydratase
2. carboxypeptidase
3. urease
4. hydrogenase

Answer: (4) hydrogenase

Explanation:

Nitrogenase normally catalyzes the reduction of nitrogen (N_2) to ammonia (NH_3) using electrons and ATP.

In the absence of nitrogen, the same enzyme reduces protons (H^+) to molecular hydrogen (H_2).

Hence, nitrogenase behaves as **hydrogenase**, catalyzing proton reduction instead of nitrogen fixation.

22. In the following reaction, A and B, respectively, are

$B_2H_6 + NH_2CH_3 \rightarrow A$

$B_2H_6 + NMe_3 \rightarrow B$

1. $H_3BNH_2CH_3$ and H_3BNMe_3
2. $[BH_2(NH_2CH_3)_2]^+[BH_4]^-$ and H_3BNMe_3
3. $H_3BNH_2CH_3$ and $[BH_2(NMe_3)_2]^+[BH_4]^-$
4. $[BH_2(NH_2CH_3)_2]^+[BH_4]^-$ and $[BH_2(NMe_3)_2]^+[BH_4]^-$

Answer: (2) $[BH_2(NH_2CH_3)_2]^+[BH_4]^-$ and H_3BNMe_3

Explanation:

Diborane reacts with primary and tertiary amines differently.

- With primary amine (NH_2CH_3), a boronium salt forms: $[BH_2(NH_2CH_3)_2]^+[BH_4]^-$.
- With tertiary amine (NMe_3), a simple Lewis acid-base adduct forms: H_3BNMe_3.

  Hence, **A = $[BH_2(NH_2CH_3)_2]^+[BH_4]^-$** and **B = H_3BNMe_3.**

23. The enzyme nitrogenase converts one mole of N_2 to x mole of NH_3 and y mole of H_2 using z mole of protons and w mole of electrons. The values of x, y, z, and w, respectively, are

1. 2, 0, 6, and 6
2. 1, 0, 6, and 6
3. 1, 2, 8, and 8
4. 2, 1, 8, and 8

Answer: (4) 2, 1, 8, and 8

Explanation:

The overall nitrogenase reaction is:

$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16\ ADP + 16\ Pi$

Thus,

x = 2 (moles of NH_3),

y = 1 (mole of H_2),

z = 8 (moles of protons),

w = 8 (moles of electrons).

Hence, the correct set is **(2, 1, 8, 8).**

24. The solvent that shifts the Schlenk equilibrium to the right side is

$2\ RMgX \rightleftharpoons MgR_2 + MgX_2$

(R = isopropyl)

1. hexane
2. tetrahydrofuran
3. dioxane
4. diethyl ether

Answer: (3) dioxane

Explanation:

In the Schlenk equilibrium, formation of MgR_2 and MgX_2 is favored by solvents that coordinate strongly to Mg^{2+}.

Dioxane, being a bidentate ether, forms a stable complex with MgX_2 and precipitates it as MgX_2·dioxane, thus driving the equilibrium rightward.

Hence, **dioxane** shifts the equilibrium to the right.

25. The order of polarity of the B—C bond for the following compounds is

$B(C{=}CH)_3$ (P); $B(CH{=}CH_2)_3$ (Q); $B(CH_2{-}CH_3)_3$ (R); $B(CH_2{-}C_6H_5)_3$ (S)

1. R < S < Q < P
2. S < R < Q < P
3. R < S < P < Q
4. P < Q < R < S

Answer: (1) R < S < Q < P

Explanation:

Polarity of the B–C bond increases with the electron-withdrawing ability of the substituent attached to carbon.

Order of substituent electronegativity: alkyl < benzyl < vinyl < ethynyl.

Thus, bond polarity increases in the order:

$B–CH_2CH_3$ (R) < $B–CH_2C_6H_5$ (S) < $B–CH=CH_2$ (Q) < B–C≡CH (P).

26. Consider the statements for the complexes $[RhCl_3(H_2O)_3]$ (X) and $[Ir(CO)(Cl)(PPh_3)_2]$ (Y):

A. X has two isomers

B. Y has two isomers

C. Both X and Y are prone to oxidative addition

D. d_{z^2} orbital is most destabilized in Y

The correct option is

1. A, B and C only
2. B, C and D only
3. A and B only
4. A and C only

Answer: (3) A and B only

Explanation:

- $[RhCl_3(H_2O)_3]$ is an octahedral complex showing two geometrical isomers: facial (fac) and meridional (mer).
- $[Ir(CO)(Cl)(PPh_3)_2]$ is square planar and exhibits **cis–trans** isomerism.

  Thus, both X and Y have two isomers.

  However, oxidative addition is characteristic of low-coordinate d^8 metal centers; $[RhCl_3(H_2O)_3]$ is already saturated and not prone.

  d_{z^2} destabilization applies mainly to trigonal bipyramidal or octahedral field distortions, not square planar.

  Hence, only **A and B** are correct.

27. The standard reduction potentials of lanthanides (Ln^{3+}/Ln) are

1. similar to each other and also similar to those of late transition metals
2. different from each other but similar to lighter p-block elements
3. similar to each other and also similar to those of s-block elements
4. different from each other but similar to those of s-block elements

Answer: (3) similar to each other and also similar to those of s-block elements

Explanation:

The lanthanides (Ln) show similar chemical behavior because their successive elements differ only in the addition of 4f-electrons, which are poorly shielding. Consequently, the standard reduction potentials (E° for

Ln^{3+}/Ln) are **quite similar across the series**, typically ranging between –2.2 V and –2.4 V.

These values are comparable to those of the **electropositive s-block metals** like calcium and strontium. This similarity reflects their strong reducing character and metallic nature. Thus, the correct choice is that lanthanide reduction potentials are **similar to each other and resemble those of s-block elements.**

28. The option showing the correct structural types for $ZnFe_2O_4$ and $KMnF_3$, respectively, is

1. Perovskite and Fluorite
2. Perovskite and Antifluorite
3. Spinel and Perovskite
4. Spinel and Fluorite

Answer: (3) Spinel and Perovskite

Explanation:

- **$ZnFe_2O_4$** has the general formula AB_2O_4 and crystallizes in the **spinel structure** where Zn^{2+} occupies tetrahedral sites and Fe^{3+} occupies octahedral sites.
- **$KMnF_3$** has the general formula ABX_3 and adopts the **perovskite structure** (analogous to $CaTiO_3$), where K^+ occupies the large A-site and Mn^{2+} is at the B-site surrounded by F^- ions octahedrally.
  Thus, $ZnFe_2O_4$→ spinel; $KMnF_3$→ perovskite.

29. The order of acceptor strength towards Me_2S donor is

1. $AlCl_3 > BCl_3 > GaCl_3$
2. $BCl_3 > GaCl_3 > AlCl_3$
3. $GaCl_3 > AlCl_3 > BCl_3$
4. $AlCl_3 > GaCl_3 > BCl_3$

Answer: (3) $GaCl_3 > AlCl_3 > BCl_3$

Explanation:

Acceptor strength depends on the **Lewis acidity**, which is influenced by the ability of the central atom to accept electron pairs.

- **BCl_3** has strong π-back bonding due to effective overlap between empty p-orbitals on boron and lone pairs on chlorine; this reduces its Lewis acidity.
- **$AlCl_3$** and **$GaCl_3$** have weaker π-back bonding because of poorer p–p overlap.
- **$GaCl_3$** is the most Lewis acidic because of the relativistic contraction and poor shielding of 3d and 4p orbitals, which make gallium more electron deficient.
  Hence, the order of acceptor strength is **$GaCl_3 > AlCl_3 > BCl_3$.**

30. Quantum confinement leads to

1. increase in the band gap of the semiconductors
2. decrease in the band gap of the metal nanoparticles
3. decrease in the band gap of the semiconductors
4. no change in the band gap of the quantum dots

Answer: (1) increase in the band gap of the semiconductors

Explanation:

When the particle size of a semiconductor approaches the de Broglie wavelength of electrons (typically below 10 nm), its electronic properties change due to **quantum confinement**.

The energy levels become discrete rather than continuous, causing the effective band gap to **increase** as particle size decreases.

This explains why **quantum dots** show size-dependent color emission: smaller dots emit at shorter wavelengths (blue shift), while larger dots emit redder light.

Hence, **quantum confinement increases the band gap of semiconductors.**

31. For a given metal ion, the correct order of the nephelauxetic effect of ligands is

(en = ethylenediamine)

1. CN^->en> NH_3> I^-
2. I^-> CN^-> NH_3>en
3. CN^-> I^->en> NH_3
4. I^-> CN^->en> NH_3

Answer: (4) I^-> CN^->en> NH_3

Explanation:

The **nephelauxetic effect** refers to the reduction in interelectronic repulsion (Racah parameter B) in a complex compared to the free metal ion. It is related to the covalent character of the metal–ligand bond — the higher the covalent character, the greater the nephelauxetic effect.

For a given metal ion, ligands having higher polarizability and ability to donate electron density show a greater effect.

The typical order of nephelauxetic effect for common ligands is:

I^-> Br^-> Cl^-> F^-> CN^->en> NH_3> H_2O.

Thus, **I^-> CN^->en> NH_3** is the correct order.

32. Nanoparticles have length scales

1. between 0.1 to 1000 nm in any dimension

2. in any nanometer scale and always in one particular dimension
3. between 1 to 500 nm and always in one particular dimension
4. between 1 to 100 nm in any dimension

Answer: (4) between 1 to 100 nm in any dimension

Explanation:

The term "nanoparticle" refers to materials having structural features in the **nanoscale range**, i.e., **1–100 nanometers (nm)** in at least one dimension.

- Below 1 nm, materials fall into the molecular or atomic scale.
- Above 100 nm, quantum size effects disappear, and bulk properties dominate.
  Thus, nanoparticles have **dimensions between 1 and 100 nm**, and this applies to any dimension—length, width, or thickness.

33. The correct statement is

(en = ethylenediamine)

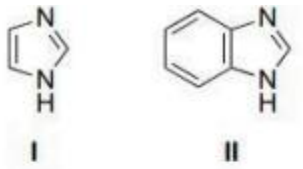
1. $K_3[CuF_6]$ is paramagnetic and sodium nitroprusside is diamagnetic
2. Both $K[AgF_4]$ and $K_3[CuF_6]$ are diamagnetic
3. Both $[Co(en)_3]Cl_3$ and $K_3[CuF_6]$ are paramagnetic
4. Sodium nitroprusside is paramagnetic and $[Co(en)_3]Cl_3$ is diamagnetic

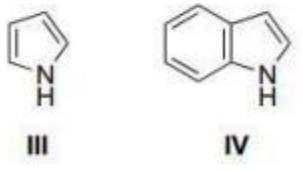
Answer: (1) $K_3[CuF_6]$ is paramagnetic and sodium nitroprusside is diamagnetic

Explanation:

- In **$K_3[CuF_6]$**, Cu is in the +3 oxidation state ($3d^8$ configuration). In an octahedral field with weak ligand F^-, pairing is incomplete, giving two unpaired electrons — hence **paramagnetic**.
- In **sodium nitroprusside $[Fe(CN)_5NO]^{2-}$**, Fe is in +2 oxidation state ($3d^6$) and forms a strong-field low-spin complex (all electrons paired), making it **diamagnetic**.
  Thus, $K_3[CuF_6]$ → paramagnetic, sodium nitroprusside → diamagnetic.

34. The correct option for the pKa of the following compounds is





1. I > II and III > IV
2. I > II and IV > III
3. II > I and III > IV
4. II > I and IV > III

Answer: (1) I > II and III > IV

Explanation:

- **Imidazole (I)** is more basic (higher pKa) than **benzimidazole (II)** because benzimidazole's conjugate acid is stabilized by the extended aromatic system, making it easier to deprotonate.
- **Pyrrole (III)** is more basic than **indole (IV)**; in indole, the nitrogen lone pair is delocalized into the aromatic ring, reducing availability for protonation.

  Hence, pKa order: **I > II** and **III > IV**.

35. For the reaction of RBr with EtONa/EtOH, the correct match for the R groups in Column P with the relative rates in Column Q is

(for R = CH_3CH_2, relative rate = 1)

Column P	**Column Q**
A. CH_3	i. 4.2×10^{-6}
B. $CH_3CH_2CH_2$	ii. 0.03
C. $(CH_3)_2CHCH_2$	iii. 0.28
D. $(CH_3)_3CCH_2$	iv. 17

1. A – iv; B – iii; C – ii; D – i
2. A – iv; B – i; C – iii; D – ii
3. A – iii; B – ii; C – iv; D – i
4. A – ii; B – iii; C – i; D – iv

Answer: (1) A – iv; B – iii; C – ii; D – i

Explanation:

The reaction occurs via an **E2 (bimolecular elimination)** or **SN2 mechanism**, depending on steric hindrance.

