PAPER : CSIR-UGC-NET/JRF DEC. 2023

CHEMICAL SCIENCES

PART-B

1. The thermodynamic variable '*X*' in the equation

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[X + \left(\frac{\partial H}{\partial P}\right)_T\right]$$ is

(a) V (b) S (c) $-V$ (d) C_p

2. 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

(a) $X_1 > X_4 > X_3 > X_2$ (b) $X_1 > X_2 > X_3 > X_4$

(c) $X_4 > X_3 > X_1 > X_2$ (d) $X_1 > X_3 > X_4 > X_2$

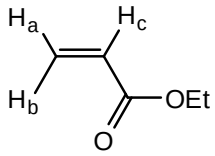
3. The option showing the ***correct*** match of metal complexes in Column-I with the corresponding Δ_0 (cm^{-1}) values in Column-II is

Column - I		Column - II	
A	$[TiF_6]^{3-}$	P	21800
B	$[MnF_6]^{2-}$	Q	17000
C	$[Co(en)_3]^{3+}$	R	9400
D	$[Fe(H_2O)_6]^{2+}$	S	24000

(a) A→Q, B→P, C→S, D→R (b) A→R, B→S, C→P, D→Q

(c) A→Q, B→P, C→R, D→S (d) A→P, B→S, C→R, D→Q

4. The ***correct*** match for the protons of ethyl acrylate given in Column P with chemical shifts (σ ppm) given in Column Q is

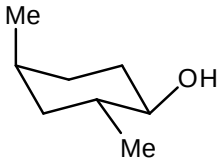


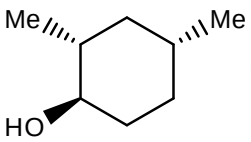
	Column **P**		Column **Q**
A.	H_a	i.	6.11 (dd, J = 16, 10 Hz)
B.	H_b	ii.	6.4 (dd, J = 16, 4 Hz)
C.	H_c	iii.	5.8 (dd, J = 10, 4 Hz)

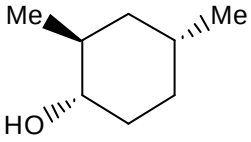
(a) A-i, B-ii, C-iii (b) A-iii, B-ii, C-i

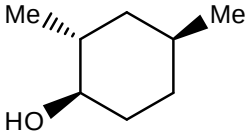
(c) A-iii, B-i, C-ii (d) A-ii, B-iii, C-i

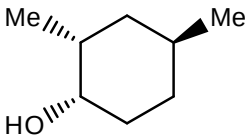
5. The structure that corresponds to the following compound is



(a) 

(b) 

(c) 

(d) 

6. 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
(a) mixing of 4f and 4d orbitals
(b) large spin-orbit coupling constant (λ)
(c) large orbital angular momentum
(d) populated ground and the excited states

7. If $H = \frac{p_x^2}{2m} + V(x)$, then $[H, p_x]$ is

(a) $i\hbar\frac{dV}{dx}$ (b) 0 (c) $-i\hbar$ (d) $-\frac{i\hbar p_x}{m}$

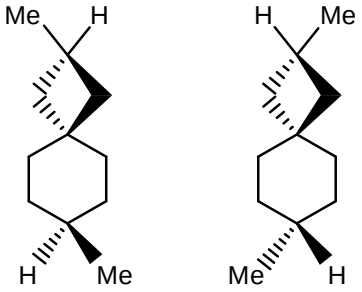
8. In a flame photometric analysis of a blood serum sample for K^+ ion, a band is obtained at 766*nm*. This band is due to
(a) absorption by K^+ ion only
(b) absorption by K atom only
(c) emission by K^+ ion only
(d) emission by K atom only

9. The ***correct*** option for the oxidation state(s) of Nb in the cluster $Na_4[Nb_6Cl_{18}]$ is
(a) two are in +3 state and four are in +2 state
(b) all are in +2 state
(c) all are in +3 state
(d) three are in +2 state and three are in +3 state

10. $[Fe(CO)_5]$ 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
(a) A, B and C only (b) A and B only (c) A, B and D only (d) B and D only

11. Of the following atomic transitions, the allowed one is
(a) $^1S \rightarrow {}^5S$ (b) $^3P \rightarrow {}^1D$ (c) $^1S \rightarrow {}^1D$ (d) $^3D \rightarrow {}^3P$

12. The following two molecules are



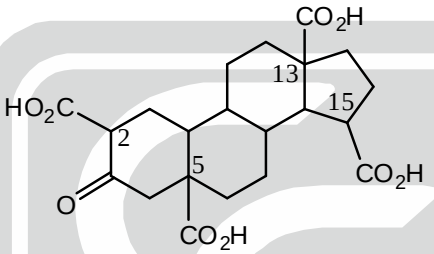
(a) Enantiomers (b) Diastereomers

(c) Homomers (Identical) (d) Constitutional isomers

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

(a) $\sqrt{2}:1$ (b) 2 : 1 (c) 1 : 2 (d) $1:\sqrt{2}$

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



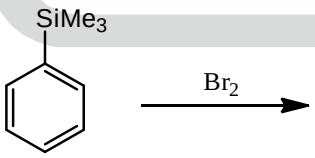
(a) C15 (b) C13 (c) C5 (d) C2

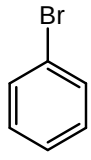
15. For 0.001 M aqueous solutions of $AlCl_3$, $CaCl_2$ and KCl at 25°C, the ***correct*** order of Debye length is

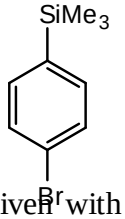
(a) $AlCl_3 < CaCl_2 < KCl$ (b) $KCl < CaCl_2 < AlCl_3$

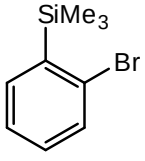
(c) $CaCl_2 < KCl < AlCl_3$ (d) $AlCl_3 < KCl < CaCl_2$

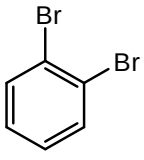
16. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

17. 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:

(a) A and B only (b) B and C only (c) A and C only (d) A and D only

18. The number of skeletal electron pairs (SEP) and the cluster type for $[B_{10}H_{10}]^{2-}$ and $[B_6H_9]^-$, respectively, are

(a) 11, *closo* and 8, *nido* (b) 11, *nido* and 8, *nido*

(c) 10, *closo* and 6, *arachno* (d) 10, *closo* and 8, *nido*

19. According to VSEPR theory, the geometries of FCIO and F_5IO, respectively, are

(a) linear and octahedral

(b) tetrahedral and octahedral

(c) tetrahedral and capped octahedral

(d) trigonal bipyramidal and capped octahedral

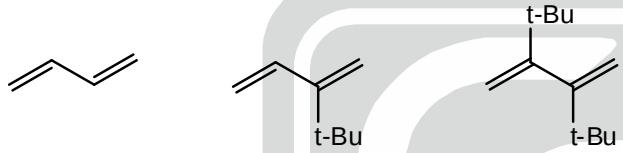
20. e^{ikx} is an eigenfunction of the linear momentum operator, $\hat{p}_x$, with the eigenvalue of

