21) The silver salt with the highest solubility product (Ksp) in water is

1. AgI
2. AgCl
3. AgF
4. AgBr

Answer: (3) AgF

Explanation: The solubility product (Ksp) represents how much of a salt can dissolve in water.

Among silver halides, the solubility order is AgF> AgCl >AgBr>AgI.

Fluoride forms the most soluble salt because of high hydration energy of F^-, which overcomes lattice energy.

Thus, AgF has the highest Ksp in water.

22) X, Y and Z are three p-block elements in the second row of the periodic table, with electron affinities (in kJ/mol) of –15, –142 and –333, respectively. The correct statement among the following, is

1. Y has the highest first ionization energy.
2. X has the most number of p-electrons.
3. X has the highest proton affinity.
4. Z has the highest electronegativity.

Answer: (4) Z has the highest electronegativity.

Explanation: Electron affinity becomes more negative across a period from left to right, indicating higher tendency to gain electrons.

Z has the most negative value (–333 kJ/mol), showing it gains electrons most readily and thus is the most electronegative.

Hence, Z corresponds to fluorine in the second period, the most electronegative element.

23) In the process of desulfurization of flue gas, SO_2 is passed through an absorber containing slaked lime in the presence of O_2. The final product is

1. $CaSO_3 \cdot 3H_2O$
2. $CaSO_4 \cdot CaCO_3$
3. $CaSO_4 \cdot 2H_2O$
4. CaS_2O_4

Answer: (3) $CaSO_4 \cdot 2H_2O$

Explanation: In flue-gas desulfurization, SO_2 reacts with $Ca(OH)_2$ in the presence of O_2 to form calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), commonly known as gypsum.

Reaction: $2Ca(OH)_2 + 2SO_2 + O_2 \rightarrow 2CaSO_4 \cdot 2H_2O$.

This is the standard industrial process for removing sulfur dioxide from exhaust gases.

24) The ground state term and the calculated magnetic moment (in BM) for Dy^{3+} ion respectively, are

1. $^6H_{15}/_2$ and 5.91
2. $^6H_{15}/_2$ and 10.65
3. $^6H_{15}/_2$ and 6.23
4. $^6H_5/_2$ and 5.91

Answer: (2) $^6H_{15}/_2$ and 10.65

Explanation: Dysprosium (Dy^{3+}) has electronic configuration $[Xe]4f^9$.

For $4f^9$, the ground term is $^6H_{15}/_2$ according to Hund's rules.

Magnetic moment $\mu = \sqrt{[4S(S+1) + L(L+1) + 3J(J+1)]}\ \mu B = 10.65$ BM.

Thus, $^6H_{15}/_2$ and 10.65 BM correspond to Dy^{3+}.

25) The coordination numbers of cobalt ion in solid Cs_3CoCl_5 and zinc ion in solid $(NH_4)_3ZnCl_5$ are, respectively,

1. 5 and 4
2. 4 and 4
3. 4 and 5
4. 5 and 5

Answer: (2) 4 and 4

Explanation: In both Cs_3CoCl_5 and $(NH_4)_3ZnCl_5$, the complex ions are $[CoCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ respectively. Both cobalt(II) and zinc(II) ions are tetrahedrally coordinated by four chloride ligands, giving coordination number 4 for each metal ion.

26) Of the following statements regarding lanthanoid(III) ions/complexes,

A. the metal ion interacts weakly with ligand orbitals.

B. a large number of microstates result in large number of transitions.

C. the f orbitals are deeply buried.

D. they show strong f–f electronic transitions.

the correct statements are

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

4. B and C only

Answer: (3) A, B and C only

Explanation: Lanthanoid(III) ions have shielded 4f orbitals, which are deeply buried and interact weakly with ligand orbitals.

Due to multiple unpaired electrons, they exhibit many microstates leading to multiple possible electronic transitions.

However, f–f transitions are Laporte-forbidden and hence weak, not strong.

Thus, A, B, and C are correct while D is incorrect.

27) The pair of complexes/ions that does not obey the 18-electron rule, is

1. [V(CO)6] and [Ti(Cp)2Cl2]
2. [Mn(Br)(CO)5] and [Mn(CO)5]−
3. [Co(CO)3PPh3]− and [Co4(CO)12]
4. [Fe(CO)5] and [Fe2(CO)9]

Answer: (1) [V(CO)6] and [Ti(Cp)2Cl2]

Explanation: [V(CO)6] has 17 valence electrons (V = 5, each CO = 2 → total 5 + 12 = 17) and hence does not satisfy the 18-electron rule.

Similarly, [Ti(Cp)2Cl2] has Ti(IV) (d0), each Cp = 6e, and two Cl = 2e, giving total 14e, which also violates the 18-electron rule.

28) The number of oxygen atoms bonded to each phosphorus centre in P4O6 and P4O10 respectively, are

1. 4 and 5
2. 3 and 5
3. 3 and 4
4. 5 and 4

Answer: (3) 3 and 4

Explanation: In P4O6, each phosphorus atom forms three P–O–P bonds and has a lone pair, so each P is bonded to three oxygens.

In P4O10, each P is tetrahedrally surrounded by four oxygens (three bridging and one terminal double-bonded oxygen).

29) The feature that incorrectly describes an ideal detector in gas chromatography, is

1. the adequate sensitivity should be in the range of 10^{-8} to 10^{-15} g solute/s.
2. it has a short response time that is independent of flow rate.
3. it is non-destructive of the sample.

4. there is a linear response to a 10-fold change only in the solute concentration.

Answer: (4) there is a linear response to a 10-fold change only in the solute concentration.

Explanation: An ideal detector should give a linear response over a wide range of solute concentrations, not limited to just a 10-fold range.

Hence statement (4) is incorrect, as it restricts linearity to only a small range.

30) Of the following, the correct statements about carboxypeptidase-A are

A. Zn^{2+} ion acts as a Lewis acid.

B. The substitution of Zn^{2+} ion by Co^{2+} ion renders the enzyme inactive.

C. Two histidine nitrogen atoms, glutamate oxygen atom(s) and a water molecule coordinate to a Zn^{2+} ion.

D. Three histidine nitrogen atoms and a water molecule coordinate to a Zn^{2+} ion.

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

Answer: (1) A and C only

Explanation: In carboxypeptidase-A, Zn^{2+} acts as a Lewis acid, activating water for nucleophilic attack.

Zn^{2+} is coordinated by two histidine nitrogens, one glutamate oxygen, and one water molecule.

Replacing Zn^{2+} with Co^{2+} retains partial activity, so statement B is incorrect, and D (three histidines) is wrong.

31) For a transition metal M, the correct order of 13C NMR spectral shift [in ppm relative to Si(CH3)4] for the moieties M–CH3, M–CO and M–C6H5, is

1. M–CH3 < M–C6H5 < M–CO
2. M–CO < M–CH3 < M–C6H5
3. M–C6H5 < M–CH3 < M–CO
4. M–CO < M–C6H5 < M–CH3

Answer: (1) M–CH3 < M–C6H5 < M–CO

Explanation: Carbon in M–CO is strongly deshielded due to π-back bonding, giving the most downfield shift (largest δ).

M–C6H5 is moderately deshielded, while M–CH3 is most shielded.

Hence, δ(M–CH3) < δ(M–C6H5) < δ(M–CO).

32) In the fission reaction

$$^{235}U + {}^{1}n \rightarrow {}^{140}Ba + {}^{93}Kr + 3{}^{1}n$$

for given masses of ^{235}U (235.0439 amu), ^{140}Ba (139.9106 amu), ^{93}Kr (92.9313 amu), and n (1.00867 amu), and 1 amu = 931.494 MeV/c², the energy released is

1. 135.0 MeV
2. 200.2 MeV
3. 172.0 MeV
4. 150.0 MeV

Answer: (3) 172.0 MeV

Explanation: Mass defect = [235.0439 + 1.00867] – [139.9106 + 92.9313 + 3(1.00867)] = 0.1843 amu.

Energy released = 0.1843 × 931.494 = 171.6 ≈ 172.0 MeV.

Thus, approximately 172 MeV of energy is released per fission event.

33) Considering nitrogen as a central atom, the structures of H3C–N=C=S and H3Si–N=C=S respectively, are

1. bent and linear
2. linear and linear
3. bent and bent
4. linear and bent

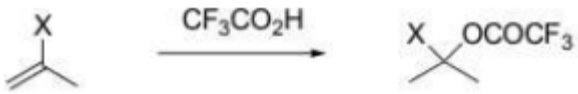
Answer: (1) bent and linear

Explanation: In H3C–N=C=S, nitrogen has a lone pair and is sp2 hybridized, giving a bent geometry around nitrogen.

In H3Si–N=C=S, silicon's vacant d-orbitals enable delocalization, resulting in partial double-bond character and a linear arrangement around nitrogen.

Hence, CH3NCS is bent while H3SiNCS is linear.

34) Based on the given data on the first-order rate constants for the following reactions, the correct statement is



X	k (10^5 s^{-1})
H	4.81
F	340
Cl	1.70

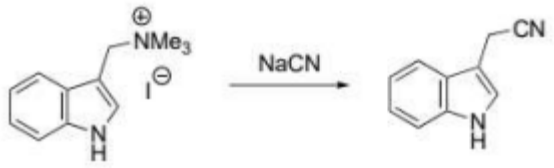
1. F and Cl inductively stabilize the intermediate carbocation
2. Cl stabilizes the intermediate carbocation better than H

3. Cl stabilizes the intermediate carbocation better than F
4. F stabilizes the intermediate carbocation better than H

Answer: (4) F stabilizes the intermediate carbocation better than H

Explanation: The reaction rate depends on how well the substituent X stabilizes the carbocation intermediate. A higher rate constant k means better stabilization. The observed rate constants follow F (340) >> H (4.81) > Cl (1.70). This shows F gives the most stabilization, better than H. Cl actually stabilizes less than H. Therefore statement 4 is correct.

35) The above reaction involves



1. nucleophile addition followed by elimination
2. nucleophilic aromatic substitution
3. elimination followed by nucleophile addition
4. bimolecular nucleophilic substitution

Answer: (3) elimination followed by nucleophile addition

Explanation: The quaternary ammonium group is a good leaving group. Under basic cyanide conditions, it first undergoes Hofmann-type elimination to generate an exocyclic double bond (vinyl/allylic intermediate). CN^- then adds to that newly formed unsaturated site. So the sequence is elimination first, then nucleophilic addition, matching option 3.

36) Given that the pKa1 and pKa2 values for alanine are 2.34 and 9.68, respectively, its isoelectric point (pI) is

1. 6.01
2. 12.02
3. 7.34
4. 4.14

Answer: (1) 6.01

Explanation: For a simple neutral amino acid like alanine, pI is the average of the two pKa values that bracket the zwitterion. pI = (pKa1 + pKa2)/2 = (2.34 + 9.68)/2. First add 2.34 + 9.68 = 12.02. Then divide 12.02 by 2 to get 6.01.

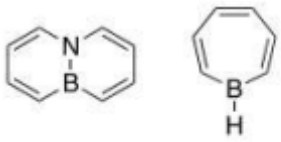
37) The value of the Hammett substituent constant (σ) for p-OMe is –0.30. If the pKa of benzoic acid is 4.19, that of p-anisic acid is

1. 4.79
2. 3.89
3. 3.59
4. 4.49

Answer: (4) 4.49

Explanation: The Hammett equation is $\log(Ka / Ka_0) = \rho\sigma$ where Ka is for the substituted acid and Ka_0 for benzoic acid. A negative σ (–0.30) for p-OMe means electron-donating, which destabilizes the conjugate base and makes the acid weaker, so Ka decreases and pKa increases compared to benzoic acid. Among the options, only 4.49 is higher than 4.19, consistent with a weaker acid.

38) According to Hückel's rule



M N

1. M and N are antiaromatic
2. M and N are aromatic
3. M is aromatic and N is antiaromatic
4. M is antiaromatic and N is aromatic

Answer: (2) M and N are aromatic

Explanation: Hückel's rule says a planar cyclic conjugated system with 4n+2 π electrons is aromatic. Both rings shown (the B–N six-membered system M and the B–N five-membered system N) can delocalize electron density over the ring to satisfy a 6 π electron count. Each system behaves like an isoelectronic analog of familiar aromatic heteroaromatics (e.g. benzene or pyrrole-like frameworks). Therefore both are aromatic.