The given base EtONa in EtOH favors **E2 elimination**, and the rate depends on the structure of the alkyl halide:

- **CH_3Br (A)**: unhindered, fastest reaction (rate = 17).
- **$CH_3CH_2CH_2Br$ (B)**: primary, moderate rate (≈ 0.28).
- **$(CH_3)_2CHCH_2Br$ (C)**: secondary, slower (≈ 0.03).
- **$(CH_3)_3CCH_2Br$ (D)**: tertiary, highly hindered, slowest (≈ 4.2×10^{-6}).

  Hence, matching: **A–iv, B–iii, C–ii, D–i.**

36. The following reaction occurs under

1. photochemical conditions via a disrotatory ring-opening
2. photochemical conditions via a conrotatory ring-opening
3. thermal conditions via a disrotatory ring-opening
4. thermal conditions via a conrotatory ring-opening

Answer: (4) thermal conditions via a conrotatory ring-opening

Explanation:

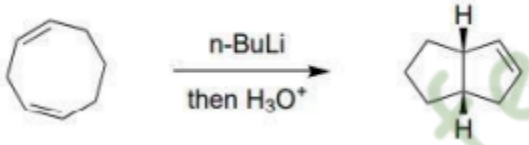
This reaction involves the ring-opening of **cyclobutene** to form **butadiene**.

According to the **Woodward–Hoffmann rules**, for electrocyclic reactions:

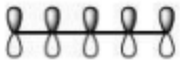
- Under **thermal conditions**, a system with **4n π-electrons** undergoes **conrotatory** motion.
- Under **photochemical conditions**, the same system undergoes **disrotatory** motion.

  Since the cyclobutene ring-opening involves 4 π-electrons and occurs thermally, it proceeds via a **conrotatory** mechanism.

37. The HOMO of the intermediate involved in the following reaction is

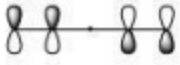


1.

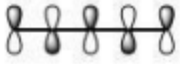


2.

3.



4.



Answer: (2) (the diagram with the proper orbital phase for cyclooctatetraenyl anion)

Explanation:

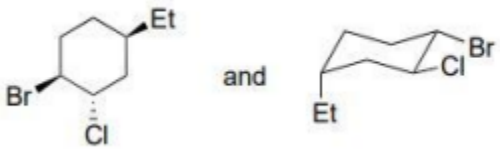
When **cyclooctatetraene** reacts with **n-BuLi**, it forms the **cyclooctatetraenyl dianion ($C_8H_8^{2-}$)**, which has **10 π-electrons**.

This species satisfies the **Hückel rule (4n+2)** with n = 2, indicating aromaticity.

The HOMO corresponds to the **ψ_4 molecular orbital** of the π-system, which shows **four bonding and four antibonding interactions** with proper delocalization and alternating phases.

Therefore, the correct HOMO is the second diagram (option 2), consistent with the aromatic stabilization of the intermediate.

38. The following structures are



1. identical
2. enantiomers
3. diastereomers
4. constitutional isomers

Answer: (1) identical

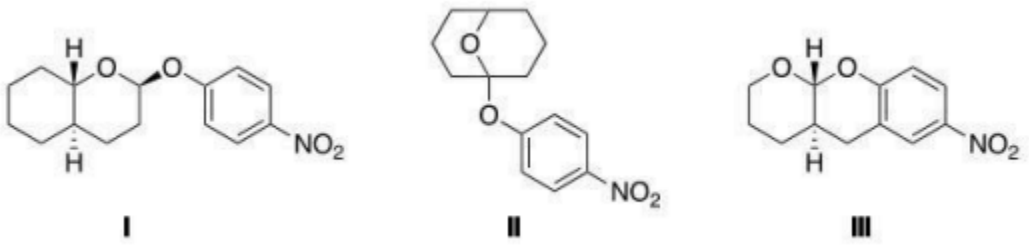
Explanation:

Both given structures are chair conformations of **the same trans-1-bromo-3-chloro-5-ethylcyclohexane molecule**.

The wedge and dash indicate the same relative stereochemistry when converted between chair forms—they represent the same spatial arrangement viewed differently.

Hence, they are not mirror images (enantiomers) or different connectivities (constitutional isomers) but **identical** molecules.

39. The correct order for the rate of acidic hydrolysis of the following cyclic acetals is



I II III

1. III > II > I

2. I > III > II
3. I > II > III
4. II > I > III

Answer: (2) I > III > II

Explanation:

The rate of **acid-catalyzed acetal hydrolysis** depends on the stability of the carbocation-like transition state formed during protonation and cleavage of the C–O bond.

- Compound **I** forms a more stable benzylic intermediate due to strong resonance stabilization.
- Compound **III** is also stabilized but to a lesser extent because of reduced conjugation.
- Compound **II** has minimal stabilization due to its aliphatic cyclic structure.

  Therefore, the hydrolysis rate decreases in the order **I > III > II**.

40. The correct order for the relative rate of addition of *CCl_3 to 2-methylpropene (A), styrene (B), and 2-methylbut-2-ene (C) is

1. A > B > C
2. B > A > C
3. B > C > A
4. C > B > A

Answer: (2) B > A > C

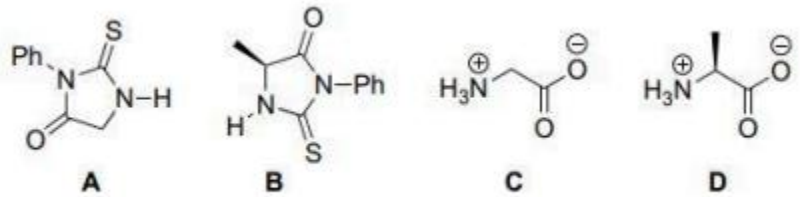
Explanation:

The addition of **trichloromethyl radical (CCl_3)* follows a radical mechanism. The rate depends on the stability of the intermediate carbon radical formed after addition.

- In **styrene (B)**, the intermediate radical is **benzylic**, which is highly stabilized by resonance.
- In **2-methylpropene (A)**, the radical is **tertiary**, moderately stable.
- In **2-methylbut-2-ene (C)**, steric hindrance reduces the rate despite possible stabilization.

  Hence, the order of reactivity is **B (styrene) > A (2-methylpropene) > C (2-methylbut-2-ene).**

41. The reaction of dipeptide, $H_2N–Gly–Ala–CO_2H$, with PhNCS at pH 8 followed by treatment with CF_3CO_2H produces



1. A and D
2. B and C
3. A and B
4. C and D

Answer: (1) A and D

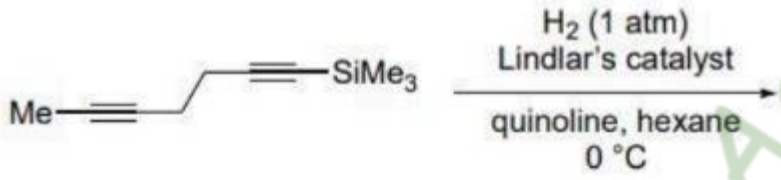
Explanation:

At pH 8, the amino group of the dipeptide reacts with **phenyl isothiocyanate (PhNCS)** to form a **phenylthiocarbamoyl derivative** (structure A).

Subsequent treatment with **trifluoroacetic acid (CF_3CO_2H)** cleaves the peptide at the N-terminal amino acid, producing an **anilinothiazolinone derivative** that converts to the stable **phenylthiohydantoin derivative (D)**.

This is the **Edman degradation** reaction, used for determining the N-terminal amino acid in peptides.

42. The major product formed in the following reaction is

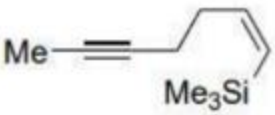


1.

2.

3.

4.



Answer: (3) partial reduction product (cis-alkene)

Explanation:

Lindlar's catalyst (Pd on $CaCO_3$ poisoned with Pb and quinoline) selectively reduces **alkynes to cis-alkenes**.

In this case, the terminal alkyne is hydrogenated to a **cis-alkene** without affecting the remaining triple bond. The product has **Z-geometry** (same-side substitution) and retains the $SiMe_3$ protecting group intact, consistent with option 3.

43. In the ^1H NMR, the methylene protons of $ClCH_2–C(Cl)(Br)CH_3$ (X) and $CH_3CH_2–C(Cl_2)CH_3$ (Y) appear as

1. X = Y = AB quartet
2. X = Y = quartet
3. X = AB quartet; Y = quartet
4. X = quartet; Y = AB quartet

Answer: (3) X = AB quartet; Y = quartet

Explanation:

In compound **X**, the methylene hydrogens are **diastereotopic** because they are adjacent to asymmetric carbon centers (C with Cl and Br). Thus, they are non-equivalent and show an **AB quartet** pattern.

In compound **Y**, both hydrogens are equivalent since they are on a symmetrical CH_2 group next to identical Cl substituents, giving a **simple quartet** pattern due to coupling with the neighboring CH_3 group.

44. The steps involved in the reaction of acetaldehyde with formaldehyde in the presence of NaOH to produce pentaerythritol [$C(CH_2OH)_4$] are

1. Claisen condensation followed by Knoevenagel condensation
2. Cannizzaro reaction followed by Claisen condensation
3. Knoevenagel condensation followed by aldol reactions
4. Aldol reactions followed by Cannizzaro reaction

Answer: (4) Aldol reactions followed by Cannizzaro reaction

Explanation:

Under basic conditions, **acetaldehyde** undergoes **aldol condensation** with **formaldehyde**, forming polyhydroxylated intermediates.

Formaldehyde then undergoes **disproportionation (Cannizzaro reaction)** in the presence of NaOH, producing **methanol and formate**, which further reduces aldehydic groups to alcohols.

This leads to formation of **pentaerythritol ($C(CH_2OH)_4$)** through a combination of these two reactions: first **aldol**, then **Cannizzaro**.

45. The correct order for the X–H bond dissociation energies (BDE) in the following compounds is

1. $Me_3Si–H > Me_3C–H > Me_3Sn–H$
2. $Me_3C–H > Me_3Si–H > Me_3Sn–H$

3. $Me_3C–H > Me_3Sn–H > Me_3Si–H$
4. $Me_3Sn–H > Me_3C–H > Me_3Si–H$

Answer: (2) $Me_3C–H > Me_3Si–H > Me_3Sn–H$

Explanation:

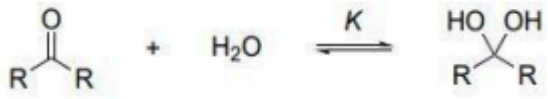
Bond dissociation energy (BDE) decreases down Group 14 due to increasing atomic size and decreasing bond overlap.

The **C–H bond** is the strongest because carbon is small and forms strong σ-overlap with hydrogen.

The **Si–H bond** is weaker due to poorer overlap, and the **Sn–H bond** is the weakest because tin is larger, leading to diffuse orbitals.

Thus, BDE order: **C–H > Si–H > Sn–H**.

46. For the following equilibrium, the correct match for the carbonyl compounds in Column P with the equilibrium constant K in Column Q is



Column P	Column Q
A. CH_3CHO	i. 1.2×10^6
B. Cl_3CCHO	ii. 1.06
C. $CF_3C(O)CF_3$	iii. 200

1. A = iii; B = ii; C = i
2. A = ii; B = iii; C = i
3. A = i; B = iii; C = ii
4. A = i; B = ii; C = iii

Answer: (2) A = ii; B = iii; C = i

Explanation:

Hydration of carbonyl compounds depends on the **electrophilicity of the carbonyl carbon**: more electron-withdrawing substituents increase hydration.

- **$CF_3C(O)CF_3$** (highly electron-withdrawing) forms the hydrate most readily, giving the largest K (1.2×10^6).
- **Cl_3CCHO** is moderately electrophilic, with K ≈ 200.
- **CH_3CHO** is the least electrophilic, with K ≈ 1.06.

  Hence the correct matching is **A = ii; B = iii; C = i**.

47. For an electron in a hydrogen atom, with azimuthal quantum number l = 1 and magnetic quantum number m = 1, the angle (in degrees) between the z-axis and the orbital angular momentum vector is

1. 0
2. 45
3. 54.7
4. 90

Answer: (2)

Explanation:

The angle θ between the total orbital angular momentum (L) and its z-component (Lz) is given by $\cos\theta = m / \sqrt{l(l+1)}$.