(a) $\hbar^2 k$ (b) $\hbar k$ (c) $\hbar k^2$ (d) $\hbar^2 k^2$

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

(a) 8 and 4 (b) 4 and 2 (c) 16 and 16 (d) 6 and 6

22. The ***correct*** order of reactivity for the following dienes with maleic anhydride is



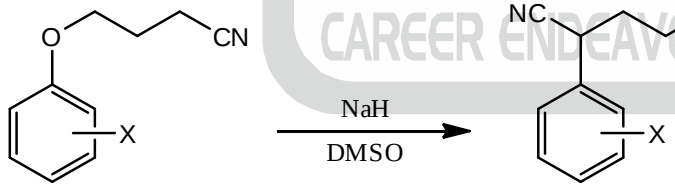
M N O

(a) M > N > O (b) N > M > O (c) N > O > M (d) O > N > M

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

(a) 400 (b) 500 (c) 600 (d) 900

24. The following reaction is the fastest when



(a) X = m-NO_2 (b) X = p-OMe (c) X = p-NO_2 (d) X = m-OMe

25. The option showing the ***correct*** match for the reactants in **Column-I** with the second-order rate constants (1 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}

(a) A-(i), B-(ii), C-(iii), D-(iv) (b) A-(iv), B-(iii), C-(ii), D-(i)

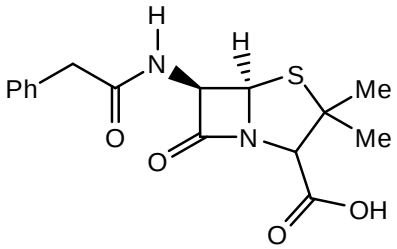
(c) A-(i), B-(ii), C-(iv), D-(iii) (d) A-(iv), B-(ii), C-(iii), D-(i)

26. The reaction of V_2O_5 with an 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 infra-red absorption in the region of 950-1035 cm^{-1}. X contains a

(a) $[V - (O)_2 - V]^{6+}$ unit (b) $[VO]^{2+}$ unit

(c) $[V(O)(O_2)]^{+}$ unit (d) $[(O)V - O - V(O)]^{4+}$ unit

27. The most effective pharmacophore that confers antibiotic activity to penicillin G is



(a) phenylacetamide (b) thiazolidine ring (c) carboxylic acid (d) β-lactam

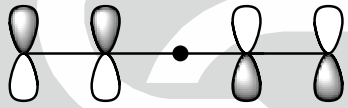
28. The number of unpaired electrons in B_2 is

(a) 0 (b) 1 (c) 2 (d) 3

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

(a) 4.54 BM (b) 1.73 BM (c) 2.83 BM (d) 3.87 BM

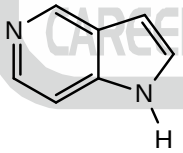
30. The following molecular orbital corresponds to

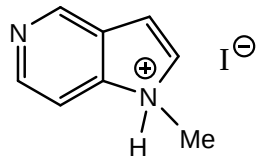


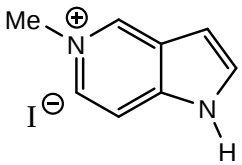
(a) HOMO of pentadienyl cation (b) HOMO of pentadienyl anion

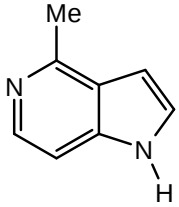
(c) LUMO of pentadienyl cation (d) LUMO of pentadienyl anion

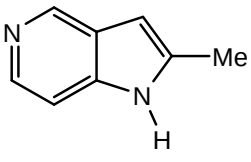
31. The reaction of the given compound with MeI produces



(a) 

(b) 

(c) 

(d) 

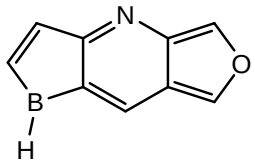
32. 2-Methylbut-2-ene is used in Pinnick oxidation [R-CHO $\rightarrow$ R-CO_2H using $NaClO_2$, Na_2HPO_4, in t-BuOH/H_2O] to scavenge

(a) HCl (b) H_3PO_4 (c) $HClO_2$ (d) HOCl

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

(a) 7 (b) 6 (c) 5 (d) 4

34. Based on Hückel rule, the following species is



(a) aromatic (b) antiaromatic (c) nonaromatic (d) homoaromatic

35. Consider the following statements,

I. Micelles form above the critical micelle concentration

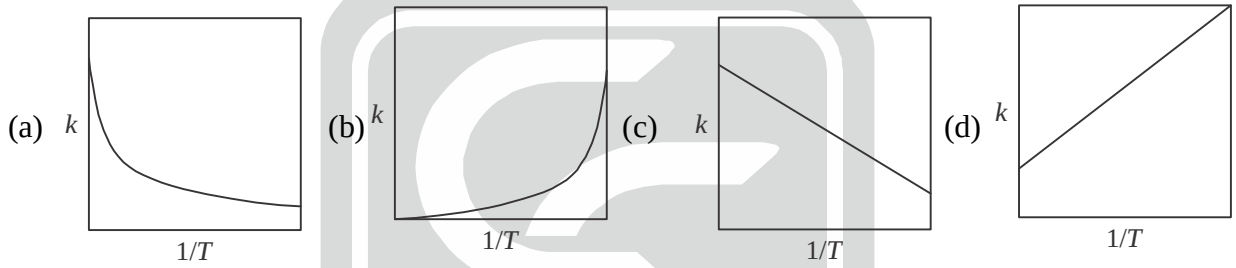
II. Micelles form above the Krafft temperature

The ***correct*** option is

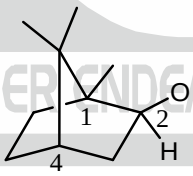
(a) Only I is true (b) Only II is true

(c) Both I and II are true (d) Both I and II are false

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

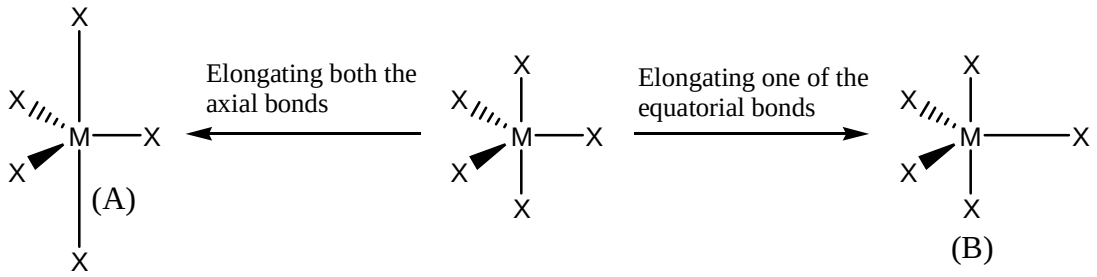


37. The ***correct*** absolute configuration for the structure shown below is



(a) 1S, 2S, 4S (b) 1S, 2R, 4R (c) 1R, 2R, 4S (d) 1S, 2S, 4R

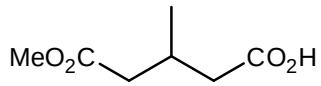
38. The molecule MX_5 belongs to the point group D_{3h}. Elongation of both the axial M-X bonds yields A and elongation of one of the M-X equatorial bonds yields B.

