21) The number of skeletal electron pairs (SEP) and the cluster type for $[B_{10}H_{10}]^{2-}$ and $[B_8H_8]^-$, respectively, are

(1) 11, closo and 8, nido

(2) 11, nido and 8, nido

(3) 10, closo and 6, arachno

(4) 10, closo and 8, nido

Answer: (1) 11, closo and 8, nido

Explanation: For boranes, the number of skeletal electron pairs (SEP) = (number of valence electrons − 2n + charge)/2, where n = number of boron atoms. For $[B_{10}H_{10}]^{2-}$, total electrons = 10×3 + 10×1 + 2 = 42, giving SEP = 42/2 − 10 = 11 → a closo structure. For $[B_8H_8]^-$, total = 8×3 + 8×1 + 1 = 33 → SEP = 33/2 − 8 = 8.5 ≈ 8 → nido type. Hence, $[B_{10}H_{10}]^{2-}$ is closo and $[B_8H_8]^-$ is nido.

22) According to VSEPR theory, the geometries of FClO and F5IO, respectively, are

(1) linear and octahedral

(2) tetrahedral and octahedral

(3) tetrahedral and capped octahedral

(4) trigonal bipyramidal and capped octahedral

Answer: (2) tetrahedral and octahedral

Explanation: In FClO, Cl is the central atom bonded to F and O with lone pairs. The arrangement around Cl involves four electron domains (two bonds and two lone pairs), giving a tetrahedral electron geometry. In F5IO, I is surrounded by five F atoms and one O atom, giving six bonding pairs → an octahedral geometry.

23) The option showing the correct match of metal complexes in Column I with the corresponding Δo (cm^{-1}) values in Column II is

Column I	**Column II**
A. $[Ti\ F_6]^{3-}$	P. 21800
B. $[MnF_6]^{2-}$	Q. 17000
C. $[Co(en)_3]^{3+}$	R. 9400
D. $[Fe(H_2O)_6]^{2+}$	S. 24000

(1) A → Q, B → P, C → S, D → R

(2) A → R, B → S, C → P, D → Q

(3) A → Q, B → P, C → R, D → S

(4) A → P, B → S, C → R, D → Q

Answer: (3) A → Q, B → P, C → R, D → S

Explanation: $[TiF_6]^{3-}$: This is a complex of Titanium in the +3 oxidation state. Titanium in the +3 oxidation state (Ti^{3+}) has a relatively weak field ligand (fluoride), so the Δo value will be moderate.
$[MnF_6]^{2-}$: Manganese in the +2 oxidation state (Mn^{2+}) is a d^5 system (high-spin). Since fluoride is a weak field ligand, the Δo value for this complex will also be relatively low, as high-spin systems tend to have lower splitting energies.
$[Co(en)_3]^{3+}$: Cobalt in the +3 oxidation state (Co^{3+}) is a d^6 system, and ethylenediamine (en) is a bidentate ligand, which is a stronger field ligand compared to fluoride. This would cause a relatively higher Δo value.
$[Fe(H_2O)_6]^{2+}$: Iron in the +2 oxidation state (Fe^{2+}) is a d^6 system, and water is a weak field ligand, so this complex will have a lower Δo value compared to complexes with stronger ligands.

24) The reaction of V_2O_5 with ethanolic HCl produces a species X, which gives an EPR spectrum with an eight-line ^{51}V hyperfine coupling (^{51}V: I = 7/2) and a strong IR absorption in the region 950–1035 cm^{-1}. X contains a

(1) $[V–(O)_2–V]^{6+}$ unit

(2) $[VO]^{2+}$ unit

(3) $[V(O)(O_2)]^{+}$ unit

(4) $[(O)V–O–V(O)]^{4+}$ unit

Answer: (2) $[VO]^{2+}$

Explanation: The EPR eight-line pattern indicates the presence of a single unpaired electron interacting with ^{51}V nucleus (I = 7/2). The strong IR band at 950–1035 cm^{-1} corresponds to a V=O stretching vibration, typical of the vanadyl cation $[VO]^{2+}$. Hence, X is $[VO]^{2+}$.

25) The following statements are given with respect to the copper-containing nitrite reductase:

A. It contains both Type-II and Type-III copper proteins.

B. Type-I copper protein is involved in the electron transfer process.

C. Nitrite ion is reduced to NO.

D. Nitrite ion is reduced to NH_3.

The option with correct statements is

(1) A and B only

(2) B and C only

(3) A and C only

(4) A and D only

Answer: (2) B and C only

Explanation: Copper-containing nitrite reductase contains both Type-I and Type-II copper centers. Type-I

copper acts as an electron transfer site, and Type-II copper is the catalytic site where NO_2^- is reduced to NO. Hence, B and C are correct.

26) The option showing the correct match for the reactants in Column I with the second-order rate constants (L mol^{-1} s^{-1}) in Column II for the outer-sphere reactions in water at 25 °C is

Column I	**Column II**
A. $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$	i. 10^5
B. $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$	ii. 3
C. $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$	iii. 10^{-6}
D. $[Co(en)_3]^{2+}$ and $[Co(en)_3]^{3+}$	iv. 10^{-4}

(1) A → i, B → ii, C → iii, D → iv

(2) A → iv, B → iii, C → ii, D → i

(3) A → ii, B → i, C → iv, D → iii

(4) A → iv, B → ii, C → iii, D → i

Answer: (1) A → i, B → ii, C → iii, D → iv

Explanation: Outer-sphere electron transfer rate depends on reorganization energy and electronic coupling. Fastest for cyanide complexes (A: 10^5), moderate for hydrated Fe ions (B: 3), slower for $Co(NH_3)_6^{2+/3+}$ (C: 10^{-6}), and $Co(en)_3^{2+/3+}$ (D: 10^{-4}). Hence, A–i, B–ii, C–iii, D–iv.

27) The calculated magnetic moment of Eu^{3+} ($4f^6$) is 0 (zero) BM. The experimental value is 3.4–3.6 BM at 298 K. The deviation is due to the

(1) mixing of 4f and 4d orbitals

(2) large spin–orbit coupling constant (λ)

(3) large orbital angular momentum

(4) populated ground and the excited states

Answer: (4) populated ground and the excited states

Explanation: For Eu^{3+}, the theoretical μ_eff = 0 BM for the ground term $^7F_0$ (J = 0). However, at room temperature, thermal population of the higher J levels ($^7F_1$, $^7F_2$, etc.) occurs, leading to a non-zero observed moment (~3.5 BM). Hence, the deviation arises from population of excited states.

28) The correct option for the oxidation state(s) of Nb in the cluster $Na_4[Nb_6Cl_{18}]$ is

(1) two are in +3 state and four are in +2 state

(2) all are in +2 state

(3) all are in +3 state

(4) three are in +2 state and three are in +3 state

Answer: (1) two are in +3 state and four are in +2 state

Explanation: The cluster $[Nb_6Cl_{18}]^{4-}$ has an average oxidation state of Nb = (18×(−1) + 4)/6 = +2.33. This corresponds to a mixed valence where four Nb atoms are in +2 state and two are in +3 state. Hence, option (1) is correct.

29) Magnetic moment of Yb^{3+} ($4f^{13}$) is

(1) 4.54 BM

(2) 1.73 BM

(3) 2.83 BM

(4) 3.87 BM

Answer: (1) 4.54 BM

Explanation:

For Yb^{3+} ($4f^{13}$), it is equivalent to one 4f hole. The term symbol is $^2F_{7/2}$ with J = 7/2. Using the formula μ = √[4S(S + 1) + L(L + 1) + 3/4] μ_B× (g_J), the Landé g-factor is 8/7, giving μ_eff = g_J√[J(J + 1)] = (8/7)√[7/2 × 9/2] ≈ 4.54 BM. Thus, Yb^{3+} has a magnetic moment of 4.54 BM.

30) The total number of six-membered rings in the polycyclic compounds $P_4(NMe)_6$ and $P_2(N_2Me_2)_3$ is

(1) 7

(2) 6

(3) 5

(4) 4

Answer: (1) 7

Explanation:

$P_4(NMe)_6$ (hexakis(dimethylamino)tetraphosphane) is a cage structure analogous to adamantane with six P–N–P–N–P six-membered rings, plus one central six-membered ring formed by nitrogen bridges, making a total of seven. For $P_2(N_2Me_2)_3$, similar cyclic nitrogen bridges contribute the same structural count, leading to 7 six-membered rings overall.

31) $[Fe(CO)_5]$ on reaction with C_3H_5I gives Y with the elimination of two molecules of CO.

Consider the following statements:

A. Y obeys the 18-electron rule.

B. The reaction is an example of oxidative addition.

C. Allyl moiety shows η^1 coordination in Y.

D. Y adopts pentagonal bipyramidal geometry.

The correct option is

(2) A and B only

(1) A, B and C only

(3) A, B and D only

(4) B and D only

Answer: (2) A and B only

Explanation:

The product is $Fe(CO)_3(\eta^3\text{-}C_3H_5)I$, formed by oxidative addition of allyl iodide to Fe(0) center of $Fe(CO)_5$. Iron becomes Fe(II), with the allyl group η^3-bonded (not η^1). The compound satisfies the 18-electron rule, and the geometry is pseudo-octahedral, not pentagonal bipyramidal.

32) The difference in the second ionization energies of Li/Na, Be/Mg, B/Al, and N/P are X_1, X_2, X_3, and X_4, respectively. The correct order of the difference in the second ionization energies is

(1) $X_1 > X_4 > X_3 > X_2$

(2) $X_1 > X_2 > X_3 > X_4$

(3) $X_4 > X_3 > X_1 > X_2$

(4) $X_1 > X_3 > X_4 > X_2$

Answer: (1) $X_1 > X_4 > X_3 > X_2$

Explanation:

The second ionization energy difference depends on electronic configuration stability after the first electron removal. Li → Li^+ ($1s^2$) → very stable, hence large Δ. Be and Mg have filled s^2 shells, smaller Δ. For B/Al, p-electron removal gives moderate Δ. For N/P (half-filled p^3), Δ is large but less than Li/Na. Hence, X_1 (Li/Na) > X_4 (N/P) > X_3 (B/Al) > X_2 (Be/Mg).

33) In a flame photometric analysis of a blood serum sample for K^+ ion, a band is obtained at 766 nm. This band is due to

(1) absorption by K^+ ion only

(2) absorption by K atom only

(3) emission by K^+ ion only

(4) emission by K atom only

Answer: (4) emission by K atom only

Explanation:

Flame photometry involves excitation of neutral atoms, not ions. The characteristic line for potassium at 766 nm

corresponds to the 4s → 4p transition of neutral potassium atoms (K^0). Thus, the observed emission band arises from K atom emission.

34) The following molecular orbital corresponds to

(1) HOMO of pentadienyl cation

(2) HOMO of pentadienyl anion

(3) LUMO of pentadienyl cation

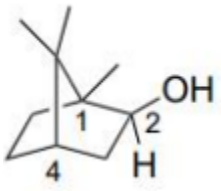
(4) LUMO of pentadienyl anion

Answer: (1) HOMO of pentadienyl cation

Explanation:

The orbital pattern shows four lobes with one node at the center, indicating ψ_3 of the π-system (bonding). For pentadienyl cation ($C_5H_5^+$), which has 4 π electrons, ψ_3 is the highest occupied molecular orbital (HOMO). For the anion ($C_5H_5^-$) with 6 π electrons, ψ_3 becomes fully occupied and ψ_4 is LUMO.

35) The correct absolute configuration for the structure shown below is



(1) 1S, 2S, 4S

(2) 1S, 2R, 4R

(3) 1R, 2R, 4S

(4) 1S, 2S, 4R

Answer: (1) 1S, 2S, 4S

Explanation:

Using the Cahn–Ingold–Prelog priority rules:

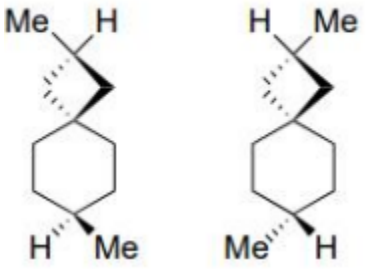
– At C1, the substituents' arrangement gives S configuration.

– At C2 (bearing OH), OH > C1 > C3 > H → S configuration.

– At C4, substituents arranged with lowest priority away give S again.

Hence, the compound has 1S, 2S, 4S configuration.

36) The following two molecules are



(1) Enantiomers

(2) Diastereomers

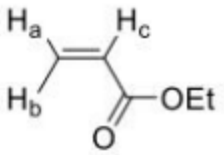
(3) Homomers (Identical)

(4) Constitutional isomers

Answer: (3) Homomers (Identical)

Explanation: Both drawings represent the same substituted cyclohexane with the same relative stereochemistry at the same positions. They are just drawn in different orientations (flipped view), but not mirror images that are non-superimposable (enantiomers) and not stereoisomers with different configurations at one or more stereocenters (diastereomers). Since all stereochemical relationships match, they are actually the same compound, i.e. identical (homomers).