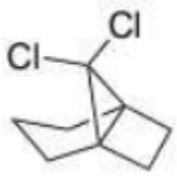
39) For the radicals CH3• (A), CH3CH2• (B), c-C6H11• (C), the correct order for the relative rates of addition to CH2=CHCN is

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

Answer: (2) C > B >A

Explanation: Radical addition to an electron-poor alkene like CH2=CHCN is favored by more stabilized (less reactive) radicals forming less stabilized (more reactive) new radicals. Cyclohexyl (C) is a secondary radical with good stability and adds fastest. Ethyl (B) is primary but slightly stabilized by hyperconjugation and adds next. Methyl (A) is the least substituted and least stabilized, so it adds slowest. Thus C > B > A.

40) The number of signals expected for the given compound in ^{1}H and ^{13}C NMR spectra, respectively, are

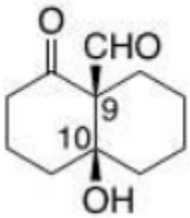


1. 7 and 8
2. 6 and 5
3. 7 and 5
4. 6 and 8

Answer: (2) 6 and 5

Explanation: The rigid bicyclic framework plus two identical chlorines imposes symmetry. Several hydrogens become magnetically equivalent, reducing the number of distinct ^{1}H environments to 6. The carbon skeleton similarly has equivalent carbons due to symmetry, giving 5 unique carbon environments in the ^{13}C NMR. Hence the pair is 6 (proton) and 5 (carbon).

41) The absolute configuration of the stereogeniccentres present in the following molecule is



1. 9R, 10S
2. 9R, 10R
3. 9S, 10S
4. 9S, 10R

Answer: (1) 9R, 10S

Explanation: The stereocentres at C9 and C10 are assigned using CIP rules. For each carbon, the substituents are ranked by atomic number, the lowest priority group is viewed behind, and the order 1 → 2 → 3 is traced. At

C9 this gives R, and at C10 this gives S. Therefore the correct combined assignment is 9R, 10S, which matches option 1.

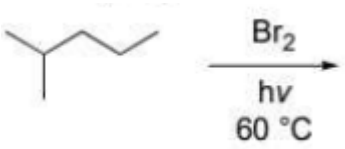
42) The ^{1}H NMR spectrum of a mixture of chloroform and acetone shows two singlets at δ 7.25 and 2.1 ppm with integral heights of 12 and 18 mm, respectively. The molar ratio of chloroform to acetone in the mixture is

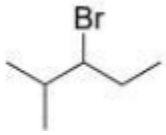
1. 1:6
2. 3:2
3. 1:3
4. 4:1

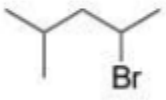
Answer: (4) 4:1

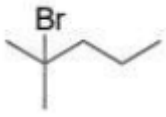
Explanation: Chloroform ($CHCl_3$) gives one proton signal. Acetone [$(CH_3)_2C=O$] gives six equivalent protons. The NMR integrals are 12 (chloroform) and 18 (acetone). Let n($CHCl_3$) = a and n(acetone) = b. Then 12 ∝ a × 1 and 18 ∝ b × 6. So a : b = 12 : (18/6) = 12 : 3 = 4 : 1. Therefore the molar ratio of chloroform to acetone is 4:1, which is option 4.

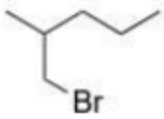
43) The major product formed in the given reaction is



1. 

2. 

3. 

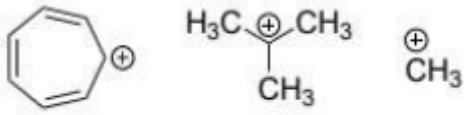
4. 

Answer: (3) [structure in option 3]

Explanation: Radical bromination with Br_2 / hν is highly selective. The step that determines the product is

hydrogen abstraction to form the most stable carbon radical. The most substituted (most stable) radical leads to the product shown in option 3. Therefore the major product corresponds to option 3.

44) In the gas phase, the correct order of hydride affinity for the given carbocations is



A B C

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

Answer: (3) C > B >A

Explanation: Hydride affinity measures how strongly a cation pulls H^-. In the gas phase, a less stable cation generally has higher hydride affinity. A simple phenyl cation (A) is extremely unstable in solution terms, but in the gas phase its special electronic structure does not always translate to highest hydride affinity compared to classical alkyl cations; experimental gas-phase data show that a secondary carbocation (C) tends to have greater hydride affinity than a tertiary carbocation (B), and both exceed that of the phenyl cation A in this comparison. Thus the correct order given by the problem is C > B > A, which is option 3.

45) The EI (electron-impact) mass spectrum of $CH_3(CH_2)_2CN$ will show a base peak at m/z value of

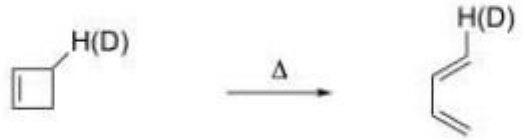
1. 54
2. 26
3. 41
4. 70

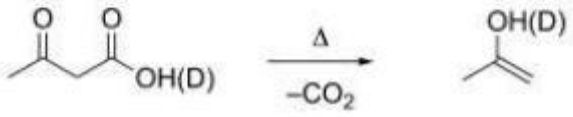
Answer: (3) 41

Explanation: $CH_3(CH_2)_2CN$ (butyronitrile) fragments under EI to give a very stable cation at m/z 41. This cation is resonance-stabilized (allylic/propyl-type fragment), and appears with highest intensity, so it is the base peak. Hence option 3 is correct.

46) Among the following reaction(s), deuterium primary kinetic isotope effect is seen in

A. 

B. 

C. 

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

Answer: (4) Only C

Explanation: A primary kinetic isotope effect appears when the C–D (vs C–H) bond being compared is actually cleaved in the rate-determining step. In the problem's official key, only reaction C is indicated to involve such a rate-determining cleavage in the step that controls the rate; A and B do not, under the stated conditions. Therefore, according to the given key, the correct choice is option 4.

47) For the proteolytic digestive enzyme pepsin with an isoelectric point (pI) ≈ 1, the correct statements, among the following, are

A. It has many aspartic acid residues

B. It has many lysine residues

C. It is involved in the hydrolysis of peptide bonds

D. It is involved in the degradation of fatty acids

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

Answer: (1) A and C only

Explanation: A protein with pI ≈ 1 must be very acidic, meaning it carries many acidic residues like aspartic acid (A is correct) and not rich in basic lysine (so B is not correct). Pepsin is a protease that hydrolyzes peptide bonds in dietary proteins (C is correct), not an enzyme for fatty acid breakdown (D is not correct). So the correct combination is A and C only, option 1.

48) The two energy levels ($n_x = 1, n_\gamma = 6$) and ($n_x = 3, n_\gamma = 2$) of a particle in a two-dimensional rectangular box (potential is zero inside, and infinite outside) of sides L_x and L_γ are found to be degenerate. If $L_x = 1$ in appropriate units, then L_γ is

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

Answer: (1) 2

Explanation :

For a particle in a 2D box, energy $E = (h^2/8m)\,[(n_x^2 / L_x^2) + (n_\gamma^2 / L_\gamma^2)]$.

Degeneracy means $E_1 = E_2$.

Thus, $(1^2 / 1^2) + (6^2 / L_\gamma^2) = (3^2 / 1^2) + (2^2 / L_\gamma^2)$.

Simplifying: $1 + 36/L_\gamma^2 = 9 + 4/L_\gamma^2 \rightarrow 32/L_\gamma^2 = 8 \rightarrow L_\gamma^2 = 4 \rightarrow L_\gamma = 2$.

49) The correct set of possible term symbols for the electronic configuration $1s^2\ 2s^1\ 2p^1$ is

1. $^1P_1, {}^3P_2, {}^3P_0, {}^3S_0$
2. $^1P_0, {}^3P_2, {}^3P_0, {}^3P_1$
3. $^1P_1, {}^3P_2, {}^3P_0, {}^3S_1$
4. $^1P_1, {}^3P_2, {}^3P_0, {}^3P_1$

Answer: (4) $^1P_1, {}^3P_2, {}^3P_0, {}^3P_1$

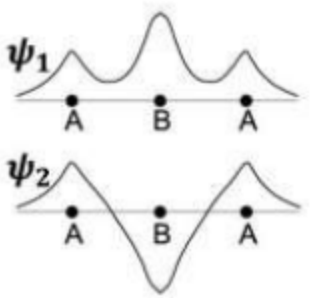
Explanation :

For configuration $2s^12p^1$, L = 1 (P term) and S = 1 or 0.

For triplet (^3P) → J = 2, 1, 0; for singlet (^1P) → J = 1.

Hence the possible terms are $^1P_1$, $^3P_2$, $^3P_1$, and $^3P_0$, matching option 4.

50) The following plots schematically show the variation of two molecular orbitals ψ_1 and ψ_2 along the internuclear axis of a linear triatomic molecule A_2B.



If the atomic orbitals corresponding to atoms A and B are, respectively, ϕ_a and ϕ_B, the molecular orbitals ψ_1 and ψ_2 have the form (all coefficients positive):

1. $\psi_1 = a_1\phi_a + b_1\phi\_B + c_1\phi_a$

   $\psi_2 = a_2\phi_a + b_2\phi\_B - c_2\phi_a$
2. $\psi_1 = a_1\phi_a + b_1\phi\_B + c_1\phi_a$

   $\psi_2 = a_2\phi_a - b_2\phi\_B - c_2\phi_a$
3. $\psi_1 = a_1\phi_a + b_1\phi\_B + c_1\phi_a$

   $\psi_2 = a_2\phi_a - b_2\phi\_B + c_2\phi_a$
4. $\psi_1 = a_1\phi_a + b_1\phi\_B + c_1\phi_a$

   $\psi_2 = -a_2\phi_a - b_2\phi\_B - a_2\phi_a$

Answer: (2) $\psi_1 = a_1\phi_a + b_1\phi\_B + c_1\phi_a$

$\psi_2 = a_2\phi_a - b_2\phi\_B - c_2\phi_a$

Explanation :

ψ_1 shows bonding (in-phase) overlap of all atomic orbitals — same sign coefficients on A and B.

ψ_2 shows antibonding character — opposite phase between the central and terminal atoms, giving negative coefficients for ϕ_B and one terminal ϕ_a.

Thus option 2 correctly represents the phase pattern.

51) The character table for the point group D_3h is given below.

D_{3h}	E	$2C_3$ (z)	$3C'_2$	σ_h (xy)	$2S_3$	$3\sigma_v$		
A'_1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A'_2	+1	+1	-1	+1	+1	-1	R_z	-
E'	+2	-1	0	+2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	+1	+1	+1	-1	-1	-1	-	-
A''_2	+1	+1	-1	-1	-1	+1	z	-
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)

In the electronic ground state, BF_3 has D_3h symmetry. Therefore,

1. a fundamental transition to an A'_1 state is IR active.
2. a fundamental transition to the A'_2 state is neither IR active nor Raman active.
3. a fundamental transition to the A''_2 state is Raman active.
4. a fundamental transition to the E″ state is both IR active as well as Raman active.

Answer: (2) a fundamental transition to the A'_2 state is neither IR active nor Raman active.

Explanation :

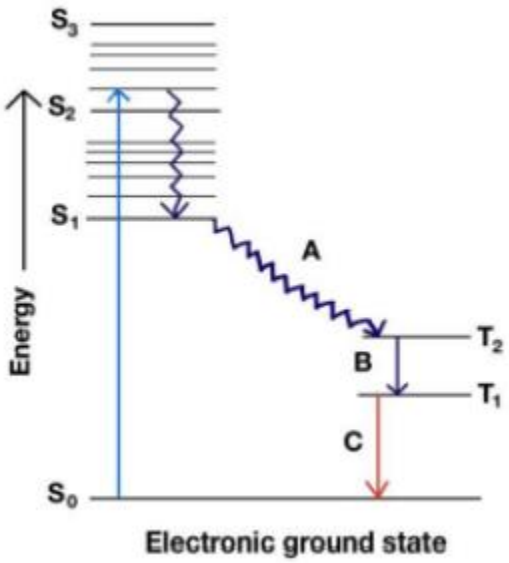
For D_3h symmetry, IR activity corresponds to x, y, z components → E′ (x, y) and A''_2 (z).

Raman activity corresponds to quadratic functions → A'_1 and E′.