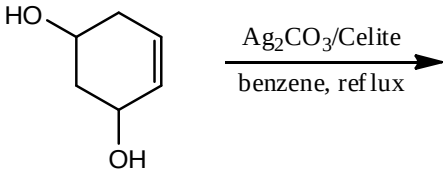


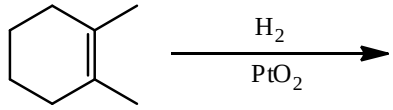
The point groups of A and B, respectively, are

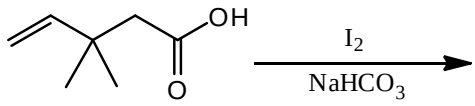
(a) C_{3v} and D_{3h} (b) D_{3h} and C_{3v} (c) C_{3v} and C_{2v} (d) D_{3h} and C_{2v}

39. Among the following, the examples of chemoselective reactions are

A. 

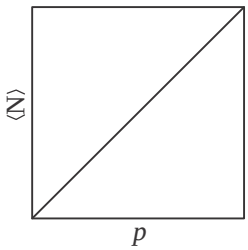
B. 

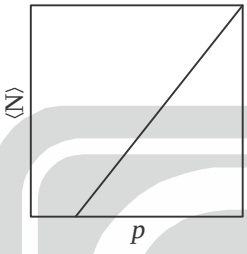
C. 

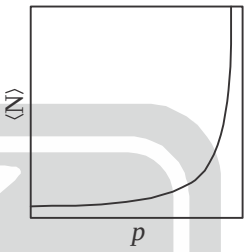
D. 

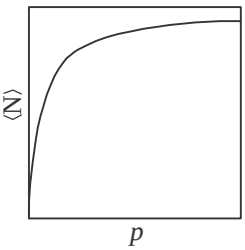
(a) A and B (b) B and C (c) A and D (d) C and D

40. For step-wise polymerization, the ***correct*** plot of chain length ($\langle N \rangle$) against degree of polymerization (p) is

(a) 

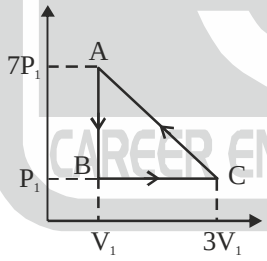
(b) 

(c) 

(d) 

PART-C

61. The total work done by the system in the cyclic process depicted above is



(a) $6\,P_1V_1$ (b) 0 (c) $-14\,P_1V_1$ (d) $12\,P_1V_1$

62. The d-orbitals of a hydrogenic atom with $n = 3$, $l = 2$, and $m = \pm 2$ are given by

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

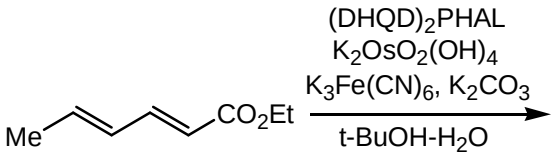
where, N is the normalization constant and $R(r)$ is the radial part of the wavefunction. An appropriate linear combination of these two wavefunctions yields the real orbitals

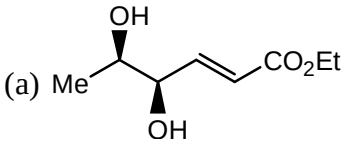
(a) d_{z^2} (b) d_{xy} (c) d_{yz} (d) d_{zx}

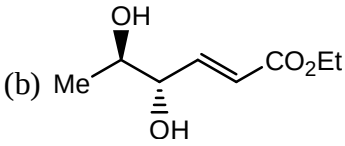
63. A molecule shows two absorption at 896 and 960 MHz in its ^{13}C NMR spectrum in a magnetic field of 3T. The corresponding chemical shifts in ppm are (^{13}C magnetogyric ratio $\gamma = 6.72\times10^{7}\ \text{radT}^{-1}s^{-1}$; $I = \frac{1}{2}$)

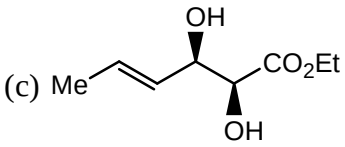
(a) 12.8 and 13.7 (b) 14 and 15 (c) 32 and 34 (d) 28 and 30

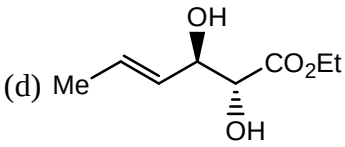
64. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

65. 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

(a) A (b) B (c) C (d) D

66. 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

(a) XeO_3, XeO_6^{4-}, and Xe (b) XeO_4, $HXeO_6^{4-}$ and Xe

(c) XeO_4, Xe and XeO_6^{4-} (d) $HXeO_4^-$, XeO_3 and XeO_6^{4-}

67. The ^{19}F NMR spectrum of $\left[XeF_5\right]^-$ ion shows, $\left[^{129}Xe, I = ½, 26.5\% \text{ abundance}\right]$

(a) a doublet with satellite peaks
(b) a triplet and a quartet with satellite peaks for both
(c) a doublet and a quintet with satellite peaks for both
(d) a singlet with satellite peaks

68. A particle of mass *m* is confined in a rectangular box with $L_x = 2L_y$. The state with the energy $\frac{10h^2}{8mL_y^2}$ has a degeneracy of

(a) 1 (b) 2 (c) 3 (d) 4

69. For a diatomic molecule, which is an anharmonic oscillator, $\bar{\nu}_e$ (vibrational wavenumber) = 536.2 cm^{-1}. The observed $\left(\bar{\nu}_{obs}\right)$ value of fundamental frequency is 529.4 cm^{-1}. The magnitude of $\bar{\nu}_{obs}\left(\text{in } cm^{-1}\right)$ for 3rd overtone is closest to

(a) 2076.8 (b) 1588.2 (c) 1567.8 (d) 2117.2

70. 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

(a) 702 cm^{-1} and $O_2^- \rightarrow$ Cu(II) charge transfer

(b) 702 cm^{-1} and $O_2^{2-} \rightarrow$ Cu(II) charge transfer

(c) 664 cm^{-1} and $O_2^- \rightarrow$ Cu(II) charge transfer

(d) 792 cm^{-1} and $O_2^{2-} \rightarrow$ Cu(II) charge transfer

71. $\left[Co\left(NH_3\right)_5\left(X\right)\right]Cl_2\left(\mathbf{1}\right)$ 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 $\left[Co\left(NH_3\right)_5\left(Z\right)\right]Cl_2\left(\mathbf{3}\right)$. 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

(a) X = Cl; Y = NO_2; Z = ONO (b) X = H_2O; Y = NO_2; Z = ONO

(c) X = Cl; Y = ONO; Z = NO_2 (d) X = H_2O; Y = ONO; Z = NO_2

72. 1 and 2 are the labels of two electrons. If ϕ_{1s} and ϕ_{2s} are the 1s and 2s wavefunctions of He atom and α and β are the spin wavefunction of an electron. The Slater determinant that correctly describes one of the symmetry-adapted excited states of He atom is

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

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

73. The following statements are given with respect to the symmetry operations and symmetry elements.

(A) BF_3 possesses S_3 axis

(B) C_2H_6 in a staggered conformation possesses an S_6 axis.

