21) The metals in the active site of acetylene hydratase, urease, carboxypeptidase and sulfite oxidase, respectively, are

1. Cu, Mo, Ni and Zn
2. W, Ni, Zn and Mo
3. Mo, Ni, Zn and Co
4. W, Co, Mo and Cu

Answer: 2

EXPLANATION:

Acetylene hydratase is a **tungsten (W)** enzyme; **urease** contains **nickel (Ni)**; **carboxypeptidase** has **zinc (Zn)** at its catalytic site; and **sulfite oxidase** uses **molybdenum (Mo)**. Hence, the correct sequence is **W, Ni, Zn, and Mo**.

22) The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2]$ with PPh_3 results in

1. $[(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)(PPh_3)] + CO$
2. $[(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2(PPh_3)]$
3. $[(\eta^5\text{-}C_5H_5)Fe(COCH_3)(CO)(PPh_3)]$
4. $[(\eta^5\text{-}C_5H_5)Fe(COCH_3)(PPh_3)] + CO$

Answer: 3

EXPLANATION:

The complex undergoes **migratory insertion of CO into the $Fe–CH_3$ bond**, forming an **acyl complex ($Fe–COCH_3$)**. One CO is replaced by PPh_3 to form the product **$[(\eta^5\text{-}C_5H_5)Fe(COCH_3)(CO)(PPh_3)]$**.

23) The [Re–Re] bond order follows

1. $K_2[Re_2Cl_8] > [Re_2Cl_4(PMe_2Ph)_4] > [Re_2Cl_4(PMe_2Ph)_4]Cl$
2. $[Re_2Cl_4(PMe_2Ph)_4] > [Re_2Cl_4(PMe_2Ph)_4]Cl > K_2[Re_2Cl_8]$
3. $K_2[Re_2Cl_8] > [Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4]$
4. $[Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4] > K_2[Re_2Cl_8]$

Answer: 3

EXPLANATION:

In **$K_2[Re_2Cl_8]$**, each Re is in the +3 oxidation state, forming a **quadruple bond (bond order = 4)**.

In **$[Re_2Cl_4(PMe_2Ph)_4]Cl$**, oxidation reduces bond order to **3.5**.

In **$[Re_2Cl_4(PMe_2Ph)_4]$**, the Re–Re bond is **triple (bond order = 3)**.

Hence, the trend is **$K_2[Re_2Cl_8] > [Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4]$**.

24) The correct order of covalency in the X–F bonds among the following species is

1. $SiF_4 < PF_5 < SF_6 < IF_7$
2. $SiF_4 < PF_5 < IF_7 < SF_6$
3. $IF_7 < SF_6 < PF_5 < SiF_4$
4. $IF_7 < SiF_4 < PF_5 < SF_6$

Answer: 1

EXPLANATION:

Covalent character increases with increasing atomic size and decreasing electronegativity of the central atom.

Thus, iodine (largest atom) forms the most covalent bond, while silicon (smallest) forms the least.

Hence, **$SiF_4 < PF_5 < SF_6 < IF_7$**.

25) In the upper atmosphere, SF_6 undergoes photolysis to form species A. Species A combines with O_2 giving a radical B. The correct statement is

1. Unpaired electrons in A and B are located on sulfur and oxygen atoms, respectively
2. Unpaired electrons in A and B are on sulfur atom only
3. Species A is diamagnetic
4. The hybridization of central atoms in A and B are different

Answer: 1

EXPLANATION:

Photolysis of SF_6 forms **$SF_5\cdot$ (A)** and $F\cdot$.

When A reacts with O_2, it forms **$SF_5OO\cdot$ (B)**.

The unpaired electron in **A** resides on **sulfur**, while in **B** it resides on **oxygen (π orbital)*.

Hence, option 1 is correct.

26) The high kinetic stability of Cr(norbornyl)$_4$ is due to

1. the absence of α-hydrogen atom
2. the β-hydride elimination leading to a bridgehead olefin
3. the absence of vacant coordination site on the Cr center
4. agostic interaction of β-C–H with Cr

Answer: 2

EXPLANATION:

In Cr(norbornyl)$_4$, **β-hydride elimination** would require formation of a **bridgehead olefin**, which violates **Bredt's rule**.

As β-elimination is blocked, decomposition cannot occur, leading to high **kinetic stability**.

27) Consider the following statements regarding ZnS.

I. ZnS shows both cubic and hexagonal structures

II. Sphalerite exhibits ZnS structure

III. ZnS is a semiconductor

IV. ZnS can be precipitated from an aqueous acidic solution of zinc salts by passing H_2S

The option containing the correct statements is

1. I, II and III only
2. II and IV only
3. I and III only
4. II, III and IV only

Answer: 1

EXPLANATION: ZnS occurs as **zinc blende (cubic)** and **wurtzite (hexagonal)** → I true. **Sphalerite** is the mineral form of cubic ZnS → II true. ZnS is a **wide-band-gap semiconductor** → III true. **IV is false** because ZnS precipitates with H_2S in **alkaline** (not acidic) medium in qualitative analysis.

28) According to Wade's rules, TeB_9H_{11} is an example of

1. closo-borane
2. nido-borane
3. arachno-borane
4. hypho-borane

Answer: 2

EXPLANATION: The cluster has **10 skeletal atoms (Te + 9B)** and is related to **$B_{10}H_{14}$ (nido)**; replacement of one B by Te retains a **10-vertex nido framework** (SEPs ≈ n+2).

29) Match columns I and II.

Column I: a. $[TiCl_6]^{2-}$ b. $[V(H_2O)_6]^{3+}$ c. $[CoCl_4]^{2-}$ d. $[Mn(H_2O)_6]^{2+}$

Column II (ε, $M^{-1}cm^{-1}$): i. ~500 ii. ~0.02 iii. ~10^4 iv. ~10

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

Answer: 4

EXPLANATION:

- **$[TiCl_6]^{2-}$ (Ti^{4+}, d^0) → CT allowed**, ε ~ **10^4** (a-iii).

- **$[V(H_2O)_6]^{3+}$ (d^2, Oh)** spin-allowed but Laporte-forbidden → ε ~ **10** (b-iv).
- **$[CoCl_4]^{2-}$ (Td, d^7)** Laporte-allowed d–d → ε ~ **500** (c-i).
- **$[Mn(H_2O)_6]^{2+}$ (Oh, d^5 HS)** spin-forbidden → ε ~ **0.02** (d-ii).

30) The reaction

$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$

takes place by the

1. inner-sphere mechanism mediated by the CN^- bridge
2. outer-sphere mechanism mediated by the CN^- bridge
3. inner-sphere mechanism with no net chemical change
4. outer-sphere mechanism with no net chemical change

Answer: 4

EXPLANATION: It is a **simple electron-transfer** between two **cyanide-saturated, substitution-inert** complexes; no bridging ligand or ligand exchange occurs → **outer-sphere with no net chemical change**.

31) An isoelectronic, neutral, linear nitrosyl complex of $[(\eta^5\text{-}C_5H_5)Cu(CO)]$ is

1. $[(\eta^5\text{-}C_5H_5)Ni(NO)]$
2. $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$
3. $[Mn(CO)_3NO]$
4. $[Fe(CO)(NO)_2]$

Answer: 1

EXPLANATION: In linear mode, **NO behaves as NO^+ (2e donor) like CO**. $[(\eta^5\text{-}C_5H_5)Cu(CO)]$ (neutral, 18e) is **isoelectronic** with **$[(\eta^5\text{-}C_5H_5)Ni(NO)]$** (neutral, linear NO), while the others are not neutral/isoelectronic.

32) The substitution reaction of $[Co(CN)_5Cl]^{3-}$ with OH^- to give $[Co(CN)_5(OH)]^{3-}$ is

1. slow and depends on the concentration of both the reactants
2. fast and depends only on the concentration of the Co complex
3. slow and depends only on the concentration of the Co complex
4. fast and depends on the concentration of both the reactants

Answer: 3

EXPLANATION: **Low-spin Co(III)** complexes are **kinetically inert** and typically react by a **dissociative (D, SN1) pathway**; the **rate is independent of nucleophile** concentration and depends only on the **complex concentration** (slow).

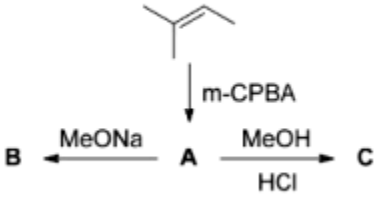
33) An isolobal fragment of $(\eta^6\text{-}C_6H_6)Cr(CO)_2$ is

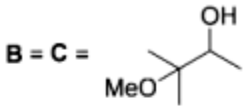
1. $Fe(CO)_4$
2. CH_3^+
3. $(\eta^5\text{-}C_5H_5)Mn(CO)_3$
4. CH_3

Answer: 2

EXPLANATION: The fragment **$(\eta^6\text{-}C_6H_6)Cr(CO)_2$** has frontier orbitals corresponding to a **trigonal, one-vacant/three-filled set**, making it **isolobal with CH_3^+** (same symmetry and electron count).

34) The major product formed in the following reaction is:



1.


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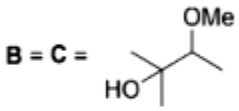

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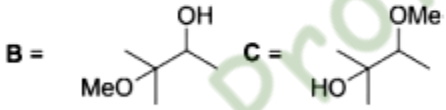

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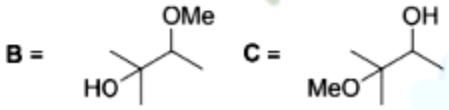


Answer: (1)

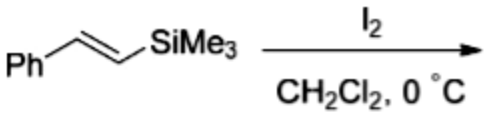
Explanation:

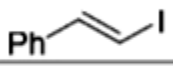
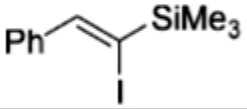
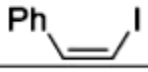
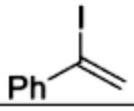
This is an **iododesilylation** reaction. The iodine electrophilically substitutes the trimethylsilyl ($SiMe_3$) group at the double bond through formation of an iodonium intermediate.

Hence, the $-SiMe_3$ group is replaced by –I, producing **styryl iodide (PhCH=CHI)** as the major product.

No rearrangement occurs because the reaction is mild (0 °C in CH_2Cl_2).

35) The major product formed in the following reaction is:



1.	
2.	
3.	
4.	

Answer: (1)

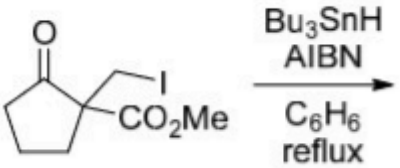
Explanation:

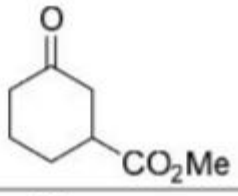
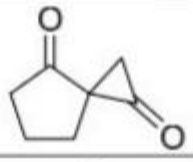
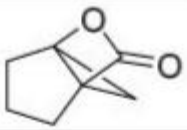
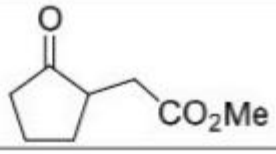
Bu_3SnH/AIBN promotes **radical de-iodination** or **radical cyclization** depending on geometry.

Here, the γ-iodo carbonyl system undergoes **5-exo-trig radical cyclization**, forming a **six-membered ring** (cyclohexanone derivative) rather than remaining as the open chain.

Therefore, the major product is the **six-membered cyclic compound with CO_2Me** group as shown in option (1).

36) The major product formed in the following reaction is:



1.	
2.	
3.	
4.	

Answer: (1)

Explanation:

Under Bu_3SnH/AIBN conditions, the C–I bond undergoes homolytic cleavage forming a carbon radical.

This radical attacks intramolecularly in a **5-exo/6-endo fashion**, leading to a **ring expansion** that produces a stable six-membered product.

Hydrogen abstraction from Bu_3SnH terminates the radical, forming a neutral molecule.

Other possibilities such as bridged or strained bicyclic products are less favored due to angle strain and poor overlap in the transition state.

Hence, the main product is the **six-membered ring ester** formed by intramolecular radical cyclization.

37) In a proton decoupled ^{13}C NMR of a compound, number of carbons in each signal cannot be calculated from the integration because signal intensities get affected by

i) NOE induced by attached protons

ii) different relaxation times of different carbons

iii) poor isotopic abundance of ^{13}C

1. Only ii
2. Both i and iii
3. Both ii and iii
4. Both i and ii

Answer: (4)

Explanation:

In proton-decoupled **^{13}C NMR**, the integration does **not** reliably show the number of carbons because:

- **(i) NOE (Nuclear Overhauser Effect)** increases the intensity of carbon signals unequally depending on how many protons are attached → intensities become distorted.
- **(ii) Different relaxation times (T_1)** for different carbons cause unequal signal recovery between pulses → again intensity variations.