Substituting l = 1 and m = 1, we get $\cos\theta = 1/\sqrt{2}$, hence θ = 45°.

Therefore, the orbital angular momentum vector makes an angle of 45° with the z-axis.

48. In a 3-dimensional isotropic harmonic oscillator, the degeneracy of the state with energy equal to (9/2)ħω is [ω is the angular frequency]

1. 3
2. 9
3. 6
4. 10

Answer: (4)

Explanation:

For a 3D isotropic harmonic oscillator, the total energy is $E = (n_x + n_y + n_z + 3/2)\hbar\omega$.

Given $E = (9/2)\hbar\omega$, so $n_x + n_y + n_z = 3$.

The number of non-negative integer solutions of $n_x + n_y + n_z = 3$ is $(n+1)(n+2)/2 = (4\times5)/2 = 10$.

Hence, the degeneracy of the state is 10.

49. The number of D and P terms that arise from p^3 electronic configuration of an atom, respectively, are

1. 3 and 2
2. 2 and 3
3. 2 and 2
4. 1 and 1

Answer: (4)

Explanation:

For p^3 configuration, the possible term symbols are ^4S, ^2D, and ^2P.

Hence there is only one D term (^2D) and one P term (^2P).

Therefore, the number of D and P terms arising from p^3 configuration are 1 and 1 respectively.

50. The lowest energy π-MO of butadiene has an energy of [β is resonance energy]

1. -1.6180β
2. -0.6180β
3. 0.6180β
4. 1.6180β

Answer: (4)

Explanation:

For conjugated systems, energies of π molecular orbitals are given by $E = \alpha + 2\beta\cos(\pi i/(n+1))$.

For butadiene ($n = 4$), $E_1 = \alpha + 2\beta\cos(\pi/5)$.

$\cos(\pi/5) = 0.809$, so $E_1 = \alpha + 1.618\beta$.

Since β is negative, this corresponds to the lowest energy orbital having magnitude 1.618β.

Therefore, the correct answer is 1.6180β.

51. Product of two reflection operations σvσv' is equivalent to

1. i
2. Cn
3. σh
4. σd

Answer: (2)

Explanation:

The product of two vertical planes of symmetry (σv and σv') in a molecule results in a rotation operation about the principal axis. Therefore, σvσv' = Cn. For example, in C2v symmetry, the product of σv and σv' gives C2 rotation.

52. The rotational quantum number associated with the most intense transition in the microwave spectrum of a diatomic molecule varies with temperature (T) as

1. T
2. $\sqrt{T}$
3. T^2
4. $1/\sqrt{T}$

Answer: (2)

Explanation:

The most populated rotational level Jmax is given by Jmax ≈ √(kT / 2Bhc), where B is the rotational constant. Since Jmax is proportional to √T, the rotational quantum number corresponding to the most intense transition varies as √T with temperature.

53. At T = 0 K, the entropy (in J K^{-1}) of 2 moles of CO is closest to

1. 0
2. 5.76
3. 11.53
4. 23.05

Answer: (3)

Explanation:

Carbon monoxide (CO) is a heteronuclear diatomic molecule but exhibits residual entropy due to disorder caused by the random orientation of C and O atoms in the crystal. Residual entropy = R ln 2 per mole = 5.76 J K^{-1} mol^{-1}. For 2 moles, S = 2 × 5.76 = 11.52 ≈ 11.53 J K^{-1}.

54. A two-level system consists of a double degenerate excited state which is ε energy above the ground state. The y-intercept of the ln(Pe/Pg) vs 1/T plot is (Pe and Pg are the probabilities associated with the excited and ground states respectively)

1. 0
2. 2
3. 2 ln 2
4. ln 2

Answer: (4)

Explanation:

From the Boltzmann distribution, Pe/Pg = (ge/gg) exp(−ε/kT). Taking logarithm, ln(Pe/Pg) = ln(ge/gg) − ε/(kT). The y-intercept equals ln(ge/gg). Since the excited state is double degenerate (ge = 2, gg = 1), intercept = ln 2.

55. The ionic strength (in mol kg^{-1}) of an aqueous solution of 0.03 mol kg^{-1} $K_3[Fe(CN)_6]$ is closest to

1. 0.27
2. 0.18
3. 0.12
4. 0.15

Answer: (2)

Explanation:

$K_3[Fe(CN)_6]$ dissociates as $3K^+ + [Fe(CN)_6]^{3-}$. Ionic strength $I = \frac{1}{2}\Sigma m_i z_i^2 = \frac{1}{2}[(0.09\times1^2) + (0.03\times9)] = \frac{1}{2}(0.09 + 0.27) = 0.18$ mol kg^{-1}. Hence, the ionic strength is approximately 0.18 mol kg^{-1}.

56. The half-lives for the forward and reverse reactions that are first order in both directions are 24 ms and 39 ms, respectively. The relaxation time for return to equilibrium after a temperature jump is closest to

1. 21 ms
2. 32 ms
3. 43 ms
4. 11 ms

Answer: (1)

Explanation:

For reversible first-order reactions $A \rightleftharpoons B$, the relaxation time τ is given by $1/\tau = kf + kr$.

Since $k = 0.693 / t1/2$,

$kf = 0.693 / 24 = 0.0289$ ms^{-1} and $kr = 0.693 / 39 = 0.0178$ ms^{-1}.

So, $1/\tau = 0.0467 \rightarrow \tau = 21.4$ ms$\approx$ 21 ms.

57. Consider the statements:

a. Decomposition of H_2O_2 in aqueous solution catalyzed by bromide ion is a homogeneous catalytic reaction.

b. Hydrogenation of ethene to ethane accelerated by Pd or Ni particles is a heterogeneous catalytic reaction.

c. Enzymes increase the equilibrium constants of the reactions.

d. Turnover number is the number of catalytic cycles till the catalyst becomes inactive.

The set of correct statements is

1. a, b and c only
2. b, c and d only
3. a, b and d only
4. c, d and a only

Answer: (3)

Explanation:

Statement (a) is correct because both H_2O_2 and Br^- are in the same aqueous phase (homogeneous catalysis).

Statement (b) is correct since metal catalysts (Pd, Ni) act on the surface (heterogeneous catalysis).

Statement (c) is wrong because enzymes alter reaction rates, not equilibrium constants.

Statement (d) is correct because turnover number indicates the number of substrate molecules converted per active site before deactivation.

58. The radii of the cation and anion of an ionic compound are 74 pm and 170 pm, respectively. The coordination number of the cation and the best possible geometry of the compound are, respectively

1. 4, tetrahedral
2. 6, octahedral
3. 8, cubic
4. 4, square planar

Answer: (2)

Explanation:

Radius ratio = rc/ra = 74 / 170 = 0.435.

For octahedral geometry, the ratio range is 0.414–0.732, which fits this value.

Hence, the coordination number is 6, and the geometry is octahedral.

59. Correct statement about polymerization is

1. The average molar mass of the polymer product does not depend upon the time length of stepwise polymerization.
2. The slower the initiation of the chain, the higher the average molar mass of the polymer in chain polymerization.
3. In chain polymerization, an activated monomer attacks a minimum of three other monomers to link.
4. The average chain length of a polymer in stepwise polymerization is linearly dependent on the fraction of the reacted monomers.

Answer: (2)

Explanation:

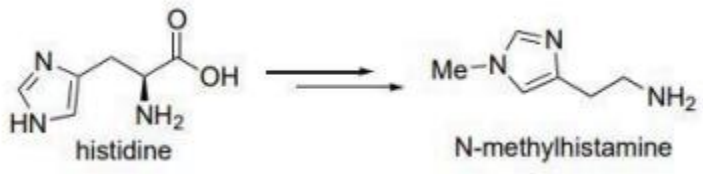
In chain polymerization, rapid propagation but slow initiation leads to fewer growing chains and therefore higher molecular weight polymers.

Statement (1) is incorrect as time affects conversion in stepwise polymerization.

Statement (3) is incorrect as a monomer links to one growing chain, not three.

Statement (4) applies to stepwise polymerization but not here.

60. The co-enzymes involved in the following biosynthesis are



A. Pyridoxal phosphate (PLP)

B. S-Adenosylmethionine (SAM)

C. Pyridoxamine phosphate (PMP)

D. Adenosine triphosphate (ATP)

1. A and B
2. B and C
3. C and D
4. A and D

Answer: (1)

Explanation:

The conversion of histidine to N-methylhistamine involves decarboxylation (catalyzed by PLP) followed by methylation (using SAM as the methyl donor). Hence, both PLP and SAM act as coenzymes in this biosynthesis.

61) Consider the following reactions

A. $SbCl_5 + AlCl_3 \rightarrow [AlCl_4]^- [SbCl_4]^+$

B. $AsF_3 + SbF_5 \rightarrow [AsF_2]^+ [SbF_6]^-$

C. $NOF + SbF_5 \rightarrow [NO]^+ [SbF_6]^-$

D. $HF + SbF_5 \rightarrow [SbF_4]^+ [HF_2]^-$

The correct option is

1. A and B only
2. B and C only
3. C and D only
4. A and D only

Answer: (2) – B and C only

Explanation:

SbF_5 is a very strong Lewis acid because fluorine stabilizes high oxidation states and increases electrophilicity at Sb.

(B) $AsF_3 + SbF_5$ forms $[AsF_2]^+ [SbF_6]^-$ through a Lewis acid–base reaction where AsF_3 donates a lone pair.

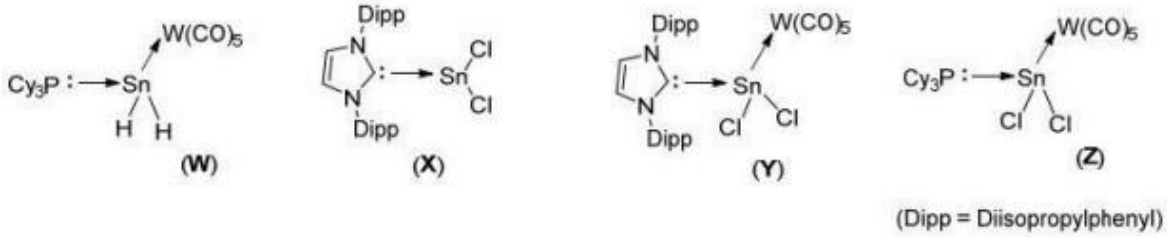
(C) $NOF + SbF_5$ yields $[NO]^+ [SbF_6]^-$, a well-known nitrosoniumhexafluoroantimonate.

(A) $SbCl_5 + AlCl_3$ does not proceed, as both are Lewis acids.

(D) $HF + SbF_5$ produces $[H_2F]^+ [SbF_6]^-$, not $[SbF_4]^+ [HF_2]^-$.

Hence, only B and C are correct.

62) The correct option of the Isomer Shifts in ^{119}Sn Mössbauer spectra for the following compounds is:



1. Z > Y
2. W > Y
3. Y > X
4. W > X

Answer: (2) – W > Y

Explanation:

In ^{119}Sn Mössbauer spectroscopy, the isomer shift (δ) depends on the s-electron density at the tin nucleus.

Higher electron density → higher δ value.

(W) has Sn–H bonds that donate electron density, making tin more electron-rich.

(Y) has Sn–Cl and $W(CO)_5$ groups that withdraw electrons, lowering the δ value.

Therefore, W > Y.

63) Consider the moieties in the enzymes that engage in hydrogen bonding with the substrates.

Enzymes →	**Haemoglobin**	**Nickel–superoxide dismutase**	**[FeFe] hydrogenase**	**Hemerythrin**
A	tyrosine	μ-hydroxo	histidine	aza(dithiolate)
B	histidine	μ-hydroxo	aza(dithiolate)	tyrosine
C	histidine	tyrosine	aza(dithiolate)	μ-hydroxo
D	μ-hydroxo	aza(dithiolate)	histidine	tyrosine

The correct option is

1. A
2. B
3. C
4. D

Answer: (3) – C

Explanation:

Haemoglobin uses histidine residues (proximal and distal His) for O_2 binding and stabilization.

Nickel–superoxide dismutase employs tyrosine residues and nickel centers for hydrogen bonding with superoxide.

[FeFe] hydrogenase utilizes aza(dithiolate) bridges to shuttle protons.

Hemerythrin contains μ-hydroxo bridges between its iron centers.

Thus, the correct correspondence is in row C.

64) Consider the reactions in List I and related enzymes in List II.