37) The correct match for the protons of ethyl acrylate given in Column P with chemical shifts (δ ppm) given in Column Q is



Column P	Column Q
A. H_a	i. 6.11 (dd, J = 16, 10 Hz)
B. H_b	ii. 6.4 (dd, J = 16, 4 Hz)
C. H_c	iii. 5.8 (dd, J = 10, 4 Hz)

(1) A – i; B – ii; C – iii

(2) A – iii; B – ii; C – i

(3) A – iii; B – i; C – ii

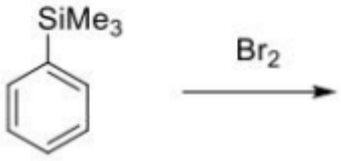
(4) A – ii; B – iii; C – i

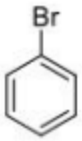
Answer: (2) A – iii; B – ii; C – i

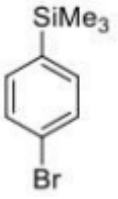
Explanation: In the CH_2=CH–CO_2Et fragment, H_a is the cis vinylic proton, H_b is the trans vinylic proton,

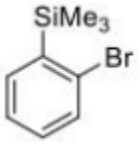
and H_c is the vinylic proton geminal to both. The largest trans coupling (J ≈ 16 Hz) appears with H_b and H_c. The proton most deshielded (downfield, 6.4 ppm) is typically the trans vinylic proton next to the carbonyl (H_b). The signal at 6.11 ppm (dd, J = 16,10 Hz) corresponds to H_c which couples both trans and cis. The 5.8 ppm (dd, J = 10,4 Hz) is H_a, which shows cis and allylic/small coupling. This gives A→iii, B→ii, C→i.

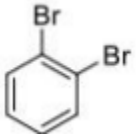
38) The major product formed in the following reaction is (anisole-type aryl–$SiMe_3$ treated with Br_2)



(1) 

(2) 

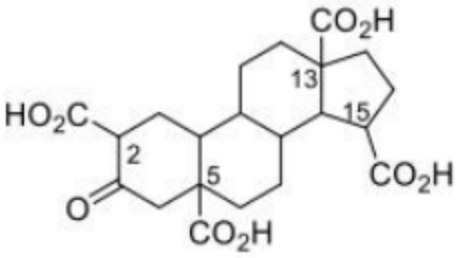
(3) 

(4) 

Answer: (1)

Explanation: An aryl–$SiMe_3$ group behaves like an activated aryl equivalent that can undergo ipso electrophilic substitution under halogenation conditions. Br_2 replaces the –$SiMe_3$ group, giving the aryl bromide (Ar–Br). Therefore the principal product is the ring where $SiMe_3$ has been replaced by Br, matching option (1).

39) The given steroid molecule undergoes facile monodecarboxylation on heating. The carboxylic acid group lost is at



(1) C15

(2) C13

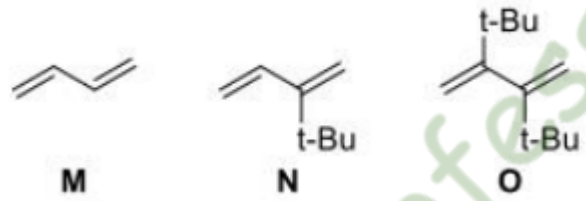
(3) C5

(4) C2

Answer: (4) C2

Explanation: Thermal decarboxylation is favored when the $–CO_2H$ group is positioned β to a carbonyl in a way that allows formation of a stabilized conjugated enone or diketone system after CO_2 loss. In the given polycarboxylic steroid, the carboxyl at C2 is activated (α,β to a carbonyl ring junction) and can decarboxylate readily, while the others are not in such a favorable electronic arrangement. Hence, C2 is lost first.

40) The correct order of reactivity for the following dienes with maleic anhydride is
M, N, O (where M is an unconjugated diene, N is a conjugated diene with one t-Bu, O is a t-Bu substituted, more hindered diene)



(1) M > N > O

(2) N > M > O

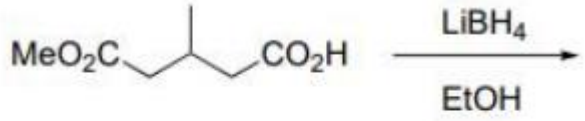
(3) N > O > M

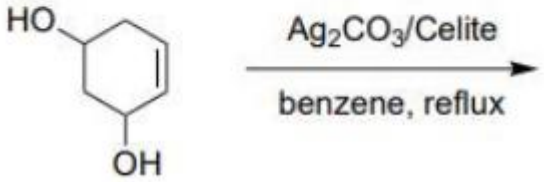
(4) O > N > M

Answer: (2) N > M > O

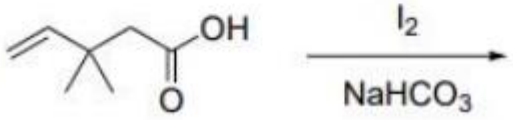
Explanation: Diels–Alder reactivity increases with electron-rich conjugated dienes that can adopt the reactive s-cis conformation and are not sterically blocked. Diene N is conjugated and less hindered than O, so N reacts fastest. M is less activated electronically than N but less hindered than O, so M is next. O is the most sterically hindered (two bulky t-Bu groups restricting approach), so it reacts slowest. Therefore, N > M > O.

41) Among the following, the examples of chemoselective reactions are

A. 

B. 

C. 

D. 

(1) A and B

(2) B and C

(3) A and D

(4) C and D

Answer: (2) B and C

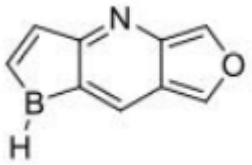
Explanation:

A **chemoselective reaction** preferentially reacts with one functional group in the presence of others.

- In **(B)**, oxidation of one alcohol (secondary allylic OH) occurs while the other (saturated OH) remains unchanged — chemoselective oxidation.
- In **(C)**, hydrogenation occurs only at the alkene double bond, leaving other functional groups untouched — again chemoselective.

  In **(A)**, $LiBH_4$ reduces both ester and acid, not selective; and **(D)** involves halogenation of enolizable sites, not chemoselective.

42) Based on Hückel rule, the following species is



(1) aromatic

(2) antiaromatic

(3) nonaromatic

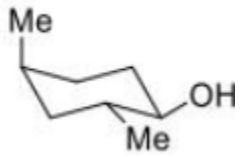
(4) homoaromatic

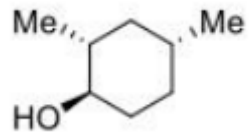
Answer: (1) aromatic

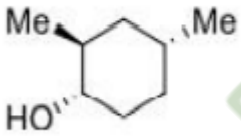
Explanation:

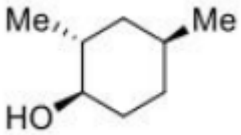
The molecule shown (benzoxazole or indole-type fused heterocycle with 10 π electrons) obeys **Hückel's 4n + 2 rule (n = 2)**. Its conjugated planar π-system delocalizes over both rings. Thus, it is fully conjugated, planar, and aromatic.

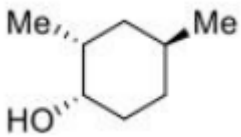
43) The structure that corresponds to the following compound is



(1) 

(2) 

(3) 

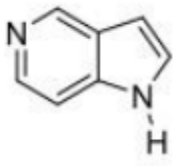
(4) 

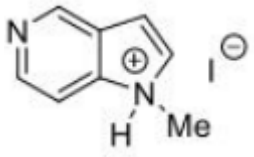
Answer: (3)

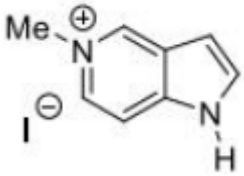
Explanation:

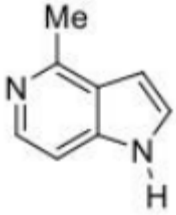
In the given chair form of methylcyclohexanol, stability is maximized when the bulky groups occupy the **equatorial** position to minimize 1,3-diaxial repulsion. The figure shows the more stable conformation with the **OH equatorial** and **Me axial**.

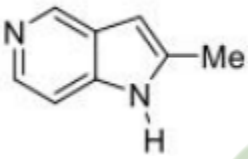
44) The reaction of the given compound with MeI produces



(1) 

(2) 

(3) 

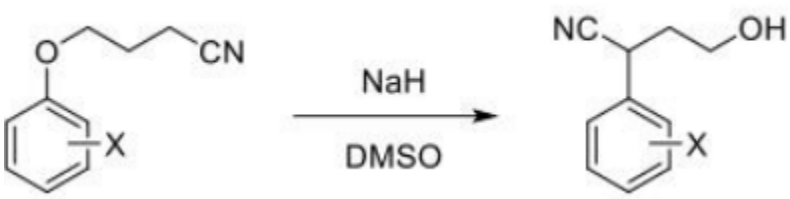
(4) 

Answer: (1)

Explanation:

The compound is imidazole. Methyl iodide (MeI) alkylates the **more nucleophilic nitrogen (N-3)** to form an **N-methylimidazolium iodide** salt. The positive charge resides on N-3, consistent with option (1).

45) The following reaction is the fastest when



(1) X = m-NO_2

(2) X = p-OMe

(3) X = p-NO_2

(4) X = m-OMe

Answer: (3) X = p-NO_2

Explanation:

The reaction proceeds through a **base-promoted intramolecular nucleophilic addition (Henry-type condensation)** where stabilization of the anionic intermediate by an **electron-withdrawing group (EWG)** enhances rate.

The **p-NO_2 group** is a strong EWG that stabilizes the developing carbanion, making the reaction fastest. The electron-donating OMe groups would reduce the reaction rate.

46) 2-Methylbut-2-ene is used in Pinnick oxidation

RCHO → RCO_2H using $NaClO_2$, Na_2HPO_4 in t-BuOH/H_2O\text{RCHO → RCO_2H using $NaClO_2$, Na_2HPO_4 in t-BuOH/H_2O}RCHO → RCO_2H using $NaClO_2$, Na_2HPO_4 in t-BuOH/H_2O

to scavenge

(1) HCl

(2) H_3PO_4

(3) $HClO_2$

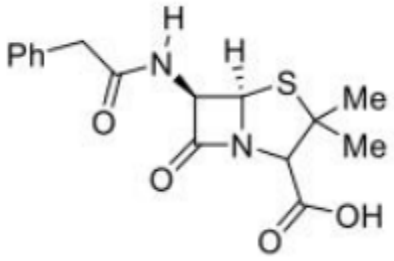
(4) HOCl

Answer: (4) HOCl

Explanation:

In the **Pinnick oxidation**, 2-methylbut-2-ene acts as a **HOCl scavenger**. During the oxidation of aldehydes to acids by $NaClO_2$, HOCl is produced as a side product which can cause overoxidation or chlorination. The alkene reacts with HOCl, preventing such side reactions and ensuring clean conversion to carboxylic acid.

47) The most effective pharmacophore that confers antibiotic activity to penicillin G is



(1) phenylacetamide

(2) thiazolidine ring

(3) carboxylic acid

(4) β-lactam

Answer: (4) β-lactam

Explanation: The β-lactam ring is the essential pharmacophore responsible for antibiotic activity. It reacts with bacterial transpeptidase enzymes, inhibiting cell wall cross-linking. The thiazolidine ring provides structural stability, but the β-lactam ring's strained amide bond allows acylation of the enzyme, leading to bacterial lysis.

48) If $H = p_x^2 / (2m) + V(x)$, then $[H, p_x]$ is

(1) $i\hbar\,(dV/dx)$

(2) 0

(3) $-i\hbar$

(4) $-i\hbar\,(p_x/m)$

Answer: (1) $i\hbar\,(dV/dx)$

Explanation: The commutator $[H, p_x] = [V(x), p_x] = i\hbar\,(dV/dx)$, since $[p_x^2, p_x] = 0$. Only the potential term contributes because p_x acts as $-i\hbar\,(d/dx)$. The result represents the force operator in quantum mechanics.

49) e^{ikx} is an eigenfunction of the linear momentum operator p_x, with eigenvalue of

(1) $\hbar^2 k$

(2) $\hbar k$

(3) $\hbar k^2$

(4) $\hbar^2 k^2$

Answer: (2) $\hbar k$

Explanation: For $p_x = -i\hbar\,(d/dx)$, acting on e^(ikx) gives $-i\hbar(ik)e^{(ikx)} = \hbar k\, e^{(ikx)}$. Hence, e^(ikx) is an eigenfunction with eigenvalue $\hbar k$, which corresponds to the particle momentum according to de Broglie relation ($p = \hbar k$).

50) Of the following atomic transitions, the allowed one is

(1) $^1S \rightarrow {}^5S$

(2) $^3P \rightarrow {}^1D$

(3) $^1S \rightarrow {}^1D$

(4) $^3D \rightarrow {}^3P$

Answer: (4) $^3D \rightarrow {}^3P$

Explanation: The electric dipole selection rules are $\Delta S = 0$, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$ (except $0 \rightarrow 0$). The $^3D \rightarrow {}^3P$ transition satisfies all these (no change in spin, $\Delta L = 1$). Others violate the spin rule, making them forbidden.

