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CSIR-UGC-NET - Chemical Science – June - 2023

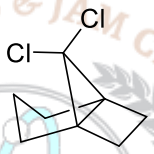
Q.1 – Q.40 Multiple Choice Question (MCQ), carry TWO marks each (for each wrong answer: –0.5). You are required to Answer Maximum 35 Questions.

1. **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**

(a) Y has the highest first ionization energy (b) X has the most number of p-electrons

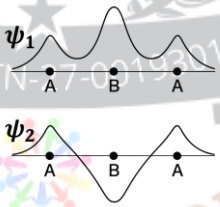
(c) X has the highest proton affinity (d) Z has the highest electronegativity

2. **The number of signals expected for the given compound in ^{1}H and ^{13}C-NMR spectra, respectively, are**



(a) 7 and 8 (b) 6 and 5 (c) 7 and 5 (d) 6 and 8

3. **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 the coefficients are positive)

(a) $\psi_1 = a_1\phi_A + b_1\phi_B + c_1\phi_A \; ; \; \psi_2 = a_2\phi_A - b_2\phi_B - c_2\phi_A$

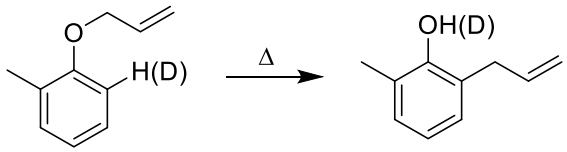
(b) $\psi_1 = a_1\phi_A + b_1\phi_B + a_1\phi_A \; ; \; \psi_2 = a_2\phi_A - b_2\phi_B + a_2\phi_A$

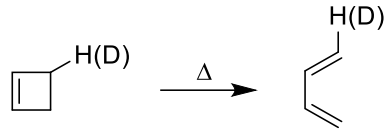
(c) $\psi_1 = a_1\phi_A + b_1\phi_B + c_1\phi_A \; ; \; \psi_2 = a_2\phi_A - b_2\phi_B + c_2\phi_A$

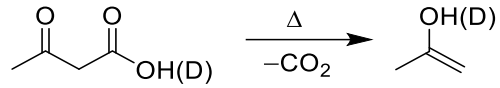
(d) $\psi_1 = a_1\phi_A + b_1\phi_B + a_1\phi_A \; ; \; \psi_2 = -a_2\phi_A - b_2\phi_B - a_2\phi_A$

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

P.



Q. 

R. 

(a) P and Q (b) Q and R (c) Only P (d) Only R

5. **Of the following, the correct statements about carboxypeptidase-A are**

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

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

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

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

(a) P and R only (b) P, R and S only (c) Q and S only (d) P and Q only

6. **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 ℃,**

(a) $\Delta S > 0$ and $\Delta G < 0$ (b) $\Delta S > 0$ and $\Delta G = 0$

(c) $\Delta S = 0$ and $\Delta G = 0$ (d) $\Delta S = 0$ and $\Delta G < 0$

7. **The number of oxygen atoms bonded to each phosphorus centre in P_4O_6 and P_4O_{10} respectively, are**

(a) 4 and 5 (b) 3 and 5 (c) 3 and 4 (d) 5 and 4

8. **The silver salt with the highest solubility product (K_{sp}) in water is**

(a) AgI (b) AgCl (c) AgF (d) AgBr

9. **Among the following, the correct thermodynamic equation of state is**

(a) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial T}{\partial S}\right)_V - P$ (b) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

(c) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial S}\right)_V - P$ (d) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial A}{\partial V}\right)_T - P$

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

(a) 5 and 4 (b) 4 and 4 (c) 4 and 5 (d) 5 and 5

11. **The feature that incorrectly describes an ideal detector in gas chromotography, is**

(a) the adequate sensitivity should be in the range of 10^{-8} to 10^{-15} g solute/s

(b) it has a short response time that is independent of flow rate

(c) it is non-destructive of the sample

(d) there is a linear to a 10-fold change only in the solute concentration

12. **For the radicals, the correct order for the relative rates of addition to $H_2C{=}CHCN$ is**

$CH_3^{\odot}$	$CH_3CH_2^{\odot}$	$c\text{-}C_6H_{11}^{\odot}$
P	**Q**	**R**

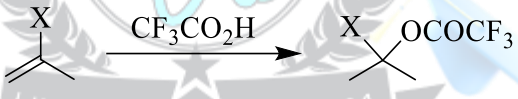
(a) P > R > Q (b) R > Q > P

(c) R > P > Q (d) Q > P > R

13. **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**

(a) 0.01 V (b) 1.56 V (c) 0.04 V (d) 1.53 V

14. **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

(a) F and Cl inductively stabilize the intermediate carbocation

(b) Cl stabilizes the intermediate carbocation better than H

(c) Cl stabilizes the intermediate carbocation better than F

(d) F stabilizes the intermediate carbocation better than H

15. **The pair of complexes/ions that does not obey the 18-electron rule, is**

(a) $[V(CO)_6]$ and $[Ti(Cp)_2Cl_2]$ (b) $[Mn(Br)(CO)_5]$ and $[Mn(CO)_5]^-$

(c) $[Co(CO)_3PPh_3]^-$ and $[Co_4(CO)_{12}]$ (d) $[Fe(CO)_5]$ and $[Fe_2(CO)_9]$

16. **In the fission reaction, $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{96}_{36}Kr + 3^{1}_{0}n$. For the given masses of**

^{235}U = 235.0439 amu n = 1.00867 amu

^{140}Ba = 139.9106 amu 1 amu = 931.494 MeV/c^2

^{93}Kr = 92.9313 amu

the energy released is

(a) 135.0 MeV (b) 200.2 MeV (c) 172.0 MeV (d) 150.0 MeV

17. For a transition metal M, the correct order of ^{13}C-NMR spectral shift [in ppm relative to $Si(CH_3)_4$] for the moieties M-CH_3, M-CO and M-C_6H_5 is