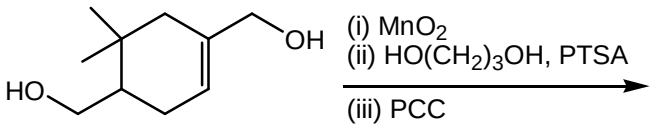
(C) Benzene molecule possesses three σ_v-planes

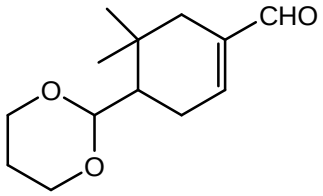
(D) Water molecule possesses C_2 axis and σ_h-plane

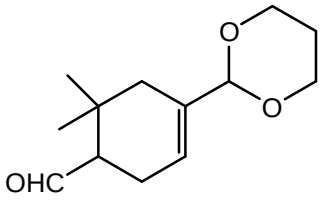
The option giving the correct statements, is

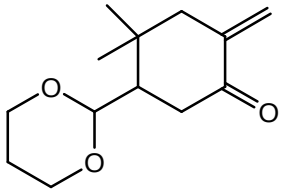
(a) B, C and D only (b) A, B and C only (c) A, B and D only (d) A, B, C and D

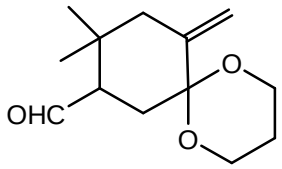
74. The major product formed in the following reaction sequence is



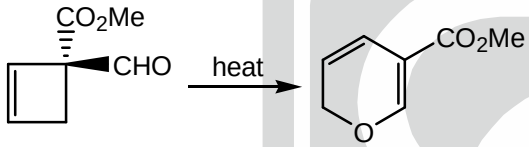
(a) 

(b) 

(c) 

(d) 

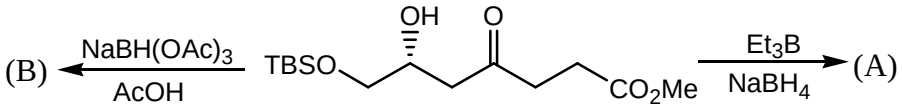
75. The mechanism of the following reaction involves

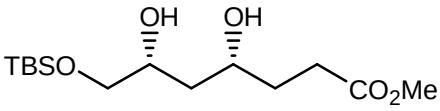


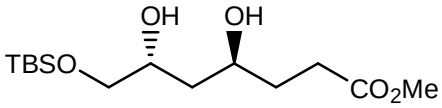
(A) 4 electron conrotatory electrocyclic reaction
(B) [2+2] cycloreversion
(C) 6 electron disrotatory electrocyclic reaction
(D) [4+2] cycloaddition

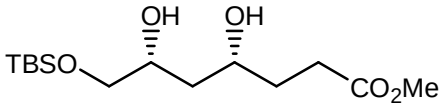
(a) A and B (b) A and C (c) B and D (d) C and D

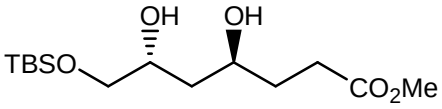
76. The major products A and B formed in the following transformations are

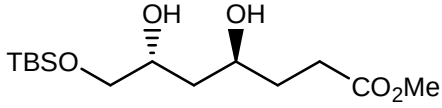


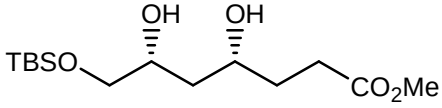
(a) A = B = 

(b) A = B = 

(c) A = 

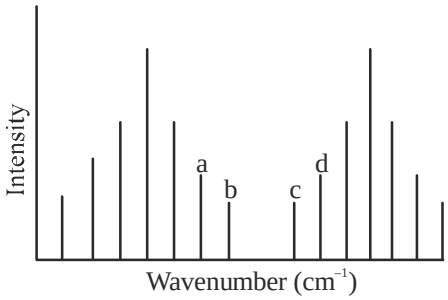
and B = 

(d) A = 

and B = 

77. 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.

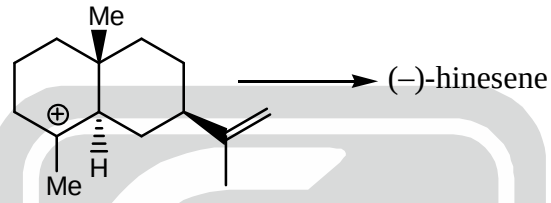
	$a\left(cm^{-1}\right)$	$b\left(cm^{-1}\right)$	$c\left(cm^{-1}\right)$	$d\left(cm^{-1}\right)$
M_1	1540	1564	1636	1660
M_2	1644	1676	1772	1804



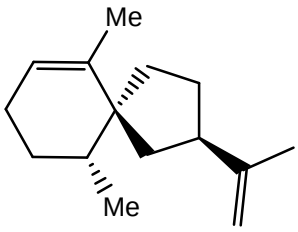
If the reduced mass of M_1 is 3-times that of M_2, the ratio of bond length of M_1 to that of M_2 is

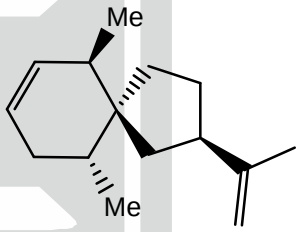
(a) 2/3 (b) 3/2 (c) 4/9 (d) 9/4

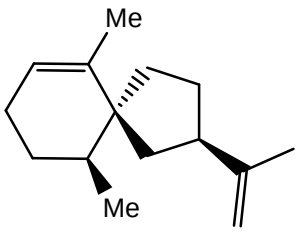
78. Upon catalysis by hinesene synthase, eudesmyl cation shown below undergoes a sequential hydride shift, ring contraction and loss of proton to form (–)-hinesene. The correct structure of (–)-hinesene is

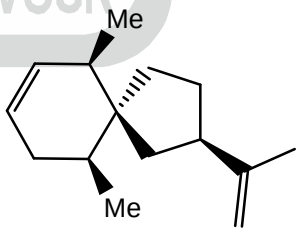


eudesmyl cation

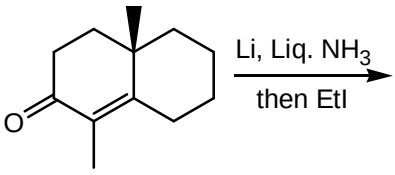
(a) 

