PAPER : CSIR-UGC-NET/JRF JUNE 2022

CHEMICAL SCIENCES

PART-B

21. What is the order of decreasing carbonyl stretching frequencies in the following species (A-D)?

(A) $\left[Mn(CO)_6\right]^{+}$ (B) $\left[Os(CO)_6\right]^{2+}$ (C) $\left[Ir(CO)_6\right]^{3+}$ (D) Free CO

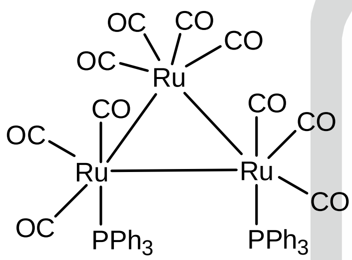
(a) B > A > C > D (b) D > C > B > A (c) A > B > C > D (d) C > B > D > A

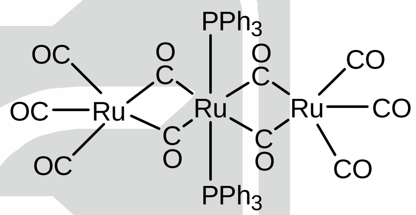
22. An octahedral d^6 complex has a single spin-allowed absorption band. The spin-only magnetic moment (B.M.) and the electronic transition for this complex, respectively, are

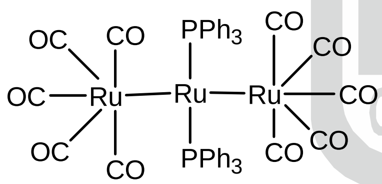
(a) 0 and $^1T_{1g} \leftarrow {}^1A_{1g}$ (b) 4.9 and $^5T_{2g} \leftarrow {}^5E_g$

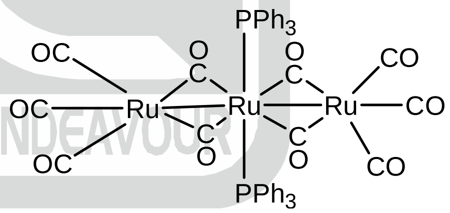
(c) 4.9 and $^5E_g \leftarrow {}^5T_{2g}$ (d) 0 and $^1T_{2g} \leftarrow {}^1A_{1g}$

23. In the solid state, the stable structure of the metal cluster $\left[Ru_3(CO)_{10}(PPh_3)_2\right]$ is

(a) 

(b) 

(c) 

(d) 

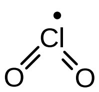
24. In the stratosphere, the radical $Cl^{\bullet}$ produced from chlorofluorocarbons reacts with O_3 as follows.

$$Cl^{\bullet} + O_3 \longrightarrow X + \text{colourless gas}$$

$$2X \longrightarrow X_2$$

$$X_2 \longrightarrow Cl^{\bullet} + Y$$

X, Y are, respectively.

(a) $ClO^{\bullet}$, 

(b) $ClO^{\bullet}$, Cl–O–$\dot{O}$ (c) Cl–O–$\dot{O}$, O_2 (d) $ClO^{\bullet}$, O_2

25. For the following nuclear decay series segment,

$$^{234}_{90}Th \longrightarrow \longrightarrow \longrightarrow {}^{230}_{90}Th$$

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

26. 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

27. Among Si_3N_4, $\alpha-BN$, A*l*N and $(SN)_X$, the compound with the highest conductivity is
(a) Si_3N_4 (b) $\alpha-BN$ (c) A*l*N (d) $(SN)_x$

28. Consider the following statements about Infrared (IR) spectroscopy.
A. It is used to determine the band gap, the band structure and the charge carrier concentration of a compound.
B. It is used to identify functional group(s) of a compound.
C. It is used to characterize different stretching and bending modes of vibration in molecules.
D. Heteronuclear diatomic molecules are IR active.
The correct statements are
(a) A, B, C and D (b) B, C and D only (c) A, B and C only (d) B and C only