(a) M-CH_3 < M-C_6H_5 < M-CO

(b) M-CO < M-CH_3 < M-C_6H_5

(c) M-C_6H_5 < M-CH_3 < M-CO

(d) M-CO < M-C_6H_5 < M-CH_3

18. If A_xB_y 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

(a) AB_3 (b) AB_2 (c) A_2B (d) A_3B

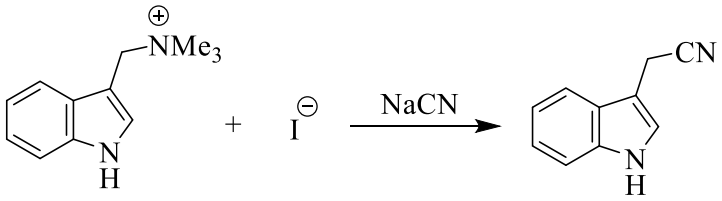
19. Transition state theory was developed to explain the empirical Arrhenius expression for rate constants. For a non-linear transition state with N atoms, the effective number of vibrational degrees of freedom used in calculating its vibrational partition function is

(a) $3N - 6$ (b) $3N - 7$ (c) $3N - 5$ (d) $3N - 8$

20. Consider the following two data sets: $A = \{x_1, x_2, \dots, x_n\}$; $B = \{\lambda x_1, \lambda x_2, \dots, \lambda x_n\}$ 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, $r_B = \frac{\sigma_B}{\langle B \rangle}$ and $r_A = \frac{\sigma_A}{\langle A \rangle}$ are related by

(a) $r_B = r_A$ (b) $r_B = r_A \frac{1}{\lambda}$ (c) $r_B = r_A \lambda$ (d) $r_B = r_A \sqrt{\lambda}$

21. The given reaction involves



(a) nucleophile addition followed by elimination

(b) nucleophilic aromatic substitution

(c) elimination followed by nucleophile addition

(d) bimolecular nucleophilic substitution

22. Given that the pK_{a1} and pK_{a2} values for alanine are 2.34 and 9.68, respectively, its isoelectric point (pI) is

(a) 6.01 (b) 12.02 (c) 7.34 (d) 4.14

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

(a) 4.79 (b) 3.89 (c) 3.59 (d) 4.49

24. **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**

(a) $CaSO_3.3H_2O$ (b) $CaSO_4.CaCO_3$ (c) $CaSO_4.2H_2O$ (d) CaS_2O_4

25. **The two energy levels $(n_x = 1, n_y = 6)$ and $(n_x = 3, n_y = 2)$ of a particle in a two dimensional rectangular box (poential is zero inside, and infinite outside) of sides L_x and L_y are found to be degenerate. If $L_x = 1$ in appropriate units, then L_y is**

(a) 2 (b) 3 (c) 4 (d) 6

26. **Considering nitrogen as a central atom, the structures of $H_3C{-}N{=}C{=}S$ and $H_3Si{-}N{=}C{=}S$ respectively, are**

(a) bent and linear (b) linear and linear (c) bent and bent (d) linear and bent

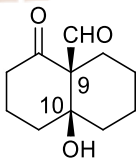
27. **The EI (electron-impact) mass spectrum of $CH_3(CH_2)_2CN$ will show a base peak at m/z value of**

(a) 54 (b) 26 (c) 41 (d) 70

28. **The correct set of possible term for the electronic configuration $1s^2 2s^1 2p^1$ is**

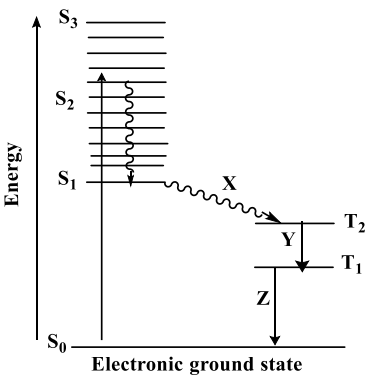
(a) $^1P_1, ^3P_2, ^3P_0, ^3S_0$ (b) $^1P_0, ^3P_2, ^3P_0, ^3P_1$ (c) $^1P_1, ^3P_2, ^3P_0, ^3S_1$ (d) $^1P_1, ^3P_2, ^3P_0, ^3P_1$

29. **The absolute configuration of the stereogenic centres present in the following molecule is**



(a) 9R, 10S (b) 9R, 10R (c) 9S, 10S (d) 9S, 10R

30. **In the Jablonski diagram given Here, 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 X, Y and Z.**



(a) X : Internal conversion
Y : Fluorescence
Z : Phosphorescence

(b) X : Inter system crossing
Y : Phosphorescence
Z : Phosphorescence

(c) X : Internal conversion
Y : Phosphorescence
Z : Phosphorescence

(d) X : Inter system crossing
Y : Fluorescence
Z : Phosphorescence

31. The character table for the point group D_{3h} is given below.

D_{3h}	E	$2C_3(z)$	$3C_2'$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$		
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,

(a) a fundamental transition to an A_1' state is IR active

(b) a fundamental transition to the A_2' state is neither IR active nor Raman active

(c) a fundamental transition to the A_2'' state is Raman active

(d) a fundamental transition to the E'' state is both IR active, as well as Raman active

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

(a) $^6H_{15/2}$ and 5.91 (b) $^6H_{15/2}$ and 10.65 (c) $^6H_{5/2}$ and 6.23 (d) $^6H_{5/2}$ and 5.91

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

P. It has many aspartic acid residues

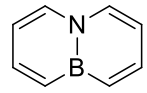
Q. It has many lysine residues

R. It is involved in the hydrolysis of peptide bonds

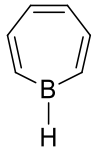
S. It is involved in the degradation of fatty acids

(a) P and R only (b) Q and R only (c) P and S only (d) Q and S only

34. According to Huckel's rule



M

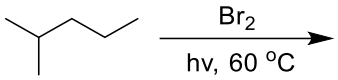


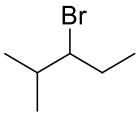
N

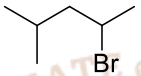
(a) M and N are antiaromatic (b) M and N are aromatic

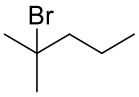
(c) M is aromatic and N is antiaromatic (d) M is antiaromatic and N is aromatic