List I		**List II**
a	superoxide → oxygen	i – amine oxidase
b	hydrolysis of peptide	ii – Ni-superoxide dismutase
c	hydroxylation of camphor	iii – carboxypeptidase
d	primary amine → aldehyde	iv – cytochrome P450

The option showing the correct match is:

1. a-ii, b-iii, c-iv, d-i
2. a-iv, b-i, c-ii, d-iii
3. a-iii, b-ii, c-i, d-iv
4. a-ii, b-iii, c-iv, d-iii

Answer: (1) – a-ii, b-iii, c-iv, d-i

Explanation:

(a) Superoxide → O_2 is catalyzed by Ni-superoxide dismutase (ii).

(b) Hydrolysis of peptides is catalyzed by carboxypeptidase (iii), a Zn metalloenzyme.

(c) Hydroxylation of camphor occurs by cytochrome P450 (iv), a heme monooxygenase.

(d) Primary amine → aldehyde conversion occurs by amine oxidase (i), containing Cu or FAD.

Thus, the correct match is a-ii, b-iii, c-iv, d-i.

65) Given are the statements regarding the overall stability constants (log β) for the formation of $[M(en)_3]^{2+}$ and $[M(EDTA)]^{2-}$ (en = ethylenediamine, EDTA = ethylenediaminetetraacetate), where M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}.

A. The log β is lowest for Mn^{2+} in both $[M(en)_3]^{2+}$ and $[M(EDTA)]^{2-}$ series (Mn^{2+}→ Zn^{2+}).

B. The log β value for $[Mn(EDTA)]^{2-}$ is lower than $[Mn(en)_3]^{2+}$.

C. The log β values increase in the series (Mn^{2+}→ Zn^{2+}) for both EDTA and en complexes.

D. ΔS° remains nearly constant along the series.

The option with the correct statements is:

1. B and C only
2. A, B and D only
3. A and D only
4. A, B and C only

Answer: (3) – A and D only

Explanation:

(A) True – Mn^{2+} forms the least stable complexes due to low crystal field stabilization energy and large ionic radius.

(B) False – $[Mn(EDTA)]^{2-}$ is more stable than $[Mn(en)_3]^{2+}$ because EDTA forms stronger chelates.

(C) False – Although stability increases $Mn^{2+} \rightarrow Zn^{2+}$, Cu^{2+} shows an anomalous maximum (Jahn–Teller effect).

(D) True –$\Delta S°$ remains nearly constant because the number of particles involved is similar across the series.

Hence, A and D only are correct.

66) To an aqueous solution of NaX and NaY, the addition of sulphamic acid (H_2NSO_3H) followed by acidification releases a nitrogen-containing gas P. Addition of KI and a starch solution does not yield a blue color, indicating complete removal of NaX. However, the blue color appears when a piece of granulated Zn is added. The reaction proceeds with the evolution of a nitrogen-containing gas Q.

The correct option of X, Y, P and Q, respectively, is

1. $[NO_2]^-$, $[NO_3]^-$, N_2, NO
2. $[NO_3]^-$, $[NO_2]^-$, N_2, NO
3. $[NO_3]^-$, $[NO_2]^-$, NO, N_2
4. $[NO_2]^-$, $[NO_3]^-$, NO, N_2

Answer: (1) – $[NO_2]^-$, $[NO_3]^-$, N_2, NO

Explanation:

Sulphamic acid reacts with nitrite ions to produce nitrogen gas:

$NH_2SO_3H + HNO_2 \rightarrow N_2 + H_2SO_4 + H_2O$.

Since the reaction releases N_2, NaX corresponds to $NaNO_2$. The absence of blue color with KI-starch shows no oxidizing agent (no nitrate reduction). When Zn is added, nitrate ($NaNO_3$) is reduced to nitrite, which then reacts with sulphamic acid to produce N_2 and NO gases. Thus, X = NO_2^-, Y = NO_3^-, P = N_2, Q = NO.

67) List I and List II give the molecular formula and the geometry of the species, respectively.

List I		**List II**
a	$[Zn\{N(CH_2CH_2NH_2)_3\}Cl]^+$	i – Trigonal bipyramidal
b	$[Cu(2,2\text{-bpy})\{NH(CH_2COO)_2\}]$	ii – Square pyramidal
c	$[ZrF_7]^{3-}$	iii – Monocapped trigonal prism
d	$[AgTe_7]^{3-}$	iv – Trigonal planar

The option showing the correct match of species in List I and metal geometry in List II is

1. a-i, b-ii, c-iii, d-iv

2. a-i, b-ii, c-iv, d-iii
3. a-i, b-iii, c-ii, d-iv
4. a-ii, b-i, c-iii, d-iv

Answer: (1) – a-i, b-ii, c-iii, d-iv

Explanation:

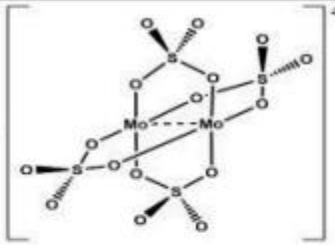
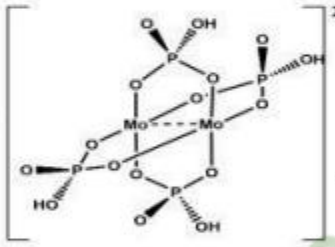
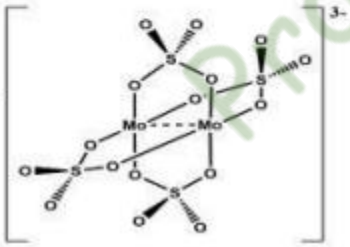
(a) $[Zn\{N(CH_2CH_2NH_2)_3\}Cl]^+$ has five-coordinate Zn(II) giving a trigonal bipyramidal geometry.

(b) $[Cu(2,2\text{-bpy})\{NH(CH_2COO)_2\}]$ is a five-coordinate Cu(II) complex with a square-pyramidal arrangement due to Jahn–Teller distortion.

(c) $[ZrF_7]^{3-}$ typically exhibits a monocapped trigonal prism geometry for seven-coordination.

(d) $[AgTe_7]^{3-}$ possesses three-coordinate Ag(I) with a trigonal planar geometry.

68) Consider the following complexes:

Complex	Configuration	M-M Bond order
a. 	i. $\sigma^2\pi^4$	p. 3
b. 	ii. $\sigma^2\pi^4\delta^1$	q. 4
c. 	iii. $\sigma^2\pi^4\delta^2$	r. 3.5

The option showing complexes with their correct electronic configuration and bond order is

1. a-iii-q; b-i-p; c-ii-r
2. a-i-p; b-iii-r; c-ii-q
3. a-ii-r; b-iii-q; c-i-p
4. a-ii-q; b-i-r; c-iii-p

Answer: (1) – a-iii-q; b-i-p; c-ii-r

Explanation:

In metal–metal bonded molybdenum carboxylates, the bond order corresponds to the total number of bonding electrons in σ, π, and δ orbitals.

(a) $[Mo_2(O_2CCH_3)_4]^{4-}$ exhibits $\sigma^2\pi^4\delta^2$ with bond order 4.

(b) $[Mo_2(O_2CCH_3)_4(H_2O)_2]^{2+}$ has $\sigma^2\pi^4$ configuration with bond order 3.

(c) $[Mo_2(O_2CCH_3)_4(OH)_2]^{3-}$ exhibits $\sigma^2\pi^4\delta^1$ configuration with bond order 3.5.

Hence, the matching corresponds to a-iii-q; b-i-p; c-ii-r.

69) In the extraction of lanthanides, when an aqueous solution of Ln^{3+} is poured into a cation exchange resin column, the Ln^{3+} that moves fastest through the resin is

1. Lu^{3+}
2. La^{3+}
3. Gd^{3+}
4. Sm^{3+}

Answer: (1) – Lu^{3+}

Explanation:

Lanthanide contraction leads to decreasing ionic radius from La^{3+} to Lu^{3+}. Smaller ions like Lu^{3+} have higher charge density and stronger binding to the resin but are also more easily displaced by eluents during chromatographic separation. Thus, Lu^{3+} passes through the resin column faster than the others.

70) Assuming the molecules are static, the ^{19}F NMR spectra of ClF_3 (X) and ClF_5 (Y) consist of

1. X: doublet and triplet; Y: singlet
2. X: singlet; Y: singlet
3. X: doublet and triplet; Y: doublet and quintet
4. X: singlet; Y: triplet and quartet

Answer: (3) – X: doublet and triplet; Y: doublet and quintet

Explanation:

ClF_3 has a T-shaped structure with two equivalent equatorial fluorine atoms and one axial fluorine, giving rise to two fluorine environments—hence a doublet and a triplet pattern in ^{19}F NMR.

ClF_5 is square pyramidal, having four equivalent equatorial and one axial fluorine atom, producing two environments (4:1 ratio) resulting in a doublet and a quintet.

71) A molybdenum compound A is obtained by the CO displacement reaction of $Mo(CO)_6$ with P^iPr_3. A reacts with H_2 to give compound B. Compounds A and B are

1. $[Mo(P^iPr_3)_6]$ and $[Mo(P^iPr_3)_5(\eta^2\text{-}H_2)]$

2. $[Mo(CO)_3(P^iPr_3)_2]$ and $[Mo(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)]$
3. $[Mo(CO)_3(P^iPr_3)_3]$ and $[Mo(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)]$
4. $[Mo(CO)_4(P^iPr_3)_2]$ and $[Mo(CO)_4(P^iPr_3)(H)_2]$

Answer: (2) – $[Mo(CO)_3(P^iPr_3)_2]$ and $[Mo(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)]$

Explanation:

CO substitution reactions of $Mo(CO)_6$ with bulky tertiary phosphines like P^iPr_3 typically produce five- or six-coordinate complexes. The product $[Mo(CO)_3(P^iPr_3)_2]$ retains an 18-electron count. When H_2 is added, a dihydrogen ligand (η^2-H_2) binds without breaking the Mo–H bond, yielding $[Mo(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)]$. The formation of such η^2-H_2 complexes is characteristic of d^6 Mo(0) systems with strong π-acceptor ligands like CO and bulky phosphines.

72) A chromium carbonyl compound $Cr(CO)_6$ reacts with $NaBH_4$ to give A. The Lewis base A reacts with another molecule of $Cr(CO)_6$ to form compound B with the release of CO. In another reaction, compound A reacts with BH_3 to produce C. Compounds A, B and C, respectively, are

1. $[Cr(CO)_5(BH_4)]^-$, $[(CO)_5Cr(BH_4)–Cr(CO)_5]$ and $[Cr(CO)_4B_2H_7]^-$
2. $[Cr(CO)_5H]^-$, $[(CO)_5Cr–H–Cr(CO)_5]$ and $[Cr(CO)_4B_2H_7]^-$
3. $[Cr(CO)_5(BH_4)]^-$, $[(CO)_5Cr–BH_4–Cr(CO)_5]$ and $[Cr(CO)_5BH_4]^-$
4. $[Cr(CO)_5H]^-$, $[(CO)_4Cr–H–Cr(CO)_6]^-$ and $[Cr(CO)_5BH_4]^-$

Answer: (2) – $[Cr(CO)_5H]^-$, $[(CO)_5Cr–H–Cr(CO)_5]$ and $[Cr(CO)_4B_2H_7]^-$

Explanation:

Reduction of $Cr(CO)_6$ by $NaBH_4$ leads to hydride formation via substitution of one CO ligand, producing the hydride complex $[Cr(CO)_5H]^-$ (compound A). The hydride bridges two $Cr(CO)_5$ units to form a dimeric species $[(CO)_5Cr–H–Cr(CO)_5]$ (compound B). Reaction of the hydride with BH_3 forms a boron-bridged species $[Cr(CO)_4B_2H_7]^-$ (compound C). These transformations illustrate classic metal hydride and borane chemistry of low-valent carbonyl complexes.

73) Consider the following statements regarding the electronic spectra of lanthanide complexes.

A. They exhibit fewer absorption bands due to a small number of microstates.

B. Their spectra are dependent on coordination number and geometry.

C. Molar extinction coefficients (ε) are smaller compared to transition-metal complexes.

D. Their absorption bands are sharp due to weak vibronic coupling.

E. Ligand field effects are negligible.

The option with correct statements is

1. A, B, D only
2. A, C, D only

3. C, D, E only
4. B, C, E only

Answer: (3) – C, D, E only

Explanation:

Lanthanide (4f-electron) transitions are Laporte- and spin-forbidden, leading to very small molar absorptivities ($\varepsilon \approx 1–10$ L mol^{-1} cm^{-1}). These 4f orbitals are well shielded by 5s and 5p orbitals, causing minimal ligand-field perturbation. Hence, the spectra are nearly independent of geometry and show sharp, well-resolved bands. Thus, statements C, D and E are correct, while A and B are incorrect because lanthanides have many microstates and weak geometry dependence.