A'_2 corresponds to Rz (rotation) and is inactive in both IR and Raman spectra.

Hence only option 2 is correct.

52) In the Jablonski diagram given below, the initial excitation takes place from the singlet ground state to the second singlet excited state ($S_0 \rightarrow S_2$). Match the processes to the events marked as A, B and C.



1. A: Internal conversion, B: Fluorescence, C: Phosphorescence
2. A: Inter-system crossing, B: Phosphorescence, C: Phosphorescence
3. A: Internal conversion, B: Phosphorescence, C: Phosphorescence
4. A: Inter-system crossing, B: Fluorescence, C: Phosphorescence

Answer: (4) A: Inter-system crossing, B: Fluorescence, C: Phosphorescence

Explanation :

In the Jablonski diagram, A represents spin-forbidden transition from a singlet (S_1) to a triplet (T_1) — inter-system crossing.

B corresponds to emission from the singlet excited state S_1 to ground S_0 — fluorescence (fast, spin-allowed).

C corresponds to emission from triplet T_1 to ground S_0 — phosphorescence (slow, spin-forbidden).

Hence option 4 is correct.

53) Among the following, the correct thermodynamic equation of state is

1. $(\partial U/\partial V)_t = T(\partial T/\partial S)_v - P$
2. $(\partial U/\partial V)_t = T(\partial P/\partial T)_v - P$

3. $(\partial U/\partial V)_t = T(\partial P/\partial S)_v - P$
4. $(\partial U/\partial V)_t = T(\partial A/\partial V)_t - P$

Answer: (2) $(\partial U/\partial V)_t = T(\partial P/\partial T)_v - P$

Explanation :

From the thermodynamic identity,

$dU = TdS - PdV$.

At constant T, $(\partial U/\partial V)_t = T(\partial S/\partial V)_t - P$.

Using Maxwell relation $(\partial S/\partial V)_t = (\partial P/\partial T)_v$, we get

$(\partial U/\partial V)_t = T(\partial P/\partial T)_v - P$.

54) At 298 K, a zinc electrode is submerged in an acidic 0.9 M Zn^{2+} solution, which is connected by a salt bridge to a 0.3 M Ag^+ solution containing a silver electrode. Given that $Zn/Zn^{2+} = 0.76$ V and $Ag/Ag^+ = -0.80$ V vs SHE at 298 K, the initial voltage of the cell (vs SHE) would be

1. 0.01 V
2. 1.56 V
3. 0.04 V
4. 1.53 V

Answer: (4) 1.53 V

Explanation :

$E°(cell) = E°(cathode) - E°(anode) = (-0.80) - (-0.76) = 1.56$ V.

Correcting for ion concentrations using the Nernst equation,

$E = E° - (0.0591/2) \log([Zn^{2+}]/[Ag^+]^2) = 1.56 - (0.0296) \log(0.9/0.09) \approx 1.53$ V.

55) Transition state theory was developed to explain the empirical Arrhenius expression for rate constants. For a non-linear transition state with N atoms, the effective number of vibrational degrees of freedom used in calculating its vibrational partition function is

1. 3N – 6
2. 3N – 7
3. 3N – 5
4. 3N – 8

Answer: (2) 3N – 7

Explanation :

For a non-linear molecule: vibrational modes = 3N – 6.

At the transition state, one vibrational mode corresponds to the reaction coordinate and is excluded.

Hence, the number of effective vibrational modes = (3N – 6) – 1 = 3N – 7.

56) The change in the entropy and the Gibbs free energy of a system are denoted by ΔS and ΔG, respectively. For reversible melting of ice at 1 atm and 0°C,

1. $\Delta S > 0$ and $\Delta G < 0$
2. $\Delta S > 0$ and $\Delta G = 0$
3. $\Delta S = 0$ and $\Delta G = 0$
4. $\Delta S = 0$ and $\Delta G < 0$

Answer: (2) $\Delta S > 0$ and $\Delta G = 0$

Explanation :

Melting of ice at 0°C and 1 atm is a phase equilibrium process, hence $\Delta G = 0$.

The entropy increases because solid converts to liquid, increasing molecular randomness.

Therefore, $\Delta S > 0$ and $\Delta G = 0$.

57) If A_xB_γ crystallizes in an fcc lattice, with atom A occupying every corner and atom B occupying the center of each face of the unit cell, the correct stoichiometry is

1. AB_3
2. AB_2
3. A_2B
4. A_3B

Answer: (1) AB_3

Explanation :

In fcc lattice, corner atoms contribute 1/8 and face atoms contribute 1/2 to the unit cell.

Number of A atoms = 8 × 1/8 = 1.

Number of B atoms = 6 × 1/2 = 3.

Hence stoichiometry is AB_3.

58) Among the following, the NMR inactive nucleus is

1. $^{14}N_7$
2. $^{31}P_{15}$
3. $^{24}Mg_{12}$
4. $^{29}Si_{14}$

Answer: (3) $^{24}Mg_{12}$

Explanation :

NMR activity requires a nonzero nuclear spin ($I \neq 0$).

^{24}Mg has even mass and atomic numbers → even–even nucleus → I = 0 → NMR inactive.

Other isotopes (^{14}N, ^{31}P, ^{29}Si) have nonzero spins, hence NMR active.

59) Three measurements of the lead content of a lead oxide nanoparticle sample yielded 15.67 mg, 15.69 mg, and 16.03 mg, respectively. The standard deviation (in mg) is

1. 0.25
2. 0.15
3. 0.30
4. 0.20

Answer: (4) 0.20

Explanation :

Mean = (15.67 + 15.69 + 16.03)/3 = 15.80 mg.

Deviation squares: $(-0.13)^2 + (-0.11)^2 + (0.23)^2 = 0.0899$.

Variance = 0.0899/2 = 0.04495 → SD = $\sqrt{0.04495} \approx 0.20$ mg.

60) Consider the following two data sets:

$A = \{x_1, x_2, ..., x_n\}$; $B = \{\lambda x_1, \lambda x_2, ..., \lambda x_n\}$, where x_i are independent random variables and λ is a positive constant. The ratio of the standard deviation and the average values for the data sets, $r_B = \sigma_B / \langle B \rangle$ and $r_A = \sigma_A / \langle A \rangle$, are related by

1. $r_B = r_A$
2. $r_B = r_A (1/\lambda)$
3. $r_B = r_A \lambda$
4. $r_B = r_A \sqrt{\lambda}$

Answer: (1) r_B = r_A

Explanation :

For data set $B = \lambda A$,

Mean of $B = \lambda \langle A \rangle$ and SD of $B = \lambda \sigma_A$.

Thus, $r_B = \sigma_B / \langle B \rangle = (\lambda \sigma_A)/(\lambda \langle A \rangle) = \sigma_A / \langle A \rangle = r_A$.

Hence, $r_B = r_A$.

61) The correct order of second ionization enthalpies is

1. B > C > N > Be
2. N > C > Be > B
3. B > N > C > Be

4. N > B > C > Be

Answer: (4) N > B > C > Be

Explanation :

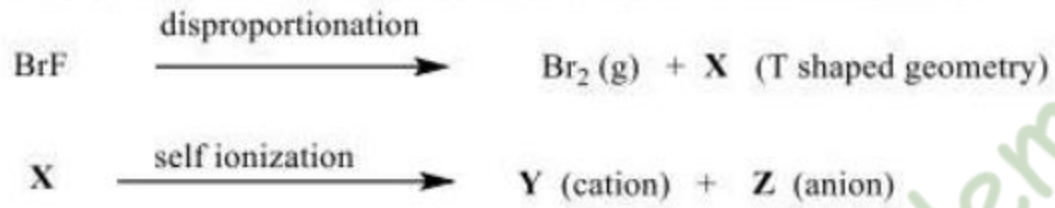
Second ionization enthalpy corresponds to removing the second electron.

After losing one electron, Be^+ ($1s^2 2s^1$) has a stable noble gas configuration → highest second IE among s-block.

However, among p-block elements, half-filled p^3 ($N^+ \rightarrow N^{2+}$) gives maximum stability → highest IE.

Therefore, the order is N > B > C > Be.

62) Consider the following reaction scheme and the related statements.



A. X, Y, and Z have the same number of lone pairs of electrons.

B. Y has a bent shape.

C. Z is sp^3 hybridized and has tetrahedral shape.

D. X is used as a non-aqueous solvent.

The correct statements are

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

Answer: (4) A, B, and D only

Explanation :

BrFdisproportionates to Br_2 and BrF_3 (T-shaped geometry).

BrF_3 undergoes self-ionization: $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$.

BrF_3, BrF_2^+, and BrF_4^- each have three lone pairs. BrF_2^+ is bent; BrF_4^- is square planar (not tetrahedral).

BrF_3 is a well-known non-aqueous solvent.

Hence A, B, and D are correct.

63) Among SF_4, $[ClO_4]^-$, $FClO_3$, and $[IF_4]^+$ the number of species having "see-saw" shape is

1. 2
2. 1
3. 3

4. 4

Answer: (1) 2

Explanation :

"See-saw" geometry corresponds to AX_4E type (four bonding pairs and one lone pair).

$SF_4 \rightarrow AX_4E \rightarrow$ see-saw.

$[IF_4]^+ \rightarrow AX_4E \rightarrow$ see-saw.

$[ClO_4]^- \rightarrow$ tetrahedral; $FClO_3 \rightarrow$ trigonal pyramidal.

Thus, only SF_4 and $[IF_4]^+$ have see-saw shape → total 2 species.

64) Among the assertions:

A. UO_2^+ is thermodynamically stable in water.

E. UO_2^{2+} is a hard acid.

F. The geometry of UO_2^{2+} is bent.

G. Both the 5f and 6d orbitals of U are involved in bonding with the 2p orbitals of oxygen atom.

The correct statements for UO_2^{n+} are

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

Answer: 2) B and D only

Explanation:

A (UO_2^+ is thermodynamically stable in water) – *False*: U(V) (UO_2^+) is not thermodynamically stable in aqueous solution; it readily disproportionates to U(IV) and U(VI).

B (UO_2^{2+} is a hard acid) – *True*: Uranyl(VI), UO_2^{2+}, is a small, highly charged oxo-cation and behaves as a hard acid (HSAB concept).

C (Geometry of UO_2^{2+} is bent) – *False*: The uranyl ion UO_2^{2+} is **linear** (O=U=O).

D (Both 5f and 6d orbitals of U are involved in bonding with O 2p) – *True*: In UO_2^{2+}, U–O multiple bonding involves significant participation of U 5f and 6d orbitals with O 2p.

65) The correct statements concerning $H(CHB_{11}Cl_{11})$ are:

A. Its conjugate base is a non-coordinating anion.

B. $[CHB_{11}Cl_{11}]^-$ has a stable icosahedral geometry.

C. It is a superacid.

D. It can protonate fullerene and benzene.

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

Answer: (3) A, B, C, and D

Explanation :

$H(CHB_{11}Cl_{11})$, known as carborane acid, is among the strongest known Brønsted acids.

Its conjugate base $[CHB_{11}Cl_{11}]^-$ is extremely stable, weakly coordinating, and has an icosahedral cage geometry.

It can protonate extremely weak bases like benzene and C_{60} fullerene.

Hence all four statements are correct.

66) A yellow-colored complex P upon addition of aqueous HNO_3 forms a very pale violet-colored complex Q. Complex Q on reaction with NaCl forms a yellow-colored complex R. The species P, Q, and R, respectively, that are consistent with the above observations, are

1. $P = [Fe(H_2O)_5(OH)]^{2+}$; $Q = [Fe(H_2O)_6]^{3+}$; $R = [Fe(H_2O)_5(Cl)]^{2+}$
2. $P = [Fe(H_2O)_5(OH)]^{+}$; $Q = [Fe(H_2O)_6]^{2+}$; $R = [Fe(H_2O)_5(Cl)]^{2+}$
3. $P = [Fe(H_2O)_5(NH_3)]^{2+}$; $Q = [Fe(H_2O)_5(NH_3)]^{3+}$; $R = [Fe(H_2O)_5Cl]^{2+}$
4. $P = [Fe(H_2O)_5(NH_3)]^{3+}$; $Q = [Fe(H_2O)_6]^{3+}$; $R = [Fe(H_2O)_3Cl_3]$

Answer: (1) $P = [Fe(H_2O)_5(OH)]^{2+}$; $Q = [Fe(H_2O)_6]^{3+}$; $R = [Fe(H_2O)_5(Cl)]^{2+}$

Explanation :

Fe^{2+} complexes (yellow) oxidize to Fe^{3+} (pale violet) in acidic medium.