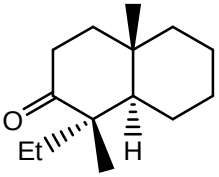
(b) 

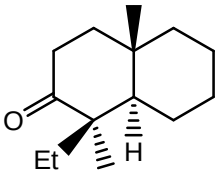
(c) 

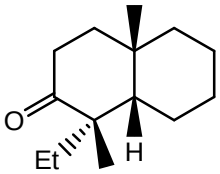
(d) 

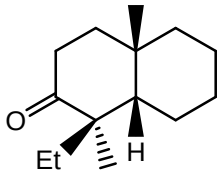
79. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

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

(a) X = $PbSO_4$, Y = $Pb(OH)_2$, Z = PbS (b) X = $ZnSO_4$, Y = $Zn(OH)_2$, Z = ZnS

(c) X = $MnSO_4$, Y = $Mn(OH)_2$, Z = MnS (d) X = $CoSO_4$, Y = $Co(OH)_2$, Z = CoS

81. σ_g and σ_u are respectively the bonding and anti-bonding molecule orbitals formed by linear combination of two 1s atomic orbitals of H-atom. The spatial part of a purely covalent wavefunction for H_2 molecule obtained according to molecular orbital theory is

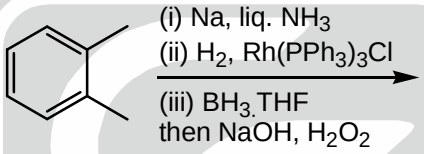
(a) $\sigma_g(1)\sigma_g(2)+\sigma_g(1)\sigma_u(2)$ (b) $\sigma_g(1)\sigma_g(2)-\sigma_g(1)\sigma_u(2)$

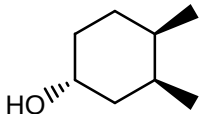
(c) $\sigma_g(1)\sigma_g(2)+\sigma_u(1)\sigma_u(2)$ (d) $\sigma_g(1)\sigma_g(2)-\sigma_u(1)\sigma_u(2)$

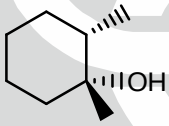
82. The percentage error in the measurements of mass and linear velocity of a particle, respectively, are 3% and 4%. The maximum percentage error in the kinetic energy of the particle is

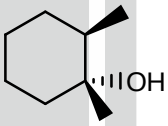
(a) 5% (b) 7 % (c) 11% (d) 24 %

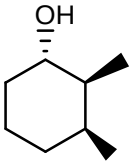
83. The major product formed in the following reaction sequence is



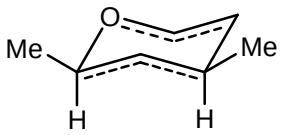
(a) 

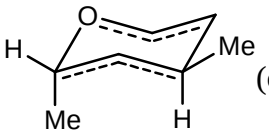
(b) 

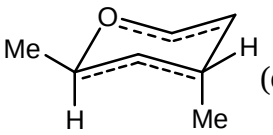
(c) 

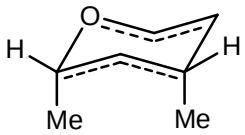
(d) 

84. The transition state (TS) structure that would lead to the product in the following reaction is

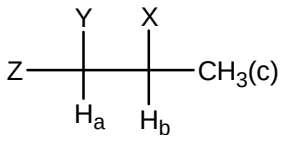
(a) 

(b) 

(c) 

(d) 

85. Consider the following compound where $^3J_{ab}$ and $^3J_{bc}$ represent three bond coupling between H_a and H_b and H_b and H_c protons, respectively.



in two different scenarios, (I) $^3J_{ab} < {}^3J_{bc}$ and (II) $^3J_{ab} = {}^3J_{bc}$

the multiplicity of H_b proton, respectively, will be

(a) I = quintet ; II = quartet of doublets (b) I = quartet of doublets; II = quintet

(c) I = triplet of triplets; II = quartet of doublets (d) I = triplet of triplets ; II = quintet

86. The correct order of relative rates of the following reaction is

(a) $k_b >> k_a;\ k_c >> k_d$ (b) $k_b >> k_a;\ k_d >> k_c$

(c) $k_a >> k_b;\ k_d >> k_c$ (d) $k_a >> k_b;\ k_c >> k_d$

87. The option showing both the complexes obeying the 18 electron rule is

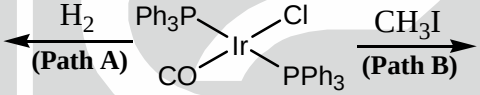
(a) $\left[\left(\eta^5\text{-}C_5H_5\right)RuCl\left(PPh_3\right)_2\right]$ and $\left[\left(\eta^5\text{-}C_5H_5\right)_2 ZrCl_2\right]$

(b) $\left[IrCl(CO)\left(PPh_3\right)_2\right]$ and $\left[Co_2(CO)_8\right]$

(c) $\left[Re(CO)_5\left(PF_3\right)\right]^+$ and $\left[Ni\left(NH_3\right)_6\right]^{2+}$

(d) $\left[\left(\eta^5-C_5H_5\right)\left(\eta^3-C_5H_5\right)Fe(CO)\right]$ and $\left[\left(\eta^3-\text{allyl}\right)Mn(CO)_4\right]$

88. In the oxidative addition of trans-$\left[IrCl(CO)\left(PPh_3\right)_2\right]$ 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



(a) $d_{x^2-y^2}(\ln A);\ d_{z^2}(\ln B)$ (b) $d_{z^2}(\ln A);\ d_{xy}$ *or* d_{xz} *or* $d_{yz}(\ln B)$

(c) d_{xy} *or* d_{xz} *or* $d_{yz}(\ln A);\ d_{z^2}(\ln B)$ (d) $d_{z^2}(\ln A);\ d_{x^2-y^2}(\ln B)$

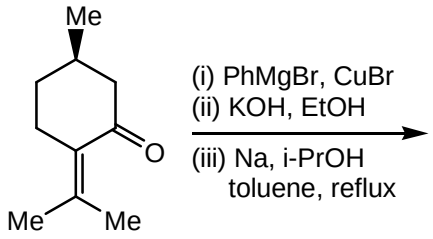
89. Some reagents and their applications are given in the table below:

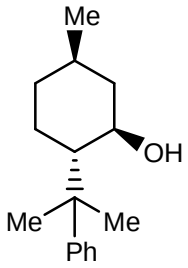
Reagents → / Applications ↓	Fricke Solution	$CuSO_4$ in basic solution	$MnSO_4$ in basic KI Solution	Ammonium $Ce(IV)$ sulfate solution
A	$[OH]$ concentration measurement	Free glucose measurement	dissolved oxygen measurement	Fe^{2+} estimate in potable water
B	Fe^{2+} estimate in potable water	Free glucose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

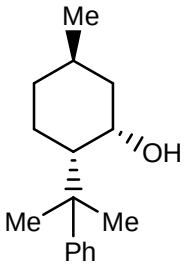
The option showing the correct match of reagents and their application, is