29. The geometry around Te in the symmetrical trimeric species of $[TeO_2F]^-$ is
(a) Square planar (b) Tetrahedral
(c) Trigonal bipyramidal (d) Octahedral

30. 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}

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

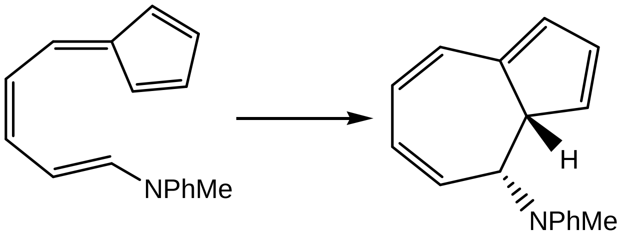
	$IE_1\ (kJ\ mol^{-1})$	$IE_2\ (kJ\ mol^{-1})$	$IE_3\ (kJ\ mol^{-1})$	$IE_4\ (kJmol^{-1})$	$IE_5\ (kJ\ mol^{-1})$
X	1086	2353	4620	6223	37830
Y	800	2427	3060	25030	32830
Z	496	4562	6910	9543	13350

The number of valence electrons in X, Y and Z are
(a) X = 2; Y = 3, Z = 4 (b) X = 4; Y = 1; Z = 1
(c) X = 4; Y = 3; Z = 1 (d) X = 1; Y = 3; Z = 4

32. The ^{1}H-NMR spectrum of $[(C_5H_5)_2Fe(CO)_2]$ 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

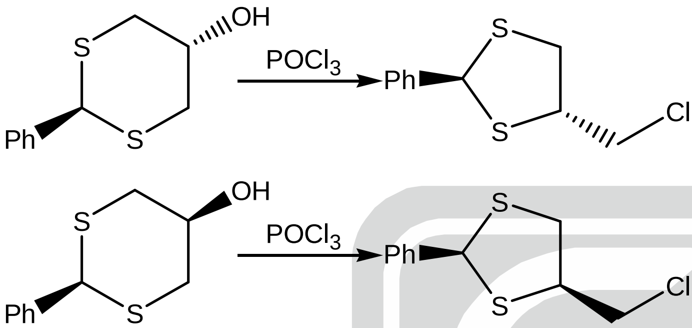
33. The number of moles of Mg-ATP needed for the reduction of one mole of nitrogen by nitrogenase enzyme is
(a) 8 (b) 16 (c) 6 (d) 2

34. The following reaction involves a



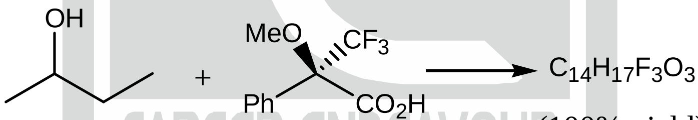
(a) photochemical 10π-electrocyclic ring closure
(b) thermal 6π-electrocyclic ring closure
(c) thermal 10π-electrocyclic ring closure
(d) photochemical 6π-electrocyclic ring closure

35. The pair of reactions depicted below are



(a) enantioselective reactions
(b) diastereospecific reactions
(c) diastereoselective reactions
(d) enantiospecific reactions

36. The products of the following reaction of a sample of 2-butanol (ee = X%) show two doublets in ^{1}H NMR spectrum in the ratio of 3:2. The value of X is ____

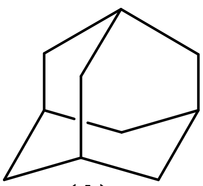


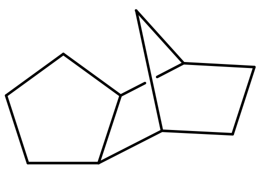
ee = X%

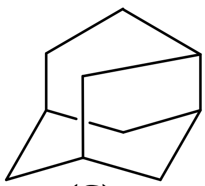
(100% yield)