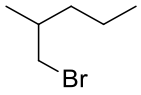
35. **The major product formed in the given reaction is**



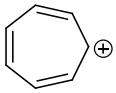
(a) 

(b) 

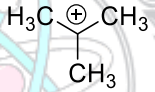
(c) 

(d) 

36. **In the gas phase, the correct order of hydride affinity for the given carbocations is**



P



Q

R

(a) P > R > Q (b) Q > R > P

(c) R > Q > P (d) R > P > Q

37. **Among the following, the NMR inactive nucleus is**

(a) $^{14}N_7$ (b) $^{31}P_{15}$ (c) $^{24}Mg_{12}$ (d) $^{29}Si_{14}$

38. **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**

(a) 1 : 6 (b) 3 : 2 (c) 1 : 3 (d) 4 : 1

39. **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**

(a) 0.25 (b) 0.15 (c) 0.30 (d) 0.20

40. **Of the following statements regarding lanthanoid (III) ions/complexes,**

P. The metal ion interacts weakly with ligand orbitals

Q. A large number of microstates result in large number of transitions

R. The f orbitals are deeply buried

S. They show strong f-f electronic transitions

The correct statements are

(a) P, R and S only (b) Q, R and S only (c) P, Q and R only (d) Q and R only

Q.41 – Q.100 Multiple Choice Question (MCQ), carry FOUR marks each (for each wrong answer: –1). You are required to Answer Maximum 25 Questions.

41. The operator for the square of the angular momentum for an electron in a hydrogenic atom is given below.

$$\hat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

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

(a) $\sin\theta\, e^{2i\phi}$ (b) $\sin\theta\, e^{i\phi}$ (c) $\cos\theta\, e^{i\phi}$ (d) $\cos\theta\, e^{2i\phi}$

42. The given reaction proceeds via

(a) A [1,3]-H shift followed by [4 + 2] cycloaddition

(b) A [1,5]-H shift followed by [4 + 2] cycloaddition

(c) A [3 + 2] cycloaddition followed by hydride shift

(d) A [4 + 2] cycloaddition followed by alkyl shift

43. The tunnelling probability of a particle with energy E incident on a potential barrier of height V_0 and width L is given by the expression

$$T(E) = 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-2kL}$$

Where k is a constant. For a certain particle with $E - \frac{V_0}{2}$, the tunnelling probability was found to be 1.6×10^{-7}. If the width of the potential is halved, then the tunnelling probability will be

(a) 3.2×10^{-7} (b) 8.0×10^{-4} (c) 6.4×10^{-7} (d) 3.2×10^{-3}

44. 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

(a) $nR\Delta S$ (b) $nR\Delta S/PV$ (c) $PV\Delta S/nR$ (d) PV/nR

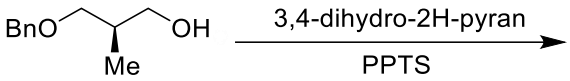
45. A perturbation $\hat{H}' = V_0(3\cos^2\phi - 1)$, where V_0 is a constant, is applied to a rigid rotator undergoing a rotational motion in a plane. The first order energy correction to the ground state is

(a) $2V_0$ (b) $\frac{1}{4}V_0$ (c) $\frac{1}{2}V_0$ (d) V_0

46. The number of unpaired electrons in $[Cp_2Fe]$, $[Cp_2Ni]$ and $[Cp_2Co]$ complexes are, respectively,

(a) 0, 0 and 1 (b) 0, 2 and 1 (c) 0, 1 and 2 (d) 2, 2 and 1

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



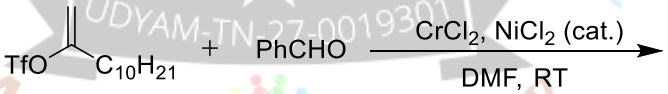
(a) a mixture of diastereomers (b) a mixture of enantiomers

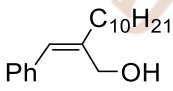
(c) a single enantiomer (d) a single diastereomer

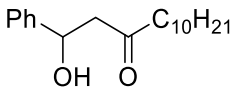
48. Five moles of $[B_9H_{14}]^-$ react with two moles of B_5H_9 at 85 °C resulting in the evolution of nine moles of H_2 and the formation of a monoanionic borane cluster that has a

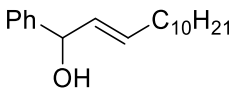
(a) Nido structure (b) Closo structure (c) Arachno structure (d) Hypo structure

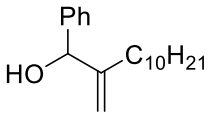
49. The major product formed in the given reaction is



(a) 

(b) 

(c) 

(d) 

50. The set of reagents required to convert ethyl benzoate to ethylbenzene is

(a) [P] MeMgI (excess);
[Q] H_3O^+;
[R] 1,2-ethanedithiol, $BF_3.Et_2O$;
[S] H_2, Raney Ni

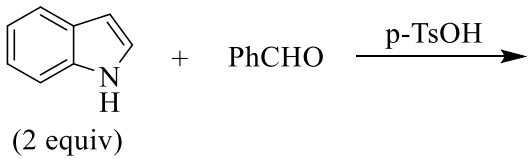
(b) [P] Me_2TiCp_2;
[Q] H_3O^+;
[R] 1,2-ethanediol, $BF_3.Et_2O$;
[S] N_2H_4, H_2O_2

(c) [P] Me_2TiCp_2;
[Q] H_3O^+;
[R] 1,2-ethanedithiol, $BF_3.Et_2O$;

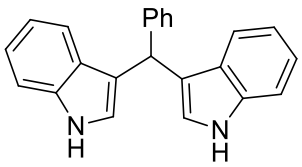
(d) [P] EtMgI (excess);
[Q] H_3O^+;
[R] 1,2-ethanediol, $BF_3.Et_2O$;

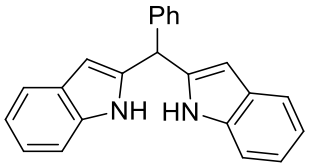
[S] H_2, Raney Ni [S] N_2H_4, H_2O_2

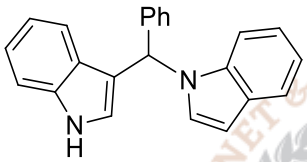
51. The major product formed in the given reaction is