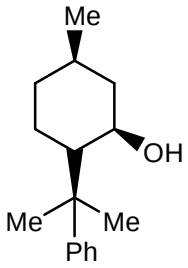
(a) A (b) B (c) C (d) D

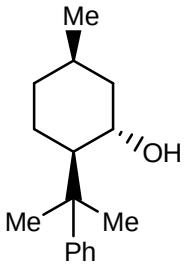
90. The major product formed in the following reaction sequene is



(a) 

(b) 

(c) 

(d) 

91. In solids, the filled molecular orbitals contribute to the

(a) Rydberg states (b) Valence band (c) Conduction band (d) Frenkel Exciton

92. According to VSEPR theory, the shapes and geometries of SeF_4 and $[BrF_4]^-$, respectively, are

(a) see-saw and trigonal bipyramidal; see-saw and trigonal bipyramidal

(b) square planar and octahedral; square planar and pentagonal pyramidal

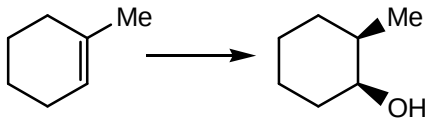
(c) see-saw and trigonal bipyramidal; square planar and octahedral

(d) square planar and square bipyramidal; square planar and octahedral

93. If E^0 for $OCl^-(aq)|Cl^-(aq)$ and $Cl^-(aq)|\frac{1}{2}Cl_2(g)$ half-cells, respectively, are 0.94 V and –1.36 V, then E^0 (in V) for the OCl^- (aq) | ½ Cl_2(g) half cell is

(a) –0.42 (b) –2.20 (c) 0.52 (d) 1.04

94. The correct set of reagents that can affect the following conversion is



(a) (i) m-CPBA ; (ii) $NaBH_3CN$, $BF_3.OEt_2$

(b) (i) OsO_4, NMO; (ii) TsCl, pyridine; (iii) $LiAlH_4$

(c) (i) m-CPBA; (ii) $LiAlH_4$

(d) OsO_4, NMO; (ii) $PhCO_2H$, PPh_3, DEAD

95. Two reactions have same pre-exponential factor, but E_a (activation energy) of the first reaction is lower than that of the second reaction by 5 kcal mol^{-1}. Given R = 1.987×10^{-3} $kcalmol^{-1}K^{-1}$. The ratio of the rate constants of the first and second reactions at 298K is closest to

(a) 4650 (b) 22025 (c) 5 (d) 150

96. The correct set of isolobal species is

(I) NH_2 ⟷ $[Fe(CO)_4]$ ⟷ $\left[Mn(CO)_4\right]^-$

(II) CH_3 ⟷ $[Mn(CO)_5]$ ⟷ $\left[CpFe(CO)_2\right]$

(III) CH_3^- ⟷ $\left[Cr(CO)_6\right]$ ⟷ $\left[Mn(CO)_6\right]^+$

(IV) BH_4^- ⟷ $\left[Co(Cp)\right]^-$ ⟷ $\left[Fe(Cp)\right]^-$

(a) I (b) II (c) III (d) IV

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

(a) 1.5 (b) 1.0 (c) 10.0 (d) 7.0

98. A linear variation is performed using two orthogonal basis functions ϕ_1 and ϕ_2 to generate two optimised energies ε_1 and ε_2 $(\varepsilon_1 \le \varepsilon_2)$. If the exact ground and the first excited state energies are E_1 and E_2, respectively, the correct statement is

(a) Both ε_1 and ε_2 are lower than E_1 (b) ε_1 lies between E1 and E2

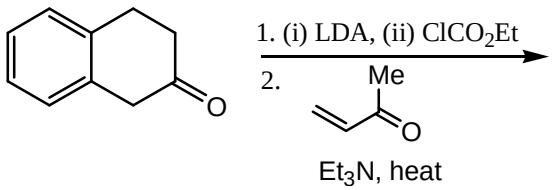
(c) $\varepsilon_1 > E_2$ (d) $\varepsilon_2 > E_2$

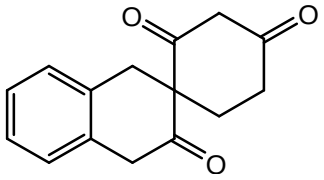
99. The rate of a surface catalyzed reaction between CO(g) and O_2(g) follows Langmuir-Hinshelwood mechanism. If O_2 gets dissociated during adsoption, the rate of the reaction is [where, p represents the partial pressure and *K* represents the surface binding constant on the species, k is a proportionality constant]

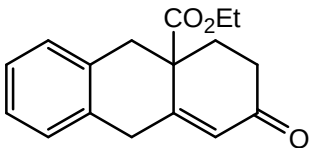
(a) $\dfrac{k \cdot K_{CO} p_{CO} \cdot K_{O_2}^{1/2}\ p_{O_2}^{1/2}}{\left(1 + K_{CO} p_{CO} + K_{O_2}^{1/2}\ p_{O_2}^{1/2}\right)^2}$ (b) $\dfrac{k \cdot K_{CO} p_{CO} \cdot K_{O_2}\ p_{O_2}}{\left(1 + K_{CO} p_{CO} + K_{O_2}\ p_{O_2}\right)}$

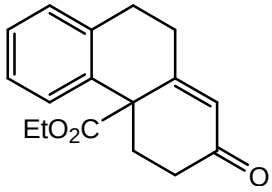
(c) $\dfrac{k \cdot p_{CO} \cdot K_{O_2}\ p_{O_2}}{1 + K_2 p_{O_2}}$ (d) $\dfrac{k \cdot K_{CO} p_{CO} \cdot K_{O_2}\ p_{O_2}}{\left(1 + K_{CO} p_{CO} + K_{O_2}\ p_{O_2}\right)^2}$

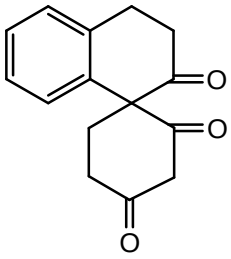
100. The major product formed in the following reaction sequence is



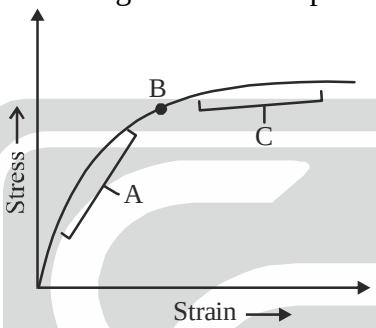
(a) 

(b) 

(c) 

(d) 

101. Identify A, B and C in the following stress-strain plot of a polymer.



(a) A: yield region, B: elastic point, C : plastic region
(b) A: plastic region, B : yield point, C : elastic region
(c) A : elastic region, B : yield point, C : plastic region
(d) A : elastic region, B : plastic point, C : yield region

102. ^{31}P NMR spectrum of P_4S_3 consists of (^{31}P, I = ½, 100 % abundance)
(a) two doublets or triplets
(b) triplet of triplets
(c) two triplets of equal intensity
(d) a doublet and a quartet

