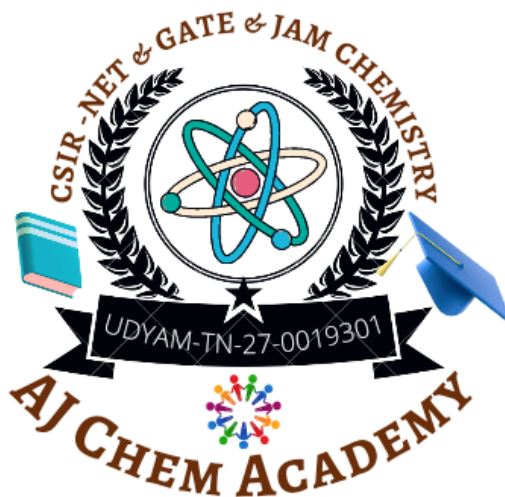


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Q.21 – Q.60 MCQ, carry TWO marks each (for each wrong answer: – 0.5). You are required to Answer Maximum 35 Questions.

21. The **base ionization constant (K_b)** of ammonia in water is 1.8×10^{-5} . The value of **acid ionization constant (K_a)** of the conjugate acid is closest to
 (a) 5.6×10^{-10} (b) 1.8×10^9 (c) 7.0×10^{-7} (d) 5.6×10^4

22. Consider the following statements about **Infrared (IR) spectroscopy**.

P. It is used to determine the band gap, the band structure and the charge carrier concentration of a compound

Q. It is used to identify functional group(s) of a compound

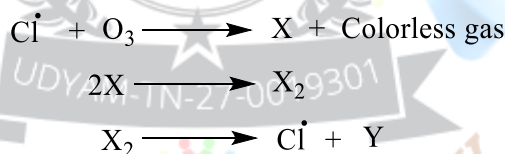
R. It is used to characterize different stretching and bending modes of vibration in molecules

S. Heteronuclear diatomic molecules are IR active

The correct statements are

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

23. In the **stratosphere**, the **Cl radical** produced from chlorofluorocarbons reacts with O_3 as follows



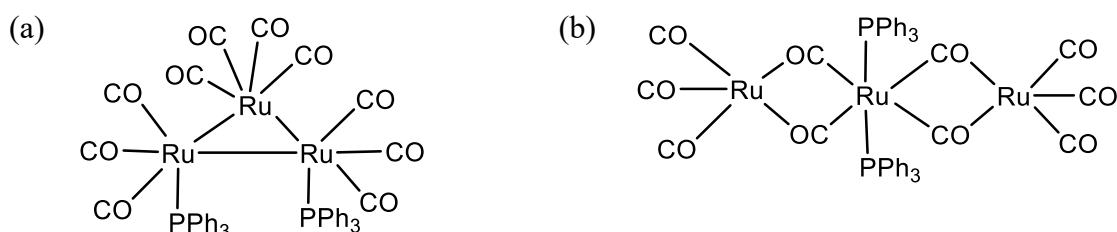
X and Y are respectively,

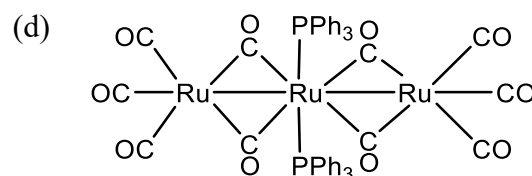
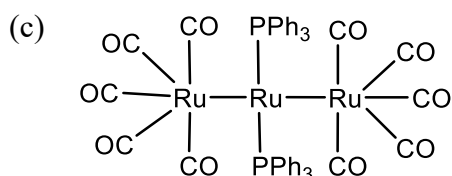
- | X | Y | X | Y |
|-----------------------------|-------------------------------|--------------------------|-------------------------|
| (a) ClO^\bullet | Cl^\bullet
O
O | (b) ClO^\bullet | Cl-O-O^\bullet |
| (c) Cl-O-O^\bullet | O_2 | (d) ClO^\bullet | O_2 |

24. The known **oxidation state(s)** of **Eu** in aqueous solution is/are

- (a) +2 and +3 (b) +3 and +4 (c) +2, +3 and +4 (d) +3 only

25. In the **solid state**, the stable structure of the metal cluster, $[\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ is





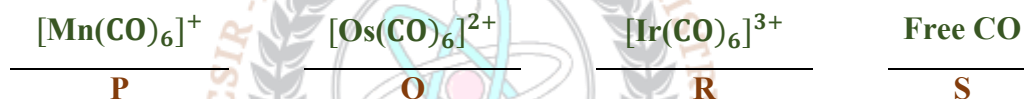
26. The number of moles of **Mg-ATP** needed for the reduction of one mole of nitrogen by **nitrogenase enzyme** is

- (a) 8 (b) 16 (c) 6 (d) 2

27. For the following nuclear decay series segment, $^{234}_{90}\text{Th} \rightarrow \rightarrow \rightarrow ^{230}_{90}\text{Th}$, the overall emitted particles are

- (a) one β , one α and one neutron (b) two β and one α
 (c) three β (d) two β and one neutron

28. What is the order of decreasing carbonyl stretching frequencies in the following species (P-S)?



- (a) $Q > P > R > S$ (b) $S > R > Q > P$ (c) $P > Q > R > S$ (d) $R > Q > S > P$

29. An octahedral d^6 complex has a single spin-allowed absorption band. The spin-only magnetic moment (B.M) and the electronic transition for this complex, respectively, are

- (a) 0 and ${}^1T_{1g} \leftarrow {}^1A_{1g}$ (b) 4.9 and ${}^5T_{2g} \leftarrow {}^5E_g$
 (c) 4.9 and ${}^5E_g \leftarrow {}^5T_{2g}$ (d) 0 and ${}^1T_{2g} \leftarrow {}^1A_{1g}$

30. The geometry around Te in the symmetrical trimeric species of $[\text{TeO}_2\text{F}]^-$ is

- (a) Square planar (b) Tetrahedral (c) Trigonal bipyramidal (d) Octahedral

31. The ${}^1\text{H-NMR}$ spectrum of $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]$ exhibits two peaks of equal intensity at room temperature, but four resonances of relative intensities 5 : 2 : 2 : 1 at lower temperature. The hapticities of C_5H_5^- are

- (a) η^5 and η^1 (b) η^5 and η^3 (c) η^3 and η^1 (d) η^3 and η^3

32. Among the given compounds, the compound with the highest conductivity is

- (a) Si_3N_4 (b) $\alpha\text{-BN}$ (c) AlN (d) $(\text{SN})_x$

33. The ionization energies (IE_1 to IE_5) of 's' and/or 'p' block elements (X, Y and Z) are given below.

IE_1	IE_2	IE_3	IE_4	IE_5
(kJ mol^{-1})	(kJ mol^{-1})	(kJ mol^{-1})	(kJ mol^{-1})	(kJ mol^{-1})

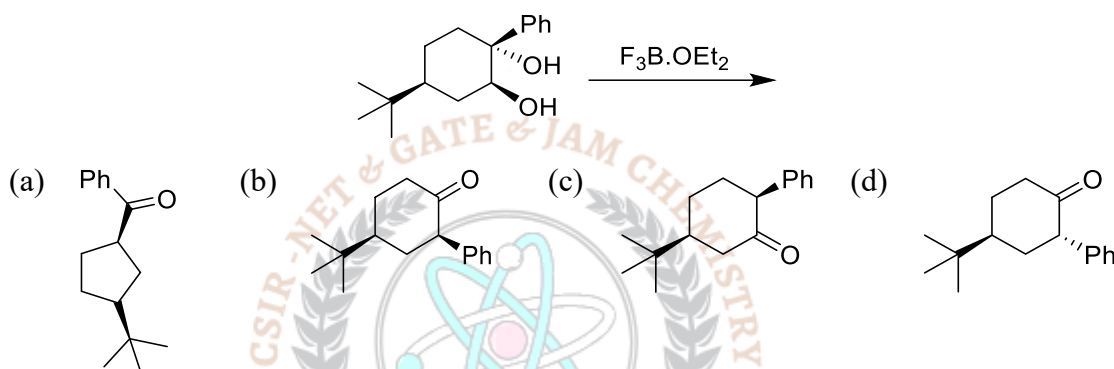


X	1086	2353	4620	6223	37830
Y	800	2427	3060	25030	32830
Z	496	4562	6910	9543	13350

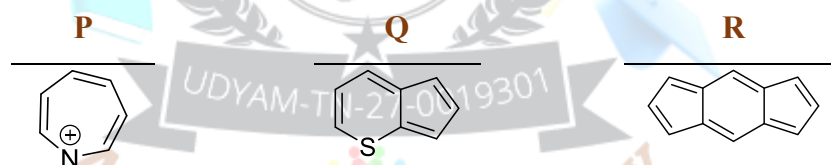
The number of valence electrons in X, Y and Z are