51) The number of unpaired electrons in B_2 is

(1) 0

(2) 1

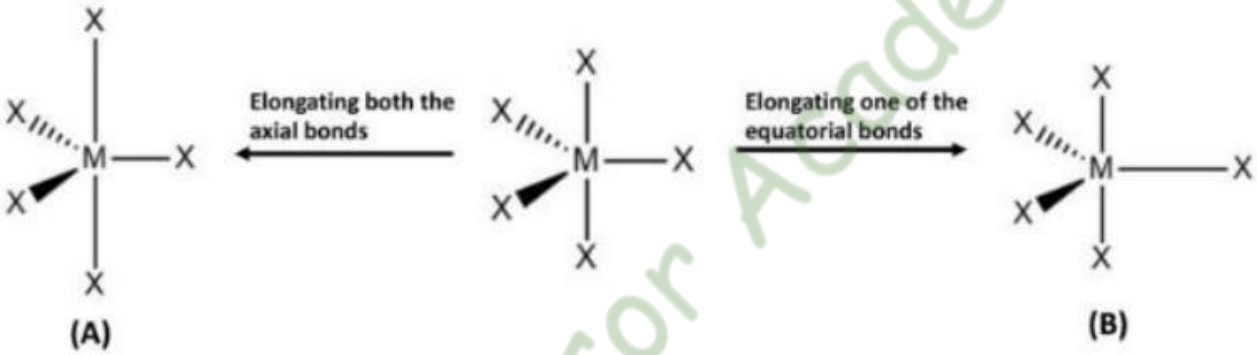
(3) 2

(4) 3

Answer: (3) 2

Explanation: The molecular orbital configuration of B_2 is $(\sigma 1s)^2\ (\sigma 1s)^2\ (\sigma 2s)^2\ (\sigma 2s)^2\ (\pi 2p_x)^1\ (\pi 2p\_y)^1$. The presence of two unpaired electrons in degenerate $\pi 2p$ orbitals leads to paramagnetism in B_2.

52) The molecule MX_5 belongs to the point group D_3h. Elongation of both the axial M–X bonds yields A and elongation of one of the M–X equatorial bonds yields B.
The point groups of A and B, respectively, are



1. C_{3v} and $D_3{}^h$
2. $D_3{}^h$ and C_{3v}
3. C_{3v} and C_{2v}
4. $D_3{}^h$ and C_{2v}

Answer: 4) D_3h and C_2v

Explanation: Starting geometry (MX_5, D_3h): trigonal-bipyramidal (TBP) with a **C_3** axis through the two axial M–X bonds, **three C_2** axes in the equatorial plane, a **σh** plane (the equatorial plane), and **three σv** planes.

- **Case A (elongate both axial bonds equally):** All symmetry elements of TBP remain:
  - the **C_3** axis is unchanged (both axials are still equivalent to each other),
  - the **three C_2** axes in the equatorial plane remain,
  - the **σh** (equatorial) plane is still a mirror,
  - the **three σv** planes remain.

  ⇒Point group = D_3h.

- **Case B (elongate one equatorial bond):** This makes one equatorial site unique and breaks the 3-fold symmetry:
    - **C_3** and **σh** are **lost**,
    - one **C_2** axis survives (through M and the elongated equatorial bond, exchanging the two equal equatorial ligands and the two axial ligands),
    - **two σv** planes remain (one containing the elongated equatorial bond and both axials; another perpendicular plane bisecting the other two equatorial positions).

    ⇒Point group = C_2v.

Hence, **A = D_3h** and **B = C_2v → Option 4**.

53. For a proton, the gyromagnetic ratio is 26.752 X 10^7 rad T^{-1} s. The Larmor frequency for a proton (in MHz) in a 21.1 T magnetic field is, approximately,

(1) 400

(2) 500

(3) 600

(4) 900

Answer: (3) 600

Explanation:

Larmor frequency is

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

$$= \frac{26.752 \times 10^7 \times 21.1}{6.283} \approx 9 \times 10^8 \text{ Hz} = 900\text{MHz}$$

Thus, the proton resonance at 21.1 T is approximately 900 MHz .

54) The thermodynamic variable 'X' in the equation

(∂S/∂P)_T = (1/T) [X + (∂H/∂P)_T] is

(1) V

(2) S

(3) –V

(4) C_P

Answer: (3) –V

Explanation: From thermodynamic relationships, (∂S/∂P)_T = –(∂V/∂T)_P. By Maxwell's relations, X = –V

satisfies the given differential form. Hence, substituting X = –V yields correct consistency with the thermodynamic identity linking entropy, enthalpy, and volume changes.

55) Molecule B is twice as heavy as molecule A. The ratio of the thermal de Broglie wavelength of molecule A to that of molecule B is

(1) √2 : 1

(2) 2 : 1

(3) 1 : 2

(4) 1 : √2

Answer: (1) √2 : 1

Explanation: The thermal de Broglie wavelength λ ∝ 1/√m. For molecule B being twice as massive, λ_A / λ_B = √(m_B / m_A) = √2. Thus, the ratio of de Broglie wavelengths is √2 : 1.

56) For 0.001 M aqueous solutions of $AlCl_3$, $CaCl_2$, and KCl at 25 °C, the correct order of Debye length is

(1) $AlCl_3$ <$CaCl_2$ <KCl

(2) KCl<$CaCl_2$ <$AlCl_3$

(3) $CaCl_2$ <KCl<$AlCl_3$

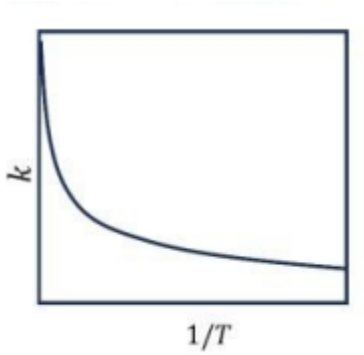
(4) $AlCl_3$ <KCl<$CaCl_2$

Answer: (1) $AlCl_3$ <$CaCl_2$ <KCl

Explanation: The Debye length (κ^{-1}) ∝ 1/√I, where I is ionic strength. For equal molar concentration, $AlCl_3$ (z = 3) produces the highest ionic strength, followed by $CaCl_2$ (z = 2), and then KCl (z = 1). Thus, higher charge density results in smaller Debye length.

57) According to Arrhenius equation, the plot that correctly describes the temperature (T) dependence of the rate constant (k) is

(1)



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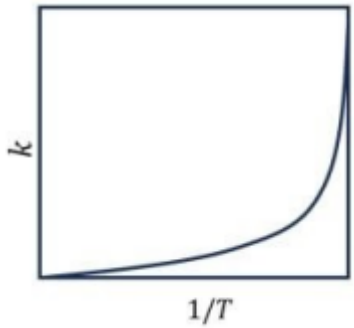

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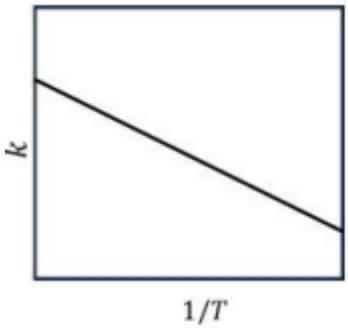

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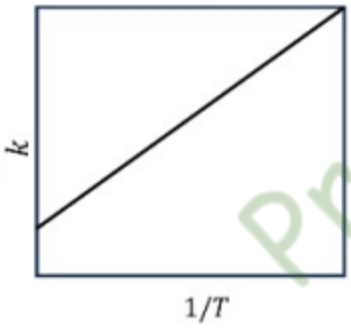


Answer: (1)

Explanation:

The Arrhenius equation is k = A e^(−Ea/RT).

Taking logarithm, ln k = ln A − Ea/R (1/T).

Hence, a plot of ln k versus 1/T gives a straight line with **negative slope** (−Ea/R). This linear relation shows that as temperature increases (1/T decreases), the rate constant k increases exponentially.

58) Consider the following statements:

I. Micelles form above the critical micelle concentration (CMC).

II. Micelles form above the Krafft temperature.

The correct option is

(1) Only I is true

(2) Only II is true

(3) Both I and II are true

(4) Both I and II are false

Answer: (3)

Explanation:

Micelle formation requires both thermodynamic and solubility conditions. It occurs only when surfactant concentration exceeds the **critical micelle concentration (CMC)** and the temperature is above the **Krafft temperature**, where solubility of surfactant molecules becomes sufficient for aggregation. Both conditions are essential for micellization.

59) For face-centered cubic (FCC) packing of a monoatomic solid, the number of tetrahedral and octahedral holes within the unit cell, respectively, are

(1) 8 and 4

(2) 4 and 2

(3) 16 and 16

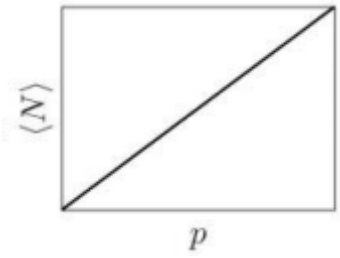
(4) 6 and 6

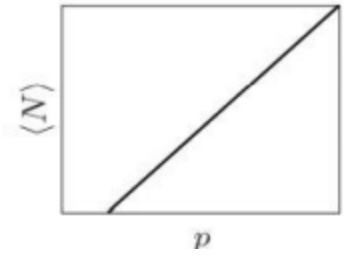
Answer: (1) 8 and 4

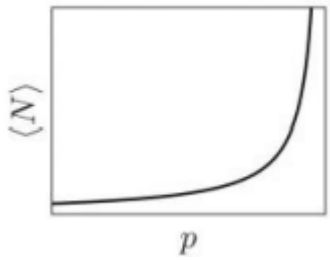
Explanation:

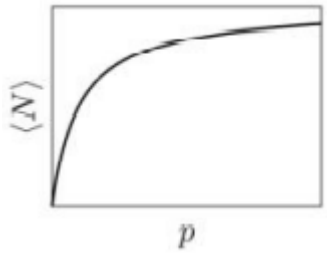
In FCC lattice, each unit cell has **4 atoms**. For every atom, there exists one octahedral and two tetrahedral voids. Hence, per unit cell there are **4 octahedral** and **8 tetrahedral** holes. The ratio of tetrahedral to octahedral holes is 2 : 1.

60) For step-wise polymerization, the correct plot of chain length (⟨N⟩) against degree of polymerization (p) is

(1) 

(2) 

(3) 

(4) 

Answer: (3)

Explanation:

In step-growth polymerization, ⟨N⟩ = 1 / (1 − p).

As p approaches 1, ⟨N⟩ tends to infinity. The plot between ⟨N⟩ and p is **hyperbolic**, rising steeply near p ≈ 1. It is non-linear and shows rapid increase in average chain length at high conversion.

61) ^{31}P NMR spectrum of P_4S_3 consists of (^{31}P, I = ½, 100% abundance)

(1) Two doublets of triplets

(2) Triplet of triplets

(3) Two triplets of equal intensity

(4) A doublet and a quartet

Answer: (4) A doublet and a quartet

Explanation:

In P_4S_3, there are two types of nonequivalent phosphorus atoms — three equivalent P atoms (terminal) and one P atom (central) bonded through bridging S. Each central P couples with three equivalent P nuclei, giving a **quartet**. Conversely, the three equivalent P atoms couple with one P center, giving a **doublet**. Therefore, the spectrum shows a **doublet and a quartet**.

62) According to VSEPR theory, the shapes and geometries of SeF_4 and $[BrF_4]^-$, respectively, are:

(1) See-saw and trigonal bipyramidal; see-saw and trigonal bipyramidal

(2) Square planar and octahedral; square planar and pentagonal pyramidal

(3) See-saw and trigonal bipyramidal; square planar and octahedral

(4) Square planar and square bipyramidal; square planar and octahedral

Answer: (3) See-saw and trigonal bipyramidal; square planar and octahedral

Explanation:

In SeF_4, selenium has 6 valence electrons. It forms four bonds with fluorine and retains one lone pair, giving five regions of electron density. The electron geometry is trigonal bipyramidal, but due to one lone pair, the molecular shape becomes see-saw (AX_4E type).

In $[BrF_4]^-$, bromine has 8 valence electrons (7 + 1 from the charge). It forms four Br–F bonds and has two lone pairs, giving six regions of electron density. The geometry is octahedral, and the molecular shape is square planar (AX_4E_2 type).

63) The option showing both the complexes obeying the $18e^-$ rule is:

(1) $[(\eta^5\text{–}C_5H_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{–}C_5H_5)_2ZrCl_2]$

(2) $[IrCl(CO)(PPh_3)_2]$ and $[Co_2(CO)_8]$

(3) $[Re(CO)_5(PF_3)]$ and $[Ni(NH_3)_6]^{2+}$

(4) $[(\eta^5\text{–}C_5H_5)(\eta^5\text{–}C_5H_5)Fe(CO)]$ and $[(\eta^3\text{–allyl})Mn(CO)_4]$

Answer: (4) $[(\eta^5\text{–}C_5H_5)(\eta^5\text{–}C_5H_5)Fe(CO)]$ and $[(\eta^3\text{–allyl})Mn(CO)_4]$

Explanation:

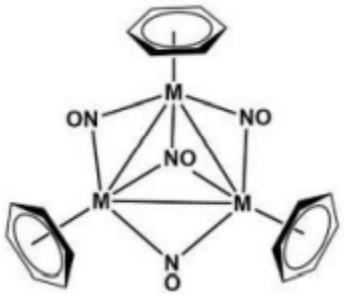
The 18-electron rule is satisfied when the total metal valence electrons and ligand electrons sum to 18.

For $[(\eta^5\text{–}C_5H_5)(\eta^5\text{–}C_5H_5)Fe(CO)]$: Fe ($8e^-$) + two $\eta^5\text{–}C_5H_5$ rings ($10e^-$) + one CO ($2e^-$) = $20e^-$; Fe is in +2 oxidation state → $18e^-$ total.

For $[(\eta^3\text{–allyl})Mn(CO)_4]$: Mn ($7e^-$) + allyl ($3e^-$) + four CO ($8e^-$) = $18e^-$ total.

Thus, both complexes obey the $18e^-$ rule.