103. 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

(a) $d_{Cr...Cr} > d_{W...W}$; A is paramagnetic and B is diamagnetic

(b) $d_{Cr...Cr} > d_{W...W}$; A is diamagnetic and B is paramagnetic

(c) $d_{W...W} > d_{Cr...Cr}$; A is diamagnetic and B is paramagnetic

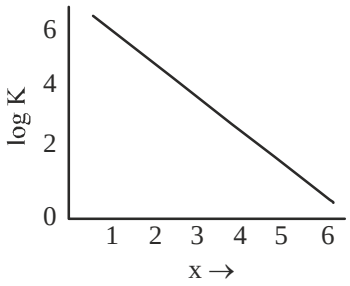
(d) $d_{W...W} > d_{Cr...Cr}$; A is paramagnetic and B is diamagnetic

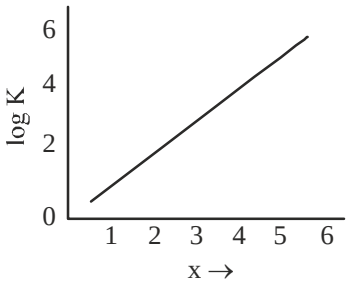
104. The application of Euler's reciprocity relation (cross-derivative rule) to the volume of 1 mole of an ideal gas results in mixed second derivative of V equal to

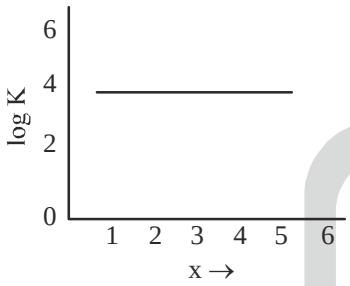
(a) $-\frac{R}{P^2}$ (b) $-\frac{RT}{P^2}$ (c) $\frac{R}{P}$ (d) $\frac{2RT}{P^3}$

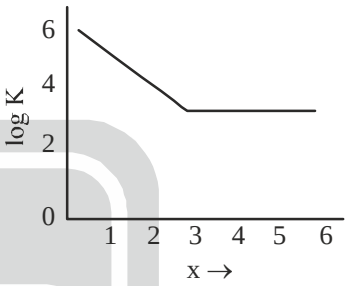
105. The correct plot of $\log K$ *vs* x (K = stepwise stability constant) for the complex

$\left[Al\left(OH_2\right)_{6-x}F_x\right]^{(3-x)^+}$ $\left(x=1-6\right)$ is

(a) 

(b) 

(c) 

(d) 

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

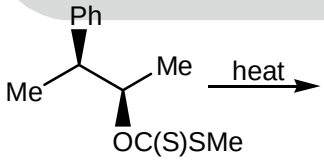
(a) ${}^6H_{5/2} \longrightarrow {}^6H_{7/2}$

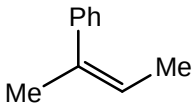
(b) ${}^6H_{5/2} \longrightarrow {}^4G_{5/2}$

(c) ${}^6H_{5/2} \longrightarrow {}^6H_{9/2}$

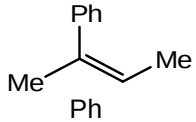
(d) ${}^4G_{5/2} \longrightarrow {}^4G_{7/2}$

107. The correct statement about the following reaction is

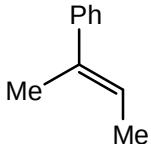


(a) 

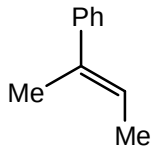
is formed through anti elimination

(b) 

is formed through syn elimination

(c) 

is formed through anti elimination

(d) 

is formed through syn elimination

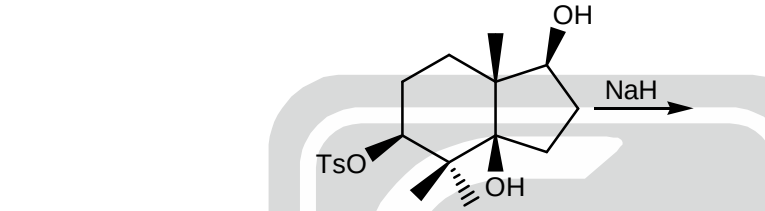
108. The character table for a particular point group is given below. The characters in the irreducible representation Γ_4 and Γ_5, respectively are

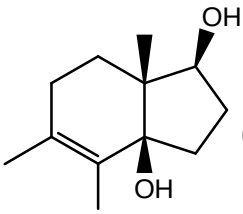
	E	$2\hat{R}_1$	$\hat{R}_2$	$2\hat{R}_3$	$2\hat{R}_4$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	−1	−1
Γ_3	1	−1	1	−1	1
Γ_4					
Γ_5					

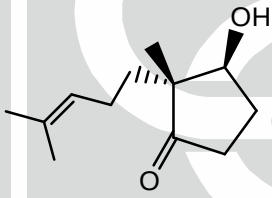
(a) $\{1,1,-1,1,-1\}$ and $\{2,-2,1,0,0\}$ (b) $\{1,-1,1,1,-1\}$ and $\{2,0,-2,0,0\}$

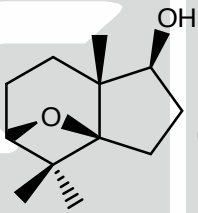
(c) $\{1,2,0,-2,1\}$ and $\{1,1,1,1,-1\}$ (d) $\{2,0,-2,0,0\}$ and $\{2,1,-1,1,-1\}$

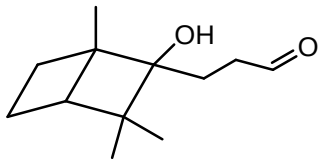
109. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

110. The temperature dependent standard electrode potential of Ag(s) | AgBr(s) | Br^- (aq) fits the expression

$$E^0(V) = 0.0713 - 4.99\times10^{-4}\left(\frac{T}{K} - 298\right) - 3.45\times10^{-6}\left(\frac{T}{K} - 298\right)^2$$

At 398 K, the entropy change, $\Delta S^0, \left(in\ JK^{-1}\ mol^{-1}\right)$ is

(a) –48.2 (b) –114.7 (c) 48.2 (d) 114.7

111. Consider a matrix representation A of the water molecule in the basis $\{\vec{V}_1, \vec{V}_2\}$, where $\vec{V}_1$ and $\vec{V}_2$, are the bond vectors along the two O–H bonds. Consider another matrix representation B of the same molecule in a new basis set $\{\vec{U}_1, \vec{U}_2\}$, such that $\vec{U}_1 = \frac{1}{\sqrt{2}}(\vec{V}_1 + \vec{V}_2), \vec{U}_2 = \frac{1}{\sqrt{2}}(\vec{V}_1 - \vec{V}_2)$. 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

(a) A_1 and B_1 (b) A_1 and B_2 (c) A_2 and B_1 (d) A_1 and A_2

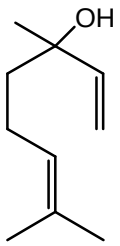
112. In the following nuclear reaction, X, Y and Z, respectively are