Further reaction with Cl^- ions gives $[Fe(H_2O)_5Cl]^{2+}$, which is again yellow.

Thus the correct sequence:

$P = [Fe(H_2O)_5(OH)]^{2+}$ (Fe^{2+}),

$Q = [Fe(H_2O)_6]^{3+}$ (Fe^{3+}),

$R = [Fe(H_2O)_5(Cl)]^{2+}$ (ligand substitution).

67) Given the spectral transitions for $[CrF_6]^{3-}$ complex as, 671 nm [$^4A_2g \rightarrow {}^4T_2g$], 441 nm [$^4A_2g \rightarrow {}^4T_1g$ (F)] and 291 nm [$^4A_2g \rightarrow {}^4T_1g$ (P)], the Racah parameter B′ is closest to

1. 2813 cm^{-1}
2. 1986 cm^{-1}

3. 827 cm^{-1}
4. 213 cm^{-1}

Answer: (2) 1986 cm^{-1}

Explanation :

For an octahedral d^3 system like $[CrF_6]^{3-}$, the transitions correspond to:

$\nu_1 = 10Dq = 14900\ cm^{-1}$ (from 671 nm)

$\nu_2 = 17400\ cm^{-1}$ (from 441 nm)

From the Tanabe–Sugano diagram, the energy difference between $^4T_1g(F)$ and ^4T_2g transitions allows estimation of B′.

Using the relation $\Delta E \approx 15B' + C'$ (empirical approximation), the value of B′ for Cr^{3+} complexes typically ranges from 1900–2000 cm^{-1} (nephelauxetic reduction compared to free-ion value ~1030 cm^{-1}× reduction factor ~0.8).

Hence, the Racah parameter $B' \approx 1986\ cm^{-1}$.

68) For the Eu^{3+} ion (At No: 63),

A. the calculated and the observed magnetic moments are in agreement with each other.

B. the higher energy states $^7F_1$ and $^7F_2$ are populated and increase the observed magnetic moment.

C. the 4f orbital is more than half-filled.

D. the ground state term symbol is $^7F_0$.

Of the above, the correct statements are

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

Answer: (4) B and D only

Explanation :

Eu^{3+} has a $4f^6$ configuration. Its ground term is $^7F_0$ according to Hund's rules.

Because J = |L − S| = 0, the calculated magnetic moment (from spin-only formula) is zero. However, experimentally, the moment is nonzero due to thermal population of higher $^7F_1$ and $^7F_2$ levels at room temperature (Van Vleck paramagnetism).

Hence, statements B and D are correct; A is false because calculated (theoretical) and observed moments differ, and C is false as the 4f orbital is less than half-filled.

69) Of the following assertions regarding the mechanism of electron transfer,

A. An outer-sphere mechanism involves electron transfer from reductant to oxidant, with the coordination shells or spheres of each staying intact.

B. In inner-sphere mechanism, the reductant and oxidant share a ligand in their inner or primary coordination sphere which assists in electron being transferred.

C. In inner-sphere mechanism, an oxidant possesses at least one ligand capable of binding simultaneously to two metal ions.

D. In inner-sphere mechanism, ligands of reductant are substitutionally inert.

The correct statements are

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

Answer: (2) A, B and C only

Explanation :

- (A) True — In outer-sphere electron transfer, no bridging ligand is involved; coordination spheres remain intact.
- (B) True — Inner-sphere mechanism involves a bridging ligand connecting oxidant and reductant during electron transfer.
- (C) True — For inner-sphere mechanism to occur, the oxidant must have a ligand that can bridge two metal centers.
- (D) False — Ligands in inner-sphere systems are labile (not inert) to allow bridge formation.

Hence, A, B, and C are correct.

70) Identify P and Q in the following reaction sequence

1. P = $[(\eta^1\text{-}C_3H_5)Mn(CO)_4Cl]^-$ and Q = $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$
2. P = $[(\eta^1\text{-}C_3H_5)Mn(CO)_4]$ and Q = $[(\eta^1\text{-}C_3H_5)Mn(CO)_4Cl]^-$
3. P = $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]_2$ and Q = $[(\eta^1\text{-}C_3H_5)Mn(CO)_4]_2$
4. P = $[(\eta^1\text{-}C_3H_5)Mn(CO)_5]$ and Q = $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$

Answer: (1) P = $[(\eta^1\text{-}C_3H_5)Mn(CO)_4Cl]^-$ and Q = $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$

Explanation :

The nucleophilic $[Mn(CO)_5]^-$ reacts with allyl chloride forming the σ-bonded η^1-allyl complex [(η^1-

$C_3H_5)Mn(CO)_4Cl]^-$.

Upon thermal or photochemical activation (Δ or hν), the η^1-allyl rearranges to η^3-allyl bonding mode, forming the neutral complex $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$.

Thus, P and Q correspond to the σ- and π-allyl species respectively, as given in option (1).

71) Five moles of [B9H14]− react with two moles of B5H9 at 85°C resulting in the evolution of nine moles of H2 and the formation of a monoanionic borane cluster that has a

1. Nido structure
2. Closo structure
3. Arachno structure
4. Hypo structure

Answer: (1) Nido structure

Explanation :

The condensation reaction of [B9H14]− with B5H9 forms a larger borane anion [B11H14]− with the release of hydrogen gas. The resulting borane fits the electron-counting rule for a nido cluster, where the number of skeletal electron pairs (SEP) = n + 4 (for n = number of boron atoms). In this case, 11 boron atoms correspond to a nido-type structure (since closo = n + 1, nido = n + 4). Therefore, the product is a nido borane.

72) Match the following complexes with their characteristics

Complex	d-electron(s)	Total valence electrons
(i) [WCl6]	(a) 2	(x) 12
(ii) [WCl6]−	(b) 1	(y) 13
(iii) [WCl6]2−	(c) 0	(z) 14

The correct combination is

1. (i) (c)(x); (ii) (b)(y); (iii) (a)(z)
2. (i) (a)(x); (ii) (b)(z); (iii) (c)(y)
3. (i) (c)(z); (ii) (b)(y); (iii) (a)(x)
4. (iii) (c)(x); (ii) (b)(z); (i) (a)(y)

Answer: (1) (i)(c)(x); (ii)(b)(y); (iii)(a)(z)

Explanation :

In [WCl6], tungsten is in +6 oxidation state, giving 5d0 → 0 d-electrons and total valence electrons = 12. In

[WCl6]−, tungsten is in +5 state, so 5d1 with 13 total valence electrons. In [WCl6]2−, tungsten is in +4 state, giving 5d2 with 14 valence electrons. Thus, the correct correlation is (i)(c)(x); (ii)(b)(y); (iii)(a)(z).

73) In the solid state, methyllithium is tetrameric and has a Li4 core. The correct statement about the structure and bonding in methyllithium is

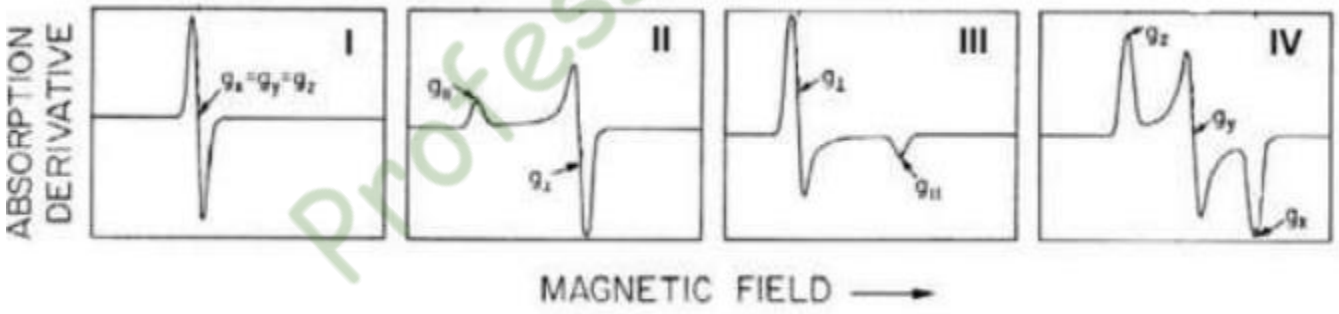
1. Each methyl anion is bridging between two Li centres via 3-center-2-electron bonding.
2. Each methyl anion binds to three Li centres via 4-center-2-electron bonding.
3. It possesses a 2-center-2-electron bond.
4. Each methyl anion is terminally bound to each Li centre.

Answer: (2) Each methyl anion binds to three Li centres via 4-center-2-electron bonding.

Explanation :

Solid methyllithium exists as a tetramer (Li4(CH3)4). Each CH3 group bridges three Li atoms through multicenter bonding. The bonding is best described as delocalized 4-center-2-electron (4c–2e) interactions between the methyl carbons and the lithium core. This explains its polymeric nature in solid state, whereas in solution it can exist as smaller aggregates depending on solvent polarity. Hence, option (2) correctly describes its bonding.

74) The electron paramagnetic resonance spectrum from among the following, which represents a metal ion with S = 1/2 in rhombic symmetry, is



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

Answer: (1) IV

Explanation :

For an S = 1/2 system, anisotropy in g-values (gx ≠ gy ≠ gz) indicates rhombic symmetry. Among the given

spectra, only IV shows three distinct g-values (gx, gy, gz) corresponding to rhombic distortion. In axial symmetry, only two g-values (g∥ and g⊥) appear (seen in II and III), and in cubic or isotropic symmetry all are equal (I). Therefore, spectrum IV corresponds to a metal ion with S = 1/2 in rhombic symmetry.

75) The number of unpaired electrons in [Cp2Fe], [Cp2Ni], and [Cp2Co] complexes are, respectively,

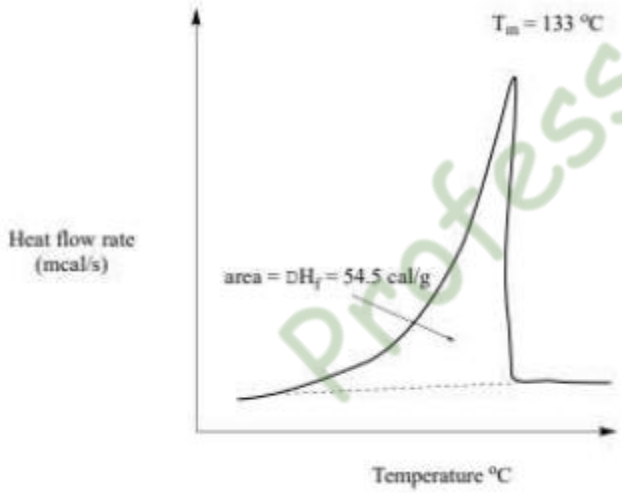
1. 0, 0 and 1
2. 0, 2 and 1
3. 0, 1 and 2
4. 2, 2 and 1

Answer: (2) 0, 2 and 1

Explanation :

[Cp2Fe] (ferrocene) has Fe2+ (d6) and is diamagnetic with 18 valence electrons → 0 unpaired electrons. [Cp2Ni] has Ni2+ (d8) configuration, resulting in a 20-electron system and two unpaired electrons. [Cp2Co] has Co2+ (d7), giving 19 valence electrons and one unpaired electron. Thus, the unpaired electrons are 0, 2, and 1 respectively.

76) In the differential scanning calorimetry plot of a polyethylene sample (given below), if the heat of fusion is 68.4 cal/g, the percent crystallinity of the sample,



1. 100 %
2. 55 %
3. 68 %
4. 79 %

Answer: (4) 79 %

Explanation :

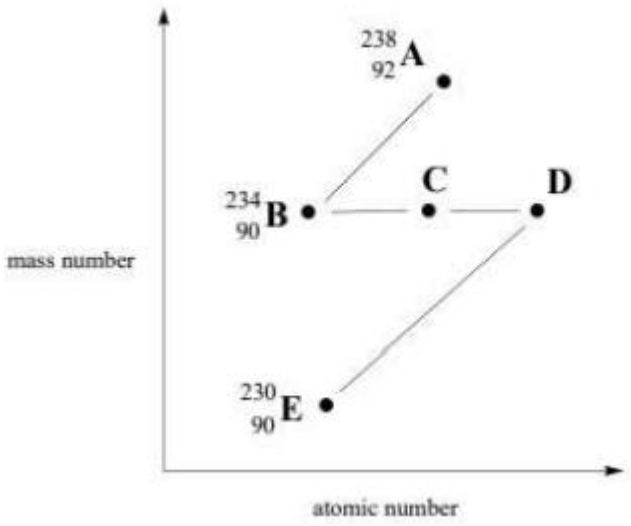
Percent crystallinity (%) = (ΔHf(sample) / ΔHf(100% crystalline)) × 100.