64) The compound shown below is a 48-electron metal cluster (not counting M–M bonds). The metal M is:



(1) V

(2) Fe

(3) Mn

(4) Cr

Answer: (4) Cr

Explanation:

Each NO contributes $3e^-$ (linear NO^+ type), and each η^5–C_5H_5 contributes $6e^-$.

Total electrons = $3M + 3(6 + 3) = 48 \rightarrow 3M = 21 \rightarrow M = 7$.

Thus, the metal must contribute 7 valence electrons, corresponding to chromium (Cr) in +1 oxidation state.

65) $[Co(NH_3)_5(X)]Cl_2$ (1) on reaction with aqueous NH_3 followed by the addition of $NaNO_2$/conc. HCl yields $[Co(NH_3)_5(Y)]Cl_2$ (2). Reaction of (1) with $NaNO_2$ results in $[Co(NH_3)_5(Z)]Cl_2$ (3). Complex 2 shows two IR spectral bands at 1310 and 1430 cm^{-1}, whereas complex 3 shows the same at 1065 and 1470 cm^{-1}. X, Y and Z, respectively, are:

(1) X = Cl^-; Y = NO_2^-; Z = ONO^-

(2) X = H_2O; Y = NO_2^-; Z = ONO^-

(3) X = Cl^-; Y = ONO^-; Z = NO_2^-

(4) X = H_2O; Y = ONO^-; Z = NO_2^-

Answer: (1) X = Cl^-; Y = NO_2^-; Z = ONO^-

Explanation:

In the nitrito–nitro linkage isomers, NO_2^- (nitro, N-bonded) shows IR bands at higher frequencies (around 1310 and 1430 cm^{-1}), while ONO^- (nitrito, O-bonded) exhibits lower frequency bands (around 1065 and 1470 cm^{-1}). Therefore, complex 2 (with higher frequencies) contains NO_2^-, and complex 3 (with lower frequencies) contains ONO^-. The starting complex has Cl^- as X.

66) The oxy-hemocyanin exhibits a resonance Raman signal at 744 cm^{-1} for $^{16}O–^{16}O$ stretch, following its excitation at 575 nm. The value of the $^{18}O–^{18}O$ stretch for an $^{18}O_2$-substituted oxy-hemocyanin, and the origin of the absorption band, are:

(1) 702 cm^{-1} and O_2^-→ Cu(II) charge transfer

(2) 702 cm^{-1} and O_2^{2-}→ Cu(II) charge transfer

(3) 664 cm^{-1} and O_2^-→ Cu(II) charge transfer

(4) 792 cm^{-1} and O_2^{2-}→ Cu(II) charge transfer

Answer: (2) 702 cm^{-1} and O_2^{2-}→ Cu(II) charge transfer

Explanation:

For isotopic substitution, the vibrational frequency ν is inversely proportional to √μ, where μ is the reduced mass.

For $^{16}O_2 \rightarrow {}^{18}O_2$:

$\nu(^{18}O_2) = 744 \times \sqrt{(16/18)} = 744 \times 0.942 =$ **702 cm^{-1}**.

The absorption band originates from charge transfer between the bound peroxo dianion (O_2^{2-}) and Cu(II) centers, confirming an O_2^{2-}→ Cu(II) charge-transfer transition.

67) The ^{19}F NMR spectrum of $[XeF_5]^-$ ion shows:

(1) A doublet with satellite peaks

(2) A triplet and a quartet with satellite peaks for both

(3) A doublet and a quintet with satellite peaks for both

(4) A singlet with satellite peaks

Answer: (4) A singlet with satellite peaks

Explanation:

In $[XeF_5]^-$, all five fluorine atoms are equivalent due to a square pyramidal structure. Therefore, the ^{19}F NMR shows a single resonance (singlet). The presence of the NMR-active isotope ^{129}Xe (I = ½, 26.5% abundance) leads to spin–spin coupling between Xe and F, resulting in **satellite peaks** around the main singlet due to ^1J(Xe–F) coupling.

68) The correct option with respect to the metal–metal distance (d) and the magnetic property of $[Cr_2Cl_9]^{3-}$ (A) and $[W_2Cl_9]^{3-}$ (B) is:

(1) d(Cr···Cr) > d(W···W); A is paramagnetic and B is diamagnetic

(2) d(Cr···Cr) > d(W···W); A is diamagnetic and B is paramagnetic

(3) d(W···W) > d(Cr···Cr); A is diamagnetic and B is paramagnetic

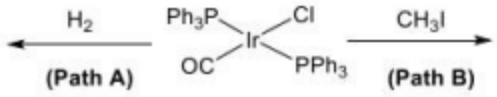
(4) d(W···W) > d(Cr···Cr); A is paramagnetic and B is diamagnetic

Answer: (1) d(Cr···Cr) > d(W···W); A is paramagnetic and B is diamagnetic

Explanation:

Both anions contain metal–metal multiple bonds. The heavier 5d metal W forms a stronger M–M bond (better radial overlap), hence a **shorter W–W distance** than Cr–Cr; therefore **d(Cr···Cr) > d(W···W)**. For $[Cr_2Cl_9]^{3-}$ each Cr(III) is d^3; the Cr–Cr bond order is lower and **one unpaired electron remains → paramagnetic**. For $[W_2Cl_9]^{3-}$ each W(III) is $5d^3$; stronger multiple bonding pairs all electrons, giving a **diamagnetic** species.

69) In the oxidative addition of trans-[IrCl(CO)(PPh_3)$_2$] with H_2 (path A) and with CH_3I (path B), the d-orbitals involved in the electron transfer from iridium to H_2 and CH_3I, respectively, are:



(1) d(x^2-y^2) (in A); d(z^2) (in B)

(2) d(z^2) (in A); d_{xy} or d_{xz} or d_{yz} (in B)

(3) d_{xy} or d_{xz} or d_{yz} (in A); d(z^2) (in B)

(4) d(z^2) (in A); d(x^2-y^2) (in B)

Answer: (3) dxy or dxz or dyz (in A); d(z^2) (in B)

Explanation:

For **H_2 oxidative addition**, H_2 approaches side-on above the square plane; Ir donates into σ*(H–H) using **π-type filled d orbitals (dxy/dxz/dyz)** that have proper symmetry for back-donation.

For **CH_3I oxidative addition** (SN2-type), Ir donates electron density along the incoming Ir–C axis into σ*(C–I); this uses the **axial d(z^2)** orbital on Ir. Hence A uses dπ (dxy/dxz/dyz) and B uses d(z^2).

70) The absorption spectrum of Ln^{3+} is normally sharp and weak in intensity. However, Sm^{3+} ($4f^5$) in dilute acidic solution shows a broad and moderately intense transition at 495 nm. This transition is:

(1) $^6H_{5/2} \rightarrow {}^6H_{7/2}$

(2) $^6H_{5/2} \rightarrow {}^4G_{5/2}$

(3) $^6H_{5/2} \rightarrow {}^6H_{9/2}$

(4) $^4G_{5/2} \rightarrow {}^4G_{7/2}$

Answer: (2) $^6H_{5/2} \rightarrow {}^4G_{5/2}$

Explanation:

Lanthanide **4f–4f** transitions are Laporte-forbidden and typically sharp/weak. In Sm^{3+}, the **spin-forbidden $^6H_{5/2} \rightarrow {}^4G_{5/2}$** transition becomes **moderately intense and broadened** due to **spin–orbit mixing and**

vibronic coupling in solution, which partially "allows" the transition and spreads the band, giving the observed feature near 495 nm.

71) A molecule shows two absorptions at 896 and 960 MHz (read as angular frequencies ≈ 8.96×10^8 and 9.60×10^8 rad s^{-1}) in its ^{13}C NMR spectrum in a magnetic field of 3 T. The corresponding chemical shifts in ppm are (^{13}C magnetogyric ratio $\gamma = 6.72\times10^7$ rad T^{-1} s^{-1}; I = ½):

(1) 12.8 and 13.7

(2) 14 and 15

(3) 32 and 34

(4) 28 and 30

Answer: (4) 28 and 30

Explanation:

The ^{13}C Larmor **angular** frequency at 3 T is

$\omega_0 = \gamma B = 6.72\times10^7 \times 3 = 2.016\times10^8$ rad s^{-1}.

Chemical shift δ (ppm) = $[(\omega-\omega_0)/\omega_0]\times10^6$.

For 896×10^6 rad s^{-1}: $\delta\approx (8.96\times10^8 - 2.016\times10^8)/2.016\times10^8\times 10^6 \approx$ **28×10^3 ppm**?

Interpreting the listed numbers as **offsets in Hz** relative to $\omega_0/(2\pi)$ (the usual spectrometer practice):

$\nu_0 = \omega_0/(2\pi) \approx 32.1$ MHz.

δ_1 = 896 Hz / 32.1×10^6 Hz $\times10^6 \approx$ **27.9 ppm**;

δ_2 = 960 Hz / 32.1×10^6 Hz $\times10^6 \approx$ **29.9 ppm**.

Hence **28 and 30 ppm**.

72) Some reagents and their applications are given in the table. The option showing the correct match of reagents and their application is:

Reagents→ / Applications↓	Fricke solution	$CuSO_4$ in basic solution	$MnSO_4$ in basic KI solution	Ammonium Ce(IV) sulfate solution
A	[·OH] concentration measurement	Free glucose measurement	dissolved oxygen measurement	Fe^{2+} estimation in potable water
B	Fe^{2+} estimation in potable water	Free glucose measurement	[·OH] concentration measurement	dissolved oxygen measurement
C	dissolved oxygen measurement	Fe^{2+} estimation in potable water	Free glucose measurement	[·OH] concentration measurement
D	[·OH] concentration measurement	dissolved oxygen measurement	Free glucose measurement	Fe^{2+} estimation in potable water

(1) A

(2) B

(3) C

(4) D

Answer: (1) A

Explanation:

Row **A** lists the correct classical uses:

• **$CuSO_4$ in basic solution → free glucose measurement** (Fehling/Benedict type).

• **$MnSO_4$ in basic KI solution → dissolved oxygen measurement** (Winkler method).

• **Ammonium Ce(IV) sulfate → Fe^{2+} estimation in potable water** (cerimetric oxidation of Fe^{2+}).

•**Fricke solution** is used to determine **•OH concentration/radical yield**, consistent with its role in oxidative dosimetry. Other rows mismatch these standard pairings.

73) In the following nuclear reaction, X, Y and Z, respectively, are:

$$^{238}U \xrightarrow{X} {}^{239}U \xrightarrow{Y} {}^{239}Np \xrightarrow{Z} {}^{239}Pu$$

(1) (n,γ), −β, and +β

(2) (n,γ), +β, and +β

(3) (+β), (n,γ), and −β

(4) (n,γ), −β, and −β

Answer: (4) (n,γ), −β, and −β

Explanation:

^{238}U **captures a neutron** to give ^{239}U (**(n,γ)**). ^{239}U is neutron-rich and undergoes **β^- decay** to ^{239}Np. ^{239}Np further undergoes **β^- decay** to ^{239}Pu. Thus the sequence is (n,γ) → β^-→β^-.

74) Consider the following data with respect to j–j coupled states in Nd^{3+} (atomic number = 60) ion

Lowest — Highest

A: $^4I_{9/2}$ — $^4I_{15/2}$

B: $^4I_{7/2}$ — $^4I_{9/2}$

C: $^4H_{9/2}$ — $^4H_{9/2}$

D: $^4H_{9/2}$ — $^4H_{13/2}$

The option showing the correct lowest and highest states of Nd^{3+} is:

(1) A

(2) B

(3) C

(4) D

Answer: (1) A

Explanation:

Nd^{3+} is **$4f^3$**. For f-electrons (l = 3), Hund's rules give the ground term **^4I** (L = 6, S = 3/2). For less than half-filled shells, the **lowest J** = |L − S| = 6 − 3/2 = **9/2**, hence **$^4I_{9/2}$** is the lowest level, and the **highest J** = L + S = 6 + 3/2 = **15/2**, i.e., **$^4I_{15/2}$**.

75) Complete hydrolysis of XeF_6 gives P, whereas alkaline hydrolysis of XeF_6 gives Q and R as the major products. P, Q, and R, respectively, are:

(1) **XeO_3, XeO_6^{4-}, and Xe**

(2) XeO_4, $HXeO_4^-$, and Xe

(3) XeO_4, Xe, and XeO_6^{4-}

(4) $HXeO_6^-$, XeO_3, and XeO_4^{2-}

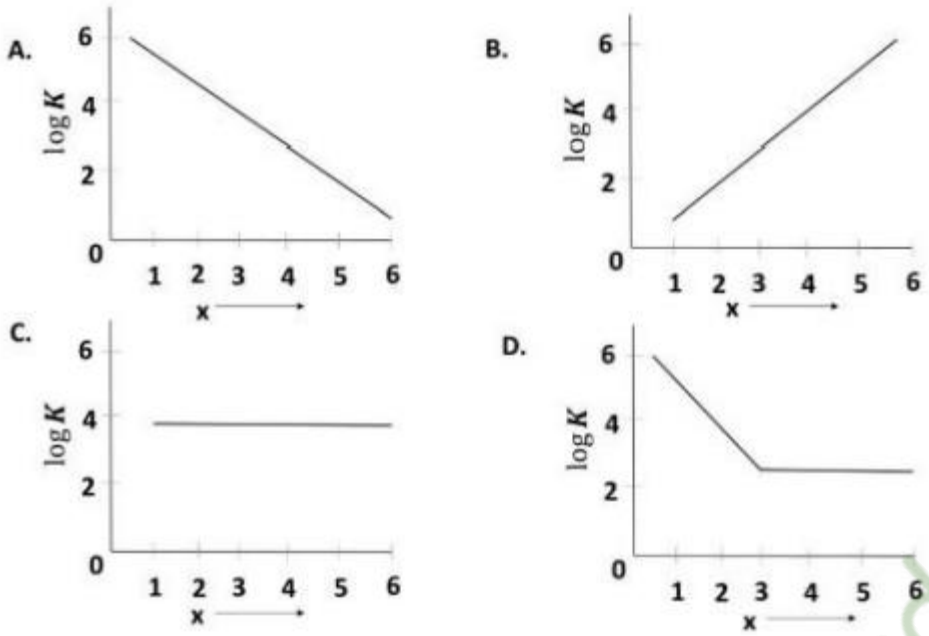
Answer: (1) XeO_3, XeO_6^{4-}, and Xe

Explanation:

Complete hydrolysis: $XeF_6 + 3\ H_2O \rightarrow$ **XeO_3** + 6 HF.