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

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

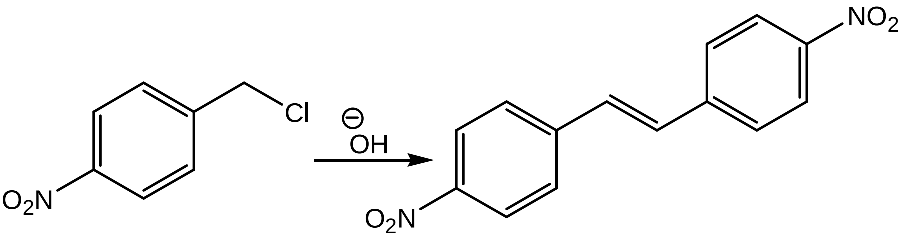

(A)

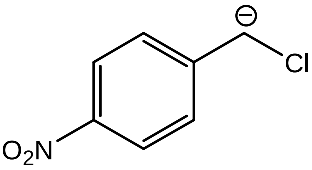

(B)


(C)

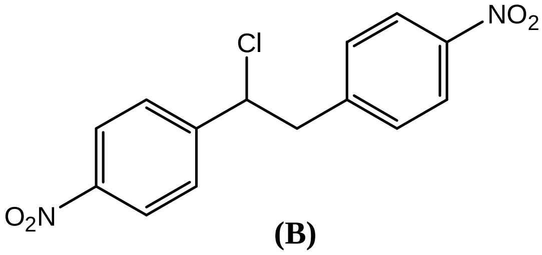
(a) A > B > C (b) B > A > C (b) C > A > B (d) A > C > B

38. The intermediate involved in the given transformation are

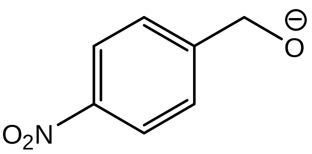




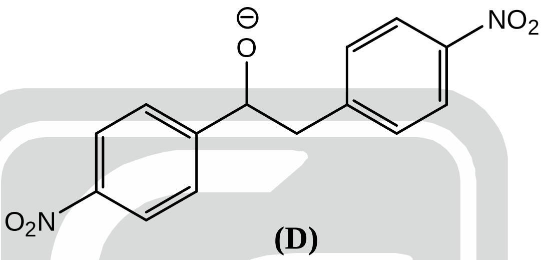
(A)



(B)



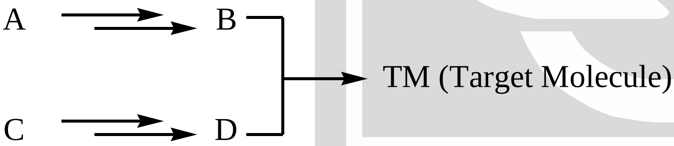
(C)



(D)

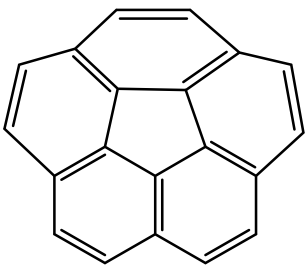
(a) A and D (b) A and B (c) C and D (c) C and B

39. The following reaction sequence is an example of



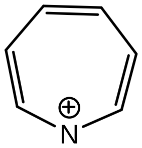
(a) convergent synthesis (b) linear synthesis
(c) diverted synthesis (d) divergent synthesis

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

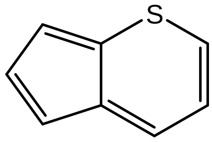


(a) 4 (b) 2 (c) 3 (d) 5

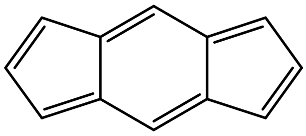
41. Which of the following species is/are aromatic?