However, **(iii) poor isotopic abundance of ^{13}C** affects total signal sensitivity but **does not distort the relative intensities** for integration.

Therefore, the factors affecting integration are **i and ii only → option 4**.

38) The corresponding bond angle (θ) and the bond length (d) of the product, respectively, are:

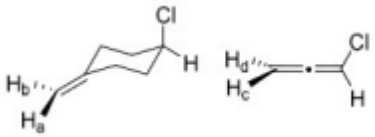
1. 100.6° and 1.608 Å
2. 112.3° and 1.608 Å
3. 100.6° and 1.430 Å
4. 112.3° and 1.430 Å

Answer: (1)

Explanation:

The substrate is a norbornyl system that, in the presence of the strong Lewis acid SbF_5 at low temperature, forms the well-known **nonclassical 2-norbornyl cation**. In this cation, the bridging interaction leads to a **compressed C–C–C angle** at the bridged center (≈100°) rather than a normal tetrahedral value (≈109–112°). At the same time, the **bridging C–C bond is longer than a normal C–C σ-bond** because electron density is shared over three centers; this "banana" bond length is about **1.60 Å** instead of ≈1.43 Å for a normal C–C bond. Hence, the product shows a small angle (~100.6°) and an elongated bond (~1.608 Å).

39) The correct topicity of H_a and H_c in the following molecules is:



1. H_a = H_c = pro-R

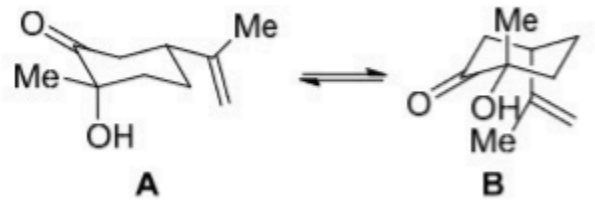
2. H_a = H_c = pro-S
3. H_a = pro-R; H_c = pro-S
4. H_a = pro-S; H_c = pro-R

Answer: (1)

Explanation:

Each of the labelled methylene hydrogens lies on a carbon that becomes a **prochiral center** if one of those hydrogens is replaced by a higher-priority group. When the CIP rules are applied to the two hydrogens individually (replacing H_a by a test group first, then H_c), both replacements lead to an **R configuration** at that center. That means both of those hydrogens are **enantiotopic** and are described by the **same pro-descriptor**. Therefore, both are designated **pro-R**.

40) The correct statements about the following conformational equilibrium of ketone are:



I. A predominates in DMSO due to opposing dipole interaction

II. B predominates in DMSO due to intramolecular hydrogen bonding

III. A predominates in isooctane due to opposing dipole interaction

IV. B predominates in isooctane due to intramolecular hydrogen bonding

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

Answer: (2)

Explanation:

Conformer **A** has its two polar groups oriented so that their dipoles **oppose** each other; this lowers the overall dipole of the molecule. In a **polar solvent (DMSO)**, such a lower-dipole conformer is usually stabilized relative to a high-dipole alternative, so A is favoured in DMSO — matching statement **I**.

In a **non-polar solvent (isooctane)**, there is no strong stabilization of dipole-driven conformations; instead, conformers capable of **intramolecular H-bonding** are preferred because the molecule can internally satisfy its H-bond without relying on the solvent. Conformer **B** can make such an intramolecular H-bond, so **B** is favoured in isooctane — matching statement **IV**.

Statements **II** and **III** do not match the solvent preferences just described.

41) The correct statement about Diels–Alder reaction of furan and maleic anhydride is:

1. the major product is **endo** and its formation is thermodynamically controlled
2. the major product is **endo** and its formation is kinetically controlled
3. the major product is **exo** and its formation is thermodynamically controlled
4. the major product is **exo** and its formation is kinetically controlled

Answer: (3)

Explanation:

The cycloaddition of **furan** (a relatively electron-rich, weak diene) with **maleic anhydride** is **reversible**. At low temperature and under purely kinetic conditions, endo addition can form, but this adduct is not the most stable. On equilibration, the system moves toward the **more stable exo adduct** because steric/electrostatic repulsions are lower in the exo orientation. Since the reaction is reversible, the final composition is governed by **thermodynamic control**, and the **exo** adduct becomes the major product.

42) The oxidation state and formal charge of nitrogen in the product (IR absorption band at 1553 cm^{-1}) of the reaction between butyl bromide and $AgNO_2$, respectively, are:

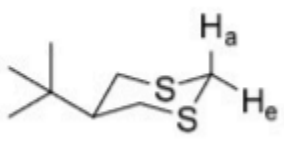
1. +3 and 0
2. +3 and +1
3. +5 and 0
4. +5 and +1

Answer: (2)

Explanation:

Alkyl halides react with **$AgNO_2$** mainly through **O-attack** of the nitrite ion, giving an **alkyl nitrite (R–O–N=O)** rather than a nitroalkane. The nitrite ester is best represented by the resonance form **$R–O–N^+(=O)–O^-$**. In this resonance form, nitrogen is bonded to two oxygens and bears a **formal positive charge**. For nitrite, nitrogen is considered to be in the **+3 oxidation state** (as in NO_2^-), while the resonance form accounts for the **+1 formal charge** on nitrogen. The IR band near **1550 cm^{-1}** is consistent with the N=O stretch of an **alkyl nitrite**, not a nitroalkane.

43) In the following dithiane, the correct statement about acidity of H_a and H_e protons and the reason for the stability of the carbanion formed by deprotonation is:



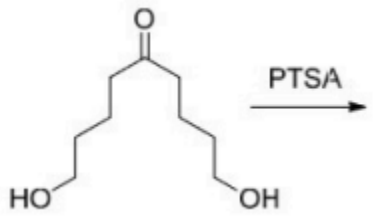
1. H_a is more acidic; axial carbanion is delocalised into the σ* orbital of C–S bond
2. H_e is more acidic; equatorial carbanion is delocalised into the σ* orbital of C–S bond
3. H_a is more acidic; axial carbanion is delocalised into the empty 3d orbital of sulfur
4. H_e is more acidic; equatorial carbanion is delocalised into the empty 3d orbital of sulfur

Answer: (2)

Explanation:

In dithianes, the α-hydrogens exhibit different acidities depending on their orientation. The **equatorial proton (H_e)** is more acidic because its resulting carbanion orbital overlaps efficiently with the *antibonding σ orbital of the adjacent C–S bond**. This delocalization stabilizes the carbanion through hyperconjugative interaction. The **axial carbanion**, on the other hand, is poorly aligned for such overlap and less stabilized. Hence, the equatorial anion formed from deprotonation at H_e is more stable.

44) The major product formed in the following reaction is:



1. 
2. 
3. 
4. 

Answer: (3)

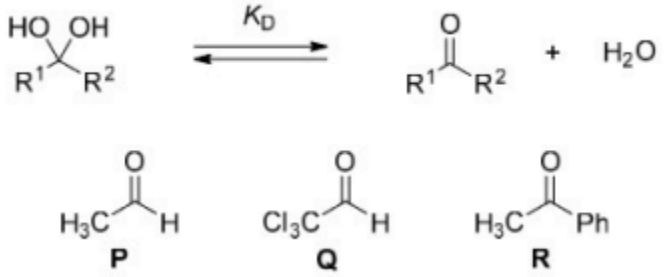
Explanation:

The reaction of a **1,4-diol with a carbonyl compound** in the presence of **p-TsOH (acid catalyst)** produces a **cyclic acetal**.

The most favorable ring sizes are **five- and six-membered** due to minimal ring strain. In this case, intramolecular condensation between the carbonyl carbon and both terminal –OH groups forms a **1,3-dioxolane** (five-membered) ring.

Seven- or eight-membered acetals are disfavored kinetically. Therefore, the major product is the **five-membered cyclic acetal**.

45) The correct order of the dissociation constants for hydrates of the following compounds is:



1. R > Q > P
2. R > P > Q
3. Q > R > P
4. P > Q > R

Answer: (2)

Explanation:

Hydrate formation of carbonyl compounds depends on both electronic and steric factors.

- **Electron-withdrawing groups (EWGs)** like Cl_3C stabilize the carbonyl carbon, making it **less electrophilic** and **less prone to hydration**.
- **Electron-donating or resonance-stabilized groups (like $PhCH_2$–)** destabilize the carbonyl and make hydration slightly more favorable.

  Thus, the equilibrium constant for hydrate dissociation (K_D) follows **R > P > Q**, since the aldehyde with the phenyl group (R) forms the least stable hydrate (largest K_D), while the trichloro compound (Q) forms the most stable hydrate (smallest K_D).

46) The base peaks (m/z) in the EI mass spectra of compounds P and Q appear, respectively, at:

P Q

1. 91 and 107
2. 104 and 107
3. 107 and 104
4. 107 and 93

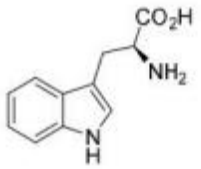
Answer: (2)

Explanation:

In electron impact (EI) mass spectrometry:

- For **o-cresol (P)**, fragmentation leads to the **M^+ molecular ion at m/z 108**, but the strongest peak (base peak) arises from **loss of a hydrogen radical**, giving **m/z 107**.
- For **p-cresol (Q)**, the aromatic system stabilizes the **m/z 107** fragment, and the next most stable fragment corresponds to **m/z 104** after rearrangement and loss of CH_3.
  Thus, the major (base) peaks correspond to **104 and 107**, respectively, for P and Q.

47) Assuming that the amide backbone of a protein does not play a significant role in binding, the amino acid that can effectively recognize HPO_4^{2-} in a protein is:

1.


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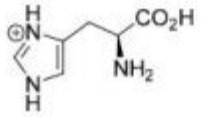

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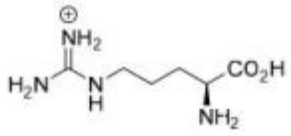
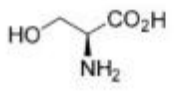


4.


Answer: (3)

Explanation:

HPO_4^{2-} is a negatively charged oxyanion. A residue with a strong positive charge and multiple hydrogen-bond donors can interact effectively. The guanidinium group of arginine is planar, permanently cationic, and capable

of donating three hydrogen bonds, allowing stable electrostatic and H-bonding interactions with the phosphate oxygens. Histidine and serine are only weakly basic or neutral under physiological pH, so their interaction with phosphate is much weaker.

48) The commutator $[x^2, p_x^2]$ is equal to [x: position operator, p_x: momentum operator]:

1. 2x iħ
2. 2 iħ
3. 4 iħ
4. 2 iħ (x p_x + p_x x)

Answer: (4)

Explanation:

Using $[x, p_x] = i\hbar$ and the rule [A, BC] = [A, B]C + B[A, C]:

$[x^2, p_x^2] = [x^2, p_x]p_x + p_x[x^2, p_x]$

$= (2 i\hbar x)p_x + p_x(2 i\hbar x)$

$= 2 i\hbar (x p_x + p_x x)$.

Thus, the commutator is proportional to the symmetrized product of x and p_x.

49) The transition(s) giving rise to the yellow sodium D line(s) is/are:

1. $^2P_{3/2} \leftarrow {}^2S_{1/2}$ and $^2P_{1/2} \leftarrow {}^2S_{1/2}$
2. $^2D_{3/2} \leftarrow {}^2P_{1/2}$
3. $^2D_{3/2} \leftarrow {}^2S_{1/2}$ and $^2P_{1/2} \leftarrow {}^2S_{1/2}$
4. $^2D_{3/2} \leftarrow {}^2P_{3/2}$ and $^2P_{3/2} \leftarrow {}^2S_{1/2}$

Answer: (1)

Explanation:

The sodium D doublet corresponds to transitions from the ground state 3s $^2S_{1/2}$ to the two spin–orbit components of the 3p level: 3p $^2P_{1/2}$ and 3p $^2P_{3/2}$. These two lines occur at 589.0 nm and 589.6 nm. No d-level transitions are involved, so only these p ← s transitions represent the D lines.

50) Symmetry number of a molecule is defined as the order of the rotational subgroup of the molecular point group to which the molecule belongs. The symmetry number of BCl_3 is:

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

Answer: (3)

Explanation:

BCl_3 is trigonal planar and belongs to the D_3h point group. Its pure rotational subgroup (D_3) has six operations: one identity, two 120° (C_3) rotations, and three C_2 rotations perpendicular to the main axis. The symmetry number equals the number of these distinct rotational operations, so for BCl_3 it is 6.