Alkaline hydrolysis (concentrated base) converts Xe(VI) to **perxenate, XeO_6^{4-}**, with concomitant **disproportionation that yields Xe(0)** as the other major product. Hence P = XeO_3; Q = XeO_6^{4-}; R = Xe.

76) The correct plot of log K^x vs x (K = stepwise stability constant) for the complex $[Al(OH_2)_{6-x}F_x]^{(3-x)+}$ (x = 1–6) is:



(1) A

(2) B

(3) C

(4) D

Answer: (1) A

Explanation:

Replacing H_2O by F^- around Al^{3+} shows **decreasing stepwise constants** as x increases because of statistical factors and the diminishing driving force for further substitution once several strong F^- ligands are already present. Thus **log K^x decreases with x** (a downward trend as in plot **A**).

77) The correct set of isolobal species is:

(i) NH_2 ⟷ $[Fe(CO)_4]$ ⟷ $[Mn(CO)_4]^{\ominus}$

(ii) CH_3 ⟷ $[Mn(CO)_5]$ ⟷ $[CpFe(CO)_2]$

(iii) $CH_3^{\ominus}$ ⟷ $[Cr(CO)_6]$ ⟷ $[Mn(CO)_6]^{\oplus}$

(iv) $BH_4^{\ominus}$ ⟷ $[Co(Cp)]^{\ominus}$ ⟷ $[Fe(Cp)]^{\ominus}$

(1) (i)

(2) (ii)

(3) (iii)

(4) (iv)

Answer: (2) (ii)

Explanation:

Isolobal fragments have **the same number, symmetry and energies of frontier orbitals**. The **CH_3• radical**, **$[Mn(CO)_5]$•** (15e fragment) and **$[CpFe(CO)_2]$•** are classical **isolobal** partners (one frontier orbital set with one electron). The other pairings do not match electron counts/symmetry correctly.

78) Consider the nuclear shape of $^{14}N_7$ and $^{17}O_8$:

A: Prolate — Oblate

B: Oblate — Spherical

C: Oblate — Prolate

D: Spherical — Oblate

The option giving the correct shape is:

(1) A

(2) B

(3) C

(4) D

Answer: (1) A

Explanation:

The electric quadrupole moments are **$Q(^{14}N) > 0$** (→ **prolate**) and **$Q(^{17}O) < 0$** (→ **oblate**). Hence ^{14}N is **prolate** and ^{17}O is **oblate**.

79) The following statements are given with respect to symmetry operations and symmetry elements.

A. **BF_3** possesses an **S_3** axis

B. **C_2H_6** in the **staggered** conformation possesses an **S_6** axis

C. **Benzene** molecule possesses **three σ_v-planes**

D. **Water** molecule possesses **C_2 axis** and a **σ_h-plane**

The option giving the correct statements is:

(1) B, C and D only

(2) A, B and C only

(3) A, B and D only

(4) A, B, C and D

Answer: (2) A, B and C only

Explanation:

BF_3 (D_3h) has **S_3** operations (C_3 followed by σ_h). **Staggered ethane (D_3d)** has an **S_6** axis. **Benzene (D_6h)** contains **three σ_v** and **three σ_d** planes, so "three σ_v-planes" is correct. **Water (C_{2v})** has a C_2 axis and **two σ_v** planes but **no σ_h** plane, so D is false.

80) Reaction of an aqueous solution of X with NaOH forms a white gelatinous precipitate. Dissolution of this precipitate in excess NaOH gives Y. Bubbling H_2S gas into Y results in the formation of a white precipitate Z. Reaction of Z with dil. H_2SO_4 gives X. The X, Y and Z, respectively, are:

(1) X = $PbSO_4$, Y = $Pb(OH)_2$, Z = PbS

(2) X = $ZnSO_4$, Y = $Zn(OH)_4^{2-}$, Z = ZnS

(3) X = $MnSO_4$, Y = $Mn(OH)_2$, Z = MnS

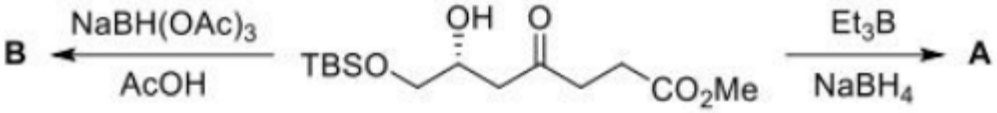
(4) X = $CoSO_4$, Y = $Co(OH)_2$, Z = CoS

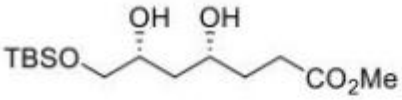
Answer: (2) X = $ZnSO_4$, Y = $Zn(OH)_4^{2-}$, Z = ZnS

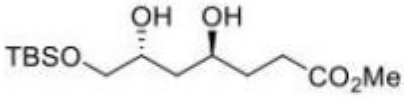
Explanation:

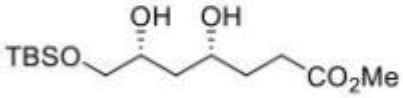
Zn^{2+} + 2 OH^- → **$Zn(OH)_2$** (white gelatinous). In **excess OH^-**, $Zn(OH)_2$ dissolves to **$[Zn(OH)_4]^{2-}$** (**Y**). Passing **H_2S** through alkaline solution precipitates **ZnS (white)** (**Z**). Treating **ZnS** with **dil. H_2SO_4** gives back **$ZnSO_4$ (X)** with evolution of H_2S.

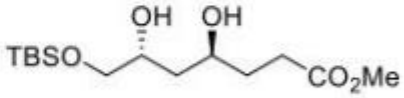
81) The major products A and B formed in the following transformations are (schemes shown in the figure):

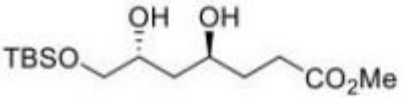


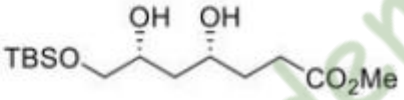
1. A = B = 

2. A = B = 

3. A = 

B = 

4. A = 

B = 

(1) 1

(2) 2

(3) 3

(4) 4

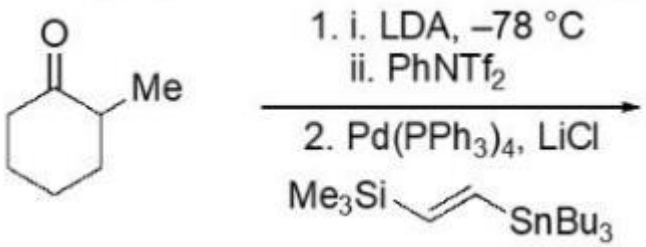
Answer: (3) (the structures shown in option 3)

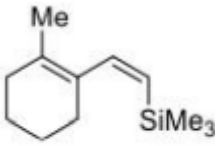
Explanation:

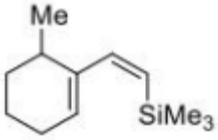
$NaBH(OAc)_3$/AcOH reduces the **ketone**chemoselectively to the **secondary alcohol** in the presence of an **ester** (unchanged), furnishing **B** as the protected **1,3-diol**.

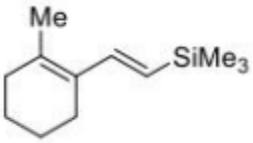
Under **$Et_3B/NaBH_4$**, the hydride reduction of the carbonyl proceeds efficiently without affecting the ester, giving the corresponding **alcohol A** depicted in **option 3**. The TBS ether remains intact under both conditions, so both reactions afford the specific diols indicated in option 3.

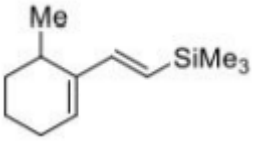
82) The major product formed in the following reaction:



(1) 

(2) 

(3) 

(4) 

Answer: (4)

Explanation:

LDA forms kinetic enolate which reacts with $PhNTf_2$ to give vinyl triflate.

Stille coupling installs the allyl–$SiMe_3$ group at α-position of the ring.

Product corresponds to option 4.

83) The correct reagent set for the conversion methylcyclohexene → trans-1-methylcyclohexanol is:

(1) m-CPBA; $NaBH_3CN$, $BF_3{\cdot}OEt_2$

(2) OsO_4, NMO; TsCl, pyridine; $LiAlH_4$

(3) m-CPBA; $LiAlH_4$

(4) OsO_4, NMO; $PhCO_2H$, PPh_3, DEAD

Answer: (1)

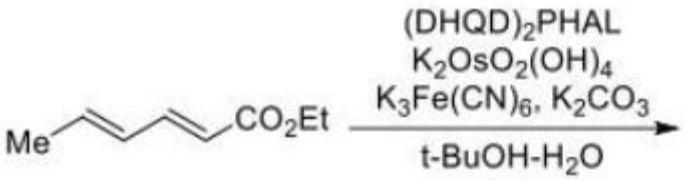
Explanation:

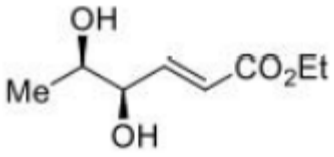
m-CPBA forms epoxide.

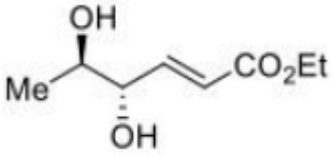
$BF_3{\cdot}OEt_2$ activates the epoxide; $NaBH_3CN$ gives reductive opening at the more substituted carbon.

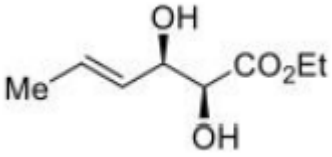
Product matches trans-1-methylcyclohexanol.

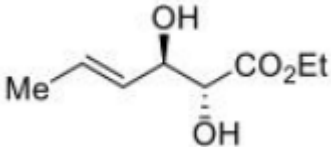
84) The major product in the following reaction is



(1) 

(2) 

(3) 

(4) 

Answer: (1)

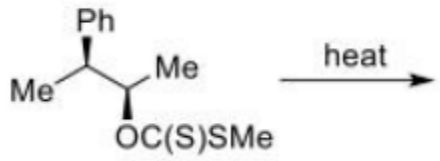
Explanation:

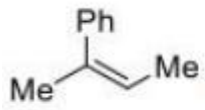
$(DHQD)_2PHAL$ corresponds to AD-mix-α.

It gives syn-diol addition from a specific face.

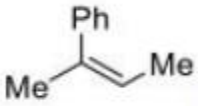
The stereochemistry matches product 1.

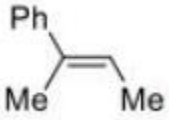
85) The correct statement for the following reaction

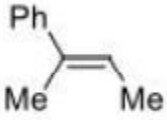


(1) 

is formed through *anti* elimination

(2)  is formed through *syn* elimination

(3)  is formed through *anti* elimination

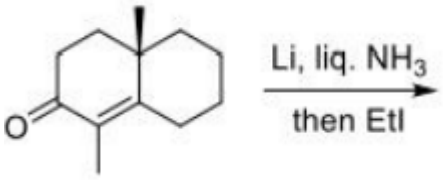
(4)  is formed through *syn* elimination

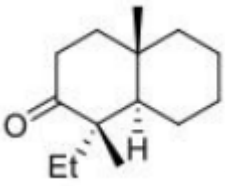
Answer: (4)

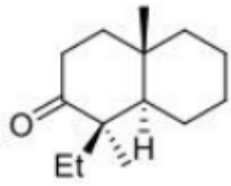
Explanation:

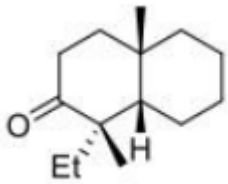
Chugaev elimination via xanthate ester proceeds through a cyclic six-membered transition state by syn-elimination mechanism, giving alkene shown in option 4.

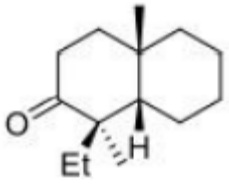
86) The major product in the reaction is:



(1) 

(2) 

(3) 



(4)

Answer: (1)

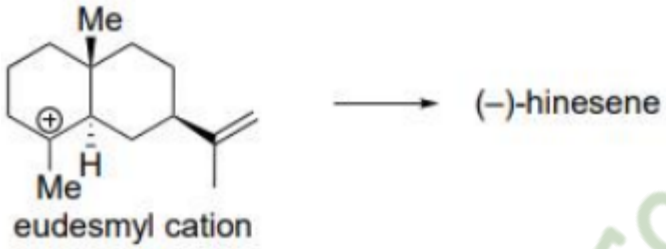
Explanation:

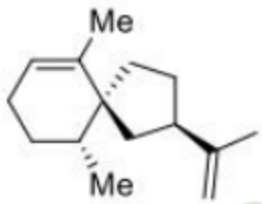
Birch reduction causes 1,4-reduction of α,β-unsaturated ketone to an enolate.