	X	Y	Z		X	Y	Z
(a)	2	3	4	(b)	4	1	1
(c)	4	3	1	(d)	1	3	4

34. The major product formed in the following reaction is

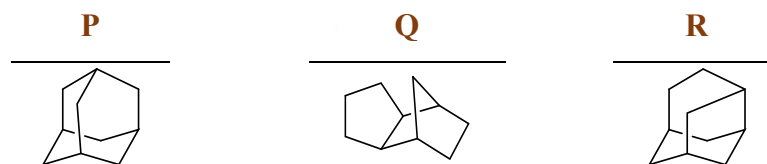


35. Which of the following species is/are aromatic?



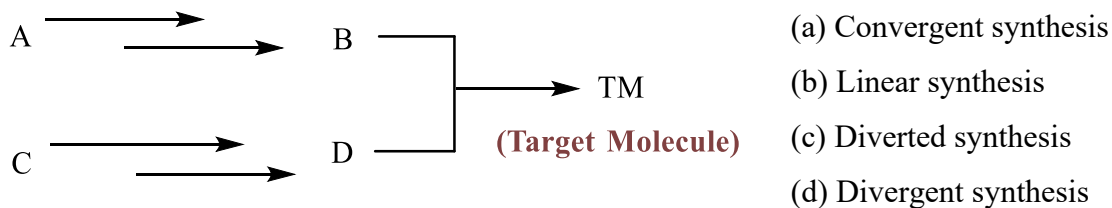
(a) only P (b) only Q (c) only Q and R (d) only P and Q

36. The correct order for the magnitude of heats of formation of the following structural isomers is



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

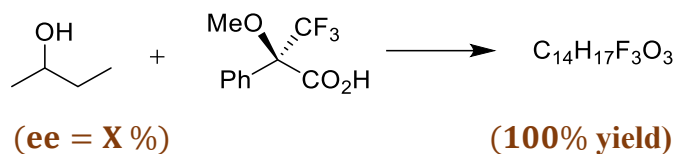
37. The following reaction sequence is an example of



38. The products of the following reaction of a sample of 2-butanol (ee = X %) show

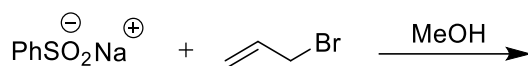


two doublets in $^1\text{H-NMR}$ spectrum in the ratio of **3 : 2**. The value of **X** is _____



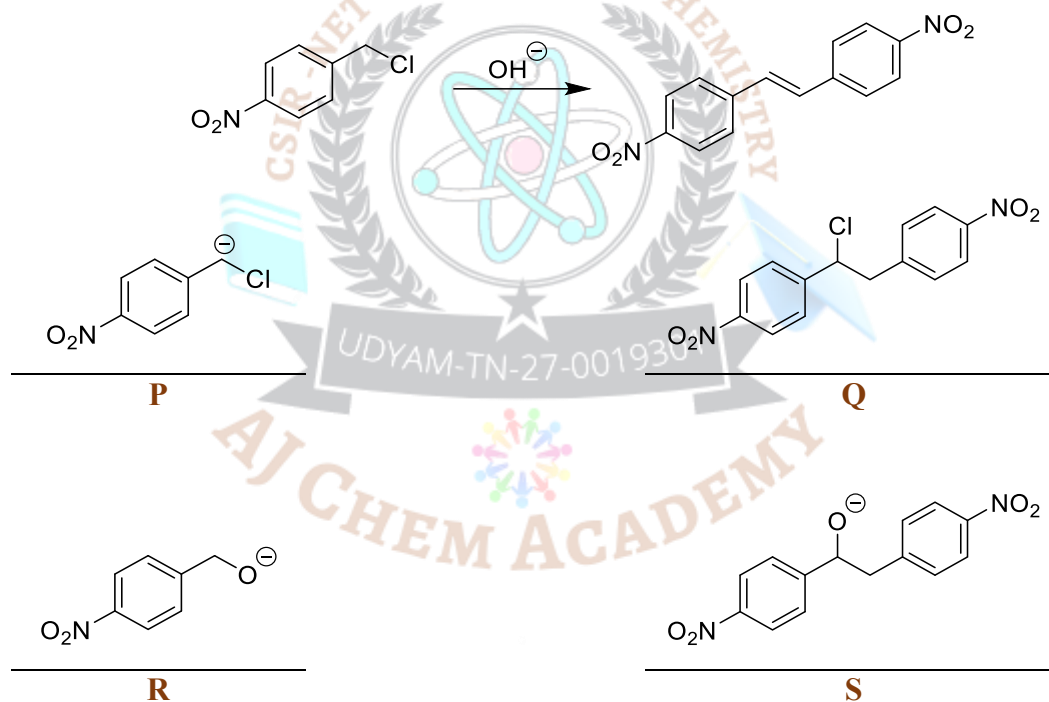
- (a) 40 (b) 60 (c) 20 (d) 80

39. The **major product** formed in the following reaction is



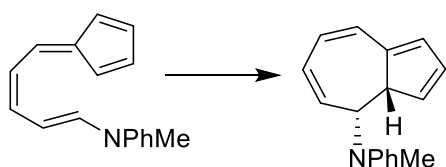
- (a) (b) (c) $\text{H}_2\text{C}=\text{CH}_2$ (d)

40. The **intermediates** involved in the given transformation are



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

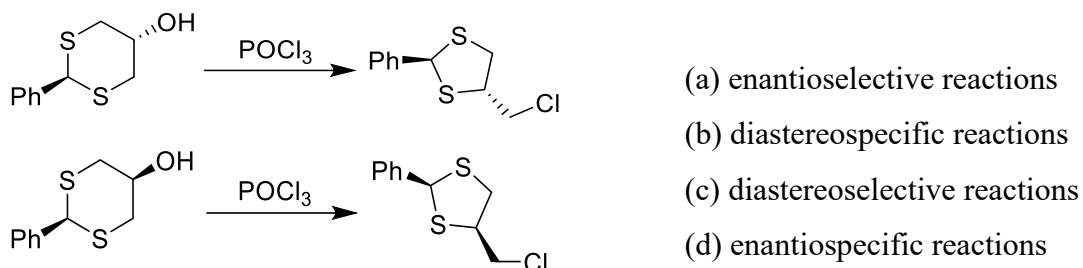
41. The following reaction involves a



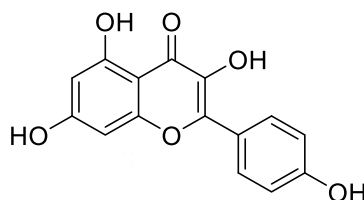
- (a) Photochemical 10π -electrocyclic ring closure
 (b) Thermal 6π -electrocyclic ring closure
 (c) Thermal 10π -electrocyclic ring closure
 (d) Photochemical 6π -electrocyclic ring closure

42. The pair of reactions depicted below are





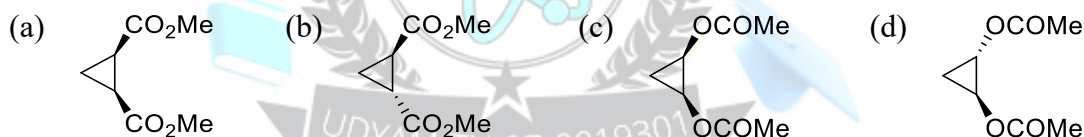
43. **Biosynthetic precursors** of the following natural product are



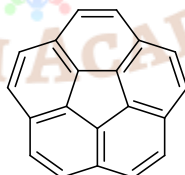
- (a) Q and S (b) Q and R (c) P and S (d) P and R

44. The structure that corresponds to the following $^1\text{H-NMR}$ spectral data is

$^1\text{H NMR}$: 3.64 (s, 6H), 2.02 (dd, 2H), 1.62 (td, 1H), 1.20 (td, 1H)

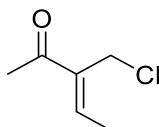


45. The number of signals observed in the proton-decoupled $^{13}\text{C-NMR}$ spectrum of the following compound is



- (a) 4 (b) 2 (c) 3 (d) 5

46. The correct **IUPAC** name of the following compound is



- (a) (E)-3-(chloromethyl)pent-3-en-2-one (b) (Z)-3-(chloromethyl)pent-2-en-4-one
 (c) (E)-3-(chloromethyl)pent-2-en-4-one (d) (Z)-3-(chloromethyl)pent-3-en-2-one

47. In the process of **polyesterification**, the **average length of polymer** formed by a **stepwise process** grows linearly with time. The **fraction condensed (extent of reaction)** and the **degree of polymerization** at time $t = 1.0$ hour, of a polymer



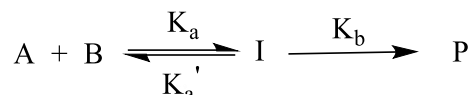
formed with $k_r = 1.80 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and initial monomer concentration of $3.00 \times 10^{-2} \text{ mol dm}^{-3}$, are respectively