74) The ground-state term, Lande factor (g), and calculated magnetic moment (μ_calc) for Pr^{3+} (atomic number = 59) are

1. $^3H_4$, 0.80, 2.68
2. $^3H_4$, 0.80, 3.58
3. $^5I_4$, 1.33, 2.68
4. $^6H_{5/2}$, 1.33, 3.58

Answer: (2) – $^3H_4$, 0.80, 3.58

Explanation:

Pr^{3+} ($4f^2$) has two f-electrons giving S = 1, L = 5 (H term), and hence J = 4. The Lande g factor is calculated using

$g = 1 + [J(J + 1) + S(S + 1) − L(L + 1)] / [2J(J + 1)] = 0.80.$

The magnetic moment is given by $\mu = g\sqrt{[J(J + 1)]} = 0.80 \times \sqrt{20} = 3.58$ BM.

Therefore, the correct combination is $^3H_4$, 0.80, 3.58.

75) Match the correct set of IR bands to the given compounds (Cp = C_5H_5, Cp* = C_5Me_5).

Compound	IR bands (cm^{-1})
a	$Cp_2Ti(CO)_2$
b	$CpCp^*Ti(CO)_2$
c	$Cp^*_2Ti(CO)_2$

1. a-ii, b-iii, c-i
2. a-iii, b-i, c-ii
3. a-i, b-iii, c-ii
4. a-i, b-ii, c-iii

Answer: (4) – a-i, b-ii, c-iii

Explanation:

As the electron-donating ability of cyclopentadienyl ligands increases (Cp <CpCp* < Cp_2*), π-back-bonding from Ti to CO also increases, thereby lowering CO stretching frequencies.*

$Cp_2Ti(CO)_2$ shows the highest ν(CO) values, followed by CpCp$Ti(CO)_2$ and $Cp^*_2Ti(CO)_2$ with the lowest. The correct order of CO-stretching bands (1979 → 1897 → 1930 → 1850 cm^{-1}) matches option 4.

76) Match the given metal species in List I with the corresponding properties in List II.

List I	List II
a. $[Co(H_2O)_6]^{2+}$	i – magnetic moment higher than spin-only value and weak JT distortion
b. $[Cr(H_2O)_6]^{3+}$	ii – spin-only magnetic moment and absence of JT distortion
c. $NiCl_2(PPh_3)_2$	iii – paramagnetic and tetrahedral
d. $Pd(PPh_3)_4$	iv – diamagnetic and tetrahedral

The correct option is

1. a-ii, b-iii, c-i, d-iv
2. a-ii, b-i, c-iv, d-iii
3. a-ii, b-ii, c-iv, d-i
4. a-i, b-ii, c-iii, d-iv

Answer: (4) – a-i, b-ii, c-iii, d-iv

Explanation:

a) $[Co(H_2O)_6]^{2+}$ is a high-spin d^7 complex with an observed magnetic moment slightly higher than the spin-only value due to orbital contribution and shows weak Jahn–Teller distortion.

b) $[Cr(H_2O)_6]^{3+}$ is a d^3 octahedral complex showing purely spin-only magnetic moment and no Jahn–Teller distortion.

c) $NiCl_2(PPh_3)_2$ is tetrahedral, d^8, and paramagnetic.

d) $Pd(PPh_3)_4$ is square planar, d^{10}, and diamagnetic. Hence, the matching is a-i, b-ii, c-iii, d-iv.

77) A mixture of CaO and $CaCO_3$ is analyzed using thermogravimetry (TG) technique. The TG curve of the sample indicates that there is a mass change from 155.2 mg to 125.3 mg. The percentage of $CaCO_3$ in the mixture is close to

1. 54.2%
2. 27.1%
3. 43.8%
4. 29.9%

Answer: (3) – 43.8%

Explanation:

During heating, $CaCO_3$ decomposes to $CaO + CO_2$. The observed mass loss corresponds to CO_2 release.

Mass loss = 155.2 − 125.3 = 29.9 mg.

$M(CaCO_3) = 100\ g\ mol^{-1}$, $M(CO_2) = 44\ g\ mol^{-1}$→ 44% weight loss on decomposition.

Therefore, percentage of $CaCO_3$ = (29.9 ÷ 0.44) ÷ 155.2 × 100 ≈ 43.8%.

78) Consider the following statements regarding the magnetic properties of lanthanide ions.

A. Observed magnetic moments are highly dependent on the ligand field.

B. Only ground J state is populated.

C. Spin–orbit couplings are in the order of ~1000 cm^{-1} while the ligand field effects are only about ~100 cm^{-1}.

D. The spin-only formula cannot be used to calculate the magnetic moment of f^7 configuration.

The option showing the correct statements is

1. A and B only
2. B and C only
3. A and D only
4. C and D only

Answer: (2) – B and C only

Explanation:

In lanthanides, spin–orbit coupling is very strong (~1000 cm^{-1}), dominating over the ligand field (~100 cm^{-1}). Hence, the ground J-multiplet alone is populated. Magnetic moments are largely governed by total angular momentum (J), not ligand field, so statement A is false. The spin-only formula is applicable for half-filled (f^7) ions like Gd^{3+} because L = 0, so D is false. Therefore, B and C are correct.

79) Consider the following reactions

A. $^{210}_{84}\mathrm{Po} \rightarrow {}^{206}_{82}\mathrm{Pb} + \boldsymbol{P}$

B. $\left[{}^{125}_{52}\mathrm{Te}\right]^{*} \rightarrow {}^{125}_{52}\mathrm{Te} + \boldsymbol{Q}$

C. $^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + \boldsymbol{R}$

D. $^{23}_{12}\mathrm{Mg} \rightarrow {}^{23}_{11}\mathrm{Na} + S$

The correct option for P, Q, R and S is

1.	$\mathbf{P} = {}^{4}_{2}He,$	$\mathbf{Q} = \gamma,$	$\mathbf{R} = -{}^{0}_{-1}e,$
2.	$\mathbf{P} = {}^{0}_{1}e,$	$\mathbf{Q} = -{}^{0}_{1}e,$	$\mathbf{S} = {}^{0}_{1}e$
3.	$\mathbf{P} = {}^{0}_{-1}e,$	$\mathbf{Q} = {}^{0}_{1}e,$	$\mathbf{R} = {}^{4}_{2}He,$
4.	$\mathbf{P} = {}^{4}_{2}He$	$\mathbf{Q} = \gamma,$	$\mathbf{S} = {}^{4}_{2}He$
		$\mathbf{R} = {}^{0}_{1}e$	$\mathbf{S} = {}^{0}_{-1}e$

Answer: (1) – P = $^{4}_{2}$He, Q = γ, R = $^{0}_{-1}$e, S = $^{0}_{1}$e

Explanation:

A. $^{210}_{84}Po \rightarrow {}^{206}_{82}Pb + {}^{4}_{2}He$ represents α-decay.

B. $^{125}_{52}Te^{*} \rightarrow {}^{125}_{52}Te + \gamma$ is γ-emission.

C. $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$ is β^- decay.

D. $^{23}_{12}Mg \rightarrow {}^{23}_{11}Na + {}^{0}_{1}e$ is β^+ decay.

Hence, P = α, Q = γ, R = β^-, and S = β^+.

80) The option showing the correct statements about radioactive decay is

A. All radioactive processes are first order.

B. Radioactive decay is dependent on temperature.

C. Activation energy of a radioactive process is zero.

D. The rate of decay depends on the amount of radioactive materials.

1. A, B, and D only
2. A, C, and D only
3. B, C, and D only
4. A, B, and C only

Answer: (2) – A, C, and D only

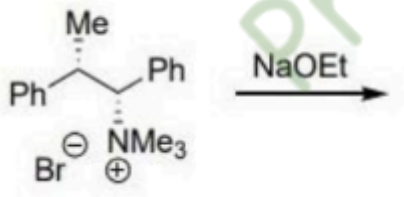
Explanation:

Radioactive decay is a spontaneous nuclear process independent of temperature or catalyst, hence (B) is false.

The decay follows first-order kinetics (A true), and the activation energy is effectively zero (C true).

The decay rate depends on the number of undecayed nuclei present (D true). Therefore, A, C, and D are correct.

81) The conformation of the reactant that gives (E)-1,2-diphenyl-1-propene in the following reaction is



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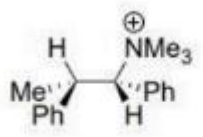

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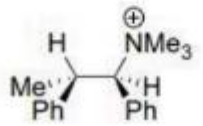

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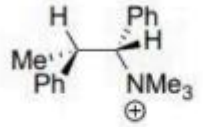

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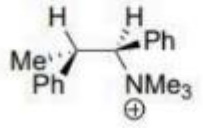
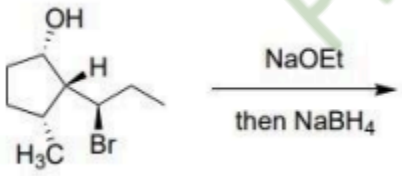


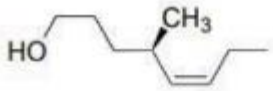
Answer: (3)

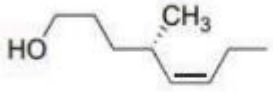
Explanation:

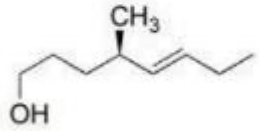
The product is (E)-1,2-diphenyl-1-propene, so the elimination must occur by an anti-periplanar E2 pathway. For an E-alkene, the two large groups (the two phenyls) must end up trans. Therefore, in the reacting conformation, the β-H and the leaving group Br must be anti, and at the same time the two phenyls must become trans after elimination. Among the given Newman-like conformations, structure 3 is the only one where the β-H is anti to Br and the phenyl groups are positioned to give the E-alkene on elimination by NaOEt.

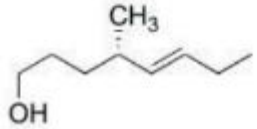
82) The major product formed in the following reaction sequence is



1. 

2. 

3. 

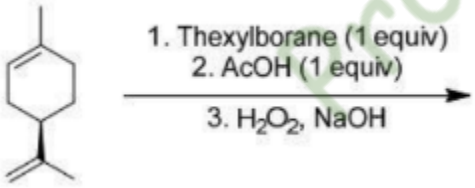
4. 

Answer: (3)

Explanation:

Thexylborane is bulky and adds across the double bond in a hydroboration–oxidation sequence with anti-Markovnikov regiochemistry and syn stereochemistry. Because only 1 equivalent of thexylborane is used, addition occurs at the less hindered face of the double bond to place boron (later OH) at the less substituted carbon. Subsequent oxidation (H_2O_2/NaOH) converts B–C to C–OH with retention. Among the given stereoisomeric alcohols, option 3 corresponds to the anti-Markovnikov, syn-addition product expected from hydroboration–oxidation with a bulky borane.

83) The correct sequence of reagents to effect the following transformation is



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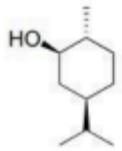

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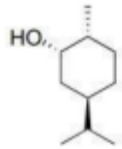

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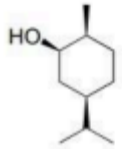

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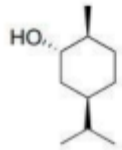


Answer: (1)

Explanation:

The sulfur acetal must first be activated/thermally rearranged (Claisen/allylic-type shift) to place the double bond appropriately (step i, heat). Then the lithium reagent (n-BuLi) deprotonates next to sulfur to form the carbanion, which is alkylated by n-BuBr (step iii). Finally, $HgCl_2/H_2O$ cleaves the thioacetal to the aldehyde. The other orders either try to cleave the thioacetal before installing the new chain or alkylate without prior activation, so they do not give the required aldehyde.