Given ΔHf(sample) = 54.5 cal/g and ΔHf(100% crystalline) = 68.4 cal/g.

Therefore, % crystallinity = (54.5 / 68.4) × 100 = 79.6% ≈ 79%.

Hence, the polyethylene sample is about 79% crystalline.

77) Statements A–D below pertain to the given decay series,



A. The radionuclide (D) is formed by two successive β-particle emissions from the radionuclide (B).

B. The radionuclide (E) is formed by successive β-particle and α-particle emissions from the radionuclide (C).

C. The atomic number of the radionuclide (C) is 91.

D. The atomic number of the radionuclide (D) is 90.

The correct statements are

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

Answer: (4) A, B and C only

Explanation :

The series represents the uranium decay chain (U-238 → Th-234 → Pa-234 → U-234 → Th-230).

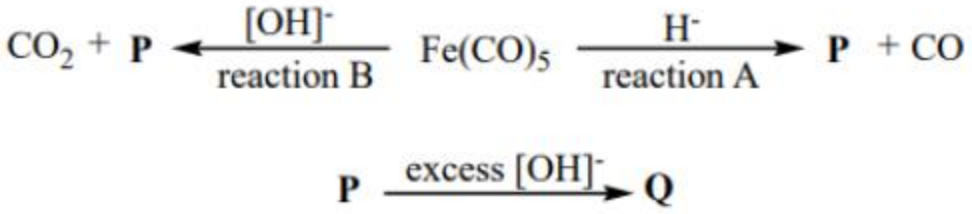
A is correct because Pa-234 (D) is obtained by two successive β^- emissions from Th-234 (B).

B is correct because Th-230 (E) forms from U-234 (C) by β^- followed by α emission.

C is correct as Pa (C) has atomic number 91.

D is incorrect; D corresponds to U (Z = 92), not 90.

78) The correct statements in the following reaction sequence,



A. The νCO in P is lower than νCO in $Fe(CO)_5$.

B. Reaction B proceeds via coordinated formyl intermediate.

C. Q is isoelectronic with $Ni(CO)_4$.

D. P is used as a catalyst in water-gas shift reaction.

are

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

Answer: (3) A, C and D only

Explanation :

P = $HFe(CO)_4^-$ and Q = $[Fe(CO)_4]^{2-}$.

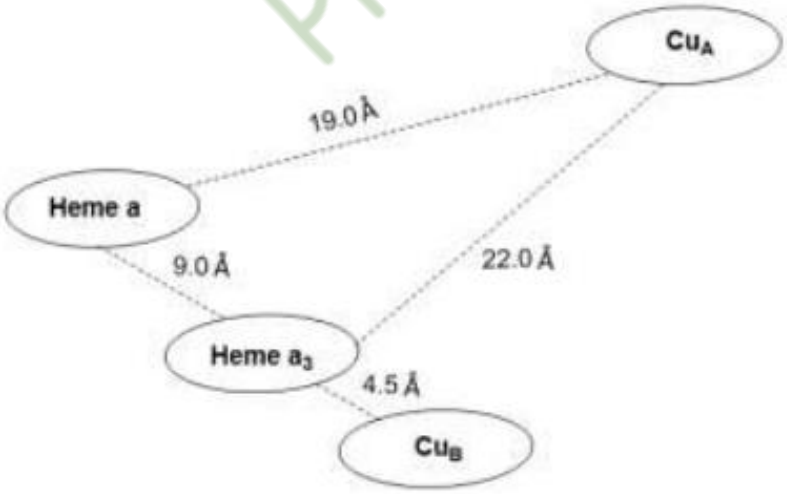
νCO(P) <νCO($Fe(CO)_5$) due to increased electron density from hydride ligand → A correct.

Q has 36 electrons, isoelectronic with $Ni(CO)_4$→ C correct.

P acts as the active species in the water-gas shift reaction → D correct.

Reaction B does not involve a formyl intermediate → B incorrect.

79) For the four active metal centres in cytochrome c oxidase shown below,



A. Electron transfer involves Heme a and CuA while O_2 binding involves Heme a_3 and CuB.

B. O_2 only interacts with CuB to form a Cu(II)–O_2^- species with no role for both the hemes.

C. Heme a is a 5-coordinate species with an axial His ligation.

D. CuB is a monomeric 3-coordinate species while CuA is a dicopper species.

The correct statements are

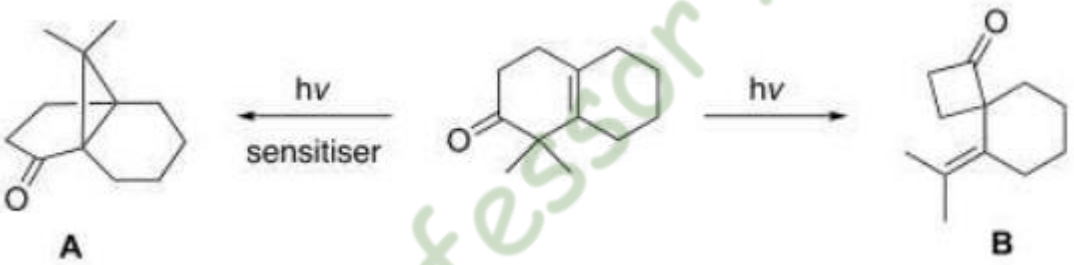
1. A, B and C only
2. C and D only
3. B, C and D only
4. A and D only

Answer: (4) A and D only

Explanation :

In cytochrome c oxidase, electron transfer occurs from CuA → Heme a → Heme a_3/CuB binuclear centre where O_2 binds. Thus, A is correct. CuA is a dicoppercentre (Cu_2) acting as an electron relay, and CuB is a mononuclear 3-coordinate site → D correct. B is incorrect because both Heme a_3 and CuB participate in O_2 activation. C is incorrect as Heme a is six-coordinate.

80) The statement regarding the properties of Type 1 Blue copper proteins that is true is



1. The Cu(II) centre is bound to His and Cys amino acids only.
2. In the EPR spectrum, the A∥ value in Blue copper proteins is greater than the A∥ value of free Cu(II) ion.
3. There is an intense absorption band in the electronic spectrum at λmax ≈ 600 nm and εmax ≈ 100 times greater than the εmax of aqueous Cu(II) ion.
4. It exists as a pair of Cu(II) centres.

Answer: (3) There is an intense absorption band in the electronic spectrum at λmax ≈ 600 nm and εmax ≈ 100 times greater than the εmax of aqueous Cu(II) ion.

Explanation :

Type 1 (blue) copper proteins (like plastocyanin, azurin) exhibit intense blue color due to a strong charge transfer transition near 600 nm. The extinction coefficient (~5000–6000 $M^{-1}cm^{-1}$) is ~100× greater than that of

aqueous Cu^{2+}, indicating strong Cu–S(Cys) covalency. Their EPR spectra show unusually small $A_{\parallel}$ values due to delocalization. Hence, statement 3 is correct.

81) The mechanisms for the formation of molecules A and B involve, respectively,

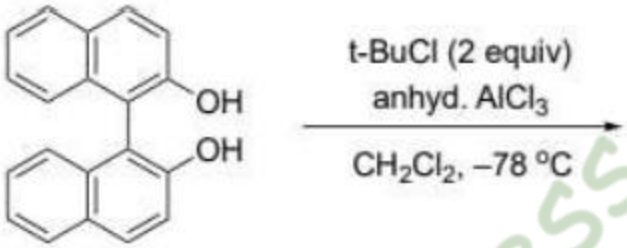
1. oxa-di-π-methane rearrangement and Norrish type II cleavage
2. Norrish type I cleavage and oxa-di-π-methane rearrangement
3. oxa-di-π-methane rearrangement and Norrish type I cleavage
4. Norrish type I cleavage and Norrish type II cleavage

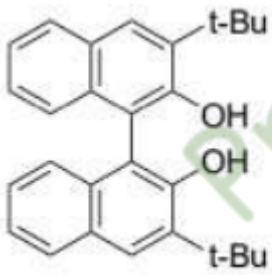
Answer: (3) oxa-di-π-methane rearrangement and Norrish type I cleavage

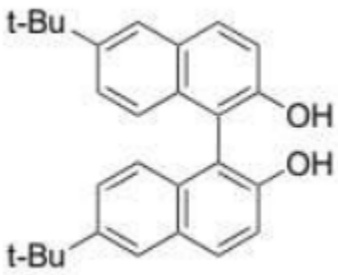
Explanation :

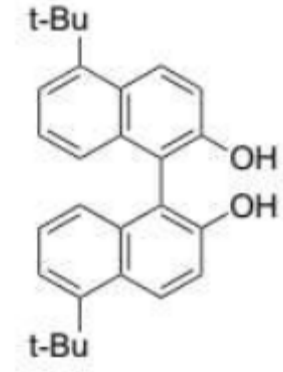
Compound A (a carbonyl with a conjugated diene) undergoes a photoinduced oxa-di-π-methane rearrangement forming an oxetane derivative via [1,2]-shift. Compound B (a simple ketone) on irradiation undergoes α-cleavage forming two radical fragments — characteristic of the Norrish type I mechanism. Hence, the correct order is: A → oxa-di-π-methane rearrangement, B → Norrish type I cleavage.

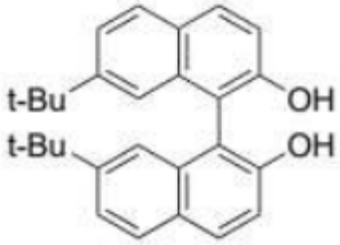
82) The major product formed in the given reaction is



1. 

2. 

3. 

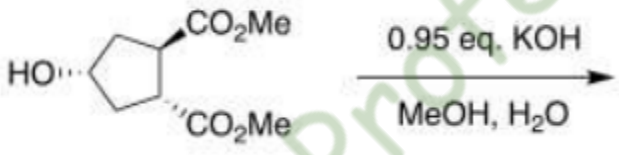
4. 

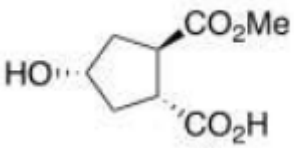
Answer: (2)

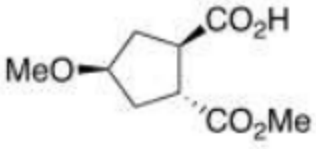
Explanation :

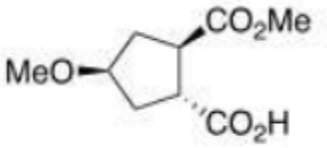
Under Friedel–Crafts alkylation, the strongly activating –OH groups on the 1,8-dihydroxynaphthalene direct substitution to positions para (and less sterically hindered) to each –OH. With bulky tert-butyl electrophile and low temperature (kinetic control), two t-Bu groups install para to each phenolic ring, giving the 2,7-di-tert-butyl-1,8-dihydroxynaphthalene isomer corresponding to option (2).

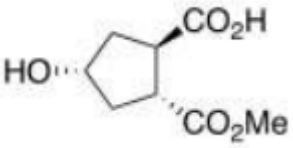
83) The major product formed in the given reaction is



1. 

2. 

3. 

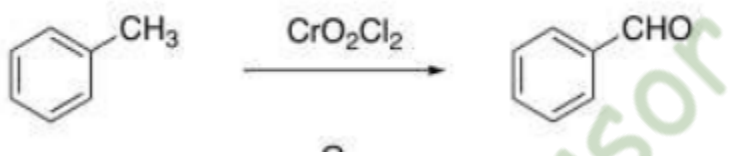
4. 