- (a) 0.66 and 2.94 (b) 0.33 and 1.50 (c) 0.16 and 1.19 (d) 0.33 and 2.94

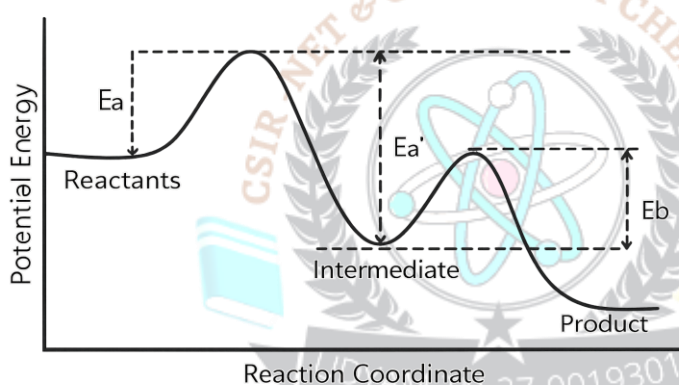
48. For the given zero-order reaction, $A \xrightarrow{k} P$, if the initial concentration of A is $[A]_0$, the time required to consume all the reactant is

- (a) $2[A]_0/k$ (b) $[A]_0/k$ (c) $[A] - [A]_0/k$ (d) $k[A]_0$

49. The effective activation energy for the reaction:

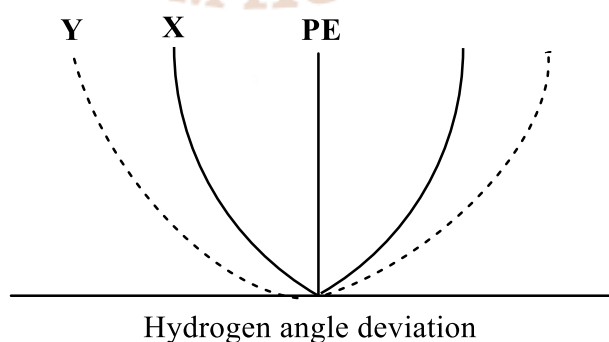


With the following potential energy versus reaction coordinate plot is



- (a) $E_a - E_a' - E_b$
 (b) $E_a + E_b - E_a'$
 (c) $-E_a + E_a' - E_b$
 (d) $E_a + E_a' - E_b$

50. Two schematic potential energy surfaces for bond bending motions are indicated as X and Y in the accompanying diagram.



The out-of-plane C-H wags in iodoform and chloroform would respectively correspond to the potential energy surfaces

- (a) X and Y (b) X and X (c) Y and X (d) Y and Y

51. The limiting molar conductivities, at 25°C , of few ionic compounds are given in the table below. The limiting molar conductivity of AgI, in units of milli-Siemens



(metre)²mol⁻¹, at 25 °C is

Ionic Compound	Molar conductivity (milli-Siemens (metre) ² mol ⁻¹)
NaI	12.69
NaNO ₃	12.16
AgNO ₃	13.34

- (a) 13.87 (b) 12.73 (c) 11.63 (d) 10.78

52. For the formaldehyde molecule (H₂CO) having C_{2v} symmetry with the character table as given below,

C _{2v}	E	C ₂	σ _v (xz)	σ _v (yz)	
A ₁	1	1	1	1	z
A ₂	1	1	-1	-1	R _z
B ₁	1	-1	1	-1	X, R _y
B ₂	1	-1	-1	1	y, R _x

The reducible representation Γ_{3N} (or) Γ_{tot} is Γ_{3N} = 4A₁ + A₂ + 4B₁ + 3B₂. The reducible representation for the vibrational modes alone, namely Γ_{vib} will be

- (a) 4A₁ + 2B₂ (b) 3A₁ + 2B₁ + B₂ (c) 3A₁ + B₁ + 2B₂ (d) 4A₁ + B₁ + B₂

53. Given that the commutator $[\hat{A}^2, \hat{B}] = [\hat{A}, \hat{B}] \hat{A} + \hat{A}[\hat{A}, \hat{B}]$, the value of $[x, [\hat{P}_x^2, x]]$ is

- (a) 2iħ² (b) 2ħ² (c) -2ħ² (d) -2iħ²

54. For a system of two fermionic particles that can be in any one of three possible quantum states each, the ratio of the probability that two particles are in the same state to that when the two particles are in different states is

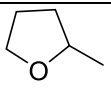
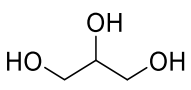
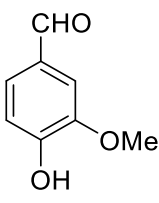
- (a) 1 (b) 1/2 (c) 0 (d) 1/3

55. The energy of an electron in a hydrogenic atom is $-13.6 Z^2/n^2$ eV, where Z is the atomic number and n is the principal quantum number. Neglecting inter-electronic repulsion, the energy of the first excited state of the He atom is

- (a) -68.0 eV (b) -13.6 eV (c) -27.2 eV (d) -108.8 eV

56. The correct match of the following fine chemicals in column-P with their sustainable feedstocks in column-Q is

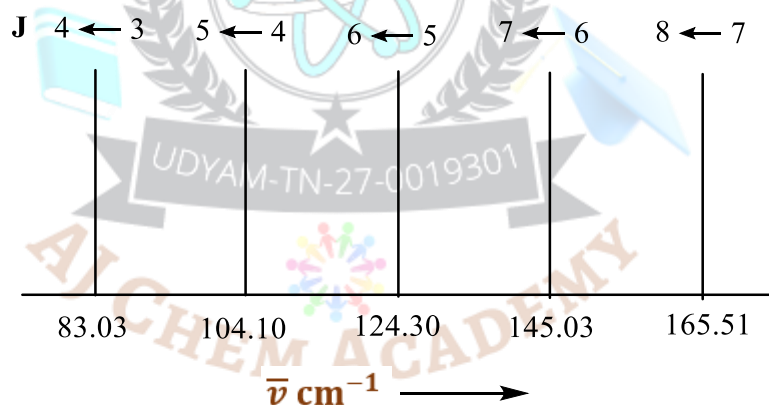
Column-P	Column-Q

X.		I.	Lignin	X	Y	Z
Y.		II.	Xylose	(a)	I ; III ; II	
Z.		III.	Vegetable oil	(b)	II ; III ; I	
				(c)	II ; I ; III	
				(d)	III ; II ; I	

57. The eigen functions of a particle in a cubic box with potential $V = 0$ in the region $0 \leq x \leq L, 0 \leq y \leq L$, and $0 \leq z \leq L$, and $V = \infty$ outside are denoted as $\Psi(n_x, n_y, n_z)$. Which of the following functions is also an eigen function of the Hamiltonian?

- (a) $\phi_1 = \Psi_{123} - \Psi_{312}$ (b) $\phi_2 = \Psi_{111} + \Psi_{222}$
 (c) $\phi_3 = \Psi_{121} - \Psi_{122}$ (d) $\phi_4 = \Psi_{212} + \Psi_{113}$

58. The rotational absorption spectrum of $^1\text{H}^{35}\text{Cl}$ shows the following lines:



Neglecting centrifugal distortion, the value of the rotational constant in units of cm^{-1} is estimated as

- (a) 3 (b) 5 (c) 10 (d) 20
59. During the phase transition, at constant temperature, of a solid from one form to another, the change in molar volume, $\Delta V_m = 1.0 \text{ cm}^3 \text{ mol}^{-1}$ is independent of pressure. The change in molar Gibbs free energy, in units of J mol^{-1} , when the pressure is increased from 1 bar to 3 bars is
- (a) 4×10^{-1} (b) 3×10^{-1} (c) 2×10^{-1} (d) 1×10^{-1}
60. Given that at 298.15 K, $E_{\text{Fe}^{3+}/\text{Fe}}^0 = -0.04\text{V}$; $E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44\text{V}$. At this temperature, the value of $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$ is



- (a) 1.24 V (b) 1.00 V (c) 0.40 V (d) 0.76 V

Q.61 – Q.120 MCQ, carry FOUR marks each (for each wrong answer: -1). You are required to Answer Maximum 25 Questions.

61. A solute S has **partition coefficient** (K_D) of 5.0 between water and chloroform. A 50 ml sample of a 0.050 M aqueous solution of the solute is extracted with 15 ml of chloroform. The **extraction efficiency for the separation** is

- (a) 50 % (b) 60 % (c) 30 % (d) 40 %

62. The nucleophilic substitution of $RR'R''SiX$ ($R, R', R'' = \text{alkyl groups}$) by a nucleophile Y gives the product $RR'R''SiY$. Among the following

P. Silylium cation is formed during the reaction

Q. It is a second order reaction

R. The cleavage of the Si–X bond is not the rate determining step

S. The product always shows inversion of configuration

Identify the correct statements.