(A)



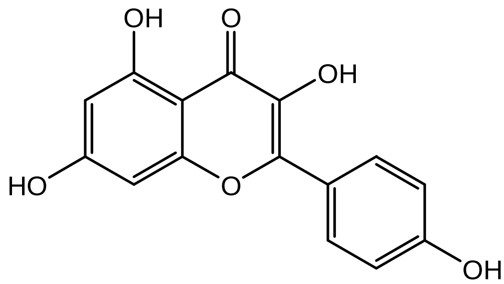
(B)



(C)

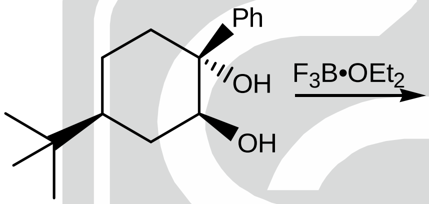
(a) only A (b) only B (c) only B and C (d) only A and B

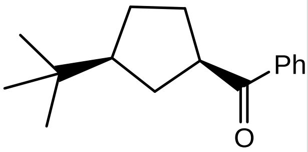
42. Biosynthetic precursors of the following natural product are

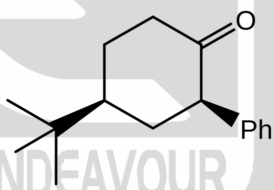


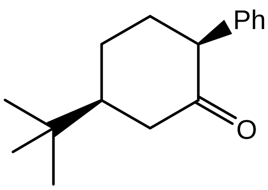
(a) phenylalanine (b) alanine (c) acetyl CoA (d) geranyl CoA

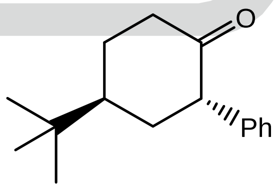
43. The major product formed in the following reaction is



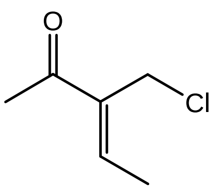
(a) 

(b) 

(c) 

(d) 

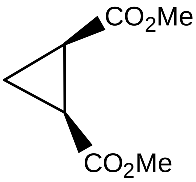
44. The correct IUPAC name of the following compound is

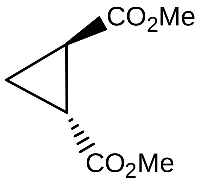


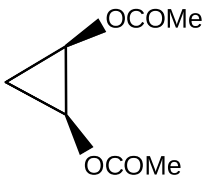
(a) (*E*)-3-(chloromethyl)pent-3-en-2-one
(b) (*Z*)-3-(chloromethyl)pent-2-en-4-one
(c) (*E*)-3-(chloromethyl)pent-2-en-4-one
(d) (*Z*)-3-(chloromethyl)pent-3-en-2-one

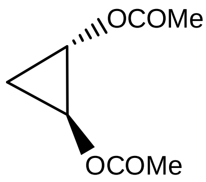
45. The structure that corresponds to the following 1H NMR spectral data is

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

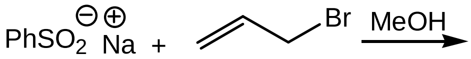
(a) 

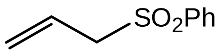
(b) 

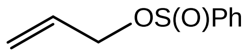
(c) 

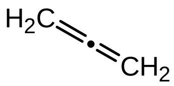
(d) 

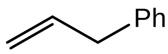
46. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

47. The energy of an electron in a hydrogenetic 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

48. The eigenfunctions of a particle in a cubic box with potential V = 0 in the region $0 \le x \le L, 0 \le y \le L$ and $0 \le z \le L$ and $V = \infty$ outside are denoted as $\psi_{n_x n_y n_z}$. Which of the following is also an eigenfunction 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) $\phi_4 = \psi_{212} + \psi_{113}$

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

(a) $2i\hbar^2$ (b) $2\hbar^2$ (c) $-2\hbar^2$ (d) $-2i\hbar^2$

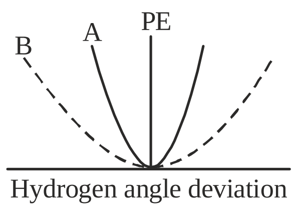
50. For a zero-order reaction $A \xrightarrow{k} P$, if the initial concentration of A is $[A]_0$, the time required to consume all the reactant is

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

51. 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

52. Two schematic potential energy surfaces for bond bending motions are indicated as A and B in the accompanying diagram