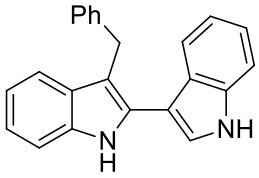


(2 equiv)

(a) 

(b) 

(c) 

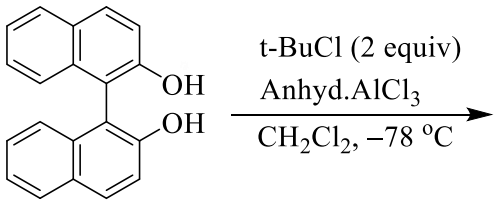
(d) 

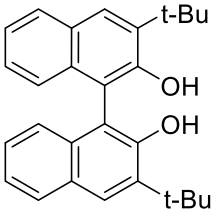
52. Identify P and Q in the following reaction sequence

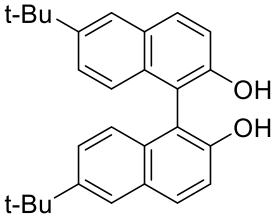
$$[Mn(CO)_5]^- + C_3H_5Cl \longrightarrow \mathbf{P} \xrightarrow{\Delta \text{ or } h\nu} \mathbf{Q}$$

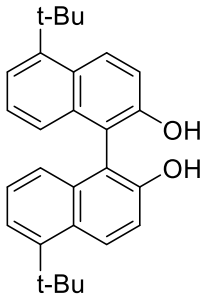
	P		Q
(a)	$[(\eta^1\text{-}C_3H_5)Mn(CO)_4Cl]^-$	and	$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$
(b)	$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$	and	$[(\eta^1\text{-}C_3H_5)Mn(CO)_4Cl]^-$
(c)	$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]_2$	and	$[(\eta^1\text{-}C_3H_5)Mn(CO)_4]_2$
(d)	$[(\eta^1\text{-}C_3H_5)Mn(CO)_5]$	and	$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$

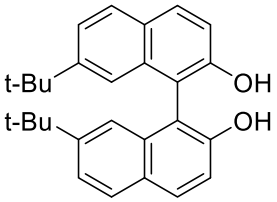
53. The major product formed in the given reaction is



(a) 

(b) 

(c) 

(d) 

54. **Among the assertions**

P. UO_2^+ **is thermodynamically stable in water**

Q. UO_2^{2+} **is a hard acid**

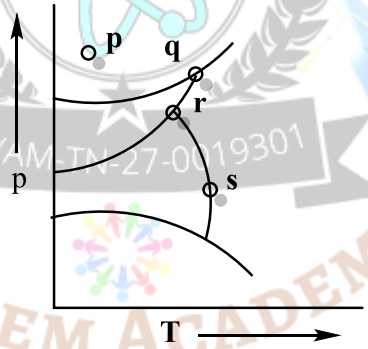
R. The geometry of UO_2^{2+} **is bent**

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

The correct statements for UO_2^{n+} **are**

(a) P and R only (b) Q and S only (c) Q, R and S only (d) P and Q only

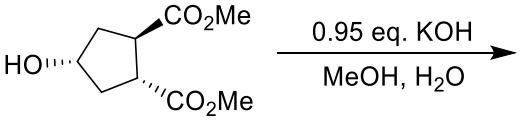
55. **The phase diagram for a one-component system is shown below.**

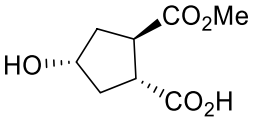


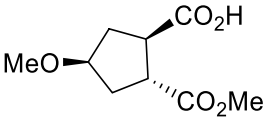
The number of degrees of freedom at the points marked p, q, r and s, respectively, are

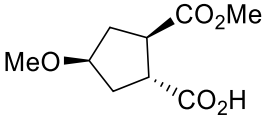
(a) 2, 0, 0, 1 (b) 1, 3, 3, 2 (c) 2, 1, 0, 1 (d) 0, 1, 2, 1

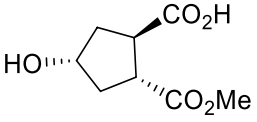
56. **The major product formed in the given reaction is**



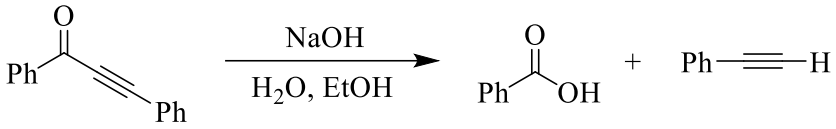
(a) 

(b) 

(c) 

(d) 

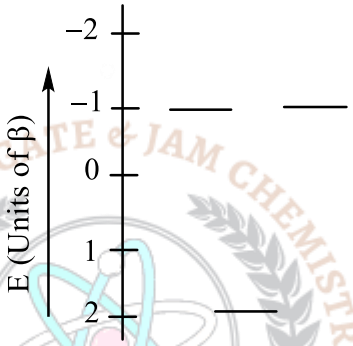
57. **The correct expression for the rate of the given reaction is**



(a) Rate = k[ketone][HO^-] (b) Rate = k[ketone]^2[HO^-]

(c) Rate = k[ketone][HO^-]^2 (d) Rate = k[ketone]

58. **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 is _____

(in units of β, where β is Huckel's constant for interaction energy)

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

59. **The difference between the lowest energy and next higher energy conformers (in kcal mol^{-1}) of meso-2, 3-dibromobutane is**

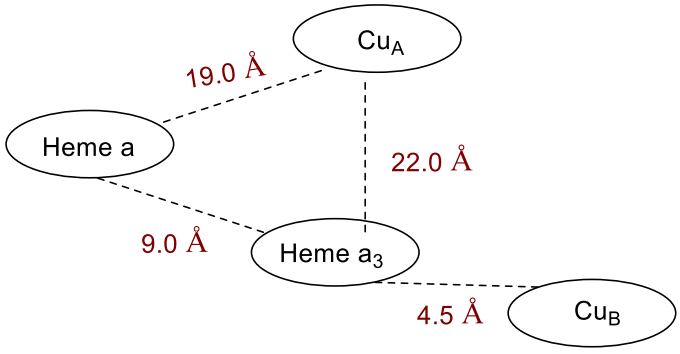
Given: Gauche interactions (kcal mol^{-1}) : Me/Me = 0.90; Me/Br = 0.25; Br/Br = 0.75