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

63. The number of electrons involved in the enzymatic action of **cytochrome c oxidase**, **carbonic anhydrase** and **photosynthetic oxygen evolving complex**, respectively, are

- (a) 2, 0, 4 (b) 4, 0, 4 (c) 4, 1, 0 (d) 2, 0, 2

64. Consider the following molecules/ions



The **Jahn-Teller effect** is expected for

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

65. The number of allowed **EPR lines** expected for a metal ion with 3 unpaired electrons is (Nuclear spin $I = \frac{7}{2}$)

- (a) 8 (b) 32 (c) 36 (d) 24

66. The statement(s) that correctly describe(s) the molecular orbital (MO) diagram of **hydroxyl radical** (OH^\cdot) is/are (consider the O-H bond to be along the x-axis)

P. The Highest Occupied Molecular Orbital (HOMO) is a non-bonded MO that is predominantly formed with $2p_z$ and $2p_y$ atomic orbitals (AOs) of O-atom

Q. The HOMO is a σ -bonded MO that is predominantly formed by the overlap of H(1s) and O(2s) AOs



R. The σ -bonding MO is formed by the overlap of H(1s) and O(2p_z) AOs

S. The σ -bonding MO is formed by the overlap of H(1s) and O(2p_x) AOs

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

67. The correct statement regarding the following physical properties is

- (a) Bond orders follows $\text{Li}_2 < \text{C}_2 < \text{B}_2 < \text{N}_2$ order
 (b) Melting point follows $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$ order
 (c) Pauling electronegativity follows $\text{Al} < \text{Si} < \text{S} < \text{P}$ order
 (d) First ionization energy follows $\text{Li} < \text{B} < \text{Be} < \text{C}$ order

68. The second order rate constants for the outer sphere self-exchange electron transfer reactions for $[\text{Ru}(\text{NH}_3)_6]^{2+}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}/[\text{Co}(\text{NH}_3)_6]^{3+}$ are $9.2 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ and $\leq 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$, respectively.

The correct rationale for the above data is

- (a) The change in the number of σ^* - electrons in Co(II)/Co(III) system
 (b) The change in the number of π^* - electrons in Co(II)/Co(III) system
 (c) The change in the number of both σ^* and π^* - electrons in Co(II)/Co(III) system
 (d) The change in the number of σ^* - electrons in Ru(II)/Ru(III) system

69. Consider the following statements about the oxo-process:

P. The reaction is first order with respect to olefin

Q. The rate is faster for terminal olefins compared to internal olefins

R. The rate is faster for internal olefins compared to terminal olefins

S. Excess of CO inhibits the reaction

The correct statements are

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

70. The electronic spectrum of an aqueous solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ shows three distinct bands:

~400 nm	~690 nm	~1070 nm
P	Q	R

The transitions assigned to P, Q and R, respectively, are

P	Q	R
(a) $T_{1g}(\text{P}) \leftarrow A_{2g}$; $T_{2g} \leftarrow A_{2g}$; $T_{1g} \leftarrow A_{2g}$		
(b) $T_{1g}(\text{P}) \leftarrow A_{2g}$; $T_{1g} \leftarrow A_{2g}$; $T_{2g} \leftarrow A_{2g}$		
(c) $T_{2g} \leftarrow A_{2g}$; $T_{1g} \leftarrow A_{2g}$; $T_{1g}(\text{P}) \leftarrow A_{2g}$		
(d) $T_{1g} \leftarrow A_{2g}$; $T_{2g} \leftarrow A_{2g}$; $T_{1g}(\text{P}) \leftarrow A_{2g}$		



71. Consider the following statements about **nanoparticles**,

P. The energy gap between the valence and conduction bands is greater for semiconductor nanoparticles than that in metal nanoparticles

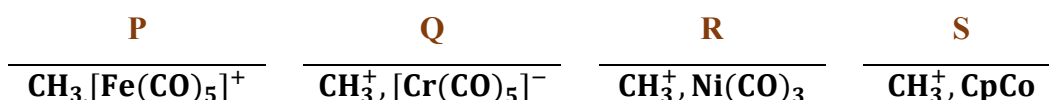
Q. Metal nanoparticles exhibit surface Plasmon resonance

R. Top-down and bottom-up synthetic methods are used to prepare nanoparticles

The correct statements are

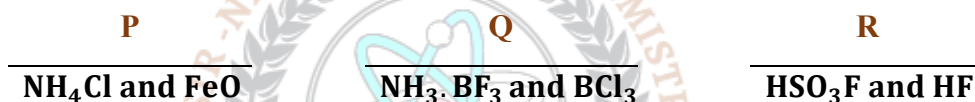
- (a) Q and R only (b) P and Q only (c) P and R only (d) P, Q and R

72. Identify the series showing **isolobal analogy**,



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

73. Consider the following pairs of compounds,



The **more acidic species** in (P), (Q) and (R) are, respectively

- (a) FeO , BCl_3 and HF (b) NH_4Cl , $\text{NH}_3 \cdot \text{BF}_3$ and HF
 (c) FeO , $\text{NH}_3 \cdot \text{BF}_3$ and HSO_3F (d) NH_4Cl , BCl_3 and HSO_3F

74. The calculated **magnetic moment (B.M)** for the ground state of a f^5 ion is

- (a) $\sqrt{35}/7$ (b) $\sqrt{35}$ (c) $\sqrt{35}/14$ (d) $35/14$

75. Consider the statements about the following species, ClF , $[\text{ClF}_2]^+$, ClF_3 , $[\text{ClF}_4]^+$ and ClF_5 . The Correct Statements are

P. There are 9 lone pairs of electrons on the chlorine atoms in the five species

Q. The species $[\text{ClF}_4]^+$ has a tetrahedral shape

R. The compound ClF_3 is a very strong fluorinated agent

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

76. Consider the following statements describing the properties of $(\text{CF}_3)_3\text{B} \cdot \text{CO}$

P. The CO stretching frequency in IR is less than 2143 cm^{-1}

Q. The ^{19}F -NMR spectrum shows one singlet resonance only

R. The point group of $(\text{CF}_3)_3\text{B} \cdot \text{CO}$ is C_{3v}

S. $(\text{CF}_3)_3\text{B} \cdot \text{CO}$ reacts with KF to form $\text{K}[(\text{CF}_3)_3\text{BC}(\text{O})\text{F}]$

The correct statements are

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



77. The reaction of HF with SnO produces X and with SnCl₄ produces Y. Reaction of one of them (X, Y) with NaF yields the species Na₄[Sn₃F₁₀]. Among the following, Identify the correct statements

P. [Sn₃F₁₀]⁴⁻ is obtained from X

Q. In the solid state, X exhibits a ring structure

R. Stereogenic lone pairs of electron are present in both X and Y

S. Y is a weaker lewis acid than X

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

78. In the following electron transfer reaction, the one in which the bridging ligand comes from the reductant is

(a) [IrCl₆]²⁻ + [Cr(OH₂)₆]²⁺ → Products

(b) [Co(NH₃)₅Cl]²⁺ + [Cr(OH₂)₆]²⁺ → Products

(c) [Fe(CN)₆]⁴⁻ + [IrCl₆]²⁻ → Products

(d) [CrO₄]²⁻ + [Fe(CN)₆]⁴⁻ → Products

79. Hydrolysis of the purple isomer of the complex [Co(tren)(NH₃)Cl]²⁺, where [tren = Tris(2-aminoethyl)amine] under basic conditions results in two products. The geometry of the intermediate involved in this reaction is

(a) Trigonal bipyramidal (b) square pyramidal (c) pentagonal planar (d) tetrahedral

80. The reaction of MoCl₂ with [Et₄N]Cl in dil. HCl and EtOH produces a dianionic hexanuclear metal clusters.

P. The cluster is [Mo₆Cl₁₄]²⁻

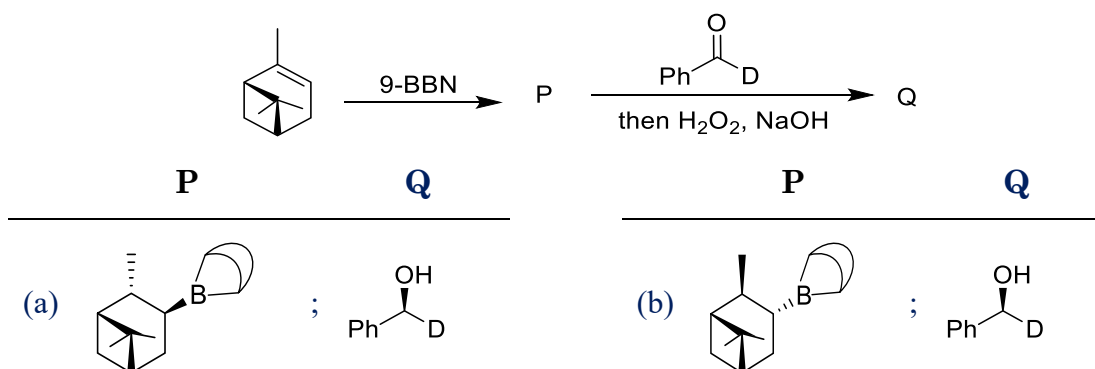
Q. The cluster has 136 valence electrons