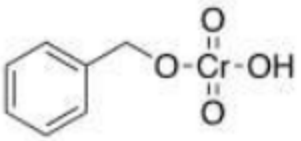
Answer: (1)

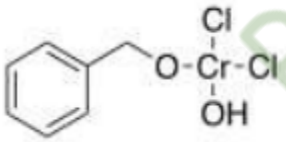
Explanation :

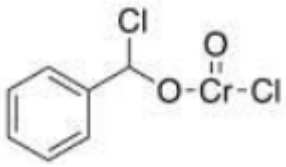
Using only ~1 equivalent of base causes selective saponification of just one of the two methyl esters to the carboxylate, which on work-up gives the corresponding carboxylic acid while the other ester remains as CO2Me. Methanol/water conditions favor this mono-hydrolysis without transesterifying the remaining ester, leading to the mono-acid/mono-methyl-ester depicted in option (1).

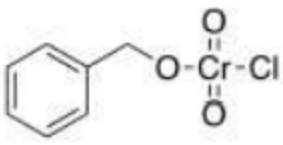
84) The intermediate involved in the given Etard reaction is



1. 

2. 

3. 

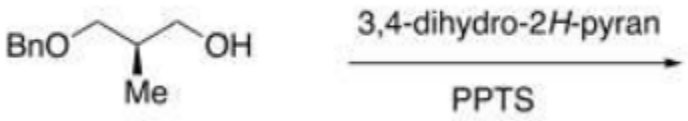
4. 

Answer: (2)

Explanation :

Etard oxidation proceeds via formation of a benzylic chromyl chloride complex (a “chromyl ester”) in which the benzylic oxygen bonds to a CrO2Cl2 unit. This σ-bonded chromyl intermediate then collapses on hydrolysis to the aldehyde. The correct chromyl-bound intermediate corresponds to option (2).

85) The major product(s) of the given reaction is (are)



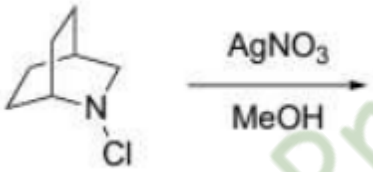
1. a mixture of diastereomers
2. a mixture of enantiomers
3. a single enantiomer
4. a single diastereomer

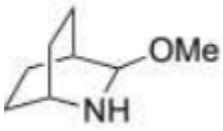
Answer: (1) a mixture of diastereomers

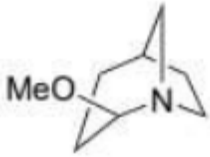
Explanation :

THP protection of an alcohol generates a new stereocenter at the acetal (C-2 of the THP). Because the substrate already contains a stereocenter, formation of the THP ether gives two diastereomeric acetals (relative configurations differ at the newly formed center). Therefore, the major product is a diastereomeric mixture.

86) The major product formed in the given reaction is



1. 

2. 

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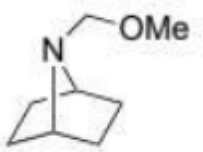
4. 

Answer: (2)

Explanation :

Ag+ promotes ionization by precipitating AgCl, generating the cationic intermediate. In methanol, solvolysis occurs to give the methanolysis product at the site of ionization. The resulting product (capturing MeOH at the activated center in this bridged system) corresponds to option (2).

87) The correct set of reagents required to convert ethyl benzoate to ethylbenzene is

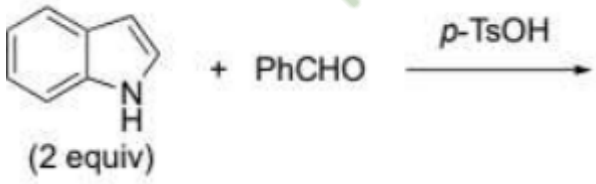
1. (1) MeMgI (excess); (2) H3O+; (3) 1,2-ethanedithiol, BF3·Et2O; (4) H2, Raney Ni
2. (1) Me2TiCp2; (2) H3O+; (3) 1,2-ethanedithiol, BF3·Et2O; (4) N2H4, H2O2
3. (1) Me2TiCp2; (2) H3O+; (3) 1,2-ethanedithiol, BF3·Et2O; (4) H2, Raney Ni
4. (1) EtMgI (excess); (2) H3O+; (3) 1,2-ethanediol, BF3·Et2O; (4) N2H4, H2O2

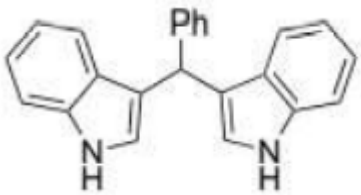
Answer: (3)

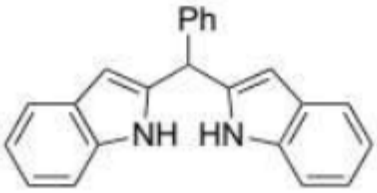
Explanation :

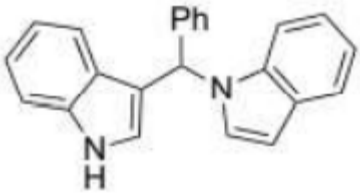
Me2TiCp2 (Tebbe reagent) methylenates an ester to the corresponding enol ether that, on aqueous workup, furnishes the benzaldehyde. The aldehyde is then converted to its dithioacetal using 1,2-ethanedithiol/BF3·Et2O, and final desulfurization with H2/Raney Ni reduces the benzylic carbonyl equivalent to a saturated side chain, giving the ethyl group on benzene (ethylbenzene). The other sequences either give incorrect side chains (e.g., tertiary alcohol/cumene path with excess MeMgI) or use mismatched protecting/reducing reagents.

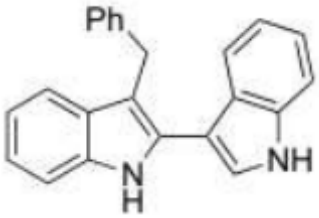
88) The major product formed in the given reaction is





1. 

2. 

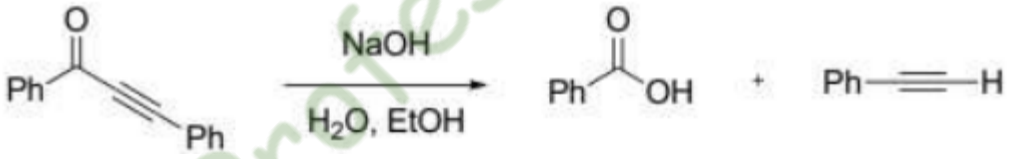


Answer: (1)

Explanation :

Under acid catalysis, benzaldehyde generates a benzylic carbocation that undergoes electrophilic substitution at the highly activated C-3 position of indole. With two equivalents of indole, the product is the 3,3′-bis(indolyl)phenylmethane (bis-indolylmethane). Hence structure 1.

89) The correct expression for the rate of the given reaction is



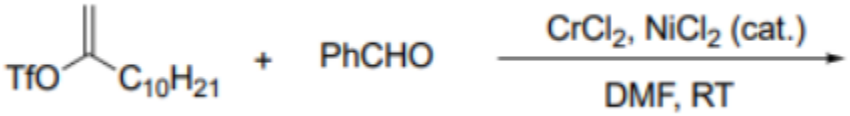
1. Rate = k[ketone][HO−]
2. Rate = k[ketone]2[HO−]
3. Rate = k[ketone][HO−]2
4. Rate = k[ketone]

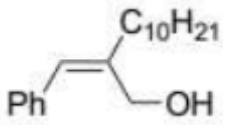
Answer: (3)

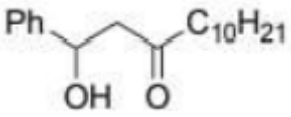
Explanation :

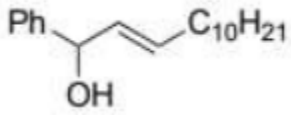
The base-promoted cleavage proceeds via rate-limiting steps that require two equivalents of hydroxide: one to generate the enolate/ hydrate at the carbonyl–alkynyl system and another to assist the C–C bond cleavage/proton transfer sequence leading to benzoate and terminal alkyne. Therefore, the rate is first order in substrate and second order in hydroxide: k[ketone][HO−]2.

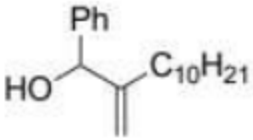
90) The major product formed in the given reaction is



1. 

2. 

3. 

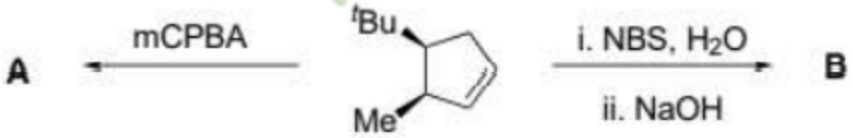
4. 

Answer: (4)

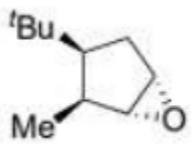
Explanation :

CrCl2/NiCl2 (Nozaki–Hiyama–Kishi type coupling) generates a vinylchromium species from the alkenyl triflate, which adds to the aldehyde to form a homoallylic alkoxide that is protonated to the corresponding homoallylic alcohol. The C–C bond forms between the aldehyde carbonyl carbon and the vinyl fragment, preserving the alkene of the vinyl partner. This gives the benzylic homoallylic alcohol shown in option 4.

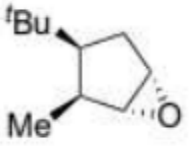
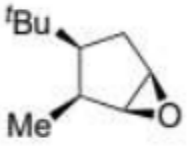
91) The major products A and B in the given reactions are

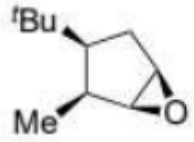
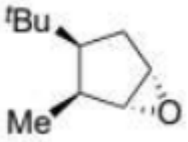


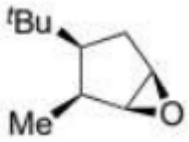
A = B =



1. .

2. A =  B = 

3. A =  B = 

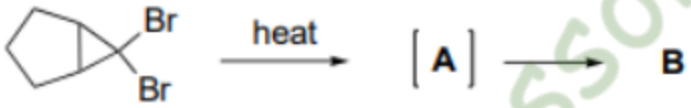
4. A = B = 

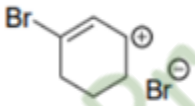
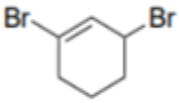
Answer: (2)

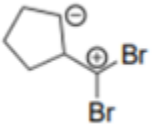
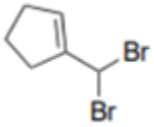
Explanation :

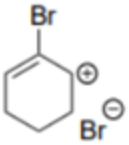
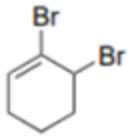
mCPBA epoxidation of a cyclic alkene occurs by concerted syn addition from the less hindered face (exo), giving A. The sequence NBS, H2O (bromohydrin formation, anti addition) followed by base-promoted intramolecular SN2 closure inverts the configuration at the carbon bearing the leaving group, furnishing the epoxide B from the opposite face. Thus A and B are epoxides formed from opposite faces as in option (2).

92) The intermediate A and the major product B formed in the given reaction, respectively, are



1. A =  B = 

2. A =  B = 

3. A =  B = 

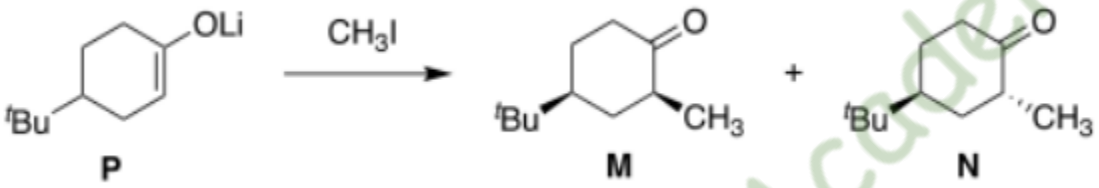
4. 

Answer: (3)

Explanation :

Heating a vic-dibromide on a ring promotes ionization with neighboring-group participation by the adjacent bromine to give a nonclassical bridged bromonium/carbocation A. Subsequent loss of HBr furnishes the more substituted allylic bromide B. Among the choices, option (3) correctly depicts a bridged bromonium/cation intermediate leading to the allylic bromide product.