(a) 1.40 (b) 1.65 (c) 1.90 (d) 0.50

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

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

61. **For the four active metal centres in cytochrome c oxidase shown below,**



P. Electron transfer involves Heme a and Cu_A while O_2 binding involves Heme a_3 and Cu_B

Q. O_2 only interacts with Cu_B to forms a Cu(II)- O_2^- species with no role for both the hemes

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

S. Cu_B is a monomeric 3-coordinate species while Cu_A is a dicopper species

The correct statements are

(a) P, Q and R only (b) R and S only (c) Q, R and S only (d) P and S only

62. The statement regarding the properties of type-I Blue copper proteins that is true is

(a) The Cu(II) centre is bound to His and Cys amino acids only

(b) In the EPR spectrum, the A_1 value in Blue copper proteins is greater than the A_1 value of free Cu(II) ion

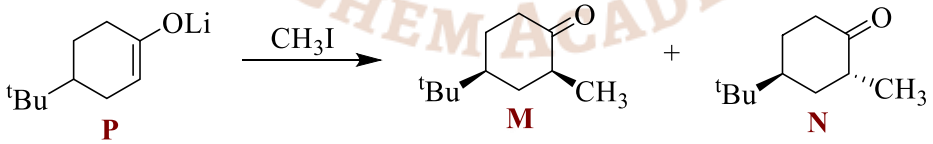
(c) There is an intense absorption band in the electronic spectrum at $\lambda_{max} \approx$ 600 nm and $\varepsilon_{max} \approx$ 100 times greater than the ε_{max} of aqueous Cu(II) ion

(d) It exists as a pair of Cu(II) centres

63. 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

(a) 2813 cm^{-1} (b) 1986 cm^{-1} (c) 827 cm^{-1} (d) 213 cm^{-1}

64. Alkylation of lithium enolate P occurs through a



(a) chair-like transition state and the major product is N

(b) chair-like transition state and the major product is M

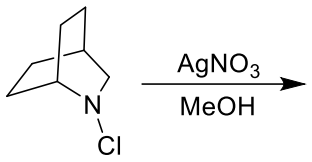
(c) twist boat-like transition state and the major product is M

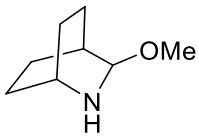
(d) twist boat-like transition state and the major product is N

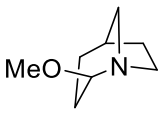
65. Acetone undergoes photodissociation upon absorption of 330 nm light. Exposure of a gaseous sample of acetone to a radiant power of 20 mW at 330 nm for a period of 3 hours results in the photodissociation of 75 µmol of acetone. The quantum yield for the photodissociation, assuming all the light is absorbed, is

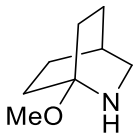
(a) 1.26×10^{-4} (b) 1.26×10^{-1} (c) 1.26×10^{-3} (d) 1.26×10^{-2}

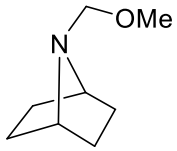
66. **The major product formed in the given reaction is**



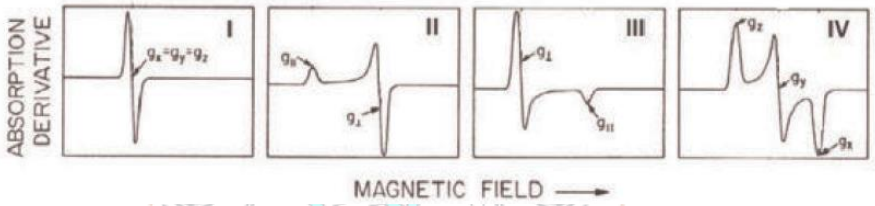
(a) 

(b) 

(c) 

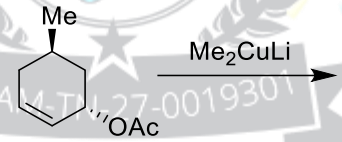
(d) 

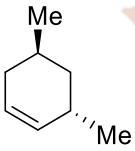
67. **The electron paramagnetic resonance spectrum from among the following, which represents a metal ion with $S = 1/2$ in rhombic symmetry, is**

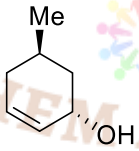


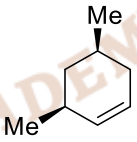
(a) IV (b) III (c) II (d) I

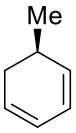
68. **The major product formed in the given reaction is**



(a) 

(b) 

(c) 

(d) 

69. **The vibrational energy for a diatomic molecule is given by,**

$$G(v) = \left(v + \frac{1}{2}\right)\nu_e - \left(v + \frac{1}{2}\right)^2 \nu_e x_e$$

where ν_e is the fundamental frequency and x_e is the anharmonicity constant. The infrared spectrum of BeO molecule in an excited state shows two transitions at $1078.48\ cm^{-1}$ and $1062.42\ cm^{-1}$, identified as transitions between vibrational levels $2 \rightarrow 3$ and $3 \rightarrow 4$, respectively. The ν_e and $\nu_e x_e$ (in cm^{-1}) for BeO molecule in this state, respectively, are

(a) 1126.66 and 8.03 (b) 1030.30 and −8.03

(c) 1174.84 and 16.06 (d) 1078.48 and 8.03

70. **The correct statements concerning $H(CHB_{11}Cl_{11})$, are**

P. Its conjugate base is a non-coordinating anion

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

R. It is a superacid

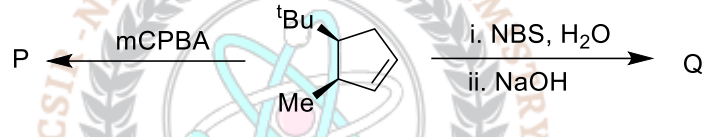
S. It can protonate fullerene and benzene