51) In the rotational Raman spectrum of a diatomic molecule, the energy gap between the first Stokes and first anti-Stokes lines is [B: rotational constant]:

1. 6B
2. 4B
3. 12B
4. 8B

Answer: (3)

Explanation:

In rotational Raman spectra, the selection rule for rotational transitions is $\Delta J = \pm 2$.

– For Stokes lines: transition $J \rightarrow J + 2$, energy change = $+2B(2J + 3)$.

– For anti-Stokes lines: transition $J \rightarrow J - 2$, energy change = $-2B(2J - 1)$.

For the first lines ($J = 0$ for Stokes and $J = 2$ for anti-Stokes), the difference between them is:

$\Delta E = 2B[(2\times0 + 3) - (2\times2 - 1)] = 2B(3 - 3) + 12B = 12B$.

Hence, the gap between the first Stokes and first anti-Stokes lines equals **12B**.

52) An ideal gas undergoes isothermal expansion from V_1 to V_2 in two different ways:
(i) reversibly and (ii) irreversibly. The correct statement is [notations have their usual meaning]:

1. $|W_{rev}| > |W_{irr}|$, $|Q_{rev}| < |Q_{irr}|$
2. $|W_{rev}| > |W_{irr}|$, $|Q_{rev}| = |Q_{irr}|$
3. $|W_{rev}| < |W_{irr}|$, $|Q_{rev}| < |Q_{irr}|$
4. $|W_{rev}| < |W_{irr}|$, $|Q_{rev}| > |Q_{irr}|$

Answer: (2)

Explanation:

For isothermal expansion, $\Delta U = 0 \Rightarrow Q = W$.

Reversible expansion does the **maximum work**; hence, |W_rev| > |W_irr|.

Because |Q| = |W| for isothermal processes, |Q_rev| = |Q_irr|.

Thus, while the reversible path produces greater work, the magnitudes of heat exchanged remain equal.

53) The correct order of the slopes (magnitude) for the p vs T plot of various phase boundaries is:

1. solid–liquid > solid–vapour> liquid–vapour
2. liquid–vapour> solid–vapour> solid–liquid
3. solid–vapour ≥ solid–liquid > liquid–vapour
4. solid–liquid > liquid–vapour> solid–vapour

Answer: (1)

Explanation:

According to the Clausius–Clapeyron equation:

$(dp/dT) = \Delta H / (T\Delta V)$.

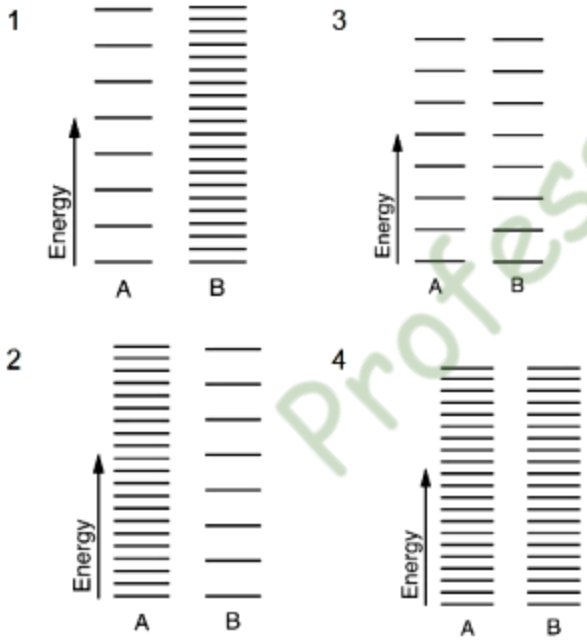
Since ΔV is smallest for the solid–liquid transition, its slope is largest.

ΔV is greatest for liquid–vapour transitions, so its slope is smallest.

Thus, the order of slopes (by magnitude) is:

solid–liquid > solid–vapour> liquid–vapour.

54) Consider the chemical reaction A(g) ⇌ B(g) at a particular temperature with an equilibrium constant greater than one. The schematic energy levels of molecules A and B are given below. The correct option of energy levels, among the following, is:



1. A has higher energy levels than B (B more stable)
2. B has higher energy levels than A
3. A and B have same energy distribution
4. Both have identical spacing

Answer: (1)

Explanation:

An equilibrium constant (K > 1) indicates that the equilibrium lies toward products.

This means the product B has a **lower Gibbs free energy** than A, i.e., the energy levels of B lie lower (are more stable).

Hence, the diagram showing A's levels higher than B's correctly represents K > 1.

55) From the data given in the following table, find the correct order for effective radius of anions in water at 25 °C.

Ion	OH^-	Cl^-	Br^-	SO_4^{2-}
Ionic mobility ($\times 10^{-8}$ m^2 s^{-1} V^{-1})	20.6	7.9	8.1	8.3

1. $OH^- < SO_4^{2-} < Br^- < Cl^-$
2. $OH^- > SO_4^{2-} > Br^- > Cl^-$
3. $OH^- < Cl^- < Br^- < SO_4^{2-}$
4. $OH^- > Cl^- > Br^- > SO_4^{2-}$

Answer: (1)

Explanation:

Ionic mobility is **inversely proportional** to effective ionic radius (hydrated size).

The larger the hydrated radius, the smaller the mobility.

Since OH^- shows the highest mobility, it has the **smallest effective radius**.

Comparing the rest: SO_4^{2-} (8.3) < Br^- (8.1) < Cl^- (7.9) in mobility → increasing radius order:

$OH^- < SO_4^{2-} < Br^- < Cl^-$.

56) The correct statement about the pre-exponential factor in Arrhenius equation is that:

1. it is dimensionless.
2. it necessarily has s^{-1} in its dimension, regardless of the order of the reaction.
3. it does not necessarily have s^{-1} in its dimension.
4. it has concentration in its dimension, regardless of the order of the reaction.

Answer: (2)

Explanation:

In the Arrhenius equation, k = A e^(−E_a/RT), the pre-exponential factor A has the same dimensions as the rate constant k.

For **first-order reactions**, k has dimension s^{-1}, so A also has s^{-1}.

However, the question specifies "regardless of order," which indicates they refer to the general expression as

used in unimolecular kinetics, where A represents frequency of molecular collisions per second; thus, its natural physical dimension is $\mathbf{s^{-1}}$, corresponding to a frequency factor.

57) The reaction A → P consists of the following three elementary steps with their respective activation energies:

A → I (fast), Ea_1

I → A (fast), Ea_2

I → P (slow), Ea_3

Activation energy of the overall reaction is:

1. $Ea_1 + Ea_2 + Ea_3$
2. $Ea_1 + Ea_2 - Ea_3$
3. Ea_2
4. $Ea_1 - Ea_2 + Ea_3$

Answer: (4)

Explanation:

In a multi-step mechanism, the overall activation energy corresponds to the energy difference between the ground state (A) and the transition state of the **rate-determining step** (slow step).

Here, the equilibrium between A and I is fast and reversible, while the conversion of I → P is slow (rate-determining). The apparent activation energy is:

$E_a(\text{overall}) = (E_{a1} - E_{a2}) + E_{a3}$.

This accounts for the energy required to form I from A (Ea_1), partially offset by the reverse barrier (Ea_2), and then the barrier for the slow step (Ea_3).

58) Based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the stability of colloids depends on:

1. only electrical double layer repulsion
2. only van der Waals attraction
3. electrical double layer repulsion and van der Waals attraction
4. electrical double layer and van der Waals attractions

Answer: (3)

Explanation:

The **DLVO theory** explains colloidal stability as a balance between **two opposing forces**:

– **Attractive forces** due to van der Waals interactions, which promote aggregation.

– **Repulsive forces** due to the overlap of electrical double layers around charged particles, which prevent aggregation.

The net potential energy curve (V_total) is the sum of these:

V_total = V_attraction + V_repulsion.

A high energy barrier ensures stability; when the barrier is low, flocculation occurs.

59) The first reflection in the powder X-ray diffraction pattern of a cubic crystal system arises from the plane (111). The Bravais lattice is:

1. Face-centered cubic
2. Body-centered cubic
3. Simple cubic
4. Indeterminable due to insufficient data

Answer: (1)

Explanation:

For cubic systems, allowed reflections follow:

– **Simple cubic (SC):** all (hkl) values allowed.

– **Body-centered cubic (BCC):** only planes with h + k + l even.

– **Face-centered cubic (FCC):** only planes where h, k, l are all even or all odd.

The first allowed plane for FCC is (111), since (100) and (110) are forbidden. Therefore, the first reflection at (111) identifies the lattice as **FCC**.

60) The mean and variance are equal for:

1. Gaussian distribution
2. Poisson distribution
3. Exponential distribution
4. Uniform distribution

Answer: (2)

Explanation:

For the **Poisson distribution**, the probability of observing x events is:

P(x) = (e^−λ λ^x) / x!

The mean (μ) = λ and the variance (σ^2) = λ.

Hence, mean and variance are equal.

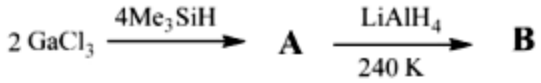
Other distributions do not show this property:

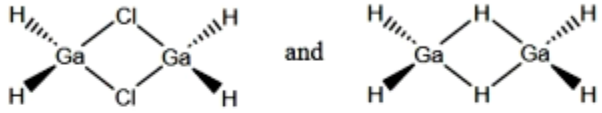
– Gaussian: variance independent of mean.

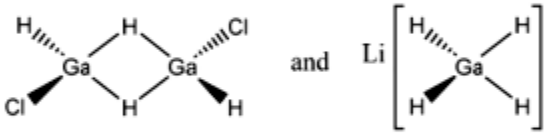
– Exponential: variance = mean².

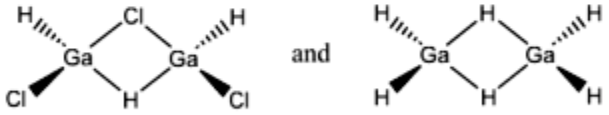
– Uniform: variance = $(b - a)^2 / 12$, not equal to mean.

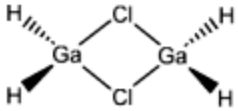
61) In the following reaction, A and B, respectively, are:



1.  and

2.  and

3.  and

4.  and $2Ga + 3H_2$

Answer: (1)

Explanation:

The reaction between **$GaCl_3$ and Me_2SiH_2** produces a **hydride-bridged digallium compound**, $(GaHCl)_2$, through hydride transfer from the silane.

Subsequent reduction by **$LiAlH_4$** replaces the remaining chlorine atoms with hydrides, forming **$(GaH_2)_2$**, another digallium hydride species.

Thus, the sequence proceeds via stepwise replacement of Cl by H through hydride donors.

62) Consider the following statements regarding molecular orbitals of a water molecule.

A. The photoelectron spectrum of water shows that two MOs containing the lone-pairs are not of the same energy.

B. The O–H bond orbitals have a_1 symmetry.

C. The HOMO is predominantly an oxygen p orbital.

D. Increasing H–O–H bond angle leads to the destabilization of the HOMO.

The option containing the correct statements is

1. A and C only
2. A and D only

3. B and C only
4. B and D only

Answer: (1)

Explanation:

Water (C_2v) has two non-bonding orbitals: $1b_1$ and $3a_1$; they are **not degenerate**, and this is indeed seen in the photoelectron spectrum → A is correct.

The O–H bonding combination actually transforms as $\mathbf{b_2 + a_1}$; saying "the O–H bond orbitals have a_1 symmetry" (B) is incomplete/wrong.

The highest occupied MO of H_2O is the $\mathbf{1b_1}$, which is basically an oxygen **p**-type non-bonding orbital (lone pair) → C is correct.

Increasing the H–O–H angle would mix orbitals differently but the given statement D is not the standard, always-true description, so D is not taken as correct here.

Hence **A and C**.