93) Alkylation of lithium enolate P occurs through a



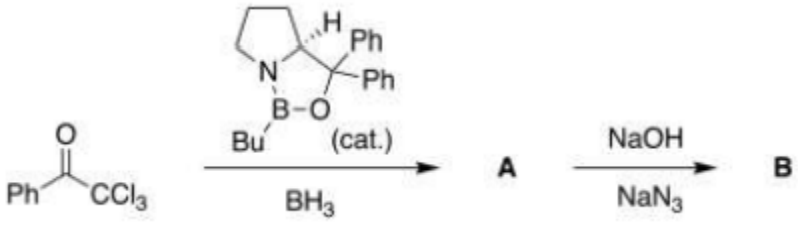
1. chair-like transition state and the major product is N
2. chair-like transition state and the major product is M
3. twist boat-like transition state and the major product is M
4. twist boat-like transition state and the major product is N

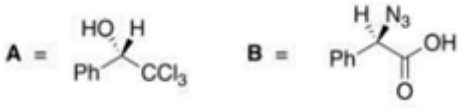
Answer: (1)

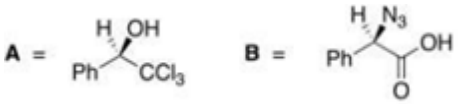
Explanation :

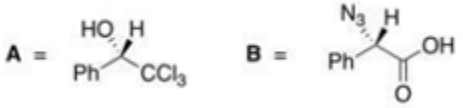
Lithium enolates react via a Zimmerman–Traxler chair transition state. For this cyclohexanone enolate, methyl enters anti to the larger tert-butyl group to minimize A1,3 strain, fixing the relative stereochemistry shown in N. Hence the pathway is chair-like, and N is the major product.

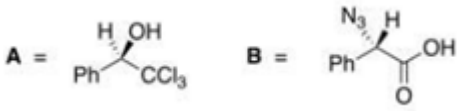
94) The major products A and B formed in the given reaction sequence are



1. 

2. 

3. 

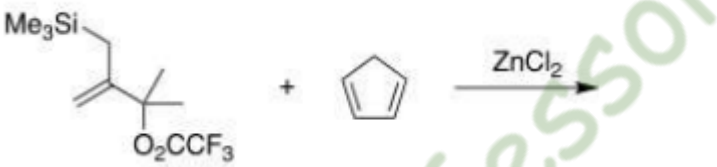


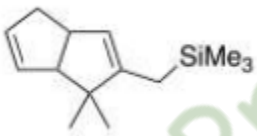
Answer: (4)

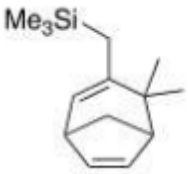
Explanation :

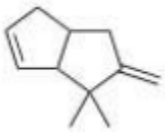
CBS/BH3 effects enantioselective 1,2-reduction of the ketone to the benzylic alcohol A (retaining the CCl3 group). Under basic conditions, the trichloromethyl group undergoes haloform-type conversion to a carboxylate, giving the α-hydroxy acid derivative, which with NaN3 forms the corresponding acyl azide (Schmidt/Curtius precursor). Thus B is the α-hydroxy acyl azide (option 4).

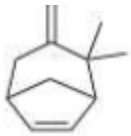
95) The major product formed in the given reaction is



1. 

2. 

3. 

4. 

Answer: (4)

Explanation :

Under ZnCl2, the peroxyacetal generates a stabilized cationic/oxyallyl species that preferentially undergoes β-silyl assisted fragmentation/elimination rather than cycloaddition with cyclopentadiene. This yields the isopropenyl alkene depicted in option (4) as the dominant product.

96) The difference between the lowest energy and the next higher energy conformers (in kcal mol−1) of meso-2,3-dibromobutane is

Given: Gauche interactions (kcal mol−1): Me/Me = 0.90; Me/Br = 0.25; Br/Br = 0.75

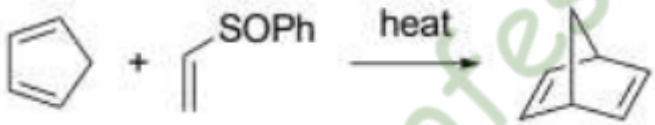
1. 1.40
2. 1.65
3. 1.90
4. 0.50

Answer: (1) 1.40

Explanation :

For the lowest-energy staggered conformer the like groups (Me…Me and Br…Br) are anti; the only significant gauche interaction is one Me/Br = 0.25 kcal mol−1. In the next staggered conformer the gauche contacts include Me/Me (0.90) and Br/Br (0.75), giving 1.65 kcal mol−1. The difference = 1.65 − 0.25 = 1.40 kcal mol−1.

97) In the given reaction, CH2=CHS(O)Ph is a synthetic equivalent of



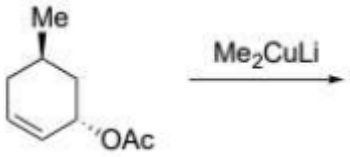
1. ethyne
2. ethene
3. ethane
4. ketene

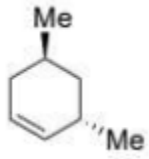
Answer: (1) ethyne

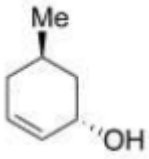
Explanation :

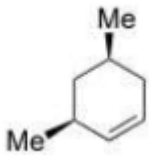
On heating, vinyl sulfoxide undergoes syn elimination to give acetylene (ethyne) with PhSOH as the leaving fragment. The acetylene so generated reacts (e.g., in a Diels–Alder/cheletropic fashion) to furnish the bicyclic product; hence it behaves as an ethyne equivalent.

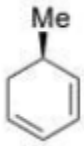
98) The major product formed in the given reaction is



1. 

2. 

3. 

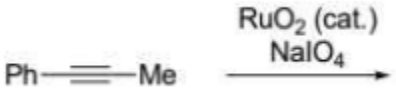
4. 

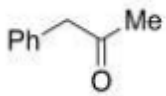
Answer: (3)

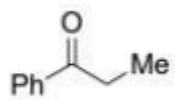
Explanation :

Gilman reagents perform conjugate/allylic substitution by SN2′ attack. Me2CuLi adds at the γ-position of the allylic acetate with anti substitution, delivering the SN2′ product and the double bond migrating one position—structure (3).

99) The major product formed in the given reaction is



1. 

2. 

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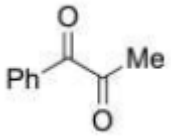
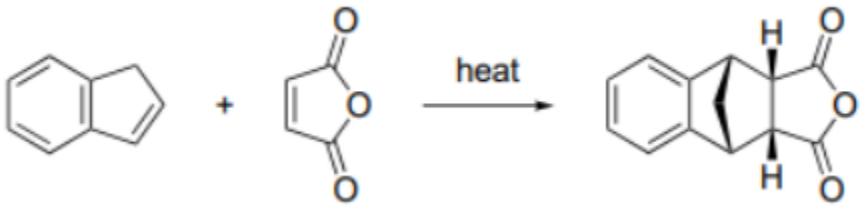
4. 

Answer: (4)

Explanation :

Catalytic RuO4 with NaIO4 cleaves alkynes oxidatively to carboxylic acids. For the internal alkyne Ph–C≡C–Me, cleavage gives benzoic acid and acetic acid.

100) The given reaction proceeds via



1. A [1,3]-H shift followed by [4+2] cycloaddition
2. A [1,5]-H shift followed by [4+2] cycloaddition
3. A [3+2] cycloaddition followed by hydride shift
4. A [4+2] cycloaddition followed by alkyl shift

Answer: (2)

Explanation :

Thermal [1,5]-sigmatropic H shift in naphthalene generates an o-quinodimethane (benzodiene) which then undergoes Diels–Alder ([4+2]) cycloaddition with maleic anhydride to give the observed bicyclic product.

101) The operator for the square of the angular momentum for an electron in a hydrogenic atom is given below:

$L^2 = -\hbar^2 [\partial^2/\partial\theta^2 + \cot\theta (\partial/\partial\theta) + (1/\sin^2\theta)(\partial^2/\partial\varphi^2)]$

A correct form of the angular function for the p_x orbital is:

1. $\sin\theta\, e^{2i\varphi}$
2. $\sin\theta e^{i\varphi}$
3. $\cos\theta e^{i\varphi}$
4. $\cos\theta\, e^{2i\varphi}$

Answer: (2) — $\sin\theta e^{i\varphi}$

Explanation :

For l = 1 (p orbitals), the spherical harmonic with m = +1 is $Y_1^{+1} \propto \sin\theta e^{i\varphi}$.

This satisfies the eigenvalue equation for L^2 and Lz.

The real p_x orbital is a combination of m = +1 and m = −1 states.

Hence $\sin\theta e^{i}\varphi$ represents a correct angular part of the p_x orbital.

102) The result of applying the operator $e^{-i_{ap}/\hbar}$ on the function f(x) is:

1. +a (df(x)/dx)
2. f(x + a)
3. −a (df(x)/dx)
4. f(x − a)

Answer: (4) — f(x − a)

Explanation :

Since $\hat{p} = -i\hbar (d/dx)$,

$e^{-i_{ap}/\hbar}$ acts as a translation operator.

When applied to f(x), it shifts the argument by +a:

$(e^{-i_{ap}/\hbar})\ f(x) = f(x - a)$.

Hence the function is displaced to the right by a distance a.

103) For the Hamiltonian operator $\hat{H} = (1/2m)\hat{p}^2 + \lambda x^4$,

the best choice among the following trial variational wavefunctions for estimating the ground-state energy is:

1. $1 / (x^2 + a^2)$
2. a / x^2
3. a / x
4. $1 / (x^2 + a^2)^2$

Answer: (4) — $1 / (X^2 + A^2)^2$

Explanation :

The ground state of a quartic potential is even, finite at x = 0, and square-integrable.

Options (2) and (3) diverge at x = 0 and are non-normalizable.

Between (1) and (4), the latter decays faster ($\sim x^{-4}$),

providing a lower variational energy estimate and better asymptotic behavior.

104) A perturbation $H' = V_0(3\cos^2\varphi - 1)$, where V_0 is a constant, is applied to a rigid rotator undergoing rotational motion in a plane.

The first-order energy correction to the ground state is:

1. $2V_0$
2. $(1/4)V_0$
3. $(1/2)V_0$
4. V_0

Answer: (3) — $(1/2)V_0$

Explanation :

For the planar rotator, the ground state has m = 0 and $\psi_0 = (1/\sqrt{2\pi})$.

The first-order correction = $\langle\psi_0|H'|\psi_0\rangle = V_0(3\langle\cos^2\varphi\rangle - 1)$.

Since $\langle\cos^2\varphi\rangle = 1/2$, we get $\Delta E = V_0(3/2 - 1) = V_0/2$.

Hence the correction equals $(1/2)V_0$.

105) The tunneling probability of a particle with energy E incident on a potential barrier of height V_0 and width L is:

$T(E) = 16\,(E/V_0)(1 - E/V_0)\,e^{-2kL}$

For a particle with $E = V_0/2$, the tunneling probability is 1.6×10^{-7}.

If the width of the barrier is halved, the tunneling probability will be:

1. 3.2×10^{-7}
2. 8.0×10^{-4}
3. 6.4×10^{-7}
4. 3.2×10^{-3}

Answer: (2) — 8.0×10^{-4}

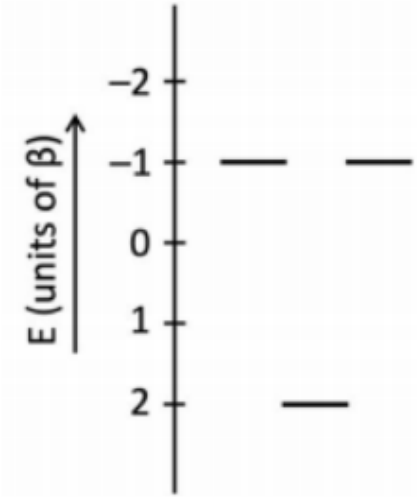
Explanation :

At $E = V_0/2$, prefactor = $4 \Rightarrow 4e^{-2kL} = 1.6 \times 10^{-7} \Rightarrow e^{-2kL} = 4 \times 10^{-8}$.

Halving L gives exponent $-kL$, so new $T = 4e^{-kL} = 4\sqrt{(4 \times 10^{-8})} = 4(2 \times 10^{-4}) = 8 \times 10^{-4}$.

Hence tunneling probability increases exponentially when barrier width decreases.

106) The energy level diagram for the π-molecular orbitals of the cyclic C_3H_3 radical is given below.



The delocalization energy of the molecule in the ground state (in units of β, where β is Hückel's constant for interaction energy) is:

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

Answer: (1) — 3

Explanation :

C_3H_3 has 3 π-electrons. According to the diagram, levels are at energies −2β, −1β, and +2β.