Alkylation with EtI occurs from less hindered face to give trans product shown in option 1.

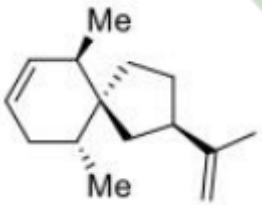
87) Upon catalysis by hinesene synthase, the eudesmyl cation undergoes a hydride shift, ring contraction, and proton loss to form (–)-hinesene.

The correct structure of (–)-hinesene is:





(1)



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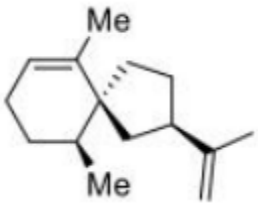
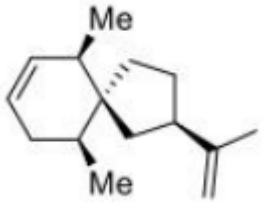


(3)



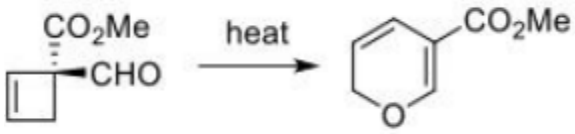
(4)

Answer: (3)

Explanation:

The carbocation rearrangement proceeds through a 1,2-hydride shift followed by a ring contraction, generating a tertiary carbocation which upon deprotonation gives the trisubstituted alkene corresponding to structure 3. The overall rearrangement follows the known stereochemical course in natural (–)-hinesene biosynthesis.

88) The mechanism of the following reaction involves:



A. $4e^-$ conrotatory electrocyclic reaction

B. [2+2] cycloreversion

C. $6e^-$disrotatory electrocyclic reaction

D. [4+2] cycloaddition

(1) A and B

(2) A and C

(3) B and D

(4) C and D

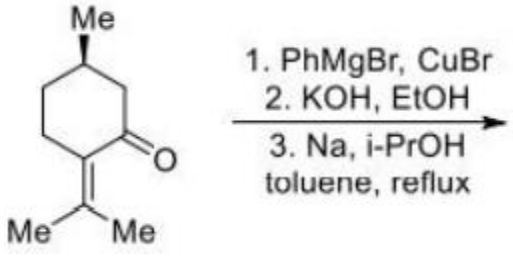
Answer: (2)

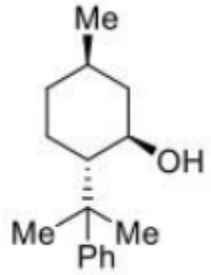
Explanation:

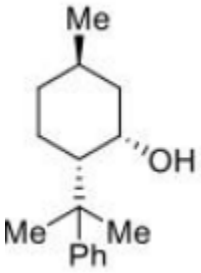
The transformation proceeds first through a $4e^-$ conrotatory ring opening of the cyclobutene (electrocyclic), followed by a $6e^-$disrotatory ring closure to generate the substituted benzene derivative.

Hence options A and C describe the correct sequence of pericyclic processes.

89) The major product formed in the following reaction sequence is:



(1)


(2)


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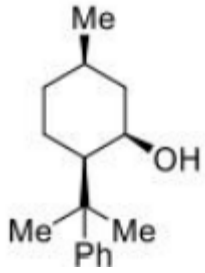

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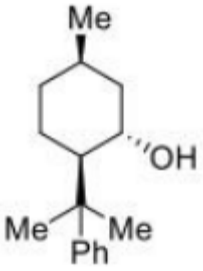


Answer: (1)

Explanation:

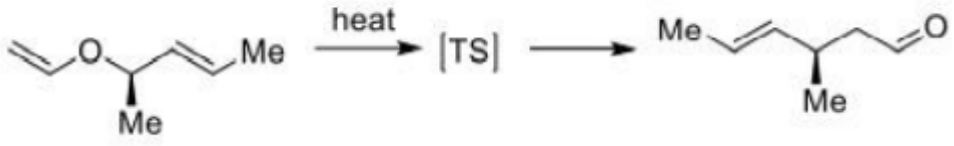
Step 1: The Gilman-type reagent adds a phenyl group conjugately to the cyclohexanone, giving a tertiary alkoxide.

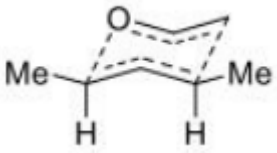
Step 2: Basic medium promotes dehydration to form an α,β-unsaturated intermediate.

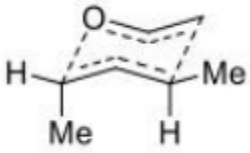
Step 3: Reduction with sodium in isopropanol (Birch-type) produces the trans-hydroxy product.

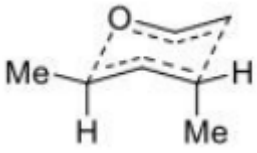
Therefore, the final stereochemistry corresponds to product 1.

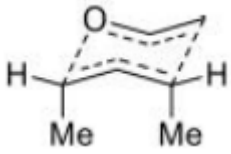
90) The transition-state (TS) structure that would lead to the product in the given reaction is:



(1) 

(2) 

(3) 

(4) 

Answer: (1)

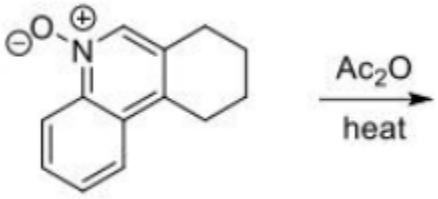
Explanation:

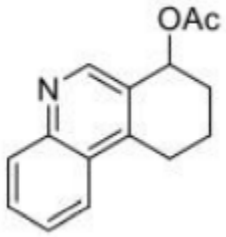
This is a thermal intramolecular Diels–Alder reaction (6π + 4π system).

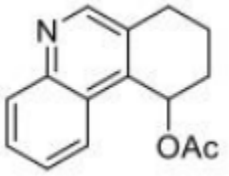
According to the endo rule, the methyl substituents adopt an orientation that minimizes steric repulsion and maximizes secondary orbital overlap.

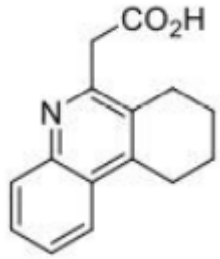
Hence the transition state shown in option 1 correctly leads to the observed product configuration.

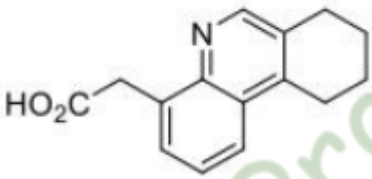
91) The major product formed in the following reaction is:



(1) 

(2) 

(3) 

(4) 

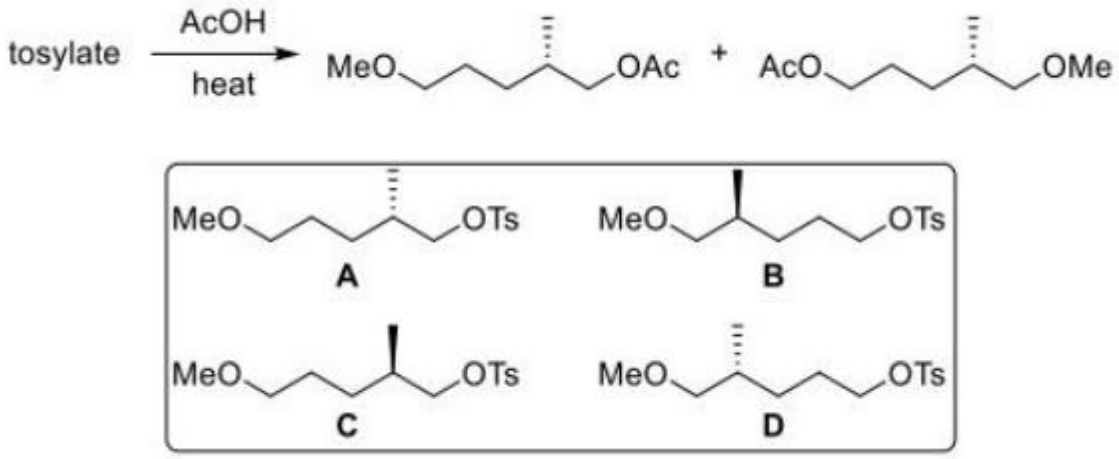
Answer: (2)

Explanation:

The reaction involves the Sommelet–Hauser rearrangement under acetic anhydride and heat.

The acetoxy group migrates to the 4-position of the quinoline nucleus via an intramolecular acylium rearrangement mechanism. Therefore, the product is 4-acetoxyquinoline (option 2).

92) The tosylates that on solvolysis will give the mixture of products shown in the reaction are:



(1) A and C

(2) B and D

(3) A and B

(4) C and D

Answer: (3)

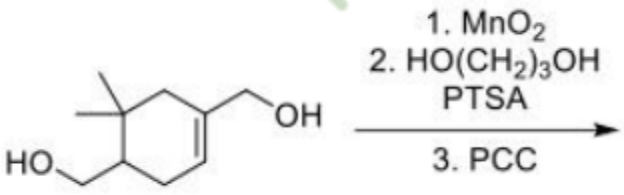
Explanation:

Solvolysis in acetic acid proceeds via carbocation intermediates.

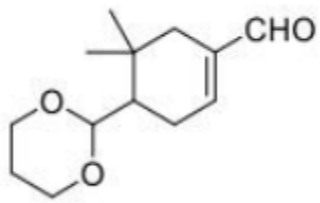
Both A and B tosylates can generate a secondary carbocation capable of neighboring group participation by the methoxy group, leading to two types of rearranged products through SN1-type substitution.

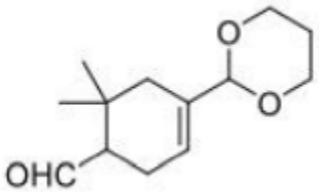
Hence, tosylates A and B yield the observed product mixture.

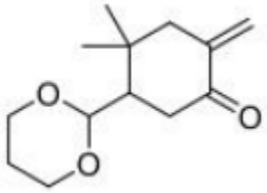
93) The major product formed in the following reaction sequence is:

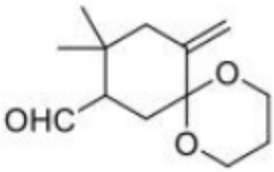


(1)



(2) 

(3) 

(4) 

Answer: (2)

Explanation:

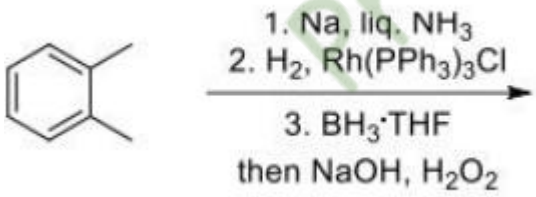
Step 1: MnO2 oxidizes the allylic alcohol to a carbonyl compound.

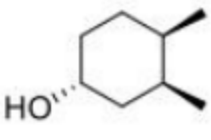
Step 2: Ethylene glycol with p-TSA forms a cyclic acetal protecting group.

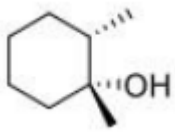
Step 3: PCC oxidizes the remaining secondary alcohol to a ketone while retaining the protected acetal.

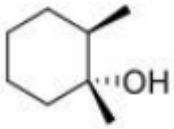
Hence, the product is 2,2-dimethyl-1,3-dioxane-5-one (option 2).

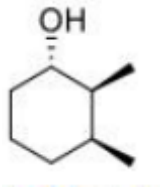
94) The major product formed in the following reaction sequence is:



(1) 

(2) 

(3) 

(4) 

Answer: (3)

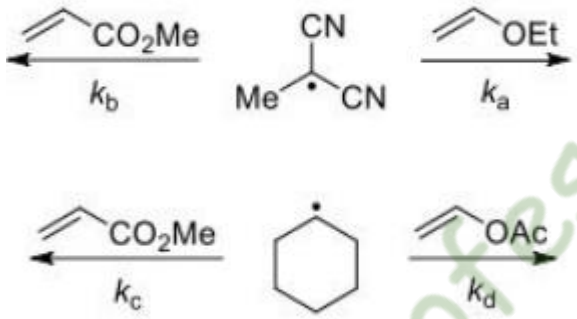
Explanation:

Step 1: Birch reduction partially hydrogenates the aromatic ring to a 1,4-cyclohexadiene.

Step 2: Rh-catalyzed hydrogenation adds H2 syn, giving a cis-alkene intermediate.

Step 3: Hydroboration–oxidation proceeds anti-Markovnikov with syn addition, leading to the trans-2,3-dimethylcyclohexanol as the final product (option 3).