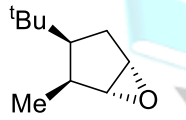
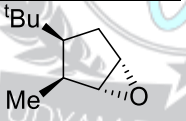
(a) P and R only (b) Q, R and S only (c) P, Q, R and S (d) P, Q and R only

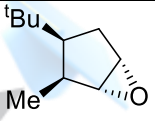
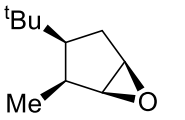
71. The transference number of the hydrogen ion in an aqueous solution containing HCl and NaCl is 0.5. The limiting molar conductivities of H^+, Na^+ and Cl^- are, respectively, $350 \times 10^{-4}\ Sm^2\ mol^{-1}$, $50 \times 10^{-4}\ Sm^2\ mol^{-1}$ and $75 \times 10^{-4}\ Sm^2\ mol^{-1}$. The ratio of the concentrations of HCl and NaCl, namely $\frac{[HCl]}{[NaCl]}$ is

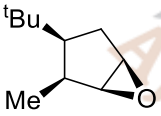
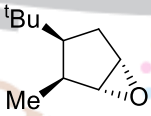
(a) $\frac{10}{11}$ (b) $\frac{11}{5}$ (c) $\frac{5}{11}$ (d) $\frac{11}{10}$

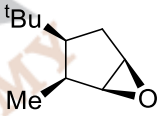
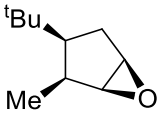
72. The major products P and Q in the given reactions are



(a) P:  ; Q: 

(b) P:  ; Q: 

(c) P:  ; Q: 

(d) P:  ; Q: 

73. The correct statements in the following reaction sequence,

Reaction X

$$Fe(CO)_5 \xrightarrow{H^-} P + CO$$

Reaction Y

$$Fe(CO)_5 \xrightarrow{[OH]^-} P + CO_2$$

$$P \xrightarrow{\text{excess } [OH]^-} Q$$

P. The ν_{CO} in P is lower than ν_{CO} in $Fe(CO)_5$

Q. Reaction Y proceeds via coordinated formyl intermediate

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

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

(a) P, Q and R only (b) Q, R and S only (c) P, R and S (d) P and R only

74. 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

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

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

(c) $P = [Fe(H_2O)_5(NH_3)]^{2+}$;
$Q = [Fe(H_2O)_5(NH_3)]^{3+}$;
$R = [Fe(H_2O)_5(Cl)]^{2+}$

(d) $P = [Fe(H_2O)_5(NH_3)]^{3+}$;
$Q = [Fe(H_2O)_6]^{3+}$;
$R = [Fe(H_2O)_3Cl_3]$

75. Consider the following reaction scheme and the related statements.

$$BrF \xrightarrow{\text{disproportionation}} Br_{2\,(g)} + X\ (\text{T shaped geometry})$$

$$X \xrightarrow{\text{Self ionization}} Y\ (\text{cation}) + Z(\text{anion})$$

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

Q. Y has a bent shape

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

S. X is used as a non-aqueous solvent

The correct statements are

(a) P and Q only (b) P and S only (c) R and S only (d) P, Q and S only

76. A particular sample of polymer has 100 chains with molecular weight 1000, 200 chains with molecular weight 10000 and 200 chains with molecular weight 100000. The polydispersity of the sample is

(a) 1.485 (b) 1.970 (c) 2.068 (d) 3.532

77. 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 $\log\left(\frac{k_1}{k_2}\right)$ in the units of the Debye-Huckel constant, B is

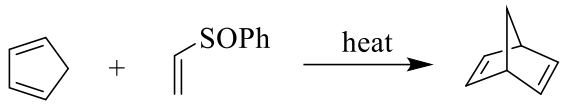
(a) -2 (b) $\frac{4}{3}$ (c) $\frac{16}{9}$ (d) -4

78. A reaction follows the rate law $-\frac{d[A]}{dt} = k[A]^2$. Starting from an initial concentration $[A]_0$, the time taken for the concentration to reduce to $\frac{[A]_0}{4}$, namely the quarter-life

of A, is

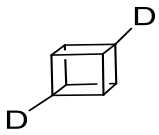
(a) $\frac{\ln k}{2}$ (b) $\frac{1}{k[A]_0}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{3}{k[A]_0}$

79. In the given reaction, $H_2C{=}CHS(O)Ph$ is a synthetic equivalent of



(a) ethyne (b) ethene (c) ethane (d) ketene

80. Sym-cubane-d_2, the structure of which is given below, is a bi-substituted isotopomer of cubane, where two hydrogens are substituted by deuterium. The point group of this molecule is



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

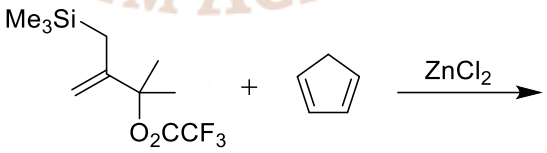
81. The number of cation vacancies per mole, when NaCl is doped with 10^{-3} mol % of BCl_3, is

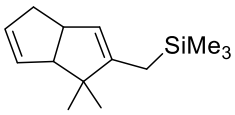
(a) 12.046×10^{23} (b) 12.046×10^{18} (c) 6.023×10^{20} (d) 6.023×10^{18}

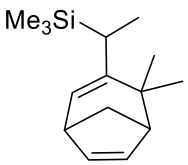
82. A three-state system with energies $E = -\varepsilon_0, 0, +\varepsilon_0$ is in a thermal equilibrium at a temperature T. If $\beta\varepsilon_0 = x$, the probability of finding the system with energy $E = 0$ is [recall, $\cosh x = \frac{1}{2}(e^x + e^{-x})$]

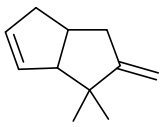
(a) $(2\cosh x)^{-1}$ (b) $\frac{1}{2}\cosh x$ (c) $(1 + 2\cosh x)^{-1}$ (d) $1 + 2\cosh x$