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

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

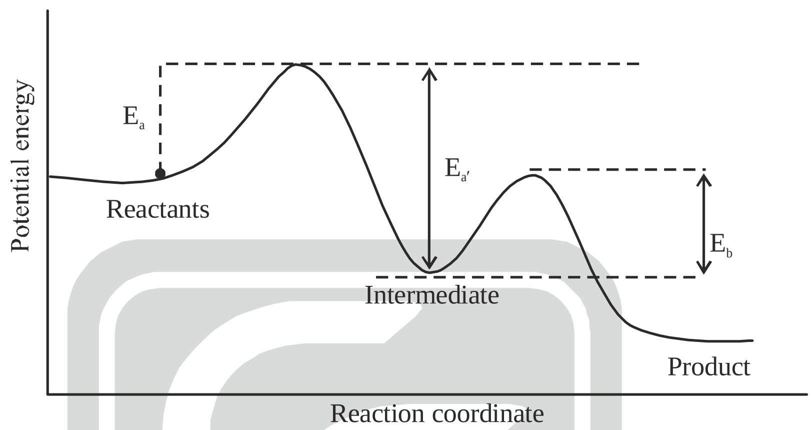
53. During the phase transition, at constant temperature, of a solid from one form to another, the change in molar volume, $\Delta V_m = 1.0\ \text{cm}^3\text{mol}^{-1}$ is independent of pressure. The change in molar Gibbs free energy, in units of J mol^{-1}, when the pressure is increased from 1 bar to 3 bars is

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

54. The effective activation energy for the reaction:

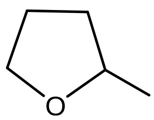
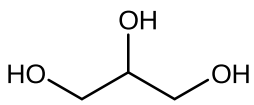
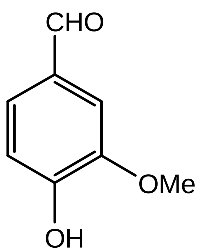
$$A + B \underset{k_{a'}}{\overset{k_a}{\rightleftharpoons}} I \xrightarrow{k_b} P$$

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) $E_a + E_{a'} - E_b$

55. The correct match of the following fine chemicals in **Column P** with their sustainable feedstocks in **Column Q** is

Column-P	**Column-Q**
(A) 	(I) Lignin
(B) 	(II) Xylose
(C) 	(III) Vegetable oil

(a) A-I, B-III, C-II (b) A-II, B-III, C-I (c) A-II, B-I, C-III (d) A-III, B-II, C-I

56. Given that at 298.15 K, $E^0_{Fe^{+3}/Fe} = -0.04V$; $E^0_{Fe^{+2}/Fe} = -0.44V$. At this temperature, the value of $E^0_{Fe^{+3}/Fe^{+2}}$ is

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

57. 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 $k_r = 1.80 \times 10^{-2}$ $dm^3mol^{-1}s^{-1}$ and initial monomer concentration of 3.00×10^{-2} $moldm^{-3}$, are respectively.

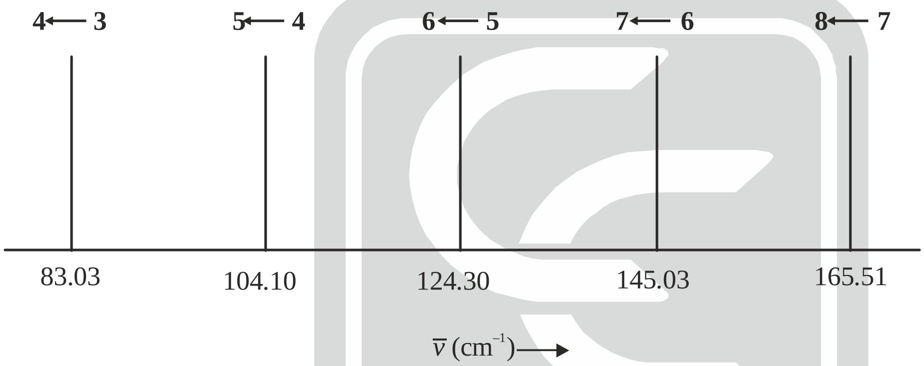
(a) 0.66 and 2.94 (b) 0.33 and 1.50 (c) 0.16 and 1.19 (d) 0.33 and 2.94