R. Each metal centre has 4 metal-metal bonds

Identify the correct statement(s) about the cluster,

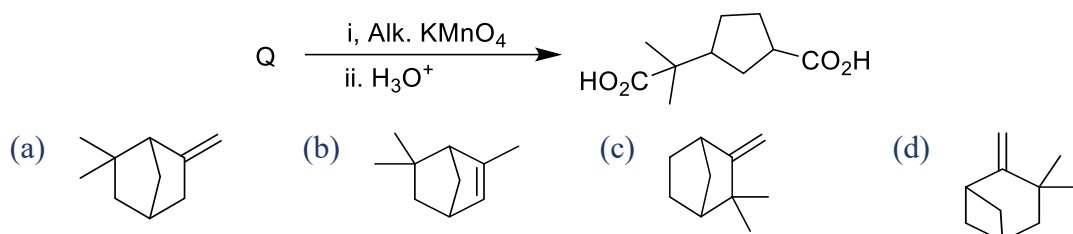
(a) Q only (b) P and R only (c) Q and R only (d) P, Q and R

81. The major products P and Q formed in the following reaction sequence are

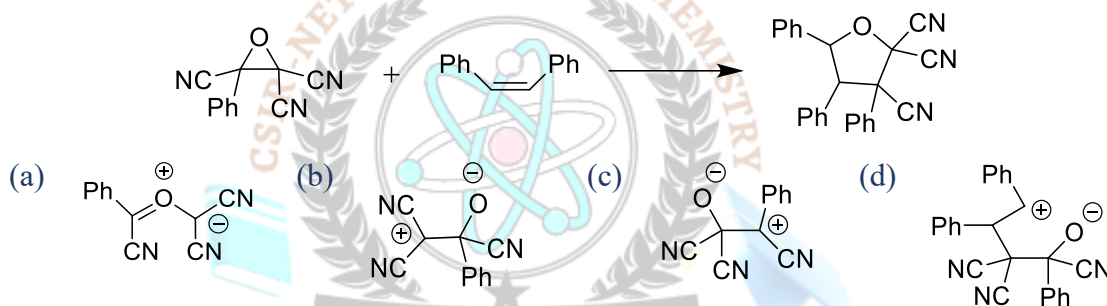




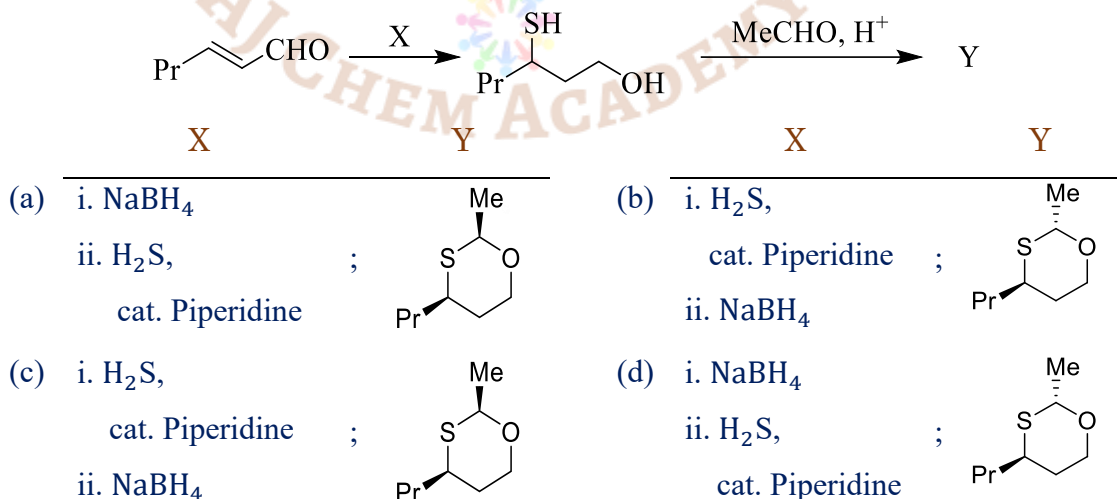
82. Structure of "Q", based on the following reaction, is



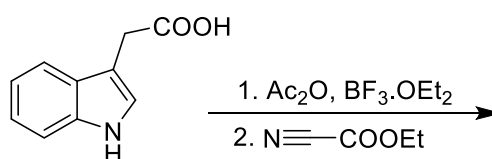
83. Considering the rate law ($\text{rate} = k[\text{epoxide}]$) for the reaction shown below, the plausible intermediate is

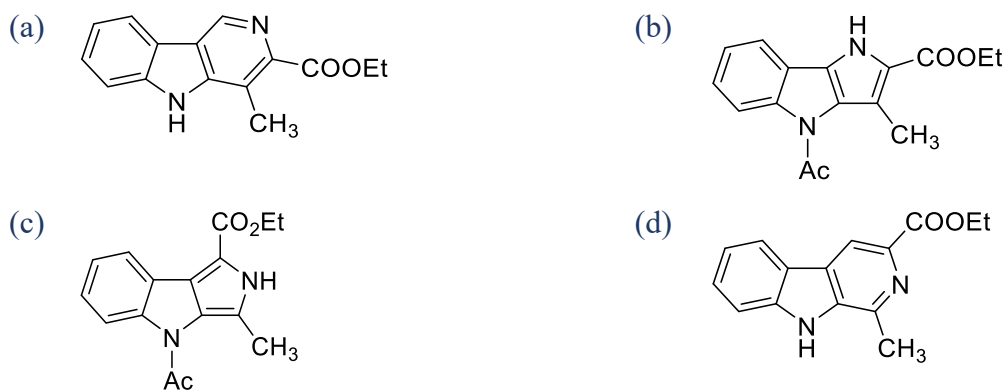


84. The reagents "X" and major product "Y" in the following reaction sequence are

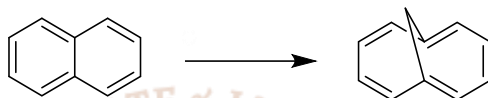


85. The major product formed in the following reaction is





86. The correct sequence of reagents to effect the following transformation is



- (a) i. $\text{CHCl}_3, \text{NaOH}$
 ii. Na/ilq. NH_3
 iii. DDQ
 iv. $\text{Na/ilq. NH}_3, \text{EtOH}$
- (b) i. DDQ
 ii. $\text{Na/ilq. NH}_3, \text{EtOH}$
 iii. $\text{CHCl}_3, \text{NaOH}$
 iv. Na/ilq. NH_3
- (c) i. $\text{Na/ilq. NH}_3, \text{EtOH}$
 ii. DDQ
 iii. $\text{CHCl}_3, \text{NaOH}$
 iv. Na/ilq. NH_3
- (d) i. $\text{Na/ilq. NH}_3, \text{EtOH}$
 ii. $\text{CHCl}_3, \text{NaOH}$
 iii. Na/ilq. NH_3
 iv. DDQ

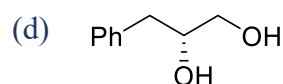
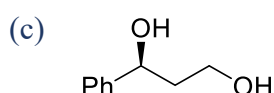
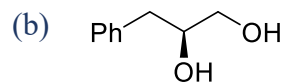
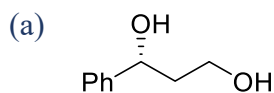
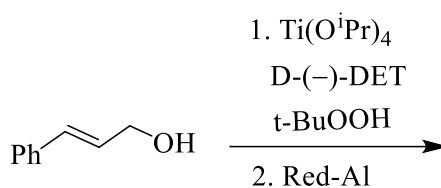
87. The correct match for the molecules given in column P with the spectral data given in column-Q is

	Column-P	Column-Q
X.	Ethyl acetate	I. $^1\text{H-NMR}$: Two singlets
Y.	2-chloropentane	II. EI-MS : M : (M + 2) is 3 : 1
Z.	1,2-dibromomethylpropane	III. IR : 1740 cm^{-1}

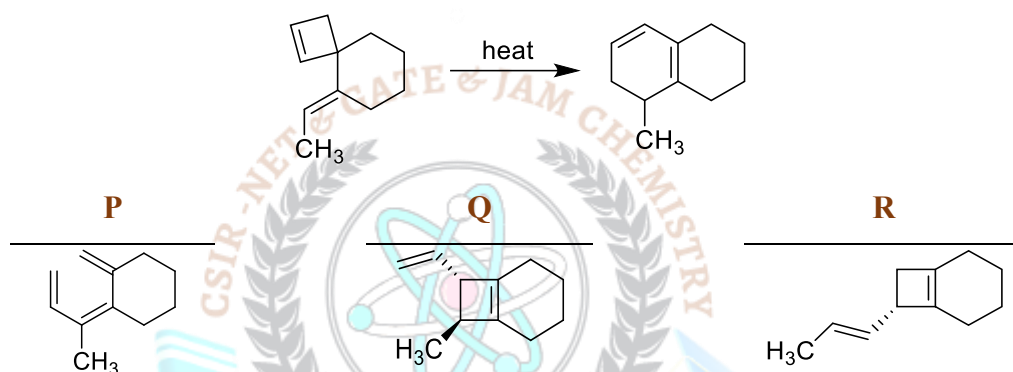
	X	Y	Z
(a)	III	I	II
(b)	I	III	II
(c)	II	III	I
(d)	III	II	I