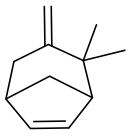
83. The major product formed in the given reaction is



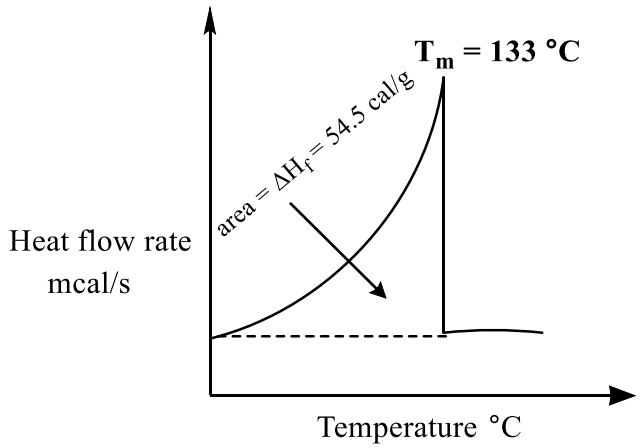
(a) 

(b) 

(c) 

(d) 

84. 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, is



(a) 100% (b) 55% (c) 68% (d) 79%

85. **For the Eu^{3+} ion (Atomic Number: 63),**

P. The calculated and the observed magnetic moments are in agreement with each Other

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

R. The 4f orbital is more than half-filled

S. The ground state term symbol is $^7F_0$

Of the above, the correct statements are

(a) P and S only (b) P and Q only (c) R and S only (d) Q and S only

86. **Consider ammonia to be an ideal gas, with each molecule of ammonia occupying an effective area of $7\ Å^2$ on barium fluoride surface. The adsorption follows the following isotherm.**

$$\frac{z}{(1-z)V} = \frac{1}{cV_m} + \frac{(c-1)z}{cV_m}$$

Where, $z = \frac{p}{p^*}$, c is a constant, and V_m is monolayer capacity (volume of the adsorbed gas) at STP. The plot of $\frac{z}{(1-z)V}$ against z gives the intercept as $4.66 \times 10^{-4}\ cm^{-3}$ and slope as $0.0761\ cm^{-3}$. The surface area of adsorption (in m^2) is close to

(a) 24.5 (b) 2.5 (c) 33.2 (d) 1.9

87. **Consider the cell, $Pt \mid H_2\ (g, p^0) \mid HCl_{(aq)} \mid\mid AgCl_{(s)} \mid Ag$, and the corresponding cell reaction $2AgCl_{(s)} + H_{2(g)} \longrightarrow 2Ag_{(s)} + 2HCl_{(aq)}$ where, p^0 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**

(a) $E = E_0 - \frac{2RT}{F}\ln(\gamma b)$ (b) $E = E_0 - \frac{RT}{F}\ln(\gamma b)$

(c) $E = E_0 - \frac{RT}{2F}\ln(\gamma b)$ (d) $E = E_0 - \frac{RT}{F}\ln(2\gamma b)$

88. **Of the following assertions regarding the mechanism of electron transfer,**

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

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

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

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

The correct statements are

(a) P and S only (b) P, Q and R only (c) Q and R only (d) Q, R and S only

89. **Match the following complexes with their characteristics**

	Complex		d-electron(s)		Total valence electrons
(i)	$[WCl_6]$	(P)	2	(X)	12
(ii)	$[WCl_6]^-$	(Q)	1	(Y)	13
(iii)	$[WCl_6]^{2-}$	(R)	0	(Z)	14

The correct combination is

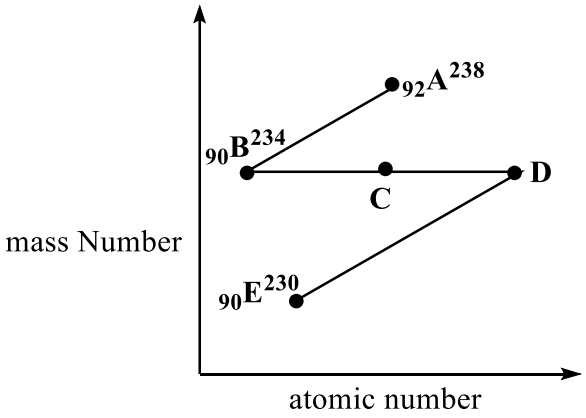
(a) i - R - X ; ii - Q - Y ; iii - P - Z

(b) i - P - X ; ii - Q - Z ; iii - R - Y

(c) i - R - Z ; ii - Q - Y ; iii - P - X

(d) iii - R - X ; ii - Q - Z ; i - P - Y

90. **Statements A-D below pertain to the given decay series,**



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

radionuclide (B)

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

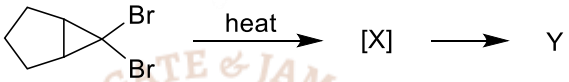
R. The atomic number of the radionuclide (C) is 91

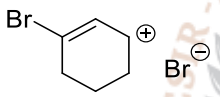
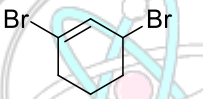
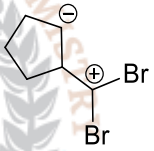
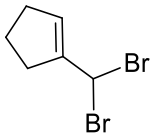
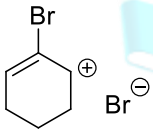
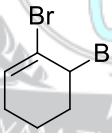
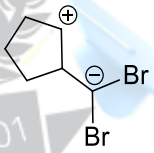
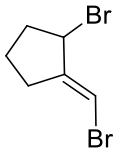
S. The atomic number of the radionuclide (D) is 90

The correct statements are

(a) P and R only (b) Q and S only (c) R and S only (d) P, Q and R only

91. **The intermediate-X and the major product-Y formed in the given reaction, respectively, are**



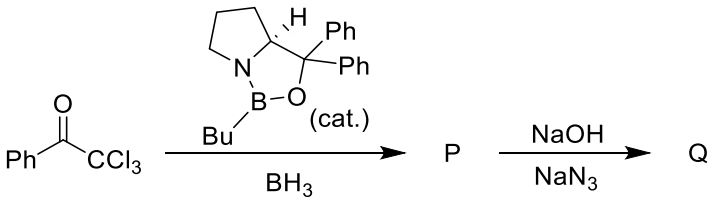
	[X]	Y		[X]	Y
(a)			(b)		
(c)			(d)		