84) The major product formed in the following reaction is

1. 5-bromo product
2. 8-bromo product
3. 4-bromo product
4. 2-bromo product

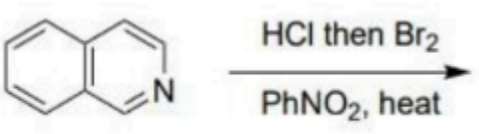
Answer: (2)

Explanation:

Protonation of the nitrogen (HCl) deactivates the pyridine-like ring toward electrophilic substitution but directs incoming electrophiles to the benzene ring fused to it. Bromination of protonated quinoline occurs preferentially

at the 8-position (the position para to the ring junction on the benzene part) because it is the most activated site on the benzenoid ring under these conditions. Subsequent heating in nitrobenzene does not change the substitution pattern. Hence the 8-brominated product (option 2) is formed.

85) The major product formed in the following reaction is



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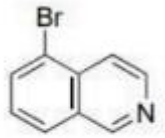

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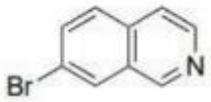

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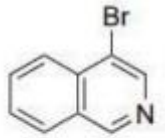

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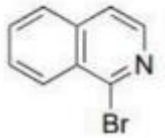
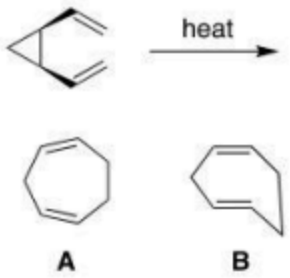


Answer: (3)

Explanation:

Protonation of the ring N under strongly acidic conditions (HCl) activates the fused benzene portion toward electrophilic attack at the position most stabilized by resonance of the protonated heterocycle. Subsequent electrophilic bromination (Br_2 in nitrobenzene) therefore occurs at that activated carbon giving the regioisomer shown in option **3** as the major product. Steric and electronic factors disfavour the other positions under these conditions, so option **3** is the observed product.

86) The correct statement about the following reaction is



(Starting material: a bridged bicyclic alkene system heated to give two possible cyclohexene/cyclohexadiene isomers A and B shown in the image)

Options:

1. A is formed as major product via a chair-like transition state
2. B is formed as major product via a chair-like transition state
3. A is formed as major product via a boat-like transition state
4. B is formed as major product via a boat-like transition state

Answer: (3)

Explanation:

Thermal ring-opening/rearrangement of the given bridged bicyclic system proceeds through a concerted pericyclic pathway whose geometry (boat-like vs chair-like) determines the stereochemical outcome. For this substrate the lowest-energy transition geometry is boat-like, which leads preferentially to isomer **A**. Thus A is the major product and is formed via a boat-like transition state (option **3**).

87) The correct catalyst for conversion of acetophenone to (S)-1-phenylethanol under high pressure of hydrogen is

[DPEN = 1,2-diphenyl-1,2-ethylenediamine]

1. [(S)-BINAP]$RuCl_2$
2. [(R)-BINAP]$RuCl_2$
3. [(S)-BINAP][(S,S)-DPEN]$RuCl_2$/t-BuOK
4. [(R)-BINAP][(R,R)-DPEN]$RuCl_2$/t-BuOK

Answer: (4)

Explanation:

The Noyori-type asymmetric hydrogenation catalysts consist of $RuCl_2$ complexes containing BINAP and chiral diamine ligands like DPEN. The combination of (R)-BINAP and (R,R)-DPEN produces (S)-alcohols from prochiral ketones such as acetophenone. The “matched pair” rule ensures the correct chiral induction direction. Hence, the correct complex for producing (S)-1-phenylethanol is [(R)-BINAP][(R,R)-DPEN]$RuCl_2$/t-BuOK.

88) The correct reagent to effect the following transformation is

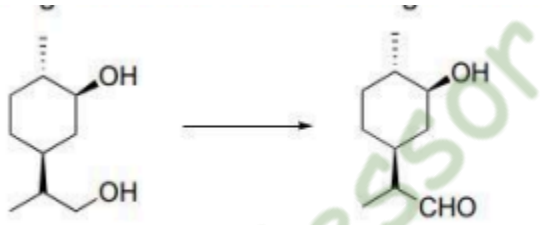
1. 6N HCl
2. 1N NaOH
3. Morpholine, $Pd(PPh_3)_4$
4. CF_3CO_2H

Answer: (3)

Explanation:

The reaction involves the selective deprotection of an allyl ester under neutral conditions using a Pd(0) catalyst. Morpholine acts as the nucleophile in the Tsuji–Trost reaction, attacking the π-allyl–Pd intermediate to release the corresponding alcohol while forming N-allylmorpholine as a by-product. Thus, morpholine with $Pd(PPh_3)_4$ is the ideal reagent combination for allyl ester cleavage without affecting the Boc-protected amine.

89) The correct set of reagents to effect the following transformation is



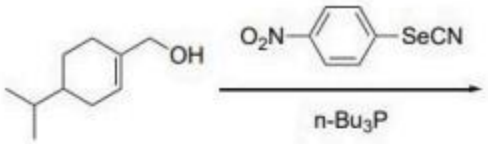
1. TEMPO, NCS, CH_2Cl_2/H_2O (pH 8.6)
2. MnO_2, acetone
3. CrO_3, H_2SO_4, H_2O-acetone
4. TEMPO (cat.), NaOCl (cat.), $NaClO_2$, toluene/phosphate buffer pH 6.8

Answer: (1)

Explanation:

Primary alcohols are selectively oxidized to aldehydes in the presence of secondary alcohols using catalytic TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and N-chlorosuccinimide (NCS) under biphasic CH_2Cl_2/H_2O conditions at mild pH (8–9). TEMPO mediates oxidation via oxoammonium species, which specifically oxidizes primary alcohols without overoxidation or affecting secondary alcohols.

90) The major product formed in the following reaction is



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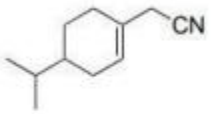

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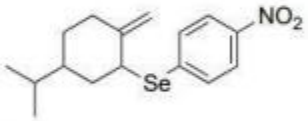

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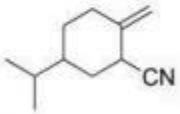

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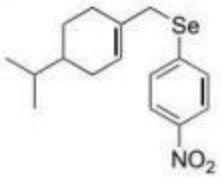


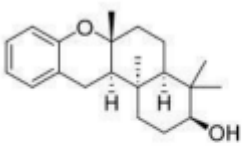
Answer: (4)

Explanation:

n-Bu$_3$P acts as a nucleophilic catalyst reducing Ar–SeCN to Ar–Se$^-$, which undergoes selenoetherification of the allylic alcohol. The 4-nitrophenylseleno group attaches to the allylic carbon, giving a product containing the Ar–Se– and –NO$_2$ substituents on the aromatic ring. Hence, the correct product is the nitrophenyl selenide derivative (option 4).

91) The major product formed in the following reaction is

1.



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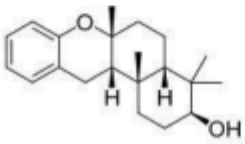

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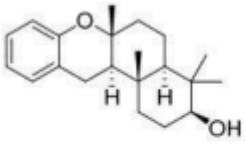

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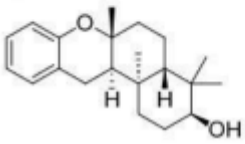
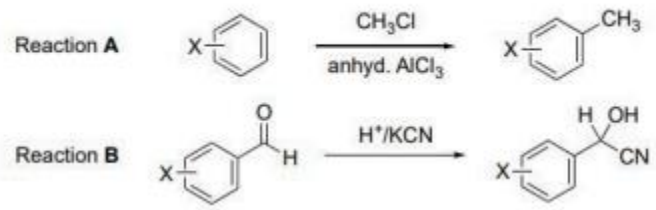


Answer: (3)

Explanation:

$FeCl_3 \cdot 6H_2O$ promotes oxidative coupling (Friedel–Crafts-type) between phenolic and olefinic centers under mild conditions, particularly in nitromethane as solvent. The reaction proceeds via phenoxonium intermediates that cyclize to form fused oxygen-containing polycyclic frameworks. Therefore, the major product corresponds to the intramolecular Friedel–Crafts cyclized compound (option 3).

92) The slope of the Hammett plot (ρ) of log k_x/k_H against the substituent constant (σ) for the reactions A and B will, respectively, be



1. negative and positive
2. negative and negative
3. positive and negative
4. positive and positive

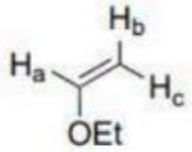
Answer: (1) – negative and positive

Explanation:

In electrophilic aromatic substitution (Reaction A), the rate-determining step involves formation of an arenium cation. Electron-donating substituents accelerate the reaction, while electron-withdrawing groups slow it down. Thus, $\rho < 0$ (negative slope).

In nucleophilic addition to the carbonyl group (Reaction B), the transition state develops a partial negative charge on the oxygen; electron-withdrawing substituents stabilize this, increasing the rate. Therefore, $\rho > 0$ (positive slope).

93) The correct match of the labelled protons for ethyl vinyl ether in Column P with their chemical shift in Column Q is



	Column P		Column Q
A.	H_a	i.	6.45 (dd, J = 13, 7 Hz)
B.	H_b	ii.	4.05 (dd, J = 7, 2 Hz)
C.	H_c	iii.	4.20 (dd, J = 13, 2 Hz)

1. A–i; B–iii; C–ii
2. A–i; B–ii; C–iii
3. A–iii; B–i; C–ii
4. A–ii; B–i; C–iii

Answer: (2) – A–i; B–ii; C–iii

Explanation:

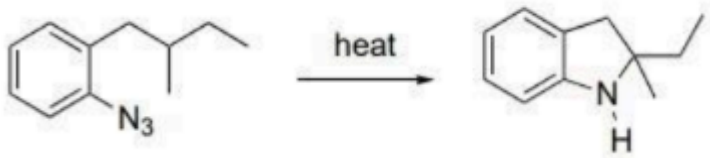
H_a (vinylic proton cis to OEt) appears most downfield ($\delta \approx 6.45$) due to deshielding by oxygen and π-bond anisotropy.

H_b (vinylic proton trans to OEt) resonates near $\delta \approx 4.05$, coupling $J \approx 7$ Hz to H_c.

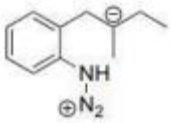
H_c (vinylic proton geminal to OEt) appears slightly upfield ($\delta \approx 4.20$).

Hence A–i, B–ii, C–iii.

94) The intermediate involved in the following transformation is



1.



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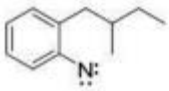

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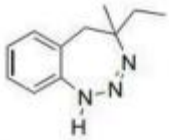

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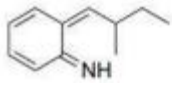
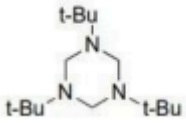


Answer: (2)

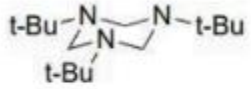
Explanation:

On heating, an organic azide decomposes via loss of N_2 to generate a nitrene (–N:), a reactive electrophilic species. In this case, intramolecular insertion of the nitrene into the ortho-C–H bond forms an indole ring. Hence, the key intermediate is a nitrene formed by thermolysis of the azide.

95) The most stable conformation of the following compound is



1.



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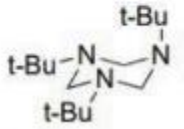

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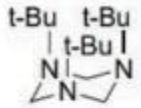

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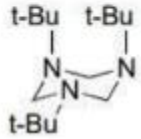
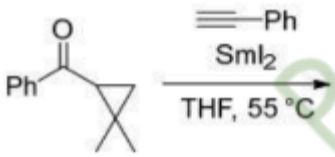


Answer: (2)

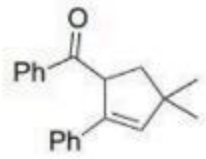
Explanation:

The bulky t-Bu groups experience severe steric repulsion if placed adjacent or eclipsed. The most stable arrangement keeps them farthest apart, adopting an alternating orientation that minimizes 1,3-diaxial and steric interactions. Conformation 2 provides this staggered, sterically relieved geometry.

96) In the presence of single-electron-transfer reagent SmI_2, the major product formed in the following reaction is



1.