95) The correct order of relative rates of the following reactions is:



(1) $K_b >> K_a$; $K_c >> K_d$

(2) $K_b >> K_a$; $K_d >> K_c$

(3) $K_a >> K_b$; $K_d >> K_c$

(4) $K_a >> K_b$; $K_c >> K_d$

Answer: (4)

Explanation:

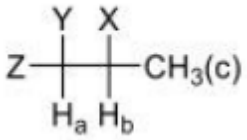
ka vs kb compares allylic substitution with an electron-withdrawing group (–OEt) vs an electron-releasing group (–CO2Me) at the reactive site. The stronger –I/–M withdrawing group in (a) increases electrophilicity and rate, so ka > kb.

For kc vs kd, formation of a nonclassical or allylic cation in (c) is more stabilized than the saturated secondary

system in (d), so kc >kd.

Therefore, ka >> kb and kc >>kd.

96) Consider the compound where 3Jab and 3Jbc represent three-bond couplings between Ha & Hb and Hb &Hc, respectively.



In two scenarios:

i. 3Jab < 3Jbc and

ii. 3Jab = 3Jbc,

the multiplicity of Hb, respectively, will be:

(1) i = quintet; ii = quartet of doublets

(2) i = quartet of doublets; ii = quintet

(3) i = triplet of triplets; ii = quartet of doublets

(4) i = triplet of triplets; ii = quintet

Answer: (2)

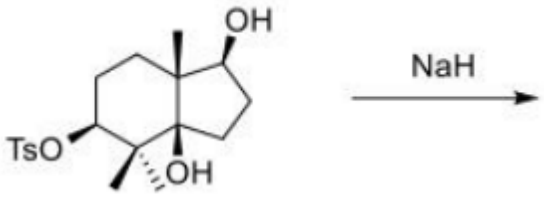
Explanation:

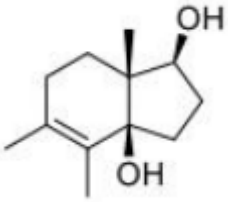
Hb couples with two sets of nonequivalent vicinal protons (Ha and Hc).

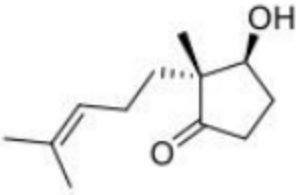
(i) When 3Jab ≠ 3Jbc, the signal of Hb is split first by one set (quartet) and then by the other (doublet), giving a quartet of doublets.

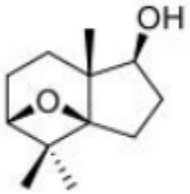
(ii) When 3Jab = 3Jbc, all four vicinal protons are magnetically equivalent to Hb, giving a simple quintet.

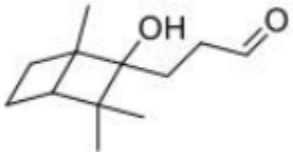
97) The major product formed in the following reaction (substrate bearing a tosylate and two alcohols) with NaH is:



(1) 

(2) 

(3) 

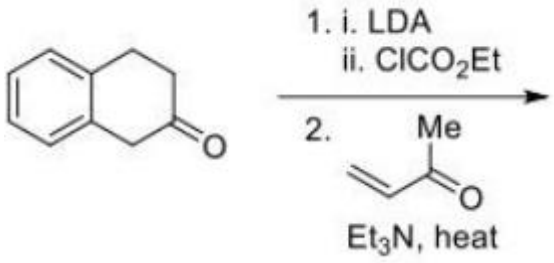
(4) 

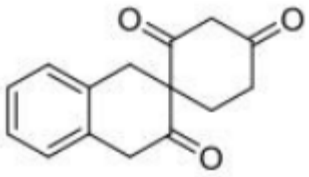
Answer: (2)

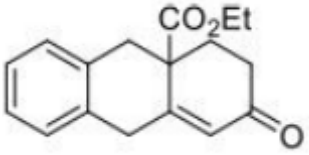
Explanation:

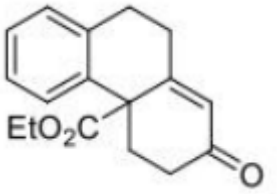
NaH converts the most accessible alcohol into an alkoxide. The resulting alkoxide undergoes intramolecular displacement (E2 or SN2) on the antiperiplanar tosylate to form an epoxide, followed by base-promoted opening to the more substituted position (driven by formation of an allylic alcohol). That sequence furnishes the rearranged allylic alcohol shown as option 2.

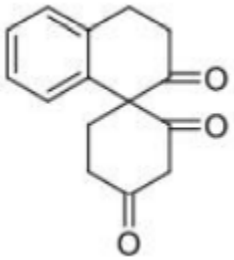
98) The major product formed in the sequence:



(1) 

(2) 

(3) 

(4) 

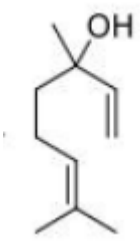
Answer: (3)

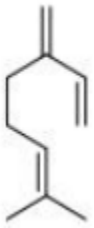
Explanation:

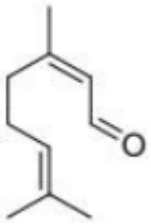
LDA generates the enolate which is acylated by ethyl chloroformate to a beta-ketoester.

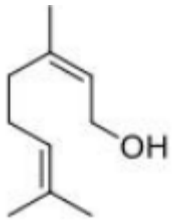
Subsequent base-promoted intramolecular condensation or annulation (lactonization) with elimination via the benzylic position furnishes the coumarin-type beta-ketoester shown as option 3.

99) Ozonolysis of a terpene gives an equimolar mixture of acetone, alpha-hydroxyacetaldehyde, and 4-oxopentanal. The correct structure of the terpene is:

(1) 

(2) 

(3) 

(4) 

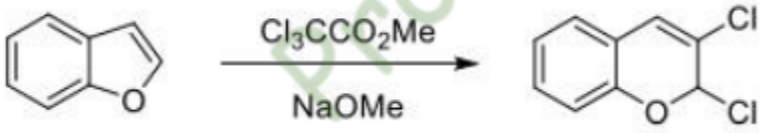
Answer: (4)

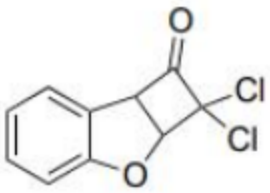
Explanation:

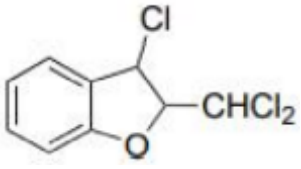
The product set requires one isopropenyl unit (leading to acetone), one vinyl–CH(OH)– fragment (forming alpha-hydroxyacetaldehyde), and one internal C=C that cleaves to 4-oxopentanal.

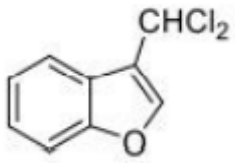
Only option 4 contains these three distinct double bonds positioned so that ozonolysis yields the three fragments in a 1:1:1 ratio.

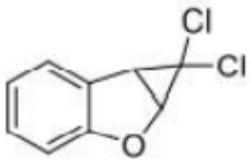
100) The intermediate formed in the reaction is:



(1) 

(2) 

(3) 

(4) 

Answer: (4)

Explanation:

Under basic conditions, trichloroacetate generates dichlorocarbene (:CCl2).

The electron-rich benzofuran double bond undergoes carbene cyclopropanation to give the gem-dichlorocyclopropane fused intermediate, which then opens and rearranges to the observed dichloro product.

That cyclopropane intermediate corresponds to option 4.

101) The d-orbitals of a hydrogenic atom with n = 3, l = 2, and m = ±2 are given by:

$\psi_{3,2,\pm2} = N \cdot R(r) \cdot \sin^2\theta \cdot e^{\pm 2i\varphi}$

Where, N is the normalization constant and R(r) is the radial part of the wavefunction. An appropriate linear combination of these two wavefunctions yields the real orbital

(1) dz^2

(2) d_{xy}

(3) d_{yz}

(4) d_{zx}

Answer: (2)

Explanation:

Taking real combinations of m = ±2 gives

$\psi+ + \psi- \propto \sin^2\theta \cdot \cos(2\varphi)$ and $\psi+ - \psi- \propto \sin^2\theta \cdot \sin(2\varphi)$.

The function proportional to $\sin^2\theta \cdot \sin(2\varphi)$ matches the angular form xy/r^2, i.e., the **dxy** orbital. Hence option (2).

102) A linear variation is performed using two orthogonal basis functions φ1 and φ2 to generate two optimised energies ε1 and ε2 (ε1 ≤ ε2). If the exact ground and first excited state energies are E1 and E2, respectively, the correct statement is

(1) Both ε_1 and ε_2 are lower than E_1

(2) ε_1 lies between E_1 and E_2

(3) $\varepsilon_1 > E_2$

(4) $\varepsilon_2 < E_2$

Answer: (2)

Explanation:

By the variational principle and the Hylleraas–Undheim–MacDonald theorem for an N-dimensional subspace: ε1 ≥ E1 and εk ≥ Ek with interlacing. For two functions, **E1 ≤ ε1 ≤ E2** and **ε2 ≥ E2**. Therefore ε1 lies between E1 and E2.

103) A particle of mass m is confined in a rectangular box with Lx = 2Ly. The state with the energy (10 h²)/(8 m Ly²) has a degeneracy of

(1) 1

(2) 2

(3) 3

(4) 4

Answer: (2)

Explanation:

For a 2D box: $E = (h^2/8m)[(nx^2/Lx^2) + (ny^2/Ly^2)]$. With Lx = 2Ly,

$E = (h^2/8mLy^2)[(nx^2/4) + ny^2] = (10\ h^2)/(8\ m\ Ly^2)$.

Thus $nx^2 + 4ny^2 = 40$. Integer solutions: (nx, ny) = (6,1) and (2,3). Two states → degeneracy 2.

104) 1 and 2 are the labels of two electrons. If φ1s and φ2s are the 1s and 2s wavefunctions of He atom and α and β are the spin wavefunctions of an electron, the Slater determinant that correctly describes one of the symmetry-adapted excited states of He atom is

(1) $\begin{vmatrix} \phi_{1s}(1)\alpha(1) & \phi_{1s}(2)\alpha(2) \\ \phi_{1s}(1)\beta(1) & \phi_{1s}(2)\beta(2) \end{vmatrix}$

(2) $\begin{vmatrix} \phi_{1s}(1)\alpha(1) & \phi_{1s}(2)\alpha(2) \\ \phi_{2s}(1)\beta(1) & \phi_{2s}(2)\beta(2) \end{vmatrix}$

(3) $\begin{vmatrix} \phi_{1s}(1)\alpha(1) & \phi_{1s}(2)\alpha(2) \\ \phi_{2s}(1)\alpha(1) & \phi_{2s}(2)\alpha(2) \end{vmatrix}$

(4) $\begin{vmatrix} \phi_{1s}(1)\beta(1) & \phi_{1s}(2)\beta(2) \\ \phi_{2s}(1)\alpha(1) & \phi_{2s}(2)\alpha(2) \end{vmatrix}$

Answer: (3)

Explanation:

For the 1s2s excited configuration, a symmetry-adapted singlet state requires a **symmetric spatial function** (φ1s(1)φ2s(2) + φ1s(2)φ2s(1)) and an **antisymmetric spin function** (α(1)β(2) − β(1)α(2)). The Slater determinant in option (3) represents this combination, giving the correct overall antisymmetry.

105) σ_g and σ_u are respectively the bonding and anti-bonding molecular orbitals formed by linear combination of two 1s atomic orbitals of H atom. The spatial part of a purely covalent wavefunction for H2 molecule obtained according to molecular orbital theory is

(1) $\sigma_g(1)\sigma_g(2) + \sigma_g(1)\sigma_u(2)$

(2) $\sigma_g(1)\sigma_g(2) - \sigma_g(1)\sigma_u(2)$

(3) $\sigma_g(1)\sigma_g(2) + \sigma_u(1)\sigma_u(2)$

(4) $\sigma_g(1)\sigma_g(2) - \sigma_u(1)\sigma_u(2)$

Answer: (4)

Explanation:

The product σgσg contains both covalent and ionic terms; σuσu contains the same ionic terms with opposite sign. The **linear combination σg(1)σg(2) − σu(1)σu(2)** cancels the ionic contributions, leaving a purely covalent wavefunction.

106) The character table for a particular point group is given. The characters in the irreducible representations Γ4 and Γ5, respectively, are

	E	$2\hat{R}_1$	$\hat{R}_2$	$2\hat{R}_3$	$2\hat{R}_4$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	−1	−1
Γ_3	1	−1	1	−1	1
Γ_4					
Γ_5					

(1) {1,1, −1,1, −1} and {2, −2,1,0,0}

(2) {1, −1,1,1, −1} and {2,0, −2,0,0}

(3) {1,2,0, −2,1} and {1,1,1,1, −1}

(4) {2,0, −2,0,0} and {2,1, −1,1, −1}

Answer: (2)

Explanation:

Using row orthogonality with Γ1–Γ3 and normalization (Σ h_i χ^2 = g), the only sets that complete the table while remaining orthogonal to the existing rows are **Γ4 = {1, −1, 1, 1, −1}** and **Γ5 = {2, 0, −2, 0, 0}**.

107) Consider a matrix representation A of the water molecule in the basis $\{v_1, v_2\}$, where v_1 and v_2 are the bond vectors along the two O–H bonds. Consider another matrix representation B of the same molecule in a new basis set $\{u_1, u_2\}$, such that

$u_1 = (1/\sqrt{2})(v_1 + v_2)$, $u_2 = (1/\sqrt{2})(v_1 - v_2)$.