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





89. **Intermediate(s) involved in the following reaction is (are)**



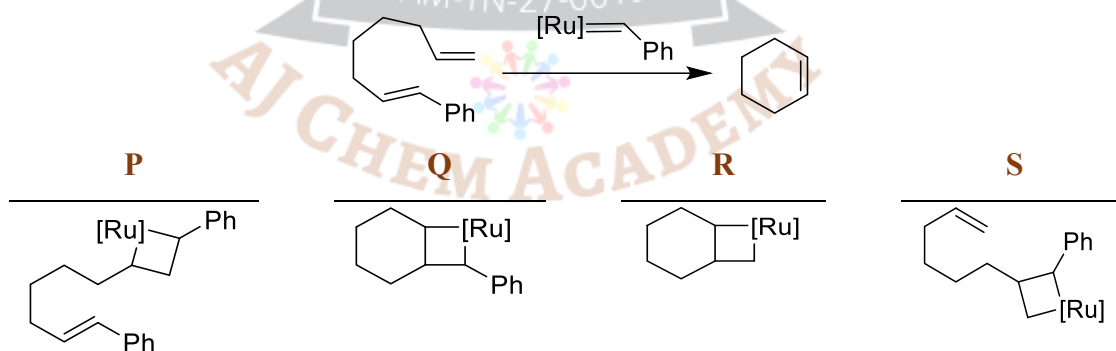
(a) P and R

(b) Q and R

(c) P only

(d) Q only

90. **The intermediates involved in the following reaction are**



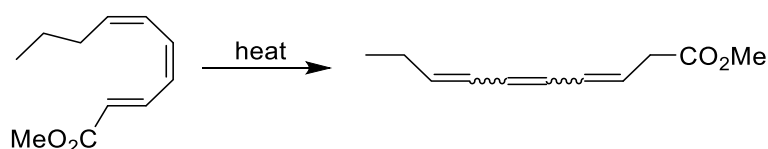
(a) Q and R

(b) Q and S

(c) P and R

(d) P and Q

91. **The stereochemistry of the double bonds in the product is**



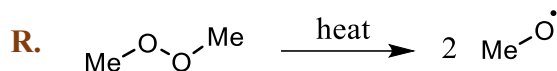
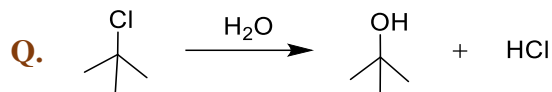
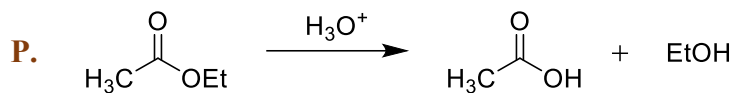
(a) 3E, 5E, 7Z

(b) 3Z, 5E, 7E

(c) 3E, 5Z, 7Z

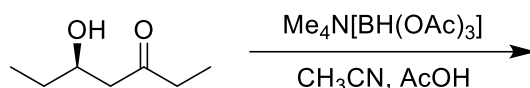
(d) 3Z, 5Z, 7E

92. **The reaction(s) with a positive entropy of activation (ΔS^\ddagger) is (are)**



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

93. The correct statement for the following reaction is

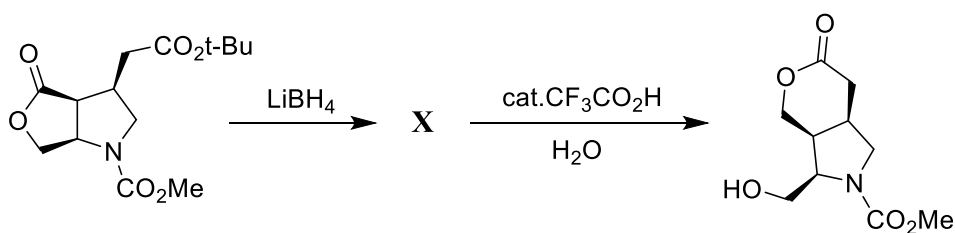


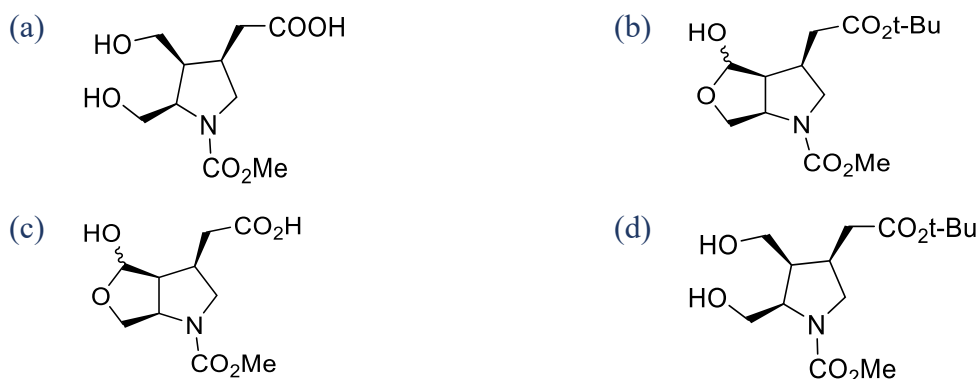
- (a) involves intermolecular hydride transfer and the product is achiral
 (b) involves intramolecular hydride transfer and the product is achiral
 (c) involves intramolecular hydride transfer and the product is chiral
 (d) involves intermolecular hydride transfer and the product is chiral
94. Given below are the bond dissociation energy (BDE; kJ mol^{-1}) values. Based on the data, the correct statement about the following equilibrium is



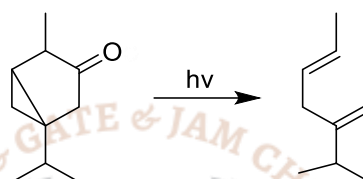
Bond	BDE (kJ mol^{-1})	Bond	BDE (kJ mol^{-1})
O-H	-460	C-C	-360
C-H	-420	C=O	-760
C-O	-380	C=C	-630

- (a) P is more stable than Q by 70 kJ mol^{-1} (b) P is more stable than Q by 130 kJ mol^{-1}
 (c) Q is more stable than P by 70 kJ mol^{-1} (d) Q is more stable than P by 130 kJ mol^{-1}
95. The structure of the compound-X in the following reaction sequence is





96. The following transformation involves



- (a) (i) Norrish type - II ; (ii) fragmentation of a cyclopropyl diradical
 (b) (i) Norrish type - I ; (ii) fragmentation of a cyclopropyl diradical
 (c) (i) Norrish type - I ; (ii) di- π -methane rearrangement
 (d) (i) Norrish type - II ; (ii) di- π -methane rearrangement

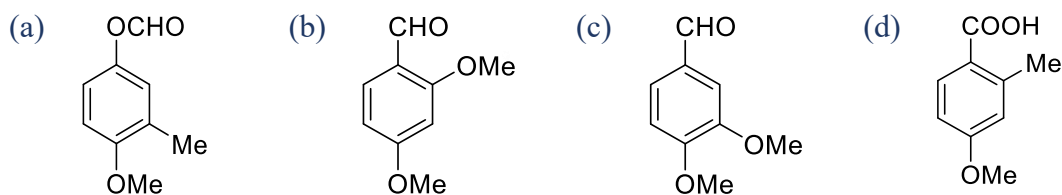
97. The correct structure that corresponds to the spectroscopic data given below is

IR (cm^{-1}) : 2720, 1710

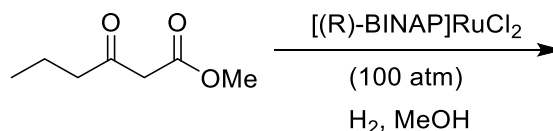
$^1\text{H-NMR}$: 9.80 (s, 1H), 7.50 (dd, $J = 8.0, 2.0$ Hz, 1H),

(δ in ppm) 7.40 (d, $J = 2.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H),

3.90 (s, 3H), 3.80 (s, 3H)