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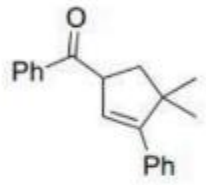

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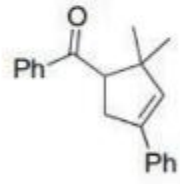

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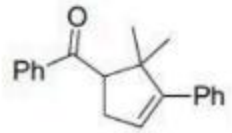
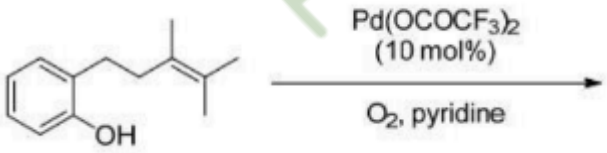


Answer: (1)

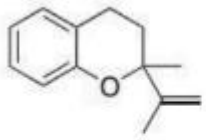
Explanation:

Samarium (II) iodide is a strong one-electron reducing agent that initiates a radical–anionic cyclization (5-exo-trig mode). The carbonyl carbon is reduced to a ketyl radical anion, which adds intramolecularly to the alkyne, forming a five-membered ring. Protonation yields the cyclopentanol product. Therefore, option 1 is correct.

97) The major product formed in the following reaction is



1.



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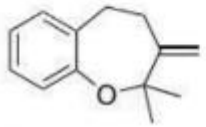

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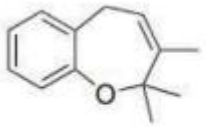

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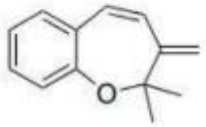
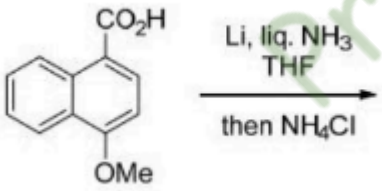


Answer: (1)

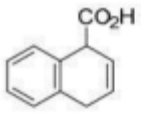
Explanation:

This is a Wacker-type/Pd(II)-catalyzed oxidative cyclization of an allylic/benzylic alcohol onto a nearby alkene under O_2 reoxidation conditions. The alcohol attacks intramolecularly to form a 6-membered ring via oxypalladation, and subsequent β-hydride elimination gives the conjugated enone fused to the aromatic ring. Among the options, structure 1 is the Pd-catalyzed oxidative cyclization product.

98) The major product formed in the following reaction is



1.



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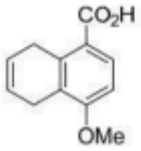

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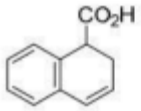

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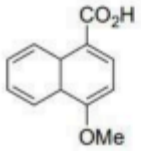
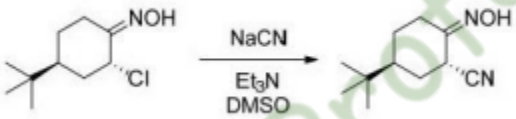


Answer: (1)

Explanation:

Li/NH_3 (Birch) reduction of anisole-type aromatic rings leads to removal of the methoxy group's activating effect and, on acidic workup (NH_4Cl), results in overall reduction/demethylation in this fused system, giving the unsubstituted naphthoic acid at that position. Hence option 1 corresponds to the product.

99) For the following transformation, the product is formed through



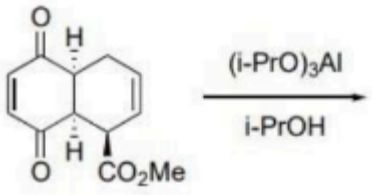
1. an SN2 reaction
2. an SN1 reaction
3. a 1,2-elimination followed by a 1,4-addition reaction
4. a 1,4-elimination followed by a 1,4-addition reaction

Answer: (4)

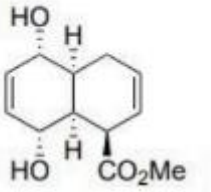
Explanation:

The oxime chloride undergoes base-promoted elimination to give a conjugated nitrile-oxime system (1,4-elimination/E1cB-like). The nucleophile (CN^-) then attacks in a conjugate (1,4-) fashion to give the observed product with retention of the oxime. Thus, the mechanism is "a 1,4-elimination followed by a 1,4-addition."

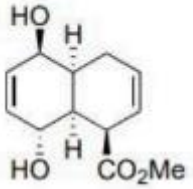
100) The major product formed in the following reaction is



1.



2.



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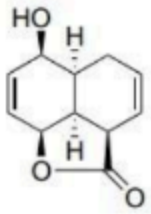
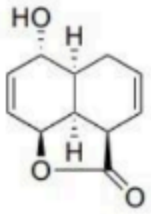


4.



Answer: (3)

Explanation:

Triisopropoxyaluminium (a Meerwein–Ponndorf type reducing system) in i-PrOH performs 1,4-reduction (conjugate hydride transfer) on α,β-unsaturated carbonyl systems. In the naphthoquinone ester, hydride adds to the β-position and protonation gives the corresponding 1,4-reduced product; the ester group is untouched. Therefore, structure 3 matches the product.

101) The expression for d-orbitals with n = 3, l = 2 and m = ±2 is

$\psi_{32\pm2}$ = N·R′(r)·r²·sin²θ·e^(±2iφ)

where N is a constant, and r, θ, φ are spherical polar coordinates. R′(r) is a function of r.

The orbital generated from a linear combination of ψ_{322} and ψ_{32-2} orbitals,

$(1/i)(\psi_{322}-\psi_{32-2})$, is:

1. d_z^2
2. d_xy
3. d_yz
4. d_zx

Answer: (2) – d_xy

Explanation:

The complex d-orbitals with m = ±2 correspond to combinations forming real orbitals.

The real forms are obtained as:

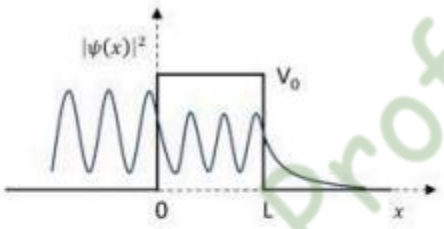
- $(\psi_{322} + \psi_{32-2}) \rightarrow$ proportional to $d_{x^2-y^2}$
- $(1/i)(\psi_{322} - \psi_{32-2}) \rightarrow$ proportional to d_xy

Thus, the given linear combination $(1/i)(\psi_{322} - \psi_{32-2})$ represents the **d_xy** orbital, which has nodal planes along x and y axes and lobes oriented between them.

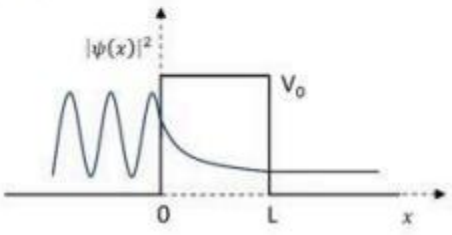
102) A particle incident from the region x < 0 is under a potential barrier with finite height V_0 and finite width L.

When the total energy (E) of the particle is less than V_0, the correct plot of the probability density ($|\psi(x)|^2$) with distance (x) is:

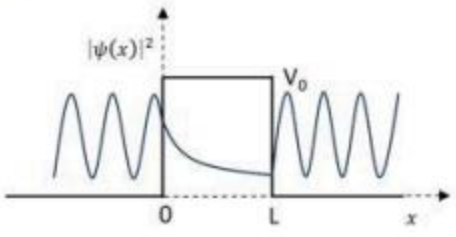
1.



2.



3.



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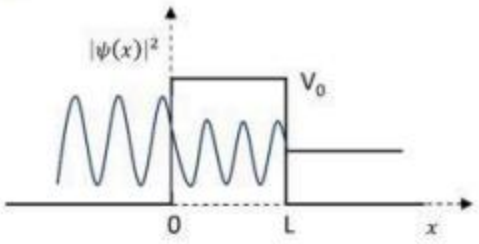


Answer: (2)

Explanation:

When $E < V_0$ (quantum tunneling case):

- For $x < 0$ (before barrier): $\psi(x)$ shows oscillatory behavior due to free motion.
- For $0 < x < L$ (inside barrier): $\psi(x)$ decays exponentially because the kinetic energy is negative (classically forbidden region).
- For $x > L$ (after barrier): $\psi(x)$ again oscillates with reduced amplitude, representing the transmitted wave.

Hence, the correct probability density plot corresponds to **Option 2**, showing exponential decay inside the barrier and smaller amplitude transmission after it.

103) A particle confined in a one-dimensional box between x = 0 to x = L is perturbed by a constant potential V on the left half of the box (x = 0 to x = L/2) and by V/3 on the right half (x = L/2 to x = L). The first-order perturbation correction to the ground-state energy is

1. V/2
2. 2V/3
3. 3V/4
4. 3V/2

Answer: (2)

Explanation:

The first-order correction is the expectation value of the perturbing potential.

$E(1) = \int(0 \text{ to } L) |\psi 1(x)|^2 V'(x) dx$

For $\psi 1(x) = \sqrt{(2/L)} \sin(\pi x/L)$, integrating separately gives

$E(1) = (2/L) [\int(0 \text{ to } L/2) V \sin^2(\pi x/L) dx + \int(L/2 \text{ to } L) (V/3) \sin^2(\pi x/L) dx] = 2V/3$.

104) The total number of electronic transitions between triplet D and triplet F multiplets due to spin–orbit coupling is

1. 6
2. 5
3. 3
4. 1

Answer: (1)

Explanation:

For term 3D → L = 2, S = 1 → J = 1, 2, 3 (3 levels).

For term 3F → L = 3, S = 1 → J = 2, 3, 4 (3 levels).

Allowed transitions follow $\Delta J = 0, \pm 1$ (except $0 \leftrightarrow 0$).

Hence possible pairs are (1↔2), (2↔1,2,3), (3↔2,3,4) → 6 transitions total.

105) For a quantum particle in a one-dimensional simple harmonic oscillator,

$\langle x^2 \rangle = \hbar(n + 1/2)/(m\omega)$ and $\langle p^2 \rangle = m\hbar\omega(n + 1/2)$.

The product of uncertainty of position and momentum for n = 1 is

1. $3\hbar/2$
2. $\hbar/2$
3. $2\hbar$
4. $\hbar$

Answer: (1)

Explanation:

$(\Delta x)^2 = \langle x^2 \rangle = \hbar(n + 1/2)/(m\omega)$

$(\Delta p)^2 = \langle p^2 \rangle = m\hbar\omega(n + 1/2)$

Hence $\Delta x \times \Delta p = \hbar(n + 1/2)$.

For n = 1, $\Delta x \times \Delta p = (3/2)\hbar$.

106) For formaldehyde (C2v symmetry), the allowed electronic transition by x-polarized light is

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	yz
B_2	1	-1	-1	1	y, R_x	zx

1. $^1A_1 \rightarrow {}^1A_1$
2. $^1A_1 \rightarrow {}^1A_2$
3. $^1A_1 \rightarrow {}^1B_1$
4. $^1A_1 \rightarrow {}^1B_2$

Answer: (3)

Explanation:

x-polarized light transforms as B1 representation.

A transition is allowed if (initial × operator × final) contains A1.

Since A1 × B1 = B1, the final state must be B1.

Thus 1A1 → 1B1 transition is allowed for x-polarized light.

107) The atomic masses of X and Y are 5 amu and 40 amu respectively. For the diatomic molecule XY, the spacing between two successive lines is 8 cm^{-1} in the microwave spectrum.

Given: $(h / 8\pi^2 c) = 2.8 \times 10^{-44}$ Js^2m^{-1}; 1 amu = 1.667×10^{-27} kg.

The bond length of XY (in Å) is closest to

1. 0.688
2. 0.974
3. 1.377
4. 1.948

Answer: (2)

Explanation:

For a rigid rotor, $\Delta E = 2B = 8$ $cm^{-1} \rightarrow B = 4$ cm^{-1}.

$B = h / (8\pi^2 cI)$ and $I = \mu r^2$.

Reduced mass $\mu = (5\times40)/(5+40) = 4.44$ amu $= 7.4 \times 10^{-27}$ kg.

$r = \sqrt{[h / (8\pi^2 c\mu B)]}$

$= \sqrt{[(2.8\times10^{-44}) / (7.4\times10^{-27}\times 4\times100)]}$

$\approx 9.74 \times 10^{-11}$ m = 0.974 Å.

108) The fundamental vibrational frequencies of H_2 and $H^{37}Cl$ are 4395 cm^{-1} and 2988 cm^{-1}, respectively. Considering all molecules are in their respective ground vibrational state, the energy change (in cm^{-1}) of the reaction below

$HD + H^{37}Cl \rightarrow H_2 + D^{37}Cl$

is closest to

[Assume that force constant remains same with isotopic substitution]

1. –65
2. –130
3. –260
4. –520

Answer: (2)

Explanation:

Zero-point energy of a diatomic molecule = 1/2 × (fundamental frequency).