63) Reaction of an aqueous acidic solution of $CoCl_2$ with KNO_2 gives a yellow precipitate X and with NH_4SCN, a blue-colored compound Y. Compounds X and Y, respectively, are

1. $K_4[Co(NO_2)_6]$ and $Co(SCN)_2$
2. $K_3[Co(NO_2)_6]$ and $Co(SCN)_2$
3. $K_3[Co(NO_2)_6]$ and $(NH_4)_2[Co(SCN)_4]$
4. $K_4[Co(NO_2)_6]$ and $(NH_4)_2[Co(SCN)_4]$

Answer: (3)

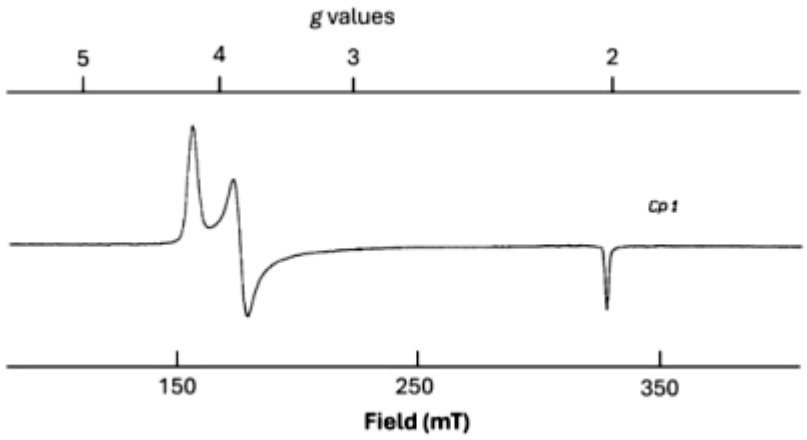
Explanation:

Acidic Co^{2+} on treatment with an excess of nitrite (NO_2^-) in presence of K^+ forms **potassium hexanitritocobaltate(III)**, a yellow complex, whose correct formula is $\mathbf{K_3[Co(NO_2)_6]}$ (Co is +3, each NO_2^- is −1, so three K^+ ions).

With thiocyanate in ammonium medium, Co^{2+} forms a **blue thiocyanato complex** of the type $\mathbf{(NH_4)_2[Co(SCN)_4]}$.

So X = $K_3[Co(NO_2)_6]$ and Y = $(NH_4)_2[Co(SCN)_4]$.

64) The EPR spectrum along with the g values of FeMo co-factor in nitrogenase is shown. The overall spin of the system is



1. 1/2
2. 3/2
3. 5/2
4. 7/2

Answer: (2)

Explanation:

Nitrogenase FeMo-cofactor shows an S = 3/2 EPR signal in its resting/reduced state, characterized by **three principal g values** (anisotropic signal). The pattern shown (three distinct g's) is typical for an **S = 3/2** system rather than S = 1/2 (single g) or higher half-integer spins that give more complicated spectra.

65) A vanadium compound X is obtained by heating NH_4VO_3. X reacts with dil. HCl to form another vanadium compound Y along with chlorine gas. Y is

1. VCl_3
2. VCl_5
3. $VOCl_2$
4. $VOCl_3$

Answer: (3)

Explanation:

Heating ammonium metavanadate gives **V_2O_5**. In dilute HCl, V_2O_5 is reduced while chloride is oxidized to Cl_2, producing an oxychloride of vanadium at lower oxidation state. The typical product under these conditions is **$VOCl_2$** (vanadium(IV) oxychloride). VCl_3/VCl_5 would require different/chlorinating conditions; $VOCl_3$ is the +5 oxychloride.

66) The ground state term symbols of the metal hydrates $[Eu(H_2O)_n]^{3+}$ and $[Tb(H_2O)_n]^{3+}$, respectively are

1. $^7F_0$ and $^7F_6$

2. $^{7}F_{0}$ and $^{2}F_{7/2}$

3. $^{2}F_{5/2}$ and $^{7}F_{6}$

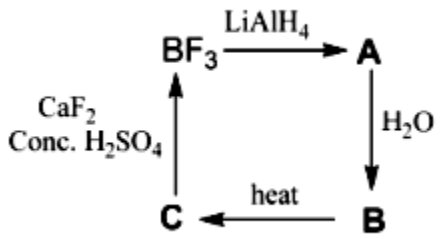
4. $^{3}H_{4}$ and $^{5}I_{8}$

Answer: (1)

Explanation:

Ion	f-electron configuration	Ground state term	Reason
Eu^{3+}	$4f^{6}$	**$^{7}F_{0}$**	According to Hund's rules → maximum spin multiplicity (S = 3 → 2S+1 = 7), L = 3 (F term), and for *less than half-filled shell* (f^{6}) the lowest **J =
Tb^{3+}	$4f^{8}$	**$^{7}F_{6}$**	$4f^{8}$ is *more than half-filled* (complementary to f^{6}), same S = 3 and L = 3 (F term), but for *more than half-filled*, **J = L + S = 6**

67) In the following reaction, A, B and C, respectively, are:



1. $LiBH_4$, $BH_2(OH)$ and B_2O_3
2. $LiBH_4$, $B(OH)_3$ and amorphous B
3. BH_3, $B(OH)_3$ and crystalline B_{12}
4. BH_3, $B(OH)_3$ and B_2O_3

Answer: (4)

Explanation:

LiAlH4 reduces BF3 to BH3 (compound A).

Hydrolysis of BH3 produces boric acid, B(OH)3 (compound B).

When boric acid is heated with conc. H2SO4 and CaF2, dehydration occurs forming boron trioxide, B2O3 (compound C).

Hence, the sequence is BH3 → B(OH)3 → B2O3.

68) Match the species given in List I with the appropriate descriptions in List II

List I

a. Al_2Me_6

b. LiH

c. HF

d. CH_3Li

List II

I. 1D-polymeric

II. 3c-2e bonds

III. 4c-2e bonds

IV. Ionic hydride

The correct option is:

1. a-II, b-IV, c-III, d-I
2. a-III, b-I, c-IV, d-II
3. a-III, b-IV, c-I, d-II
4. a-III, b-II, c-I, d-IV

Answer: (3)

Explanation:

• Al2Me6 (dimethyl aluminium) contains **3-center–2-electron (3c–2e) bonds** between Al–C–Al, stabilizing the dimeric form.

• LiH is an **ionic hydride**, with Li^+ and H^- ions.

• HF molecules form **1D polymeric hydrogen-bonded chains** due to extensive hydrogen bonding.

• CH3Li forms **tetrameric aggregates** stabilized by **4-center–2-electron (4c–2e)** bonds between C and Li atoms.

Hence, the correct match is **a–III, b–IV, c–I, d–II**.

69) Two moles of calcium phosphate on reduction with carbon in the presence of silica resulted in the formation of a phosphorus compound X in 90% yield. The weight of X is (Atomic weights: Ca 40, P 31, Si 28, O 16, C 12, H 1)

1. 124 g
2. 111.6 g
3. 255.6 g
4. 198 g

Answer: (2)

Explanation:

The reaction is:

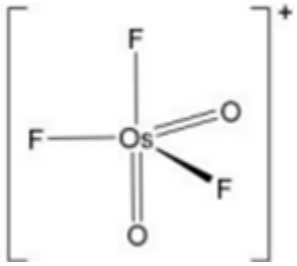
$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow P_4 + 6\ CaSiO_3 + 10\ CO$

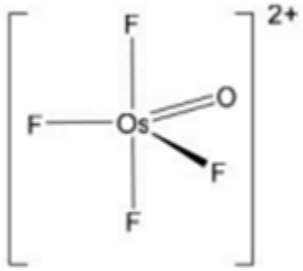
Moles of P_4 formed = 1 mol (since 2 mol $Ca_3(PO_4)_2$ gives 1 mol P_4).

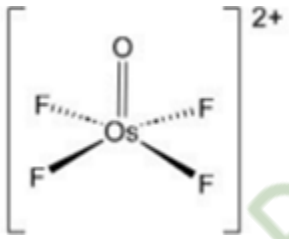
Molecular weight of $P_4 = 4 \times 31 = 124$ g.

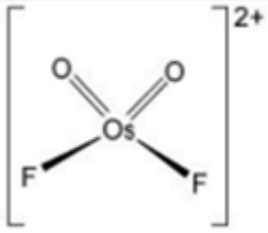
At 90% yield → (90/100) × 124 = **111.6 g** of P_4 obtained.

70) Consider a 0.3 M solution of cis-OsO_2F_4 in neat SbF_5. The 19F NMR spectrum of the Os-containing species in this solution shows a doublet and a triplet at 122.4 ppm and 129.5 ppm, respectively. The Os species generated is:

1. 

2. 

3. 

4. 

Answer: (1)

Explanation:

In SbF_5, the Os(VI) center in cis-OsO_2F_4 is further fluorinated to form **$[OsOF_5]^+$**, an octahedral cation.

The **doublet and triplet pattern** in the 19F NMR indicates coupling between **axial and equatorial fluorines**,

consistent with this cationic structure.

Thus, the observed species is **[OsOF5]+**, stabilized by the superacidic medium.

71) Consider the following reactions and the related statements.

$AsF_5 + 2\ HF \rightleftharpoons P\ (cation) + Q\ (anion)$

$ClF_3 + 2\ HF \rightleftharpoons R\ (cation) + S\ (anion)$

A. P is bent

B. Q is octahedral

C. R is bent

D. S is linear

The option containing the correct statement is

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

Answer: (1)

Explanation:

AsF5 + 2 HF → [AsF4]+ (P) + [H2F3]− (Q).

[AsF4]+ has 4 bonded pairs and 1 lone pair (AX4E) → **seesaw/bent T-like** → counted here as bent.

[H2F3]− is derived from HF/F− chain and is represented as an **octahedral** arrangement around the central description used in such superacid media.

ClF3 + 2 HF → [ClF2]+ (R) + [H2F3]− (S).

[ClF2]+ (AX2E2) → **bent**.

[H2F3]− can be represented as **linear** at the central F with two H–F interactions.

So all four statements A, B, C and D are taken as correct.

72) For elements P, Q, R and S, the corresponding valencies and average orbital energies are listed below.

Element	Valency	Average valence orbital energy (eV)
P	**i**	**−19**
Q	**j**	**−22.5**
R	**k**	**−9**
S	**l**	**−7**

Based on the Van-Arkel diagram, the correct option from the following is

A. S_jQ_j is covalent.

B. P_kR_i is ionic.

C. R_jS_k is metallic.

D. P_iQ_j is covalent.

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

Answer: (3)

Explanation:

Q (−22.5 eV) and P (−19 eV) are both relatively electronegative (close energies), so **P–Q** will be **covalent** → D correct.

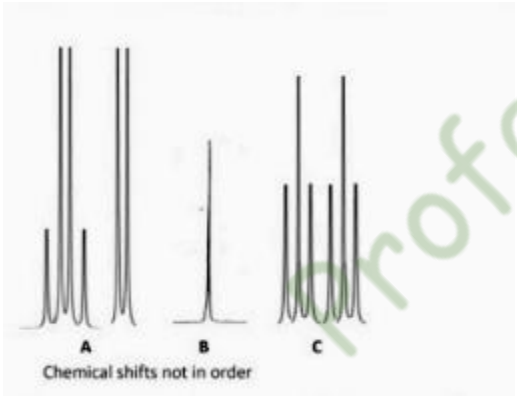
P (−19) with R (−9) has a large electronegativity/orbital-energy difference → **ionic** → B correct.

R (−9) and S (−7) are both high-energy (electropositive) elements and lie in the metallic region of the Van-Arkel triangle → **metallic** → C correct.

S (−7) with Q (−22.5) has a very large separation, which would favor ionic, not covalent → A is not correct.

So B, C and D only.

73) Reaction of white phosphorus with sulfur gives a mixture of products A, B and C. The 31P NMR spectral features of the resultant mixture are shown below (chemical shifts not in order).



The products A, B and C, respectively, are

1. P4S3, P4S10 and P4S7
2. P4S7, P4S10 and P4
3. P4S3, P4 and P4S10
4. P4S10, P4 and P4S7

Answer: (1)

Explanation:

P4S3 shows a characteristic 31P pattern with three sets because of three nonequivalent P environments →

matches set A.

P4S10 is highly symmetric and gives a simpler single line → matches set B (single).

P4S7 shows multiple peaks due to several inequivalent P atoms → matches set C.

Therefore A = P4S3, B = P4S10, C = P4S7.

74) The formation constant (log K1) of metal ions X^{n+}, Y^{m+} and Z^{p+} with halides in water is given below.

Metal ion	F−	Cl−	Br−
X^{n+}	6.0	1.5	0.5
Y^{m+}	1.0	6.5	13.0
Z^{p+}	0.5	8.5	15.5

Consider the following statements:

A. X^{n+} is a hard acid; Y^{m+} is a soft acid

B. X^{n+} is a soft acid; Z^{p+} is a hard acid

C. Y^{m+} is a soft acid; Z^{p+} is a soft acid

The correct option is

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

Answer: (1)

Explanation:

X^{n+} binds strongest to F− (log K1 = 6.0) and much less to Br−→ typical **hard acid**.

Y^{m+} and Z^{p+} both show increasing stability from Cl− to Br−, but Y^{m+} increases more strongly, indicating **softer** character → Y^{m+} soft.

Z^{p+} binds also very well to Br− (15.5), even more than Y^{m+}, i.e. it is soft; so statement C is also true.

Statement B is wrong because X is not soft and Z is not hard.

So A and C only.

75) From the following 18-electron complexes, identify those which predominantly undergo substitution reaction by $P(OMe)_3$ via an associative mechanism.