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

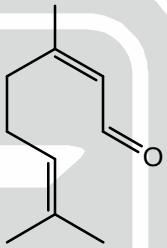
(a) $(n), -\beta$, and $+\beta$ (b) $(n,\gamma), +\beta$, and $+\beta$

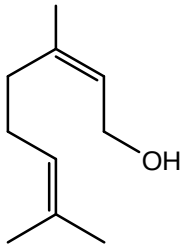
(c) $(+\beta),(n,\gamma)$, and $-\beta$ (d) (n,γ), $-\beta$ and $-\beta$

113. Ozonolysis of a terpene gives equimolar mixture of acetone, α-hydroxyacetaldehyde and 4-oxopentanal. The correct structure of terpene is

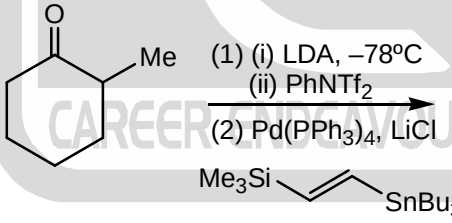
(a) 

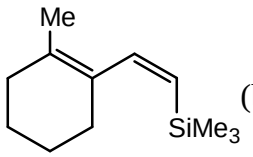
(b) 

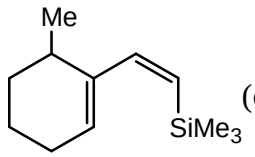
(c) 

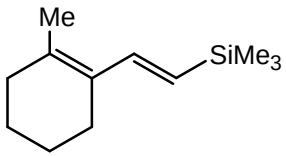
(d) 

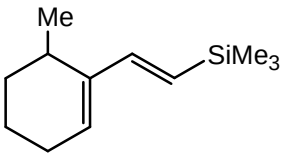
114. The major product formed in the following reaction sequence is



(a) 

(b) 

(c) 

(d) 

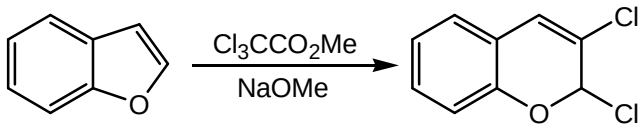
115. Consider the nuclear shape of $^{14}N_7$ and $^{17}O_8$

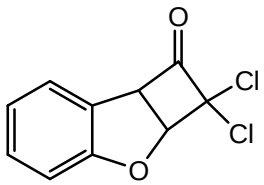
	$^{14}N_7$	$^{17}O_8$
A	Prolate	Oblate
B	Oblate	Spherical
C	Oblate	Prolate
D	Spherical	Oblate

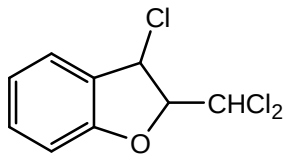
The option giving the correct shape, is

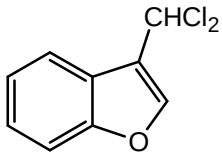
(a) A (b) B (c) C (d) D

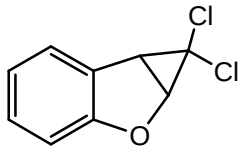
116. The intermediate formed in the following reaction is



(a) 

(b) 

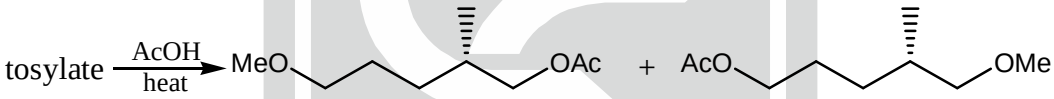
(c) 

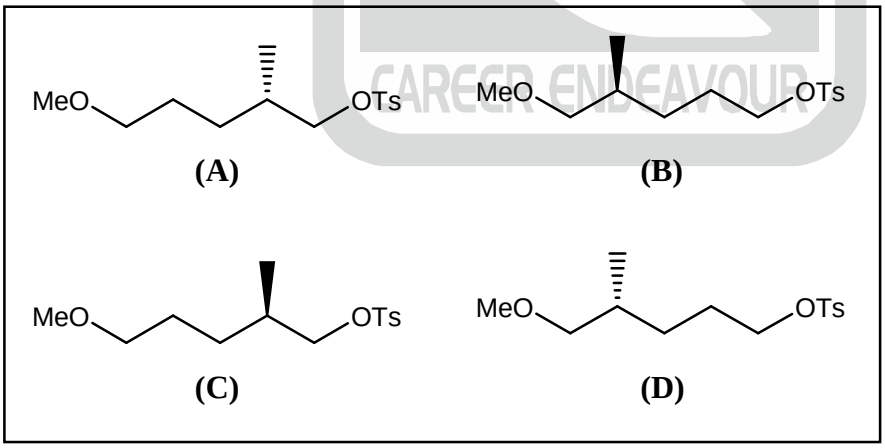
(d) 

117. 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 unit of 10^{-21} J) is closest to [$k_B = 1.38\times10^{-23}$ JK^{-1}]

(a) 1.44 (b) 2.87 (c) 5.74 (d) 11.48

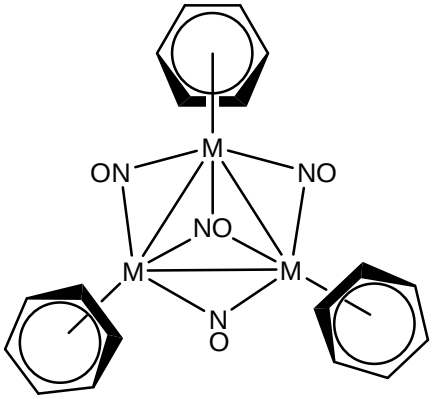
118. The tosylates that on solvolysis will give the mixture of products as shown in the reaction are





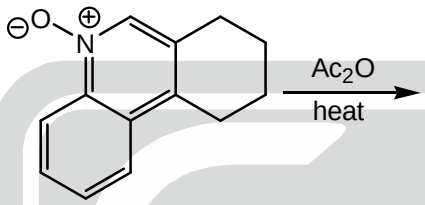
(a) A and C (b) B and D (c) A and B (d) C and D

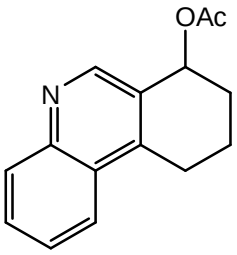
119. The compound shown below is a 48-electron metal cluster (not counting M-M bonds). The metal M is

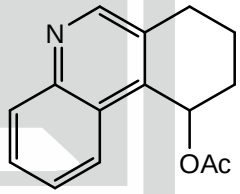


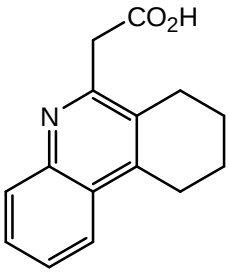
(a) V (b) Fe (c) Mn (d) Cr

120. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d)