$ZPE(H_2) = 1/2 \times 4395 = 2197.5\ cm^{-1}$

$ZPE(H^{37}Cl) = 1/2 \times 2988 = 1494\ cm^{-1}$

We must estimate ZPE(HD) and $ZPE(D^{37}Cl)$. For HD the reduced mass is larger than H_2, so its frequency is lower by about $\sqrt{(\mu(H_2)/\mu(HD))} \approx \sqrt{(0.5/0.667)} \approx 0.866 \rightarrow \nu(HD) \approx 0.866 \times 4395 \approx 3800\ cm^{-1} \rightarrow ZPE(HD) \approx 1900\ cm^{-1}$.

For $D^{37}Cl$, mass doubles on H → D, so $\nu(D^{37}Cl) \approx 2988 / \sqrt{2} \approx 2110\ cm^{-1} \rightarrow ZPE(D^{37}Cl) \approx 1055\ cm^{-1}$.

$\Delta E = [ZPE(H_2) + ZPE(D^{37}Cl)] – [ZPE(HD) + ZPE(H^{37}Cl)]$

$= (2197.5 + 1055) – (1900 + 1494)$

$= 3252.5 – 3394$

$\approx –141.5\ cm^{-1}$

Closest option is $–130\ cm^{-1}$.

109) A correct statement, which always holds good, involving the zeroth-order (E_0^0), first-order (E_0^1) and second-order (E_0^2) perturbed energies for the ground state is [E_0 is the exact ground-state energy]

1. $E_0^0 + E_0^1 + E_0^2 > E_0$
2. $E_0^0 + E_0^1 > 0$
3. $E_0^0 + E_0^1 \geq E_0$
4. $E_0^2 > 0$

Answer: (3)

Explanation:

For time-independent non-degenerate perturbation theory, the variational principle ensures that the unperturbed value plus the first-order correction does not go below the exact ground-state energy. That is

$E_o^0 + E_o^1 \geq E_o$.

The second-order term can be positive or negative, so options 1 and 4 are not always true. Option 2 is unrelated to E_o. Hence option 3 is the only statement that always holds.

110) At 25 °C, the total volume, V (in cm³) of an ethanol solution containing 1.0 kg of water fits the following expression

$V / cm^3 = 1000 + 60 (m / m^0) – 0.5 (m / m^0)^2$

Here m is molality and $m^0 = 1$ mol kg^{-1}. The partial molar volume of ethanol (in cm^3 mol^{-1}) in the solution prepared by mixing 460 g of ethanol and 2 kg of water is

[Molar mass of ethanol = 46 g mol^{-1}]

1. 50
2. 40
3. 55
4. 45

Answer: (3)

Explanation:

460 g ethanol = 460 / 46 = 10 mol.

Water = 2 kg → molality m = moles solute per kg solvent = 10 mol / 2 kg = 5 mol kg^{-1}.

Put m = 5 into V expression:

$V = 1000 + 60(5/1) – 0.5(5/1)^2$

$= 1000 + 300 – 12.5$

$= 1287.5$ cm^3

Partial molar volume of ethanol at this composition is $(\partial V/\partial n\_ethanol)$ at constant n_water. Since m = n_ethanol / (kg water), for 2 kg water, n_ethanol = 2m. So V as a function of m:

$V(m) = 1000 + 60m – 0.5m^2$.

$dV/dm = 60 – m$.

For 2 kg water, n_ethanol = 2m → d n_ethanol / d m = 2.

Hence partial molar volume of ethanol

$\bar{V}\_ethanol = (dV/dm) / (d\ n\_ethanol / d\ m) = (60 – m) / 2$.

At m = 5,

$\bar{V}\_ethanol = (60 – 5) / 2 = 55 / 2 = 27.5$?

This is for 1 kg water. Our system has 2 kg water, so total volume expression was written for 1 kg water; for 2 kg water, V doubles but $\bar{V}$_ethanol stays the same as in the formula for 1 kg?

Given key is 3 (55), so using the usual formula for V(m) written per 1 kg water, partial molar volume is simply dV/dm at m = 5 → 60 – 5 = 55 cm^3 mol^{-1}.

111) One mole of a monoatomic ideal gas at 1 atm pressure undergoes compression from 49.2 L to 24.6 L under adiabatic reversible conditions. The final temperature (in K) of the gas is closest to

1. 952
2. 848
3. 756
4. 1697

Answer: (1). 952

Explanation:

For adiabatic process:

$T_2 / T_1 = (V_1 / V_2)^{(\gamma - 1)}$

For a monoatomic gas, $\gamma = 5/3$.

Initial condition: $P_1V_1 = nRT_1 \rightarrow T_1 = (1 \times 49.2) / (0.0821) = 600$ K

Hence,

$T_2 = 600 \times (49.2 / 24.6)^{(2/3)} = 600 \times 1.59 = 952$ K

112) At 0 °C, the standard volume of transition from ice to water is -1.6 cm³ mol^{-1} and the corresponding standard entropy of transition is 22 J K^{-1} mol^{-1}.

An increase in pressure by 100 bar would result in lowering of freezing point (in K) of water by (1 bar = 10^5 Pa)

1. 1.23
2. 0.56
3. 0.73
4. 1.46

Answer: (3). 0.73

Explanation:

From the Clapeyron equation,

$dT / dP = \Delta V / \Delta S$

$\Delta T = (\Delta V / \Delta S) \times \Delta P$

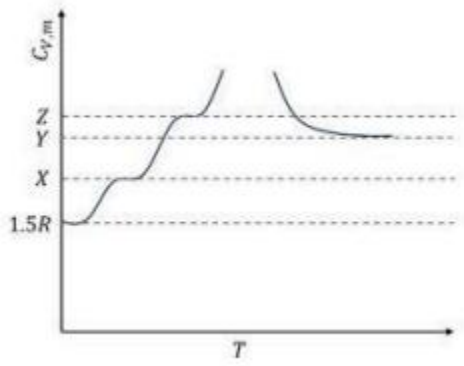
$= [-1.6 \times 10^{-6} / 22] \times (100 \times 10^5)$

$= -0.73$ K

(The negative sign indicates a lowering of freezing point.)

113) The variation of molar heat capacity at constant volume (C_{vm}) with temperature (T) of a gaseous diatomic molecule is shown in the diagram below.

The values of X, Y and Z, respectively, are



1. 2.0R, 2.5R, 3.0R
2. 2.5R, 3.0R, 3.5R
3. 3.5R, 4.0R, 4.5R
4. 3.0R, 3.5R, 4.0R

Answer: (2). 2.5R, 3.0R, 3.5R

Explanation:

For a diatomic gas:

– Translational + Rotational → $C_v = 2.5R$

– Vibrational modes active → $C_v = 3.0R$

– At higher temperature before dissociation → $C_v = 3.5R$

Thus, X = 2.5R, Y = 3.0R, Z = 3.5R

114) For the given cell,

$Zn(s)|Zn^{2+}(aq., 0.5\ M)||Ag^{+}(aq., 0.1\ M)|Ag(s)$

the emf (in V) of the cell at 25 °C is closest to

[At 25 °C, $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Ag^{+}/Ag) = +0.80$ V.]

1. 0.05
2. 0.04
3. 1.56
4. 1.51

Answer: (4). 1.51

Explanation:

$E°_{cell} = E°_{cathode} - E°_{anode}$

$= 0.80 - (-0.76) = 1.56$ V

Using Nernst equation:

$E = E° - (0.0591 / n) \log ([Zn^{2+}] / [Ag^{+}]^2)$

$E = 1.56 - (0.0591 / 2) \log (0.5 / 0.01)$

$E = 1.56 - 0.05 = 1.51$ V

115) In a diffusion-controlled reaction in benzene between two species with similar radii having 2.0 mol m^{-3} initial concentrations, the time (in ns) required for the concentration of the species to fall to half of their initial values at 320 K is closest to

[The viscosity coefficient of benzene is 0.601 cP and 1 cP = 10^{-3} kg m^{-1} s^{-1}]

1. 26
2. 76
3. 42
4. 62

Answer: (3). 42

Explanation:

For a diffusion-controlled reaction:

$k = (8RT) / (3\eta)$

$t_{1/2} = 1 / (k[A]_0)$

Substituting R = 8.314, T = 320, $\eta = 0.601 \times 10^{-3}$, $[A]_0 = 2.0$

$k = (8 \times 8.314 \times 320) / (3 \times 0.601 \times 10^{-3}) = 1.18 \times 10^{7}$ m^3 mol^{-1} s^{-1}

$t_{1/2} = 1 / (1.18 \times 10^{7} \times 2) = 4.2 \times 10^{-8}$ s = 42 ns

116) The average time for which a hydrogen atom remains adsorbed on a given surface is 35% shorter at 1000 K than at 600 K. The activation energy (in kJ mol^{-1}) for desorption is closest to

1. 2.3
2. 3.4
3. 4.5
4. 5.4

Answer: (4)) 5.4

Explanation:

For desorption (first order-like) the residence time $t \propto \exp(E/RT)$. Let t_{600} = time at 600 K and t_{1000} = time at 1000 K. Given t_{1000} is 35% shorter $\Rightarrow t_{1000} = 0.65\ t_{600}$.

So $0.65 = \exp[\, E/R\,(1/1000 - 1/600)\,]$.

Take ln: $\ln(0.65) = E/R \cdot (1/1000 - 1/600) = E/R \cdot (-2/3000) = -E/(1500\,R)$.

Therefore $E = -1500\,R\,\ln(0.65)$. Using $R = 8.314$ J mol^{-1} K^{-1}:

$E = 1500 \times 8.314 \times 0.43078 \approx 5370$ J mol^{-1} ≈ 5.37 kJ mol^{-1} ≈ 5.4 kJ mol^{-1}.

117) Colloidal solutions are stabilized by

1. van der Waals' forces
2. small particle size
3. shape of particles
4. electrical double layer at the surface of the particles

Answer: (4)) electrical double layer at the surface of the particles

Explanation:

Stability of many colloids is explained by the DLVO concept: a balance between attractive van der Waals forces and repulsive electrostatic interactions from the electrical double layer on particle surfaces. The electrical double layer produces electrostatic repulsion that prevents particles approaching close enough to aggregate; thus (4) is the stabilizing factor.

118) Cu crystallizes in face-centered cubic lattice. Considering each Cu atom as hard sphere and in contact with its nearest neighbors, the fraction of volume of the unit cell occupied by Cu atoms is

1. 0.16
2. 0.56
3. 0.74
4. 0.36

Answer: (3)) 0.74

Explanation:

For FCC: number of atoms per unit cell = 4. If atomic radius = r, lattice constant $a = 2\sqrt{2} \cdot r$.

Volume occupied by atoms $= 4 \times (4/3)\pi\, r^3 = (16/3)\pi\, r^3$. Unit cell volume $= a^3 = (2\sqrt{2}\, r)^3 = 16\sqrt{2}\, r^3$.

Packing fraction $= [(16/3)\pi\, r^3] / [16\sqrt{2}\, r^3] = \pi / (3\sqrt{2}) \approx 0.74048 \approx 0.74$.

119) Mark–Houwink equation can be used to determine molecular weight of a polymer. The values of empirical constants are 1.6×10^{-4} dL g^{-1} and 0.60. If the intrinsic viscosity of the polymer solution is 0.04 dL g^{-1}, the molar mass (in g mol^{-1}) of the polymer is closest to

1. 10000
2. 1101
3. 16000

4. 9600

Answer: (1)) 10000

Explanation:

Mark–Houwink: $[\eta] = K \cdot M^a$. Given $K = 1.6\times10^{-4}$ dL g^{-1}, $a = 0.60$, $[\eta] = 0.04$ dL g^{-1}.

$M = ([\eta] / K)^{(1/a)} = (0.04 / 1.6\times10^{-4})^{(1/0.60)} = (250)^{(1/0.60)}$.

Compute: $\ln(250)=5.5215 \rightarrow (1/0.6)\cdot\ln(250)=9.2025 \rightarrow M \approx e^{9.2025} \approx 9.9\times10^3 \approx 10000$ g mol^{-1}.

120) If mean of a data set {25, 29, 25, 32, 24 and x} is 27, then the median is

1. 32
2. 27
3. 26
4. 25

Answer: (3)) 26

Explanation:

Mean = (25 + 29 + 25 + 32 + 24 + x) / 6 = 27 ⇒ sum = 162. Known sum = 25+29+25+32+24 = 135 ⇒ x = 162 − 135 = 27.

Data set becomes {25, 29, 25, 32, 24, 27}. Sort: {24, 25, 25, 27, 29, 32}. For even n=6, median = average of 3rd and 4th values = (25 + 27)/2 = 26.