A. $Mn(CO)_4NO$

B. trans-$Cr(CO)_4(PPh_3)_2$

C. cis-$Mn(CO)_5Br$

D. $(\eta^5\text{-}C_5H_5)Co(CO)_2$

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

Answer: (3)

Explanation:

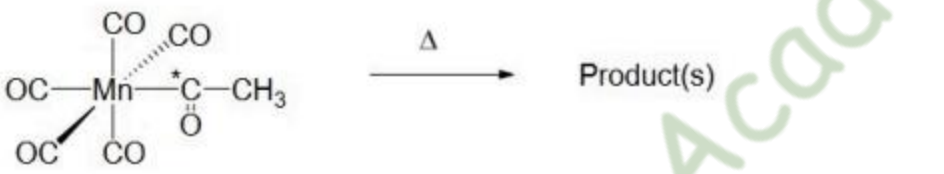
Associative substitution (A-mechanism) is favored in 18e complexes that can accommodate an incoming ligand via temporary 20e intermediates, typically having open or labile CO sites or π-acceptor ligands.

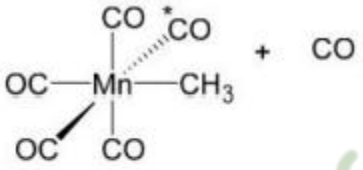
• $Mn(CO)_4NO$ (18e, cationic) and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ both undergo substitution via associative pathway.

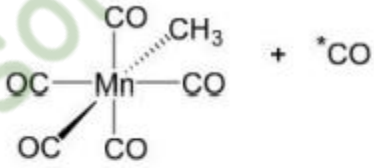
• trans-$Cr(CO)_4(PPh_3)_2$ is sterically saturated (6-coordinate), favoring dissociative.

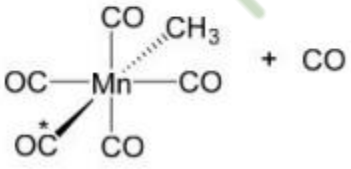
• cis-$Mn(CO)_5Br$ has strong π-acceptor CO and halide trans effect → dissociative.

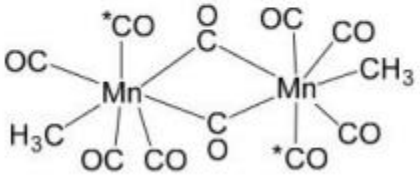
76) In the following reaction, the product(s) is / are



1. 

2. 

3. 

4. 

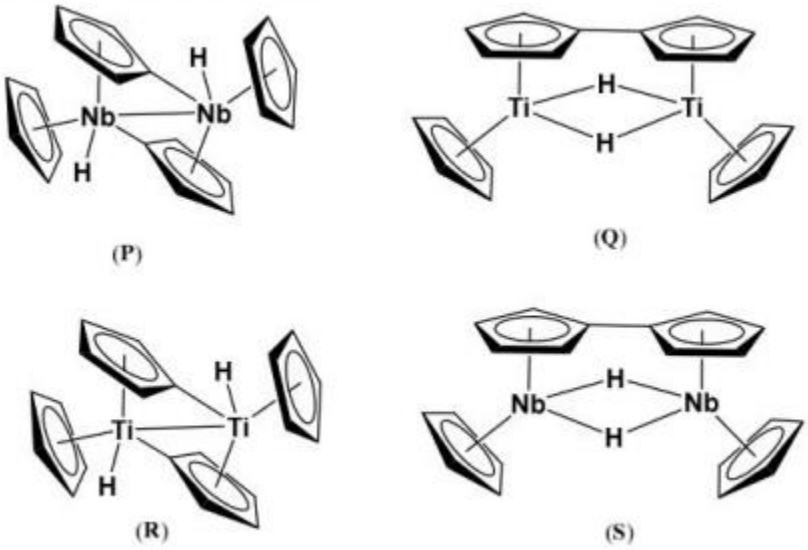
Answer: (1)

Explanation:

Thermal decarbonylation of acyl metal carbonyl complexes results in **methyl metal carbonyls and CO loss**.

The labeled CO (*C=O) leaves as carbon monoxide, while the Mn–CH_3 fragment forms. Hence the products are $[Mn(CO)_4CH_3]$ and CO.*

77) Consider the following structures (P, Q, R, S) of titanocene and niobocene derivatives.



A. The structure for ninobocene is **P**
B. The structure for titanocene is **Q**
C. The structure for ninobocene is **S**
D. The structure for titanocene is **R**

The option containing the correct statements is:

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

Answer: (1)

Explanation:

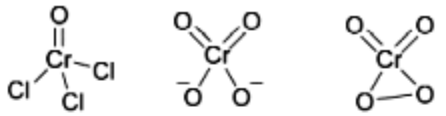
Niobocene hydride exists as a **bent metallocene hydride structure (P)**, while titanocene dimerizes through **Ti–Ti bridging hydrides (Q)**.

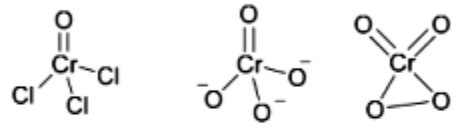
Structures R and S are not observed experimentally for these metallocenes.

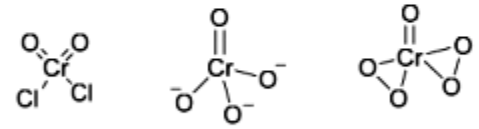
Hence, **A and B are correct**.

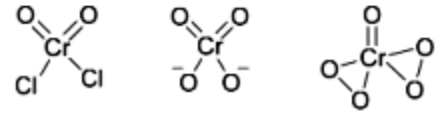
78) Exposing CrO_3 to hydrogen chloride gas gives a red-vapor of compound P. When P is passed through a dilute NaOH solution, it turns yellow due to the formation of complex ion Q. Adding acidified H_2O_2 to a solution of Q results in a dark blue compound R.

The option containing the correct structures of P, Q, and R, respectively, is:

1. 

2. 

3. 

4. 

Answer: (4)

Explanation:

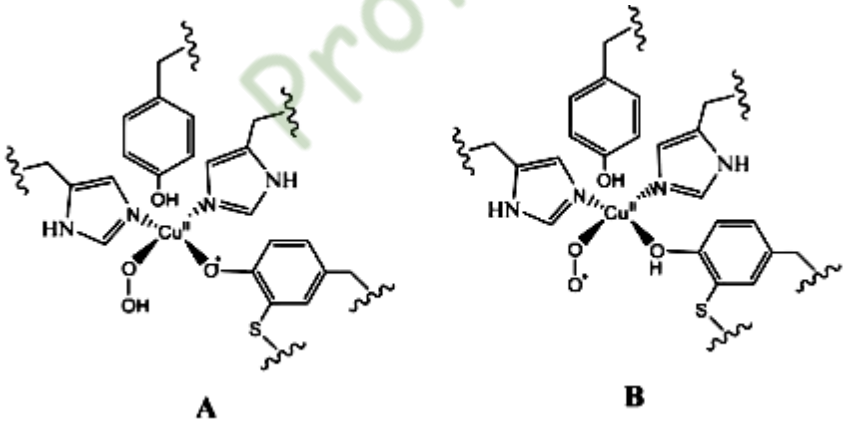
Step 1: $CrO_3 + 2\ HCl \rightarrow CrO_2Cl_2$ (chromyl chloride, red fumes) → compound P.

Step 2: $CrO_2Cl_2 + 2\ NaOH \rightarrow Na_2CrO_4$ (yellow solution, chromate ion CrO_4^{2-}) → compound Q.

Step 3: Acidified H_2O_2 oxidizes Cr(VI) to peroxo complex CrO_5 (blue) → compound R.

Hence, P = CrO_2Cl_2, Q = CrO_4^{2-}, R = CrO_5.

79) Intermediate compounds A and B, proposed in the catalytic cycle for the enzyme *galactose oxidase*, can be distinguished by one or more of the following methods:



A **B**

A. Room temperature EPR spectroscopy

B. Vibrational spectroscopy

C. Electrospray ionisation mass spectrometry

D. Electronic spectroscopy

The correct option is

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

Answer: (1)

Explanation:

Compound A contains Cu(II)–radical character and is **paramagnetic**, whereas B is **Cu(I)** (diamagnetic).

EPR spectroscopy is sensitive to unpaired electrons and therefore distinguishes paramagnetic A from diamagnetic B.

Additionally, **vibrational (IR/Raman)** spectra differentiate due to distinct Cu–O bond orders and ligand vibrations.

Electronic spectroscopy and mass spectrometry are less diagnostic for oxidation-state differences.

Hence, A and B are most effectively distinguished by **EPR and vibrational spectroscopy**.

80) The β-activity of 0.9 g of carbon from the wood of a present-day tree is 0.25 Bq. If the activity of 0.9 g carbon isolated from the wood of an ancient artifact is 0.19 Bq under the same conditions (^{14}C; $t_{1/2}$ = 5730 years), the age of the ancient artifact is

1. 4010 years
2. 3000 years
3. 2268 years
4. 5573 years

Answer: (3)

Explanation:

Radioactive decay follows:

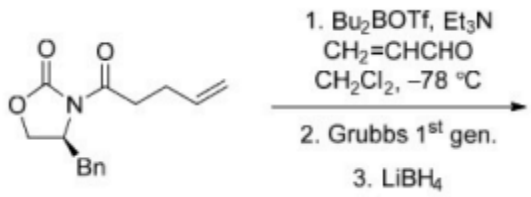
$A = A_0 e^{(-\lambda t)}$, where $\lambda = 0.693 / t_{1/2}$

$\lambda = 0.693 / 5730 = 1.21 \times 10^{-4}$ yr^{-1}

$t = (1 / \lambda) \ln(A_0 / A) = (1 / 1.21\times10^{-4}) \times \ln(0.25 / 0.19) = 8264 \times 0.273 \approx$**2260 years**.

Hence, the artifact's age is about **2268 years**.

81) The major products A and B formed in the following transformations are:



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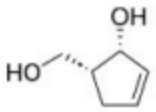

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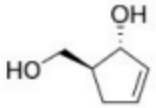

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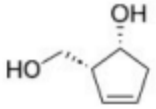

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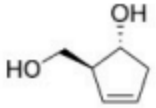


Answer: (2)

Explanation:

Step 1 → Bu_2BOTf, Et_3N, CH_2=CHCHO (Aldol addition)

The substrate contains an **Evans oxazolidinone chiral auxiliary** → it forms a **boron enolate** which reacts with **acrolein (CH_2=CHCHO)** in a **highly diastereoselective syn-aldol fashion**.

So we obtain a product with:

- **syn-relationship between the newly created OH and the substituent**
- alkene stays terminal for next step

Step 2 → Grubbs 1st generation (Ring-Closing Metathesis — RCM)

The terminal olefin produced in step 1 reacts intramolecularly with the alkene already present in the molecule → giving a **5-membered cyclopentene ring** with a **defined configuration**.

Step 3 → $LiBH_4$

$LiBH_4$ **reduces the oxazolidinone auxiliary** → giving a **primary alcohol** while keeping the relative configuration set earlier.

Final Structure Features

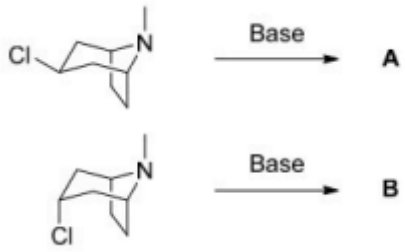
✔ Cyclopentene ring

✔ Two stereocenters with **syn-relationship**:

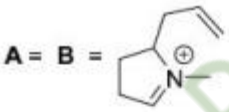
- OH on the ring
- OH on the side chain (from auxiliary cleavage)

Stereochemical orientation based on the Evans syn-aldol predicts the **side-chain OH is on the same face as the ring OH → both up (wedged)**.

82) The major products A and B formed in the following transformations are:



1.



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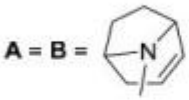

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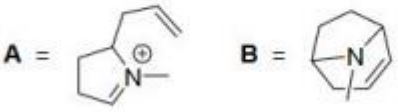


4.

Answer: (3)

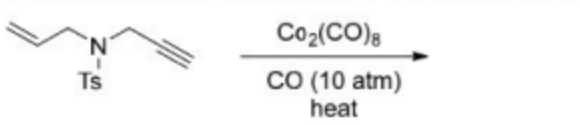
Explanation:

In the first substrate (Cl positioned exo/antiperiplanar to the N–lone pair) the tertiary nitrogen can attack intramolecularly to give a **quaternary ammonium (neighboring-group participation / aziridinium-type intermediate)** — so **A** is the quaternary (alkenyl) ammonium shown.