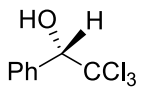
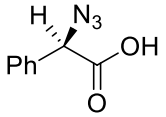
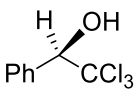
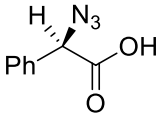
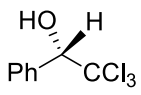
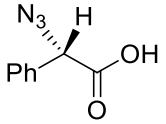
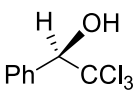
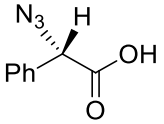
92. **The correct order of second ionization enthalpies, is**

(a) B > C > N > Be (b) N > C > Be > B

(c) B > N > C > Be (d) N > B > C > Be

93. **The major products P and Q formed in the given reaction sequence are**

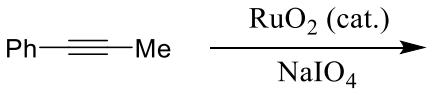


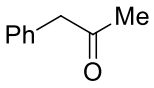
	P	Q		P	Q
(a)			(b)		
(c)			(d)		

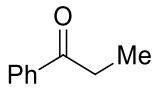
94. For the Hamiltonian operator $\hat{H} = \frac{1}{2m}\hat{p}^2 + \lambda\hat{x}^4$, the best choice among the following trial variational wavefunctions for estimating the ground state energy is

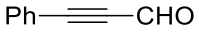
(a) $\frac{1}{x^2+a^2}$ (b) $\frac{a}{x^2}$ (c) $\frac{a}{x}$ (d) $\frac{1}{(x^2+a^2)^2}$

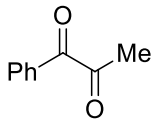
95. The major product formed in the given reaction is



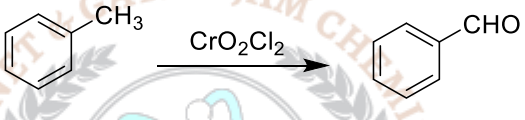
(a) 

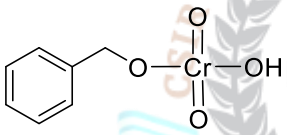
(b) 

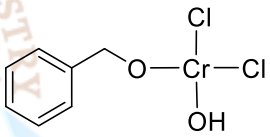
(c) 

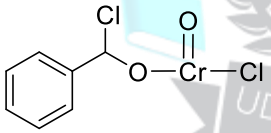
(d) 

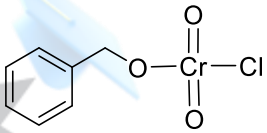
96. The intermediate involved in the given Etard reaction is



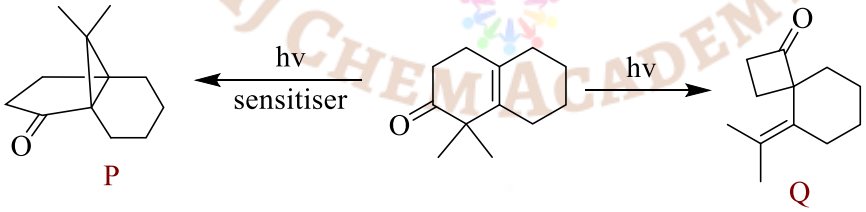
(a) 

(b) 

(c) 

(d) 

97. The mechanisms for the formation of molecules P and Q involve, respectively,



(a) oxa-di-π-methane rearrangement and Norrish type II cleavage

(b) Norrish type I cleavage and oxa-di-π-methane rearrangement

(c) oxa-di-π-methane rearrangement and Norrish type I cleavage

(d) Norrish type I cleavage and Norrish type II cleavage

98. Consider four non-interacting ^4He 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

(a) 4 (b) 12 (c) 2 (d) 1

99. The result of applying the operator $e^{-ia\hat{p}/h}$ on the function $f(x)$ is

(a) $+a\frac{df(x)}{dx}$ (b) $f(x+a)$ (c) $-a\frac{df(x)}{dx}$ (d) $f(x-a)$

100. In the solid state, methyllithium is tetrameric and has a Li_4 core. The correct statement about the structure and bonding in methyllithium is

(a) Each methyl anion is bridging between two Li-centres via 3-center-2-electron bonding

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

(c) It possesses a 2-center-2electron bond

(d) Each methyl anion is terminally bound to each Li-centre

Answer Key

PART - B

Q.No	Ans
1.	d
2.	b
3.	b
4.	d
5.	a
6.	b
7.	c
8.	c
9.	b
10.	b

Q.No	Ans
11.	d
12.	b
13.	d
14.	d
15.	a
16.	c
17.	a
18.	a
19.	b
20.	a

Q.No	Ans
21.	c
22.	a
23.	d
24.	c
25.	a
26.	a
27.	c
28.	d
29.	a
30.	d

Q.No	Ans
31.	b
32.	b
33.	a
34.	b
35.	c
36.	c
37.	c
38.	d
39.	d
40.	c

PART - C

Q.No	Ans
41.	b
42.	b
43.	b

Q.No	Ans
56.	a
57.	c
58.	b

Q.No	Ans
71.	c
72.	b
73.	c

Q.No	Ans
86.	a
87.	a
88.	b

44.	c
45.	c
46.	b
47.	a
48.	a
49.	d
50.	c
51.	a
52.	d
53.	b
54.	b
55.	a

59.	a
60.	a
61.	d
62.	c
63.	c
64.	a
65.	b
66.	b
67.	a
68.	c
69.	a
70.	c

74.	a
75.	d
76.	c
77.	*
78.	d
79.	a
80.	b
81.	b
82.	c
83.	d
84.	d
85.	d

89.	a
90.	d
91.	c
92.	d
93.	d
94.	d
95.	d
96.	b
97.	c
98.	c
99.	d
100.	b