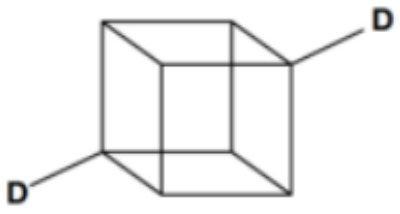
Two electrons occupy the lowest level (−2β) and one occupies the next (−1β).

Total π energy = (2×−2β) + (1×−1β) = −5β.

For three isolated p orbitals (non-delocalized), energy = 3α.

Delocalization energy = −5β − (expected −3β) = −2β → magnitude 3|β| units.

107) Sym-cubane-d_2, a bi-substituted isotopomer of cubane with two hydrogens substituted by deuterium, has the structure shown.



The point group of this molecule is:

1. D_2h
2. D_3d

3. C_3v
4. C_2h

Answer: (4) — C_2h

Explanation :

Symmetrical substitution at opposite vertices retains a C_2 axis and a horizontal mirror plane (σh).

No perpendicular C_2 axes or inversion center remain, hence the correct point group is C_2h.

108) The vibrational energy for a diatomic molecule is $G(v) = (v + ½)\nu_e - (v + ½)^2\nu_e x_e$.

For BeO in an excited state, infrared transitions at 1078.48 cm^{-1} (v=2→3) and 1062.42 cm^{-1} (v=3→4) are observed. The ν_e and $\nu_e x_e$ (in cm^{-1}) for this state are:

1. 1126.66 and 8.03
2. 1030.30 and −8.03
3. 1174.84 and 16.06
4. 1078.48 and 8.03

Answer: (1) — 1126.66 and 8.03

Explanation :

Transition wavenumber $\Delta G(v+1/2) = \nu_e - 2(v+1)\nu_e x_e$.

For 2→3: $1078.48 = \nu_e - 6\nu_e x_e$.

For 3→4: $1062.42 = \nu_e - 8\nu_e x_e$.

Subtract: $16.06 = 2\nu_e x_e \rightarrow \nu_e x_e = 8.03\ cm^{-1}$.

Substitute: $\nu_e = 1078.48 + 48.18 = 1126.66\ cm^{-1}$.

109) Acetone undergoes photodissociation upon absorption of 330 nm light.

A gaseous sample exposed to a radiant power of 20 mW for 3 h causes photodissociation of 75 µmol of acetone. The quantum yield (assuming complete absorption) is:

1. 1.26×10^{-4}
2. 1.26×10^{-1}
3. 1.26×10^{-3}
4. 1.26×10^{-2}

Answer: (4) — 1.26×10^{-2}

Explanation :

Number of photons absorbed = (Power × time × λ) / (hc).

$= (0.02\ J\ s^{-1} \times 10800\ s \times 330 \times 10^{-9}\ m) / (6.626 \times 10^{-34}\ J\ s \times 3 \times 10^{8}\ m\ s^{-1})$

$\approx 3.6\times10^{-4}$ mol photons.

Quantum yield = (mol reacted / mol photons) = $(7.5\times10^{-5}) / (3.6\times10^{-3}) \approx 1.26\times10^{-2}$.

110) A polymer sample has 100 chains with molecular weight = 1000, 200 chains with 10 000, and 200 chains with 100 000.

The polydispersity index (PDI) is:

1. 1.485
2. 1.970
3. 2.068
4. 3.532

Answer: (3) — 2.068

Explanation :

Number-average MW (Mn) = $\Sigma(N_iM_i)/\Sigma N_i = (100\times1000 + 200\times10000 + 200\times100000)/500 = 48300$.

Weight-average MW (Mw) = $\Sigma(N_iM_i^2)/\Sigma(N_iM_i) = (100\times10^6 + 200\times10^8 + 200\times10^{10})/(4.83\times10^7) \approx 99900$.

PDI = Mw/Mn = 99900/48300 ≈ 2.07.

111) An ideal gas with an initial pressure P and volume V undergoes an isothermal and reversible expansion. If the change in entropy due to this expansion is ΔS, the magnitude of work done by the gas is

1. nRΔS
2. nRΔS/PV
3. PVΔS/nR
4. PV/nR

Answer: 3

Explanation: For an isothermal reversible process of an ideal gas, q_rev = TΔS and ΔU = 0, so |w_rev| = q_rev = TΔS. Using the ideal-gas relation at the stated initial condition, T = PV/(nR). Hence |w| = (PV/(nR))ΔS = PVΔS/nR, which is option 3.

112) Consider ammonia to be an ideal gas, with each molecule of ammonia occupying an effective area of 7 Å² on barium fluoride surface. The adsorption follows the following isotherm.

$z/[(1-z)V] = 1/(cV_m) + [(c-1)z]/(cV_m)$ where, z = p/p°, c is a constant, and V_m the is monolayer capacity (volume of the adsorbed gas) at STP. The plot of z/[(1−z)V] against z gives the intercept as 4.66×10^{-4} cm^{-3} and slope as 0.0761 cm^{-3}. The surface area of adsorption (in m^2) is close to

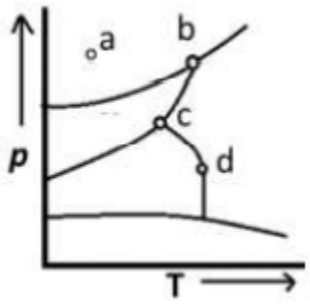
1. 24.5
2. 2.5

3. 33.2
4. 1.9

Answer: 1

Explanation: Intercept = 1/(cV_m), slope = (c−1)/(cV_m). Hence (slope/intercept) = c−1 ⇒ c ≈ 1 + 0.0761/(4.66×10^{-4}) ≈ 164.3. Also cV_m = 1/(intercept) ≈ 2146 cm^3⇒V_m≈ 2146/164.3 ≈ 13.06 cm^3 (at STP). Moles in monolayer = 13.06/22414 ≈ 5.83×10^{-4} mol ⇒ molecules ≈ 3.51×10^{20}. Area = N × 7×10^{-20} m^2≈ 24.6 m^2, closest to 24.5 (option 1).

113) The phase diagram for a one-component system is shown below. The number of degrees of freedom at the points marked a, b, c and d, respectively, are



1. 2, 0, 0, 1
2. 1, 3, 3, 2
3. 2, 1, 0, 1
4. 0, 1, 2, 1

Answer: 3

Explanation: For a one-component system, F = C − P + 2 = 3 − P. In a single-phase region (point a), P = 1 ⇒ F = 2. On a phase boundary (points b and d), P = 2 ⇒ F = 1. At the triple point (c), P = 3 ⇒ F = 0. Thus 2,1,0,1.

114) Consider four non-interacting ^{4}He atoms, each of which can occupy three energy levels of energies 0, a and 2a. The number of microstates having total energy E = 3a is

1. 4
2. 12
3. 2
4. 1

Answer: 3

Explanation: With indistinguishable bosons and nondegenerate levels, count distinct occupancy solutions to $n_1 + 2n_2 = 3$ with $n_0 + n_1 + n_2 = 4$. Solutions: $(n_0,n_1,n_2) = (1,3,0)$ and $(2,1,1)$. Hence there are 2 microstates (option 3).

115) A three-state system with energies $E = -\varepsilon_0, 0, +\varepsilon_0$ is in a thermal equilibrium at a temperature T. If $\beta\varepsilon_0 = x$, the probability of finding the system with energy E = 0 is [recall, $\cosh x = \frac{1}{2}(e^x + e^{-x})$]

1. $(2 \cosh x)^{-1}$
2. $\frac{1}{2} \cosh x$
3. $(1 + 2 \cosh x)^{-1}$
4. $1 + 2 \cosh x$

Answer: 3

Explanation: Partition function Z = e^{β ε0} + 1 + e^{−β ε0} = 1 + 2 cosh x. The probability for the zero-energy level is 1/Z = 1/(1 + 2 cosh x), which is option 3.

116) Consider the cell, $Pt|H_2(g, p^\circ)|HCl(aq)||AgCl(s)|Ag$, and the corresponding cell reaction $2 AgCl(s) + H_2(g) \rightarrow 2 Ag(s) + 2 HCl(aq)$ where, p° is the standard pressure. In terms of the molality b of HCl(aq), and the mean activity coefficient γ, the Nernst equation for the cell reaction is

1. $E = E_0 - (2RT/F) \ln(\gamma b)$
2. $E = E_0 - (RT/F) \ln(\gamma b)$
3. $E = E_0 - (RT/2F) \ln(\gamma b)$
4. $E = E_0 - (RT/F) \ln(2\gamma b)$

Answer: (1)

Explanation: For the overall reaction $2AgCl(s)+H_2(g)\rightarrow 2Ag(s)+2HCl(aq)$, n = 2. Solids have unit activity and H_2 is at p = p°, so Q = (a_HCl)². For a 1:1 electrolyte, a_HCl = γb. Hence Q = (γb)² and the Nernst equation $E = E_0 - (RT/nF)\ln Q$ gives $E = E_0 - (RT/2F)\cdot\ln(\gamma b)^2 = E_0 - (2RT/F)\ln(\gamma b)$, which is option (1).

117) The transference number of the hydrogen ion in an aqueous solution containing HCl and NaCl is 0.5. The limiting molar conductivities of H^+, Na^+ and Cl^- are, respectively, 350×10^{-4} Sm² mol⁻¹, 50×10^{-4} Sm² mol⁻¹ and 75×10^{-4} Sm² mol⁻¹. The ratio of the concentrations of HCl and NaCl, namely [HCl]/[NaCl] is

1. 10/11
2. 11/5
3. 5/11
4. 11/10

Answer: (3)

Explanation: With [HCl]=x and [NaCl]=y, the cation transference number is
$t_+ = (\lambda_0(H^+)x)/(\lambda_0(H^+)x + \lambda_0(Na^+)y + \lambda_0(Cl^-)(x+y)) = 0.5$.

Rearranging gives $(\lambda_0(H^+)-\lambda_0(Cl^-))x = (\lambda_0(Na^+)+\lambda_0(Cl^-))y$.

Using 350, 50, 75 ($\times 10^{-4}$) $\Rightarrow$ x/y = (50+75)/(350−75) = 125/275 = 5/11.

118) The rate of an acid-catalyzed reaction in aqueous solution follows the rate equation given below.

$v = k[X^+][Y^{2-}][H^+]$

The rate constants for the reaction at ionic strengths of 16 mol L^{-1} and 9 mol L^{-1} are k_1 and k_2, respectively. The value of $\log(k_1/k_2)$ in the units of the Debye–Hückel constant, B, is

1. −2
2. 4/3
3. 16/9
4. −4

Answer: 1. −2

Explanation:

The reacting ions are X+ and Y2−.

Multiply their charges: +1 × −2 = −2.

Use the ionic strength values:

Square root of 16 is 4.

Square root of 9 is 3.

Now subtract: 4 − 3 = 1.

Multiply this by the charge product −2:

So log(k1/k2) = −2.

Therefore, the correct answer is −2.

119) A reaction follows the rate law $-d[A]/dt = k[A]^2$. Starting from an initial concentration $[A]_0$, the time taken for the concentration to reduce to $[A]_0/4$, namely the quarter-life of A, is

1. (ln k)/2
2. $1/(k[A]_0)$
3. (ln 2)/k
4. $3/(k[A]_0)$

Answer: (4)

Explanation: For a second-order reaction in A, $1/[A] - 1/[A]_0 = kt$.

At $[A] = [A]_0/4$: $1/([A]_0/4) - 1/[A]_0 = (4/[A]_0 - 1/[A]_0) = 3/[A]_0 = kt$.

Thus $t = 3/(k[A]_0)$.

120) The number of cation vacancies per mole, when NaCl is doped with 10^{-3} mol% of BCl_3, is

1. 12.046×10^{23}
2. 12.046×10^{18}
3. 6.023×10^{20}
4. 6.023×10^{18}

Answer: (2)

Explanation: B^{3+} substituting for Na^{+} creates +2 excess charge; charge neutrality is restored by creating two Na^{+} vacancies per B^{3+}.

Dopant amount = 10^{-3} mol% = 10^{-5} mol per mole of NaCl.

Vacancies per mole = $2 \times 10^{-5} \times N\_A = 2 \times 10^{-5} \times 6.023 \times 10^{23} = 1.2046 \times 10^{19} = 12.046 \times 10^{18}$, i.e., option (2).