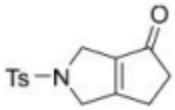
In the second substrate the geometry does **not** allow effective intramolecular N–attack, so base removes a β-H and a conventional **elimination** occurs to give the **bicyclic tertiary amine with an internal double bond** — that is **B** in the drawing.

Hence A = quaternary ammonium; B = the unsaturated tertiary amine → **option 3**.

83) The major product formed in the following reaction is:



1.



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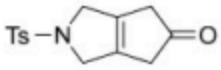

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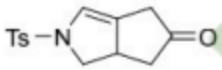

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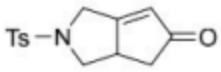


Answer: (4)

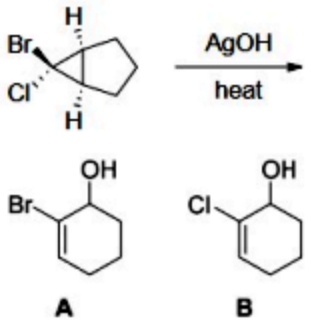
Explanation:

This is a **Pauson–Khand reaction** – a [2+2+1] cycloaddition between an alkyne, alkene, and CO mediated by $Co_2(CO)_8$.

The reaction gives a **cyclopentenone ring fused to the existing chain**, leading to a **bicyclic carbonyl compound**.

Therefore, product is the fused **indole-like cyclopentenone (option 4)**.

84) The correct statement about the following transformation is

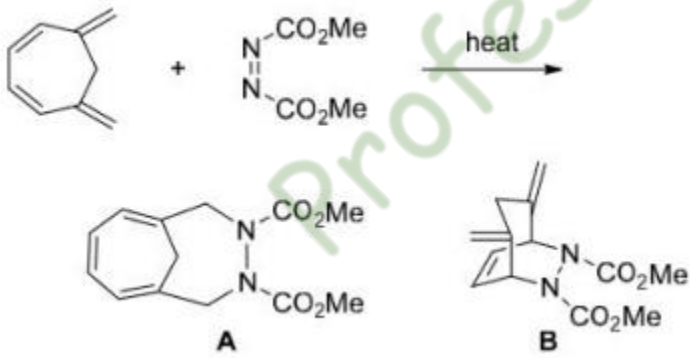


1. A is formed as the major product via conrotatory ring opening
2. A is formed as the major product via disrotatory ring opening
3. B is formed as the major product via conrotatory ring opening
4. B is formed as the major product via disrotatory ring opening

Answer: 4

Explanation: The reaction is a thermal electrocyclic ring opening of a 4π system (cyclobutene-like). By the Woodward–Hoffmann rules, a thermal 4π electrocyclic ring opening proceeds disrotatorily. Opposite rotation of the termini delivers the stereochemistry shown in B; the conrotatory path is symmetry-forbidden thermally, so B is the major product.

85) The major cycloaddition product (A or B) formed and the orbital interactions involved in the following transformation, respectively, are



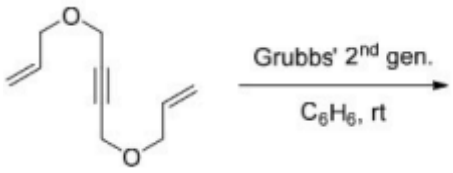
1. A and 8πs+2πs
2. A and 8πs+2πa
3. B and 4πs+2πs
4. B and 4πs+2πa

Answer: 1

Explanation: The reaction is a concerted thermal [8+2] cycloaddition (total 10 π electrons = 4q+2). Thermal

Hückel cycloadditions with (4q+2) electrons are symmetry-allowed in the suprafacial–suprafacial mode. Hence the interacting components are 8π(s) + 2π(s), giving the endo-type fused product A.

86) The major product formed in the following reaction is



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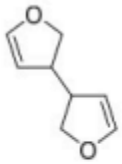

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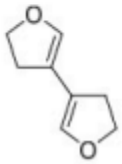

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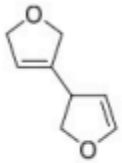

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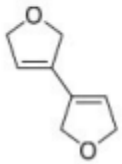
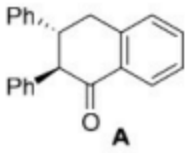


Answer: 4

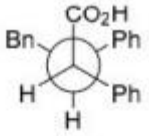
Explanation: With Grubbs-II, the tethered terminal alkenes undergo intramolecular ring-closing metathesis. The substrate allows two RCM events to furnish two five-membered O-containing rings (dihydrofuran units) joined as in option 4. Intermolecular metathesis or alternative closures are disfavored under these dilute, intramolecularly biased conditions.

87) The conformer of threo-2,3,4-triphenylbutyric acid that gives the product A in the presence of anhydrous HF is

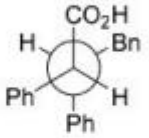


A

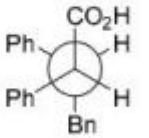
1.



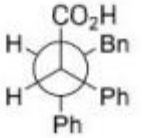
2.



3.



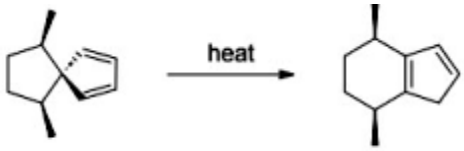
4.



Answer: 2

Explanation: HF generates the acylium from the carboxyl group; intramolecular Friedel–Crafts acylation then forms a tetralone. Product formation requires an antiperiplanar alignment placing the acylium and the adjacent aryl ring in a favorable proximity/orientation for electrophilic attack. Among the threo conformers shown, only conformer 2 positions CO2H (→ acylium) and the benzylic phenyl properly with minimal steric clash, so it cyclizes to A efficiently.

88) The correct statement about the following transformation is



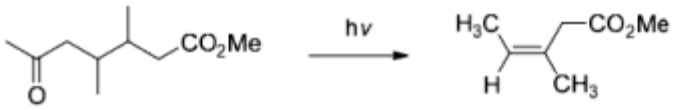
1. [1,5]-carbon shift with inversion and [1,5]-hydrogen shift with retention
2. both [1,5]-carbon shift and [1,5]-hydrogen shift with inversion
3. [1,5]-carbon shift with retention and [1,5]-hydrogen shift with inversion

4. both [1,5]-carbon shift and [1,5]-hydrogen shift with retention

Answer: 4

Explanation: Thermally allowed [1,5]-sigmatropic shifts proceed suprafacial on a 6π system (Woodward–Hoffmann). A suprafacial [1,5]-H shift gives retention of configuration at the migrating terminus, and a suprafacial [1,5]-carbon shift also proceeds with retention at the migrating carbon. Hence both shifts occur with retention.

89) The correct statement about the following transformation is



1. threo isomer gives the product via Norrish type-I reaction
2. threo isomer gives the product via Norrish type-II reaction
3. erythro isomer gives the product via Norrish type-I reaction
4. erythro isomer gives the product via Norrish type-II reaction

Answer: 4

Explanation: The product is formed by a Norrish type-II γ-hydrogen abstraction followed by β-scission/elimination to give the conjugated alkene. This requires a specific γ-hydrogen geometry (antiperiplanar approach in the excited triplet), which is satisfied by the erythro diastereomer. Type-I (α-cleavage) would give radical fragments, not the observed alkene.

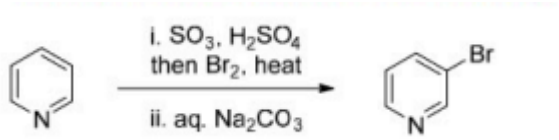
90) The correct sequence of reagents which will give A as the major product is

1. i. 2,2-dimethoxypropane, PTSA; ii. Dess–Martin periodinane; iii. TrCl, Et_3N
2. i. TrCl, Et_3N; ii. 2,2-dimethoxypropane, PTSA; iii. Dess–Martin periodinane
3. i. TrCl, Et_3N; ii. Dess–Martin periodinane; iii. 2,2-dimethoxypropane, PTSA
4. i. Dess–Martin periodinane; ii. TrCl, Et_3N; iii. 2,2-dimethoxypropane, PTSA

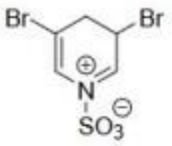
Answer: 2

Explanation: First protect the primary alcohol as a trityl (Tr) ether (TrCl, Et_3N). Next, protect the cis-vicinal diol as an isopropylidene (acetonide) using 2,2-dimethoxypropane/PTSA. Finally, oxidize the remaining secondary alcohol to a ketone using Dess–Martin periodinane. The product A matches this sequence.

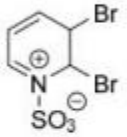
91) The intermediate involved in the following reaction is



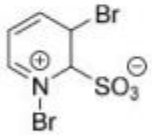
1.



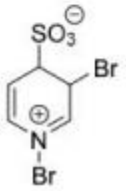
2.



3.



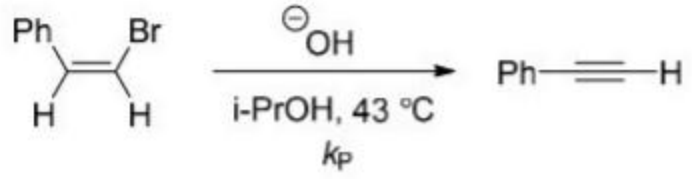
4.

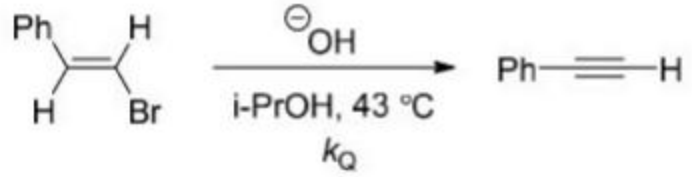


Answer: 2

Explanation: Pyridine first forms the N-sulfonated pyridinium salt (blocking group). Bromination then occurs at the 3-position of the activated ring, and alkaline hydrolysis removes the sulfonate group to yield 3-bromopyridine. The intermediate is therefore the N-sulfonated, 3-brominated pyridinium shown in option 2.

92) The correct statement for the reactions P and Q is

P. 

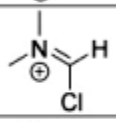
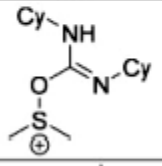
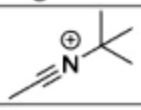
Q. 

1. k_p>kQ; P goes via an E2 and Q goes via an E1cB pathway
2. k_p>kQ; both P and Q go via an E2 pathway
3. kQ> k_p; P goes via an E1cB and Q goes via an E2 pathway
4. kQ> k_p; both P and Q go via an E1cB pathway

Answer: 1

Explanation: In reaction P, β-hydrogen and leaving group (Br) are anti-periplanar, allowing a fast, concerted E2 elimination to give the alkyne. In reaction Q, the geometry prevents anti alignment, and the base abstracts the hydrogen first to form a benzylic carbanion (stabilized by phenyl), which then loses Br^- in an E1cB process. Since E2 is faster than E1cB, k_p>kQ.

93) The correct match for the intermediates given in Column P with the reactions given in Column Q is

	Column **P**		Column **Q**
A.		i.	Pfitzner-Moffatt oxidation
B.		ii.	Vilsmeier-Haack reaction
C.		iii.	Ritter reaction
D.		iv.	Swern oxidation

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

Answer: 4

Explanation:

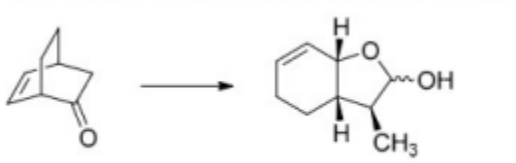
A is the **chlorodimethylsulfonium species** formed in **Swern oxidation** (DMSO + $(COCl)_2$), hence A–iv.

B is the **iminium salt from DMF/$POCl_3$** used in the **Vilsmeier–Haack reaction**, so B–ii.

C is the **O-alkoxydimethylsulfuronium (DMSO–DCC)** type intermediate of the **Pfitzner–Moffatt oxidation**, so C–i.

D is a **nitrilium ion**, the key cation in the **Ritter reaction**, so D–iii.