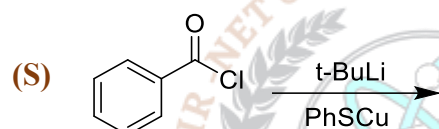
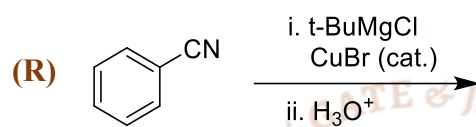
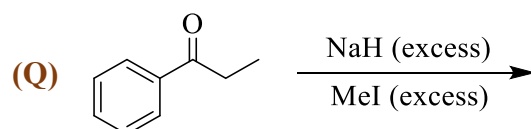
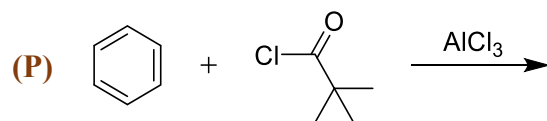


98. The major product formed in the following reaction is



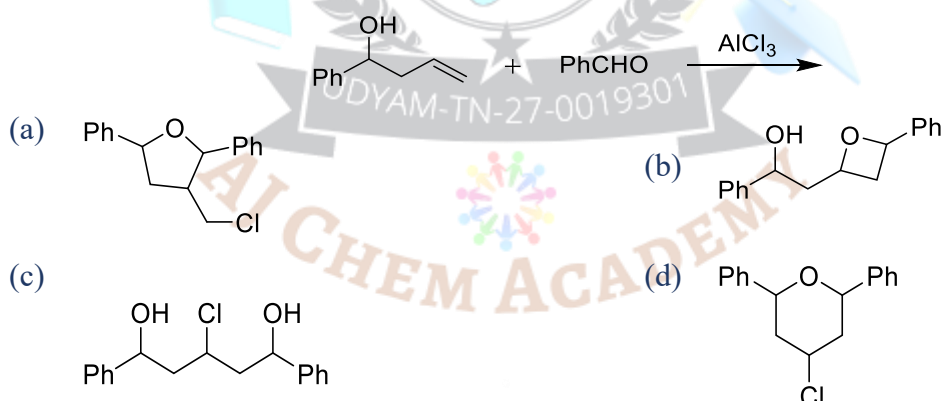


99. The reactions that will furnish **t-BuCOPh** as the major product are

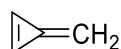


- (a) Only P, Q and R (b) Only Q, R and S (c) Only P and R (d) Only Q and S

100. The major product formed in the following reaction is



101. For the molecule methylenecyclopropene (structure given below), the roots obtained from the Huckel secular determinant can be approximated as $x = -2.0, -0.30, +1.0, +1.5$, where $x = \frac{\alpha-E}{\beta}$, with E being the energy of a π orbital.



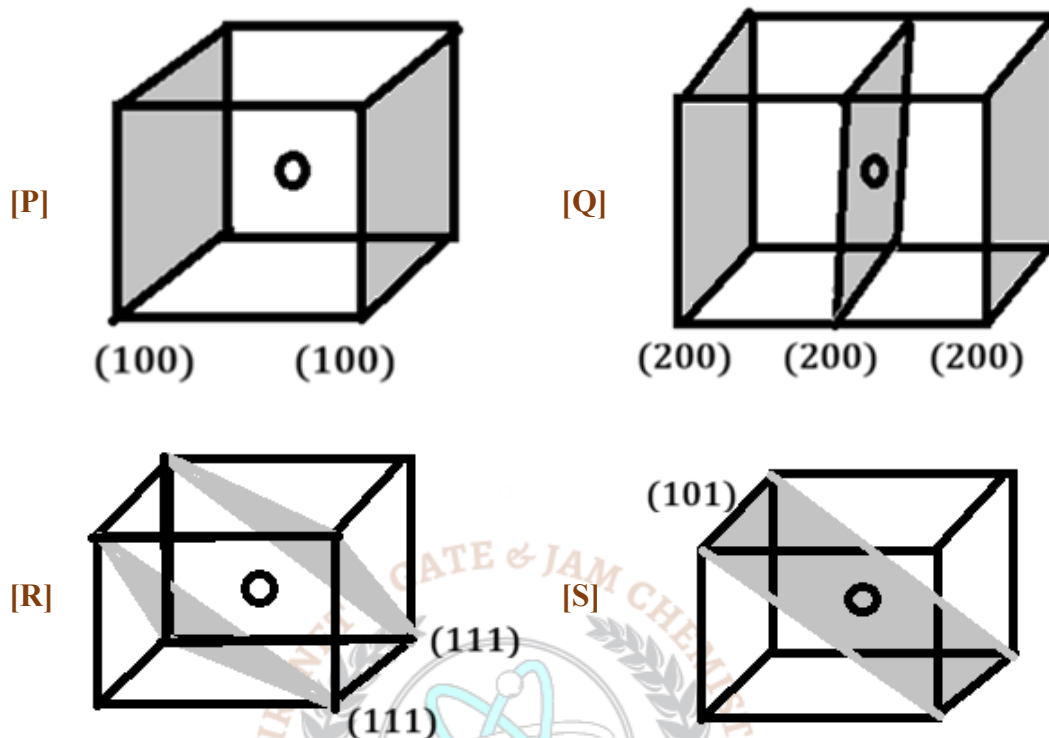
The delocalization energy of methylenecyclopropene is:

(Given the energy of the ground state π orbital of ethylene is $E = \alpha + \beta$)

- (a) $2\alpha + 2.6\beta$ (b) $-(2\alpha + 1.7\beta)$ (c) 0.6β (d) 0.3β

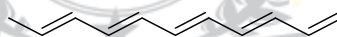
102. The lattice structure of α -Fe (bcc) with some lattice planes are shown in the figure. The planes that will not show X-ray reflections are





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

103. Given below is a conjugated system of 11 carbon atoms



Assume the average C–C bond length to be 1.5 \AA and treat the system as a 1D box. The frequency of radiation required to cause a transition from the ground state of the system to the first excited state (take $\frac{h^2}{8m} = k$) is

- (a) $\frac{13}{225} \frac{k}{h}$ (b) $\frac{11}{225} \frac{k}{h}$ (c) $\frac{9}{225} \frac{k}{h}$ (d) $\frac{7}{225} \frac{k}{h}$

104. For a C-H bond with a stretching frequency 3000 cm^{-1} , what is the expected isotope (deuterium) effect $\frac{K_H}{K_D}$ at 298 K for a full bond homolysis?

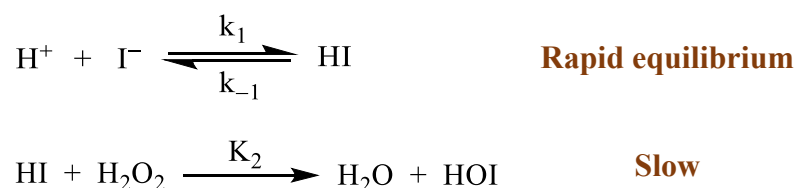
Given $h = 6.63 \times 10^{-34} \text{ Js}$, $c = 3 \times 10^{10} \text{ cm/s}$, $k_B = 1.38 \times 10^{-23} \text{ J/K}$.

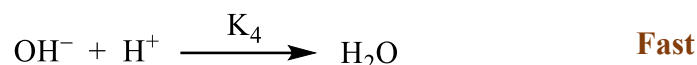
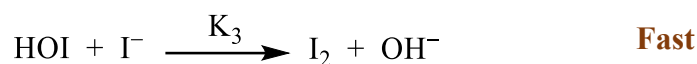
- (a) e (b) 1 (c) e^4 (d) e^2

105. The predicted rate law, using the steady state approximation, for the reaction



Following the possible mechanism is,





- (a) $\frac{k_1 k_2 [\text{H}^+][\text{I}^-][\text{H}_2\text{O}_2]}{K_{-1} + K_2 [\text{H}_2\text{O}_2]}$ (b) $k_2 [\text{HI}][\text{H}_2\text{O}_2]$
 (c) $k_1 K_{-1} k_2 [\text{HI}][\text{H}_2\text{O}_2]$ (d) $\frac{k_2 k_1}{[K_{-1} + K_4]} [\text{H}^+][\text{I}^-][\text{H}_2\text{O}_2]$

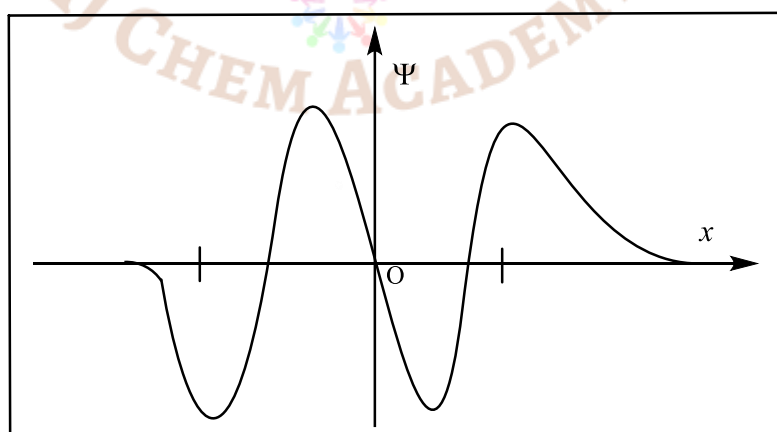
106. What is the cell potential (in V) at 298 K and 1 bar for the following cell?