58. The limiting molar conductivities, at 25ºC, 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 25ºC is

Ionic Compound	Molar conductivity $\left(\text{milli-Siemens (metre)}^2\text{mol}^{-1}\right)$
NaI	12.69
$NaNO_3$	12.16
$AgNO_3$	13.34

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

59. The rotational absorption spectum of $H^{35}Cl$ 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

60. For the formaldehyde molecule H_2CO having C_{2v} symmetry with the character table as given below,

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

the reducible representation Γ_{3N} (or Γ_{tot}) is $\Gamma_{3N} = 4A_1 + A_2 + 4B_1 + 3B_2$. The reducible representation for the vibrational modes alone, namely Γ_{vib} will be

(a) $4A_1 + 2B_2$ (b) $3A_1 + 2B_1 + B_2$ (c) $3A_1 + B_1 + 2B_2$ (d) $4A_1 + B_1 + B_2$

PART-C

61. Consider the following pairs of compounds.
(i) NH_4Cl and FeO
(ii) $H_3N{\bullet}BF_3$ and BCl_3
(iii) HSO_3F and HF
The more acidic species in (i), (ii) and (iii) are, respectively
(a) FeO, BCl_3 and HF
(b) NH_4Cl, $H_3N{\bullet}BF_3$ and HF
(c) FeO, $H_3N{\bullet}BF_3$ and HSO_3F
(d) NH_4Cl, BCl_3 and HSO_3F

62. Consider the statements about the following species, ClF, $[ClF_2]^+$, ClF_3, $[ClF_4]^+$ and ClF_5.
(A) There are 9 lone pairs of electrons on the chlorine atoms in the five species.
(B) The species $[ClF_4]^+$ has a tetrahedral shape
(C) The compound ClF_3 is a very strong fluorinating agent.
The correct statements are
(a) B and C only
(b) A and C only
(c) A and B only
(d) A, B and C

63. Identify the series showing isolobal analogy.
(A) $CH_3, \left[Fe(CO)_5\right]^+$
(B) $CH_3^+, \left[Cr(CO)_5\right]^-$
(C) $CH_3^+, Ni(CO)_3$
(D) $CH^+, CpCo$
(a) A and B only
(b) A, C and D only
(c) B and C only
(d) A and D only

64. The second order rate constants for the outer sphere self-exchange electron transfer reactions for $\left[Ru(NH_3)_6\right]^{2+}/\left[Ru(NH_3)_6\right]^{3+}$ and $\left[Co(NH_3)_6\right]^{2+}/\left[Co(NH_3)_6\right]^{3+}$ are $9.2\times10^2\ M^{-1}sec^{-1}$ and $\leq 10^{-9}\ M^{-1}\ sec^{-1}$, 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

65. Consider the following molecules/ions
(A) $\left[Mn(H_2O)_6\right]^{3+}$ (B) $\left[Ni(H_2O)_6\right]^{2+}$ (C) VCl_4
The Jahn-Teller effect is expected for
(a) A and C only (b) A only (c) C only (d) A and B only

66. The electronic spectrum of an aqueous solution of $\left[Ni(H_2O)_6\right]^{2+}$ shows three distinct bands:
(A) (~400 nm) (B) (~690 nm) and (C) (~1070 nm)
The transitions assigned to A, B and C, respectively, are
(a) $T_{1g}(P) \leftarrow A_{2g}, T_{2g} \leftarrow A_{2g}$, and $T_{1g} \leftarrow A_{2g}$
(b) $T_{1g}(P) \leftarrow A_{2g}, T_{1g} \leftarrow A_{2g}$, and $T_{2g} \leftarrow A_{2g}$
(c) $T_{2g} \leftarrow A_{2g}, T_{1g} \leftarrow A_{2g}$ and $T_{1g}(P) \leftarrow A_{2g}$