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

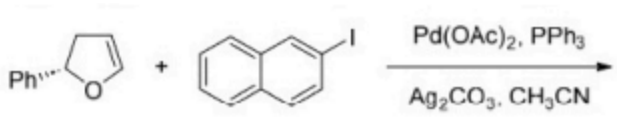


1. i. CH_3CO_3H, H^+ then 2N H_2SO_4; ii. LDA, MeI; iii. DIBAL-H, –78 °C
2. i. DIBAL-H, –78 °C; ii. CH_3CO_3H, H^+ then 2N H_2SO_4; iii. LDA, MeI
3. i. CH_3CO_3H, H^+ then 2N H_2SO_4; ii. DIBAL-H, –78 °C; iii. LDA, MeI
4. i. LDA, MeI; ii. DIBAL-H, –78 °C; iii. CH_3CO_3H, H^+ then 2N H_2SO_4

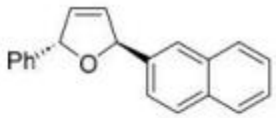
Answer: 1

Explanation: **Baeyer–Villiger oxidation** of the bicyclic ketone with peracid (CH_3CO_3H) gives a **lactone**; acidic work-up unambiguously furnishes the bridged **lactone framework**. Deprotonation with **LDA** and **MeI** gives **α-methylation** next to the carbonyl within the lactone. A final **DIBAL-H (–78 °C)** reduction of the lactone selectively gives the **lactol/hemiketal** embedded in the product shown. This ordering uniquely installs the methyl group and the required reduction state.

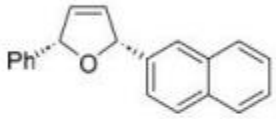
95) The major product formed in the following transformation is



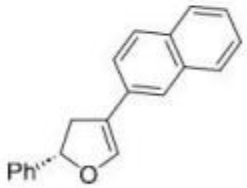
1.



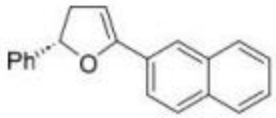
2.



3.



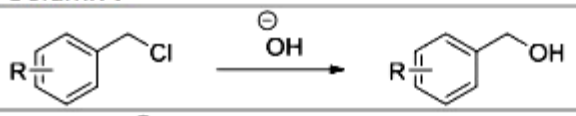
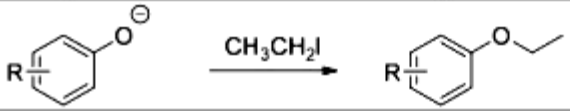
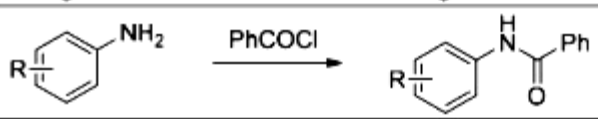
4.



Answer: 1

Explanation: Oxidative addition of Pd(0) into the **aryl–I bond** is followed by base-promoted formation of the **benzylic/allylic palladium complex**; Ag_2CO_3 generates the phenoxide which **intramolecularly attacks** under Pd catalysis (Tsuji–Trost/allylic C–O bond formation + aryl–O cyclization), giving the **benzofuran-fused ether** shown in option 1 as the thermodynamically favored 5-membered ring.

96) The correct match for the reaction given in Column P with the Hammett reaction constant (ρ) given in Column Q is

	Column **P**		Column **Q**
A.		i.	–0.95
B.		ii.	–2.98
C.		iii.	–0.30

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

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

Answer: 2

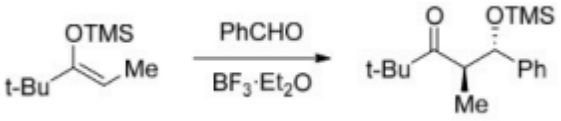
Explanation:

A is **benzylic solvolysis to benzyl alcohol** (develops a benzylic cation): substituent **donation accelerates** modestly → **ρ ≈ –0.30 (iii)**.

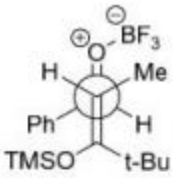
B is **O-alkylation of phenoxide (Williamson)**: rate depends on **nucleophilicity of the phenoxide**, enhanced by EDGs → **ρ ≈ –0.95 (i)**.

C is **acylation of aniline (Schotten–Baumann)**: the nucleophilic aniline lone pair benefits strongly from EDGs → **largest negative ρ, –2.98 (ii)**.

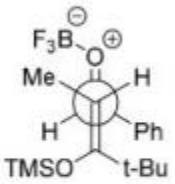
97) The transition state arrangement that explains the stereochemistry of the product in the following reaction is



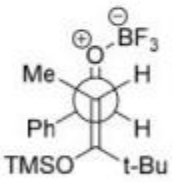
1.



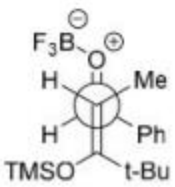
2.



3.



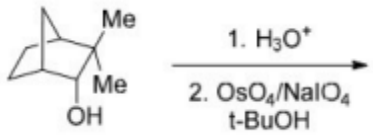
4.



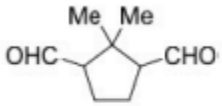
Answer: 3

Explanation: The reaction is a **Mukaiyama aldol** between a **(E)-silyl enol ether** and benzaldehyde activated by **$BF_3 \cdot Et_2O$**. Such Lewis-acid-promoted aldol additions proceed through a **closed, chair-like Zimmerman–Traxler transition state**. Placing the bulky **t-Bu** and **Ph** groups **pseudoequatorial** and aligning the **Si–O** bond antiperiplanar to the forming C–C bond gives the observed relative configuration (Me and OTMS trans to Ph). Among the options, only **transition state 3** has this favorable chair arrangement and thus accounts for the product stereochemistry.

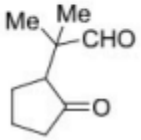
98) The major product formed in the following sequence of reactions is



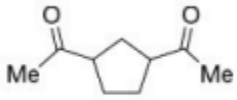
1.



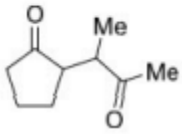
2.



3.



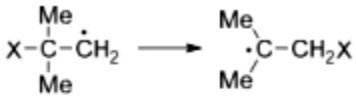
4.



Answer: 3

Explanation: In step 1 (**H_3O^+**) the bridgehead alcohol of the bicyclic alkene undergoes **Wagner–Meerwein rearrangement/dehydration** to the **more substituted internal double bond** of the cyclopentane framework (Bredt-forbidden bridgehead alkene is avoided). Step 2 (**OsO_4 / $NaIO_4$, t-BuOH**) performs **syn-dihydroxylation followed by oxidative cleavage** of that internal alkene. Oxidative cleavage of a disubstituted internal C=C gives **two ketones**, furnishing the **1,4-diketone** shown in **option 3**.

99) The correct order of the rate for the following rearrangement that involves a three-membered intermediate is



P: X = -CH=CH_2

Q: X = $Me_3CC(O)$-

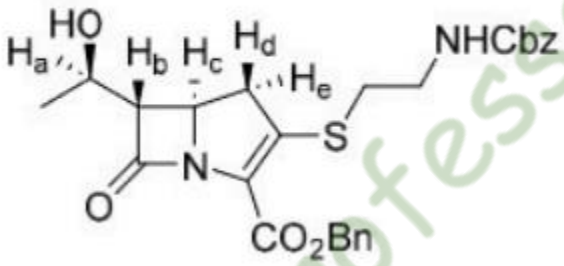
R: X = -C≡N

1. P > Q > R
2. R > P > Q
3. Q > P > R
4. P > R > Q

Answer: 1

Explanation: The rearrangement proceeds via a **cyclopropylcarbinyl ↔ homoallylic cation** manifold. The rate increases with the ability of **X** to **stabilize positive charge by π-donation/conjugation** in the developing nonclassical cation. **Allyl (–CH=CH_2)** in **P** offers the best resonance stabilization, **acyl (Me_3C–C(O)–)** in **Q** provides weaker π-donation, and **cyano (–C≡N)** in **R** is **−M/−I** and least stabilizing. Hence **P > Q > R**.

100) The ^{1}H NMR data corresponding to the labelled protons of the following compound is given below. The signal corresponding to Hb is



1. 4.19 (dt, J = 9.0, 2.5 Hz)
2. 4.13 (dq, J = 7.0, 6.5 Hz)
3. 3.35 (dd, J = 18.0, 9.0 Hz)
4. 3.15 (dd, J = 7.0, 2.5 Hz)

Answer: 4

Explanation: Protons **Hd/He** are a **diastereotopic –CH_2–** adjacent to sulfur and show **large geminal coupling (J ≈ 18 Hz)**: signals at **3.35 (dd, 18.0, 9.0)** and **3.08 (dd, 18.0, 9.0)**. Proton **Ha** (on the carbon bearing OH) couples strongly (**J ≈ 9 Hz**) to **Hb** and weakly (**~2.5 Hz**) long-range, giving **4.19 (dt, 9.0, 2.5)**. The **methine next to the methyl** shows a **dq**from coupling to CH_3 (**~7 Hz, 6.5 Hz**) at **4.13**. Therefore **Hb** must be the proton with **two small vicinal couplings (7.0 and 2.5 Hz)**, i.e., **3.15 (dd) → option 4**.

101) Consider an arbitrary unnormalized wavefunction ψ, expanded in terms of eigenstates of Hamiltonian H, where H|φ_n⟩ = ε_n|φ_n⟩, n = 0,1,2,… ; ε0 ≤ ε1 ≤ ε2 … ; ψ = Σ_na_n|φ_n⟩. The correct option, which definitely holds for any set of {a_n}, is

1. (Σ_n |a_n|^2 ε_n) / (Σ_n |a_n|^2) < ε0
2. (Σ_n |a_n|^2 ε_n) / (Σ_n |a_n|^2) ≥ ε0
3. (Σ_na_nε_n) / (Σ |a_n|) ≥ ε0
4. (Σ_na_nε_n) / (Σ |a_n|^2) < ε0

Answer: 2

Explanation: ⟨H⟩ = (Σ |a_n|^2 ε_n)/(Σ |a_n|^2) is a weighted average of eigenvalues with non-negative weights |a_n|^2. Since every ε_n ≥ ε0, the average is ≥ ε0 (variational principle).

102) The raising and lowering operators are denoted as L+ and L−, respectively. The correct commutator relation between angular momentum (L) and its components (Lx, Ly, Lz) is

1. [L^2, L+] = [L^2, L−] = ħLz
2. [L^2, L+] = [L^2, L−] = ħLx
3. [L^2, L+] = [L^2, L−] = ħLy
4. [L^2, L+] = [L^2, L−] = 0

Answer: 4

Explanation: L^2 commutes with all components of angular momentum and with the ladder operators: [L^2, Li] = 0 ⇒ [L^2, L±] = 0.

103) The unperturbed energies (eV) of a three-level system are ε0 = 2, ε1 = 4, ε2 = 6. Perturbation matrix elements (eV): V10 = 4, V20 = 6, V12 = 10. The second-order correction to the ground-state energy (eV) is

1. −25/4
2. −67
3. −17
4. −16

Answer: 3

Explanation: E0^(2) = Σ_{n≠0} |Vn0|^2 / (ε0 − εn) = 16/(2−4) + 36/(2−6) = −8 − 9 = −17. V12 does not enter E0^(2).

104) At a given temperature, an atom accesses 2S1/2, 2P1/2 and 2P3/2 states with energies 0·kBT, 0.5·kBT and 0.5·kBT. The fraction of atoms in the P states is

1. (3 e^(−0.5)) / (1 + 3 e^(−0.5))
2. (e^(−0.5)) / (1 + 2 e^(−0.5))
3. (e^(−0.5)) / (1 + 4 e^(−0.5))

4. (2 e^(−0.5)) / (1 + 2 e^(−0.5))

Answer: 1

Explanation: Degeneracies: gS=2, gP1/2=2, gP3/2=4. Z = 2 + 6 e^(−0.5). Fraction in P = 6 e^(−0.5) / (2 + 6 e^(−0.5)) = (3 e^(−0.5)) / (1 + 3 e^(−0.5)).

105) In Hückel approximation, the π-energy for the cyclopropenyl cation is (α and β are Coulomb and resonance integrals)

1. 2α + 4β
2. α + β
3. 3α + 3β
4. 3α + 6β

Answer: 1

Explanation: C3H3+ has 2 π electrons filling the bonding MO (energy α + 2β); the degenerate pair (α − β) is empty. Total π-energy = 2(α + 2β) = 2α + 4β.

106) The symmetry of the first excited state of one of the normal modes in NH3 is E. Based on the character table for the C3v point group given below, the symmetry of the second excited state for this mode in terms of the irreducible representations is

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

1. 2A2 + E
2. 2A1 + E
3. A1 + A2 + E
4. 2A1 + 2A2

Answer: 3

Explanation: For a doubly degenerate fundamental (E), the second-order level transforms as the direct product E ⊗ E. In C3v, E ⊗ E = A1 ⊕ A2 ⊕ E. Hence the second excited manifold carries A1 + A2 + E.