(given; $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.762\text{V}$, $E_{\text{AgBr}/\text{Ag}}^0 = +0.730\text{V}$, γ_{\pm} of ZnBr_2 solution = 0.462)

- (a) 0.298 (b) 2.198 (c) 0.531 (d) 1.566
107. The state of an electron in a hydrogenic atom is given by the un-normalized wave function, $\phi = \left\{ Y_{10}(\theta, \phi) + \frac{1}{\sqrt{2}} Y_{11}(\theta, \phi) \right\} R(r)$ where $Y_{lm}(\theta, \phi)$ are spherical harmonics and $R(r)$ is the radial function. The probability that a measurements of L_z will give an eigen value of \hbar is
- (a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) $\frac{1}{3}$ (d) $\frac{1}{\sqrt{3}}$
108. For a particle exhibiting simple harmonic motion in 1-dimension, the uncertainty in its position in the state having the following schematic wave function is _____

(zero point energy $E_0 = 1/2\hbar\omega$)



- (a) $\frac{7E_0}{k}$ (b) $\sqrt{\frac{14E_0}{k}}$ (c) $\frac{14E_0}{k}$ (d) $\sqrt{\frac{7E_0}{k}}$
109. Carbonic anhydrase ($2.5 \times 10^{-9} \text{ mol dm}^{-3}$) catalyses hydration of CO_2 in red blood cells at pH 7.1 and 274 K. The rate of the reaction, v (in $\text{mol dm}^{-3}\text{s}^{-1}$) reaches its maximum value when varied with the substrate (S) concentration



(in mmol dm^{-3}) according to the following equation

$$\frac{1}{v} = 4 \left\{ 1 + \frac{10}{[S]_0} \right\}$$

The catalytic efficiency of the enzyme (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) is

- (a) 4×10^5 (b) 10^6 (c) 10^7 (d) 10^4

110. A protein has 3 tyrosine residues and 'n' tryptophan residues both of which are the only amino acids absorbing at 280 nm. If the absorbance of the protein having a concentration of $10 \mu\text{M}$ (in a cuvette of path length 2 cm) is 0.59, the number of tryptophane residues in the protein must be,

$$[\epsilon_{280}(\text{Tyrosine}) = 1500 \text{ M}^{-1} \text{ cm}^{-1}; \epsilon_{280}(\text{Tryptophane}) = 5000 \text{ M}^{-1} \text{ cm}^{-1}]$$

- (a) 11 (b) 5 (c) 2 (d) 7

111. A symmetric top molecule with moments of inertia $I_x = I_y$ and I_z in the body-fixed axes is described by the Hamiltonian $\mathbf{H} = \frac{1}{2I_x} (\mathbf{L}_x^2 + \mathbf{L}_y^2) + \frac{1}{2I_z} \mathbf{L}_z^2$. If $l_x = 1$ & $l_z = \frac{1}{2}$, the eigen values for the levels with quantum numbers $l = 1$, $m_l = 1$, and $l = 1$, $m_l = 0$, are respectively,

- (a) $\frac{3\hbar^2}{2}$ and $-\hbar^2$ (b) \hbar^2 and $-\hbar^2$ (c) $\frac{3\hbar^2}{2}$ and \hbar^2 (d) $-\hbar^2$ and \hbar^2

112. The partition function for a gas is given by,

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} (V - Nb)^N e^{\frac{\beta a N^2}{V}}$$

The internal energy of the gas is

- (a) $\frac{3}{2} Nk_B T + \frac{2aN}{V}$ (b) $\frac{1}{2} Nk_B T - \frac{aN^2}{V}$ (c) $\frac{3}{2} Nk_B T - \frac{aN^2}{V}$ (d) $\frac{3}{2} NRT - \frac{2aN}{V}$

113. 1 mole of $^{16}\text{O}_2$ and 1 mole of $^{18}\text{O}_2$ in two different containers of the same volume have the same entropy. Assuming there are no rotational and vibrational contributions to the entropy, if the temperature of $^{16}\text{O}_2$ is 300 K what is the temperature of $^{18}\text{O}_2$ in K?

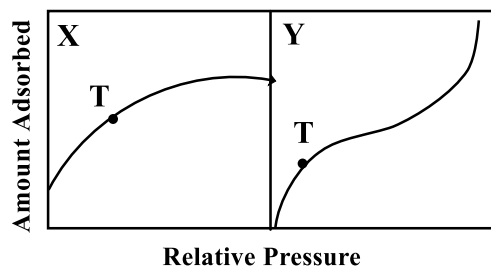
- (a) 37.54 (b) 300.10 (c) 266.66 (d) 273.48

114. The Gibbs free energy of mixing for a regular binary solution of components A and B, at temperature T, on the basis of the Margules equation for activity coefficient, is (in standard notation)

- (a) $nRT (x_A \ln x_A + x_B \ln x_B)$ (b) $nRT (x_A \ln x_A + x_B \ln x_B + \xi x_A x_B)$
 (c) $nRT (x_A \ln \gamma_A + x_B \ln \gamma_B)$ (d) $nRT \xi x_A x_B$



115. Which of the following statements corresponding to the accompanying figures displaying isotherms is/are correct?



- P. Fig X represents an isotherm of type II and point T shows near complete coverage of the surface
- Q. Fig Y represents an isotherm of type II and point T shows near complete coverage of the surface
- R. Fig X represents an isotherm of type I and point T shows near complete coverage of the surface
- S. Fig Y represents an isotherm of type III and point T shows beginning of the multilayer formation
- (a) only statement S is correct (b) statement R and S are correct
(c) statement Q and R are correct (d) statement P and Q are correct
116. The effective rate constants for a gaseous unimolecular reaction: $A \rightarrow P$ following the Lindemann-Hinshelwood mechanism are $1.70 \times 10^{-3} \text{s}^{-1}$ and $2.20 \times 10^{-4} \text{s}^{-1}$ at $[A] = 4.37 \times 10^{-4} \text{mol dm}^{-3}$ and $1.00 \times 10^{-5} \text{mol dm}^{-3}$, respectively. The rate constant for the activation step in the mechanism is approximately equal to (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$).
- (a) 12.3 (b) 49.4 (c) 6.1 (d) 24.7
117. Six distinguishable particles are distributed over 3 non-degenerate levels, of energies 0, ϵ and 2ϵ . The most probable value for the total energy is
- (a) 5ϵ (b) 7ϵ (c) 8ϵ (d) 6ϵ
118. The vibrational energy of the n^{th} state of HCl is approximately given as

$$G(n) = 3000 \left(n + \frac{1}{2} \right) - 50 \left(n + \frac{1}{2} \right)^2 \text{ cm}^{-1}$$

The vibrational quantum number, n_{max} , beyond which HCl undergoes dissociation is

- (a) 29 (b) 59 (c) 119 (d) 19
119. The molecular weight of polyethene determined in five individual experiments is



given below,

Experiment No.	Molecular weight (g/mole)
1	10,000
2	11,000
3	9,000
4	10,500
5	11,500

The standard deviation in the above measurements is closest to

- (a) 850 g/mol (b) 2000 g/mol (c) 1600 g/mol (d) 500 g/mol

120. In the reaction between two ions, the rate constant is k_r when the ionic strength (I) is 0.004. And the rate constant is k_r^0 when the activity coefficient is 1. The ratio $k_r/k_r^0 = 0.884$. If the charge of one ion is +1. The charge of other ion is close to (Debye-Hukel constant = 0.509 at 298 K; $\log 0.884 = -0.05$)

- (a) -1.554 (b) -1.395 (c) -0.777 (d) -0.389

Answer Key

PART - B

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

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

Q.No	Ans
41.	c
42.	b
43.	d
44.	a
45.	c
46.	d
47.	a
48.	b
49.	b
50.	a

Q.No	Ans
51.	a
52.	b
53.	b
54.	c
55.	a
56.	b
57.	a
58.	c
59.	c
60.	d



PART - C

Q.No	Ans
61.	b
62.	a
63.	b
64.	a
65.	d
66.	b
67.	d
68.	a
69.	a
70.	b
71.	d
72.	b
73.	d
74.	a
75.	b

Q.No	Ans
76.	b
77.	a
78.	d
79.	a (or) b
80.	d
81.	b
82.	c
83.	c
84.	c
85.	d
86.	d
87.	d
88.	c
89.	d
90.	d

Q.No	Ans
91.	d
92.	b
93.	c
94.	a
95.	d
96.	b
97.	c
98.	c
99.	b
100.	d
101.	c
102.	b
103.	b
104.	d
105.	a

Q.No	Ans
106.	d
107.	c
108.	d
109.	c
110.	b
111.	c
112.	c
113.	c
114.	b
115.	c
116.	d
117.	d
118.	a
119.	a
120.	c

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