(d) $T_{1g} \leftarrow A_{2g}, T_{2g} \leftarrow A_{2g}$ and $T_{1g}(P) \leftarrow A_{2g}$

67. The statement(s) that correctly describe(s) the molecular orbital (MO) diagram of HO•(hydroxyl radical) is/are (consider the O–H bond to be along the x-axis).
(A) 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.
(B) The HOMO is a σ- bonded MO that is predominantly formed by the overlap of H(1s) and O(2s) AOs.
(C) The σ- bonding MO is formed by the overlap of H(1s) and $O(2p_z)$ AOs.
(D) The σ- bonding MO is formed by the overlap of H(1s) and $O(2p_x)$ AOs.
(a) A and C only (b) A and D only (c) B only (d) D only

68. A solute S has partition coefficient (*KD*) 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%

69. Consider the following statements about nanoparticles.
A. The energy gap between the valence and conduction bands is greater for semiconductor nanoparticles than that in metal nanoparticles.
B. Metal nanoparticles exhibit surface plasmon resonance.
C. Top-down and bottom-up synthetic methods are used to prepare nanoparticles.
The correct statements are
(a) B and C only (b) A and B only (c) A and C only (d) A, B and C

70. Hydrolysis of the purple isomer of the complex $[Co(tren)(NH_3)Cl]^{2+}$ [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

71. 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

72. 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) $35/14$

73. Consider the following statements describing the properties of $(CF_3)_3B{\bullet}CO$.
(A) The CO stretching frequency in IR is less than 2143 cm^{-1}.
(B) The ^{19}F NMR spectrum shows one singlet resonance only
(C) The point group of $(CF_3)_3B{\bullet}CO$ is C_{3v}.
(D) $(CF_3)_3B{\bullet}CO$ reacts with KF to form $K[(CF_3)_3BC(O)F]$
The correct statements are
(a) A, C and D only (b) C and D only (c) A, B and C only (d) A and D only

74. The reaction of HF with SnO produces **P** and with $SnCl_4$ produces **Q**. Reaction of one of them (**P, Q**) with NaF yields the species $Na_4[Sn_3F_{10}]$. Among the following
(A) $[Sn_3F_{10}]^{4-}$ is obtained from **P**.
(B) In the solid state, **P** exhibits a ring structure
(C) Stereogenic lone pairs of electron are present in both **P** and **Q**.
(D) **Q** is a weaker Lewis acid than **P**.

Identify the correct statements.
(a) A and B only (b) C and D only (c) A, B and C only (d) B, C and D only

75. 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.
(A) Silylium cation is formed during the reaction
(B) It is a second order reaction
(C) The cleavage of the Si-X bond is not the rate determining step
(D) The product always shows inversion of configuration
Identify the correct statements.
(a) B and C only (b) A and B only (c) C and D only (d) B, C and D only

76. Consider the following statements about the Oxo-process:
A. The reaction is first order with respect to olefin.
B. The rate is faster for terminal olefins compared to internal olefins.
C. The rate is faster for internal olefins compared to terminal olefins.
D. Excess of CO inhibits the reaction.
The correct statements are
(a) A, B and D only (b) C and D only (c) A and B only (d) A and D only

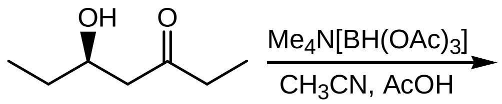
77. The reaction of $MoCl_2$ with $[Et_4N]Cl$ in dil. HCl and EtOH produces a dianionic hexanuclear metal cluster.
(A) The cluster is $[Mo_6Cl_{14}]^{2-}$
(B) The cluster has 136 valence electrons.
(C) Each metal centre has 4 metal-metal bonds
Identify the correct statement(s) about the cluster
(a) B only (b) A and C only (c) B and C only (d) A, B and C