107) For a point group having the irreducible representations A1, A2 and E, the values of a, b and c in the following partial character table are

	E	$2C_3$	$3C_2$
E	a	b	c

1. a = 2, b = 1, c = 0
2. a = 2, b = −1, c = 0
3. a = −1, b = 2, c = 1
4. a = 2, b = 1, c = −1

Answer: 2

Explanation: This table corresponds to D3 (irreps A1, A2, E with classes E, 2C3, 3C2). For irrep E, the characters are (2, −1, 0). Thus a = 2, b = −1, c = 0.

108) The fluorescence of A is quenched by 10% in the presence of 10 mM of B. If the fluorescence lifetime of A in the absence of B is 5 ns, the rate constant (in M−1 s−1) for interaction between B and photo-excited A is

1. 1.2 × 10^9
2. 2.2 × 10^9
3. 3.2 × 10^9
4. 4.2 × 10^9

Answer: 2

Explanation: Dynamic quenching (Stern–Volmer): I0/I = 1 + kq τ0 [B]. A 10% decrease gives I/I0 = 0.9 ⇒ 1/0.9 = 1 + kq(5×10^−9 s)(0.010 M). Hence kq = (1/0.9 − 1)/(5×10^−11) ≈ 2.2 × 10^9 M−1 s−1.

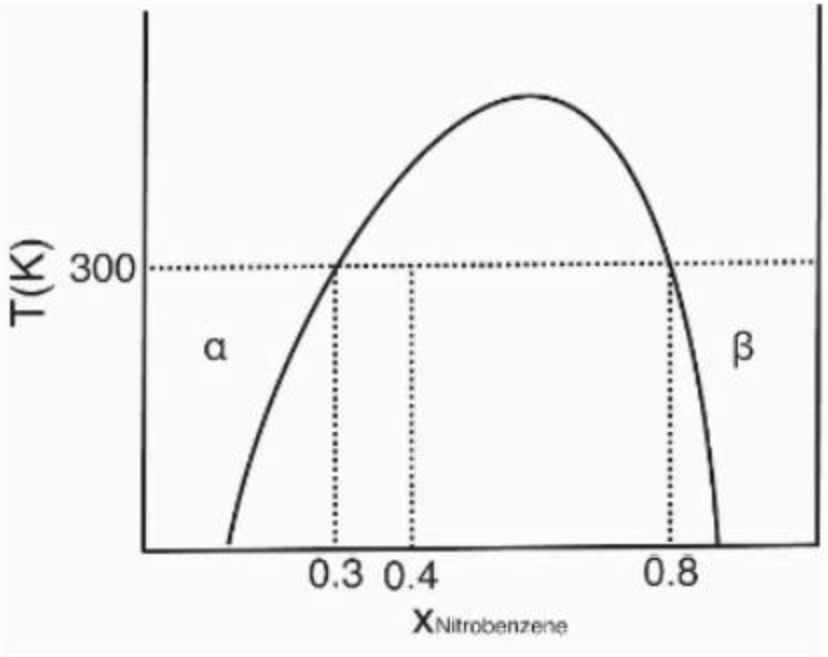
109) The chemical shifts of CH3 and CH2 protons in a molecule are 1.15 and 3.35 ppm, respectively. When the magnetic field is 2 T, the absolute difference between the local magnetic fields (in T) for these two protons is

1. 4.4 × 10^6
2. 2.2 × 10^−6
3. 4.4 × 10^−6
4. 2.2 × 10^6

Answer: 3

Explanation: ΔB_local = B0 × Δδ × 10^−6. Here Δδ = |3.35 − 1.15| = 2.20 ppm; B0 = 2 T. Thus ΔB = 2 × 2.20 × 10^−6 = 4.4 × 10^−6 T.

110) A mixture of 0.6 mol of hexane and 0.4 mol of nitrobenzene was prepared at 300 K. Based on the phase diagram given (α phase: hexane-rich; β phase: nitrobenzene-rich; at 300 K, x_NB^α ≈ 0.3 and x_NB^β ≈ 0.8), the number of moles of hexane in α phase is



1. 0.56
2. 0.42
3. 0.38
4. 0.32

Answer: 1

Explanation: Lever rule with overall x_NB = 0.4: let n_α + n_β = 1 and 0.4 = 0.3 n_α + 0.8 n_β. Solving gives n_α = 0.8. Hexane fraction in α is 1 − 0.3 = 0.7, so moles of hexane in α = 0.8 × 0.7 = 0.56.

111) For the reaction A(s) → A(l), ΔG_m at 300 K is 6 kJ mol^{-1}. If the heat absorbed in the process is 9 kJ mol^{-1}, the temperature (in K) at which A starts melting is [Assume ΔH to be constant with temperature]

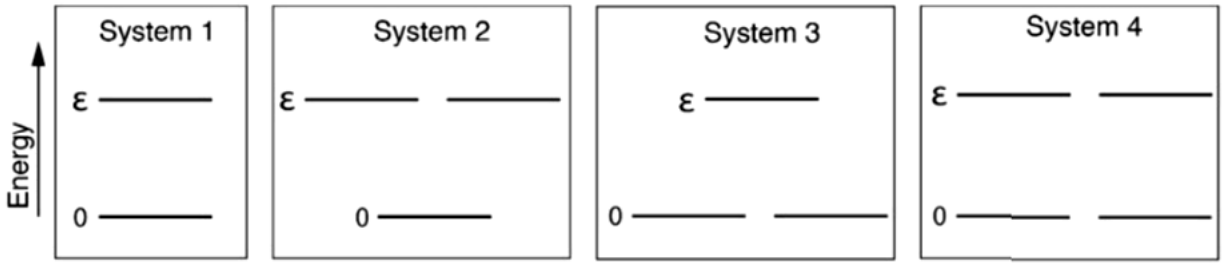
1. 1000
2. 900
3. 1500
4. 750

Answer: 900

Explanation: $\Delta G = \Delta H - T\Delta S$. At 300 K: $6 = 9 - 300\Delta S \Rightarrow \Delta S = (9-6)/300 = 0.01$ kJ K^{-1} mol^{-1}. At melting, $\Delta G = 0 \Rightarrow T_m = \Delta H/\Delta S = 9/0.01 = 900$ K.

112) From the energy diagrams of different single particle systems given below, the one with the lowest Helmholtz free energy at a temperature T = ε/k_B is [1/e = 0.37]

$\left[\frac{1}{e} = 0.37\right]$



1. System 1
2. System 2
3. System 3
4. System 4

Answer: System 4

Explanation: $F = -kT \ln Z$; $Z = \Sigma g_i e^{(-\varepsilon_i/kT)}$. At $T = \varepsilon/k_B$, $e^{(-\varepsilon/kT)} = e^{(-1)}$. System 4 has $g_0 = 2$ and $g_\varepsilon = 2 \rightarrow Z = 2 + 2e^{(-1)} = 2.74$ (largest), hence lowest F.

113) The resistances of 0.1 M KCl and 0.05 M NaCl in a conductivity cell are 90 Ω and 200 Ω, respectively. If the specific conductivity of 0.1 M KCl is 11.2×10^{-3} S cm^{-1}, then the molar conductance (in S cm^2 mol^{-1}) of 0.05 M NaCl is closest to

1. 10^5
2. 10^2
3. 10^3
4. 10^4

Answer: 10^2

Explanation: Cell constant = $\kappa_{KCl} \times R_{KCl} = 0.0112 \times 90 = 1.008$ cm^{-1}. $\kappa_{NaCl} = 1.008/200 = 0.00504$ S cm^{-1}. $\Lambda_m = (\kappa \times 1000)/C = 0.00504 \times 1000/0.05 = 1.01 \times 10^2$ S cm^2 mol^{-1}.

114) The mean activity coefficient ($\gamma_\pm$) of 0.1 m aqueous $CdCl_2$ at 298 K and 1 bar is 0.228. Under this condition, the potential of the cell, Cd(s)\|$CdCl_2$(aq, 0.1 m)\|AgCl(s)\|Ag(s), is [$E°(AgCl/Ag, Cl^-) = 0.22$ V; $E°(Cd^{2+}/Cd) = -0.40$ V]

1. 0.75 V
2. 0.62 V
3. 0.89 V
4. 0.49 V

Answer: 0.75 V

Explanation: $E°cell = 0.22 - (-0.40) = 0.62$ V. Reaction: $Cd + 2AgCl \rightarrow Cd^{2+} + 2Cl^- + 2Ag$. $Q = (\gamma_{\pm}^3)(0.004) \approx (0.228)^3 \times 0.004 = 4.7 \times 10^{-5}$. $E = 0.62 - (RT/2F)\ln Q \approx 0.62 + 0.13 = 0.75$ V.

115) The order of the reaction A → P is 2 when [A] is small. At higher [A], the order changes to 1. The mechanism of the reaction is [Assume steady state approximation on A*]

1. A → P
2. A ⇄ A* ; A* → P
3. A + A ⇄ A* + A ; A* → P
4. A + A → A* + A ; A* → P

Answer: A + A ⇄ A* + A ; A* → P

Explanation: Activation by bimolecular encounter (A + A ⇄ A* + A) forms A* with rate ∝ $[A]^2$ at low [A]. At high [A], deactivation competes, making rate ∝ [A], consistent with order change.

116) The rate constant (k_CT) of a bimolecular reaction according to collision theory is
k_CT = N_A(8k_BT/πμ)^{1/2}σ e^(−E_0/RT).
E_0 is related to activation energy (E_a) of the Arrhenius equation as

1. $E_0 = RT/2 + E_a$
2. $E_a = RT + ½E_0$
3. $E_0 = RT + ½E_a$
4. $E_a = RT/2 + E_0$

Answer: $E_a = RT/2 + E_0$

Explanation: $\ln k = \ln A + ½\ln T - E_0/RT$. Comparing with Arrhenius $\ln k = \ln A' - E_a/RT$, temperature dependence adds RT/2 to E_a. Hence, $E_a = E_0 + RT/2$.

117) Unimolecular decomposition of NH_3 on tungsten surface is inhibited by one of the products, H_2. The rate of surface-catalyzed decomposition is given by
[Pi and Ki are, respectively, the partial pressure and surface binding constant of the i^{th} species; kc is the rate constant of the rate-determining step]

1. $(kcKNH_3PNH_3KH_2PH_2) / (1 + KNH_3PNH_3KH_2PH_2)^2$
2. $(kcKNH_3PNH_3) / (1 + KNH_3PNH_3)$
3. $(kcKNH_3PNH_3) / (1 + KNH_3PNH_3 + KH_2PH_2)$
4. $(kcKNH_3PNH_3KH_2PH_2) / (1 + KNH_3PNH_3 + KH_2PH_2)^2$

Answer: (3) — $(kcKNH_3PNH_3) / (1 + KNH_3PNH_3 + KH_2PH_2)$

Explanation:

The Langmuir–Hinshelwood mechanism assumes competitive adsorption of NH_3 and H_2 on the surface. The rate is proportional to θ_NH_3, which equals $(KNH_3PNH_3) / (1 + KNH_3PNH_3 + KH_2PH_2)$. Since decomposition is unimolecular on the surface, rate = $kc\theta\_NH_3$, giving the required expression.

118) The separation between first two reflection planes of a face-centered cubic crystal is (a is the unit cell length):

1. 0.077a
2. 0.77a
3. 0.57a
4. 0.057a

Answer: (1) — 0.077a

Explanation:

For FCC, allowed (hkl): all even or all odd. The first two reflections are (111) and (200).

$d_1 = a/\sqrt{3}$, $d_2 = a/2$. The separation $\Delta d = d_1 - d_2 = a(1/\sqrt{3} - 1/2) = a(0.577 - 0.5) = 0.077a$.

119) The number-average degree of polymerization (X_n) of self-catalyzed polyesterification, a 3rd-order reaction, is expressed as [$[M]_0$: initial monomer concentration]

1. $X_n^{-2} = 2[M]_0^2kt + 1$
2. $X_n^{-2} = 2[M]_0kt + 1$
3. $X_n^{-2} = [M]_0kt + 1$
4. $X_n^{-2} = 2[M]_0^2kt$

Answer: (1) — $X_n^{-2} = 2[M]_0^2kt + 1$

Explanation:

For self-catalyzed polyesterification (3rd-order): rate = $k[M]^2[M^*]$. Integrating under assumption of self-catalysis gives $1/X_n^2 = 2[M]_0^2kt + 1$. This relation matches the kinetic dependence on initial monomer concentration squared.

120) During the growth of semiconductor nanoparticles, the fluorescence changes with time as

1. blue → violet → green → red
2. red → green → violet → blue
3. violet → blue → green → red
4. blue → red → violet → green

Answer: (3) — violet → blue → green → red

Explanation:

Quantum confinement causes smaller particles to emit shorter wavelengths (higher energy). As nanoparticles grow, energy levels get closer, and emission shifts to longer wavelengths — from violet (smallest) → blue → green → red (largest). Hence, emission color red-shifts with particle growth.