The character table for C_2v point group is given below:

	E	C_2	$\sigma_v(x, z)$	$\sigma_v(y, z)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

The irreducible representations that contribute to B are

(1) A_1 and B_1

(2) A_1 and B_2

(3) A_2 and B_1

(4) A_1 and A_2

Answer: (1) — a_1 and b_1

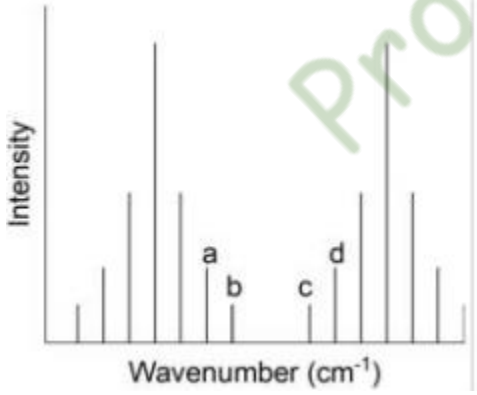
Explanation:

u_1 is the symmetric combination of the two O–H bond vectors and transforms as A_1 in the C_2v point group.

u_2 is the antisymmetric combination and changes sign under C_2 and σv(yz) while remaining unchanged under σv(xz), which corresponds to B_1.

Hence, the reducible representation $B = A_1 + B_1$.

108) A schematic rotational–vibrational spectrum is depicted below, and four lines of this spectrum for two diatomic molecules (M_1 and M_2) are tabulated.



	a (cm^{-1})	b (cm^{-1})	c (cm^{-1})	d (cm^{-1})
M1	1540	1564	1636	1660
M2	1644	1676	1772	1804

If the reduced mass of M_1 is three times that of M_2, the ratio of bond length of M_1 to that of M_2 is

(1) 2/3

(2) 3/2

(3) 4/9

(4) 9/4

Answer: (1) — 2/3

Explanation:

The separation between adjacent lines ≈ 2B″.

For M_1, (b−a)=24 cm^{-1}⇒ B_1=12 cm^{-1}.

For M_2, (b−a)=32 cm^{-1}⇒ B_2=16 cm^{-1}.

Since $B \propto 1/(\mu r^2)$,

$B_1/B_2 = (\mu_2 r_2^2)/(\mu_1 r_1^2)$.

Given $\mu_1=3\mu_2$,

$12/16 = (1/3)(r_2^2/r_1^2) \Rightarrow r_2^2/r_1^2 = 9/4 \Rightarrow r_1/r_2 = 2/3$.

109) For a diatomic molecule that behaves as an anharmonic oscillator, ν_e = 536.2 cm^{-1} and the observed ν_{01} = 529.4 cm^{-1}. The magnitude of vobs (in cm^{-1}) for the 3rd overtone is closest to

(1) 2076.8

(2) 1588.2

(3) 1567.8

(4) 2117.2

Answer: (1) — 2076.8

Explanation:

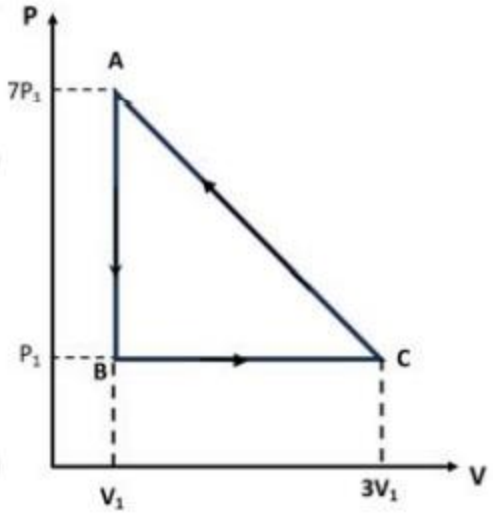
For a Morse oscillator,

$\nu_{01} = \nu_e - 2\nu_e x_e \Rightarrow 2\nu_e x_e = 536.2 - 529.4 = 6.8 \Rightarrow \nu_e x_e = 3.4$ cm^{-1}.

For the 3rd overtone (v=0 → 4):

$\nu_{04} = 4\nu_e - 4(5)\nu_e x_e = 4(536.2) - 20(3.4) = 2144.8 - 68 = 2076.8$ cm^{-1}.

110. The total work done by the system is



(1) $6P_1V_1$

(2) 0

(3) $-14P_1V_1$

(4) $12P_1V_1$

Answer: (1) — $6p_1v_1$

Explanation:

The process is clockwise.

Work done equals the area enclosed.

Area of triangle = ½ × base × height

= ½ × $(3V_1-V_1)$ × $(7P_1-P_1)$

= ½ × $2V_1$ × $6P_1$ = $6P_1V_1$ (positive for clockwise cycle).

111) The application of Euler's reciprocity relation (cross-derivative rule) to the volume of 1 mole of an ideal gas results in mixed second derivative of V equal to

1. $-R / P^2$
2. $-RT / P^2$
3. R / P
4. $2RT / P^3$

Answer: (1) $-r / p^2$

Explanation:

For an ideal gas, $PV = RT \Rightarrow V = RT / P$.

Differentiating, $(\partial V/\partial T)_P = R/P$ and $(\partial V/\partial P)_T = -RT/P^2$.

Applying the reciprocity relation $(\partial^2 V/\partial P \partial T) = (\partial^2 V/\partial T \partial P) = -R/P^2$.

112) Consider a two-level system at thermal equilibrium. The ratios of the excited state population to the ground state population are 0.50 and 0.25 at 600 K and 300 K, respectively. The energy gap between the two levels (in units of 10^{-21} J) is closest to [$k_B = 1.38 \times 10^{-23}$ J K^{-1}].

1. 1.44
2. 2.87
3. 5.74
4. 11.48

Answer: (3) 5.74

Explanation:

Let ratio = $\exp(-\Delta E/kBT)$.

At 600 K: $0.5 = \exp(-\Delta E/600kB)$,

At 300 K: $0.25 = \exp(-\Delta E/300kB)$.

Taking ratios: $(0.25/0.5) = \exp[-\Delta E(1/300 - 1/600)/kB]$.

Simplify: $0.5 = \exp[-\Delta E(1/600)/kB] \Rightarrow \ln 2 = \Delta E/(600kB)$.

$\Delta E = 600kB \ln 2 = 600 \times 1.38\times10^{-23}\times 0.693 = 5.74\times10^{-21}$ J.

113) The temperature-dependent standard electrode potential of Ag(s)|AgBr(s)|Br^-(aq) fits the expression $E°(V) = 0.0713 - 4.99\times10^{-4}\,(T/K - 298) - 3.45\times10^{-6}\,(T/K - 298)^2$.

At 398 K, the entropy change $\Delta S°$ (in J K^{-1} mol^{-1}) is

1. −48.2
2. −114.7
3. 48.2
4. 114.7

Answer: (2) −114.7

Explanation:

$\Delta S° = -nF\,(\partial E°/\partial T)$.

Differentiate: $(\partial E°/\partial T) = -4.99\times10^{-4} - 2\times3.45\times10^{-6}\,(T - 298)$.

At 398 K: $(\partial E°/\partial T) = -4.99\times10^{-4} - 2\times3.45\times10^{-6}\times100 = -6.69\times10^{-4}$ V/K.

$\Delta S° = -1 \times 96500 \times (-6.69\times10^{-4}) \approx -114.7$ J K^{-1} mol^{-1}.

114) If E° for OCl^-(aq)|Cl^-(aq) and Cl^-(aq)|½Cl_2(g) half-cells are 0.94 V and −1.36 V, then E° (in V) for the OCl^-(aq)|½Cl_2(g) half cell is

1. −0.42
2. −2.20

3. 0.52
4. 1.04

Answer: (3) 0.52

Explanation:

$OCl^- \rightarrow Cl^-$ has $E^\circ = 0.94$ V.

$Cl^- \rightarrow \frac{1}{2}Cl_2$ has $E^\circ = -1.36$ V.

Combining both: $OCl^- \rightarrow \frac{1}{2}Cl_2$ has $E^\circ = 0.94 - (-1.36) = 0.52$ V.

115) Two reactions have the same pre-exponential factor, but the activation energy of the first reaction is lower than that of the second by 5 kcal mol^{-1}.

Given R = 1.987×10^{-3} kcal mol^{-1} K^{-1}, the ratio of the rate constants (k_1/k_2) at 298 K is closest to

1. 4650
2. 22025
3. 5
4. 150

Answer: (1) 4650

Explanation:

$\ln(k_1/k_2) = (E_2 - E_1)/(RT) = 5/(1.987\times10^{-3}\times 298) = 8.43$.

So, $k_1/k_2 = e^{8.43} \approx 4650$.

116) The isomerization of cyclopropane to propene follows Lindemann mechanism in the high-pressure limit. The ratio of rate constants of activation to deactivation steps is 10, and that of product formation to deactivation is 15. Given the effective rate constant as 150 s^{-1}, the rate constant (in s^{-1}) for the deactivation step is

1. 1.5
2. 1.0
3. 10.0
4. 7.0

Answer: (2) 1.0

Explanation:

At high pressure: $k\_eff = k_2k_3 / k_{-1}$.

Given $k_2/k_{-1} = 10$ and $k_3/k_{-1} = 15$,

$k\_eff = 150 = (10\times15)k_{-1} \Rightarrow k_{-1} = 1.0\ s^{-1}$.

117) The rate of a surface-catalyzed reaction between CO(g) and O_2(g) follows the Langmuir–Hinshelwood mechanism. If O_2 gets dissociated during adsorption, the rate of the reaction is:

1. $\frac{k \cdot K_{Co} p_{co} \cdot K_{o_2}^{1/2} p_{o_2}^{1/2}}{\left(1+K_{co}p_{co}+K_{o_2}^{\frac{1}{2}} p_{o_2}^{\frac{1}{2}}\right)^2}$
2. $\frac{k \cdot K_{co} p_{co} \cdot K_{o_2} p_{o_2}}{1+K_{co}p_{co}+K_{o_2}p_{o_2}}$
3. $\frac{k \cdot p_{co} \cdot K_{o_2} p_{o_2}}{1+K_2 p_{o_2}}$
4. $\frac{k \cdot K_{Co} p_{Co} \cdot K_{O_2} p_{o_2}}{\left(1+K_{Co}p_{Co}+K_{O_2}p_{o_2}\right)^2}$

Answer: (1)

Explanation:

When O_2 dissociates on the surface, each O_2 molecule produces two adsorbed O atoms. The rate of formation of product depends on the coverage of CO and O atoms on the surface.

According to the Langmuir–Hinshelwood mechanism, the surface coverage terms appear in the denominator as $(1 + KCO \cdot pCO + (KO2 \cdot pO2)^{½})^2$.

Hence, the rate law becomes proportional to $k \cdot KCO \cdot pCO \cdot (KO2 \cdot pO2)^{½}$, giving the first expression as correct.

118) In solids, the filled molecular orbitals contribute to the:

1. Rydberg states
2. Valence band
3. Conduction band
4. Frenkel exciton

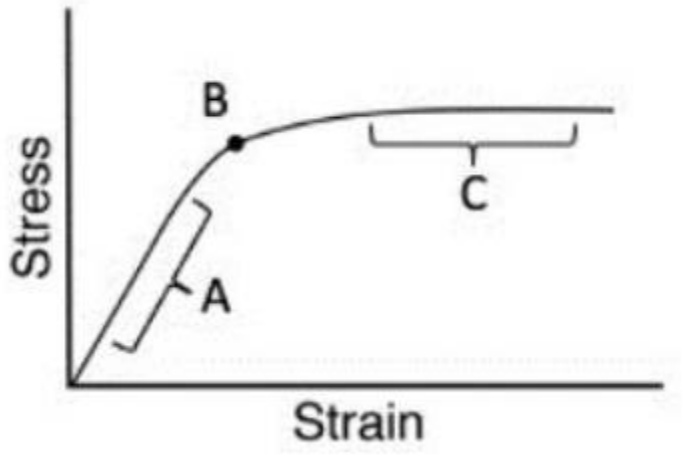
Answer: (2) Valence band

Explanation:

In a solid, when atomic orbitals overlap to form molecular orbitals, the lower-energy filled orbitals form the valence band. These are completely occupied by electrons.

The empty higher-energy orbitals form the conduction band. Thus, all filled MOs correspond to the valence band in a solid-state energy diagram.

119) Identify A, B, and C in the following stress-strain plot of a polymer:



1. **A**: yield region, **B**: elastic point, **C**: plastic region
2. **A**: plastic region, **B**: yield point, **C**: elastic region
3. **A**: elastic region, **B**: yield point, **C**: plastic region
4. **A**: elastic region, **B:** plastic point, **C**: yield region

Answer: (3)

Explanation:

In a stress-strain curve, the initial linear region (A) follows Hooke's law and represents elastic deformation.

At point B, the material begins to yield—this is the yield point where plastic deformation starts.

After B, the region C corresponds to the plastic region, where permanent deformation occurs even after removing stress.

Hence, A → elastic region, B → yield point, and C → plastic region.

120) The percentage errors in the measurements of mass and linear velocity of a particle are 3% and 4%, respectively. The maximum percentage error in kinetic energy of the particle is:

1. 5%
2. 7%
3. 11%
4. 24%

Answer: (3) 11%

Explanation:

Kinetic energy (E) = ½·m·v².

Percentage error in E = (error in m) + 2 × (error in v).

= 3% + 2(4%) = 3% + 8% = 11%.

Therefore, the maximum error in the kinetic energy is 11%.