78. The number of allowed EPR lines expected for a metal ion with 3 unpaired electrons and a nuclear spin (*I*) of 7/2 is
(a) 8 (b) 32 (c) 36 (d) 24

79. In the following electron transfer reactions, the one in which the bridging ligand comes from the reductant is
(a) $[IrCl_6]^{2-} + [Cr(OH_2)_6]^{2+} \longrightarrow \text{products}$
(b) $[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} \longrightarrow \text{products}$
(c) $[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \longrightarrow \text{products}$
(d) $[CrO_4]^{2-} + [Fe(CN)_6]^{4-} \longrightarrow \text{products}$

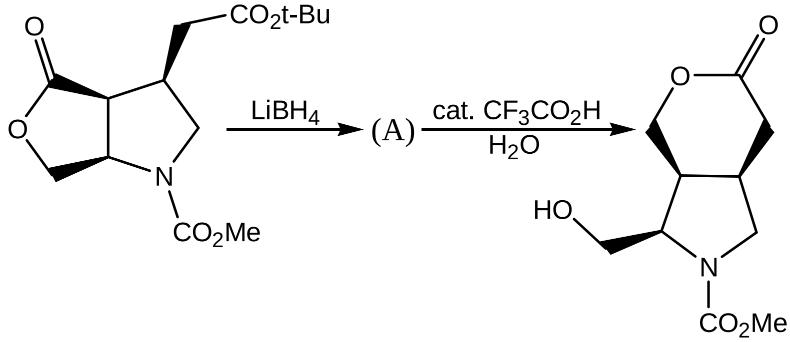
80. The correct statement regarding the following physical properties is
(a) Bond order follows $Li_2 < C_2 < B_2 < N_2$ order.
(b) Melting point follows $NH_3 < PH_3 < AsH_3 < SbH_3$ order.
(c) Pauling electronegativity follows Al < Si < S < P order.
(d) First ionization energy follows Li < B < Be < C order.

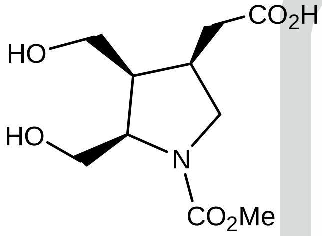
81. The correct statement for the following reaction is

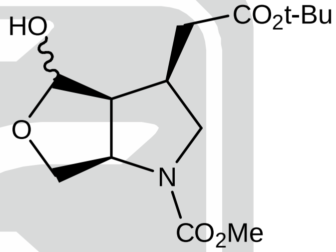


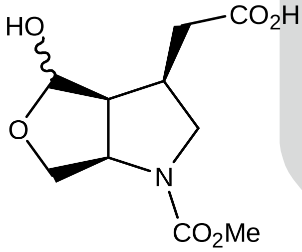
(a) involves intermolecular hydride transfer and the product is achiral
(b) involves intramolecular hydride transfer and the product is achiral
(c) involves intramolecular hydride transfer and the product is chiral
(d) involves intermolecular hydride transfer and the product is chiral

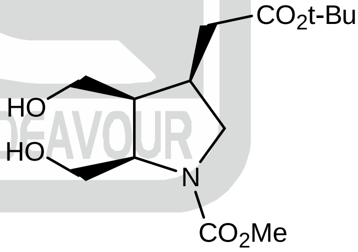
82. The structure of the compound A in the following reaction sequence is



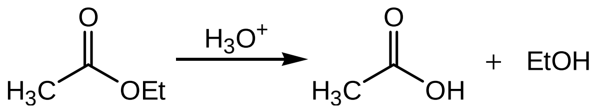
(a) 

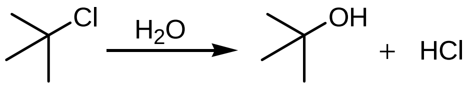
(b) 

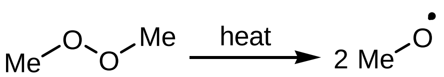
(c) 

(d) 

83. The reaction(s) with a positive entropy of activation $(\Delta S^{\#})$ is(are)

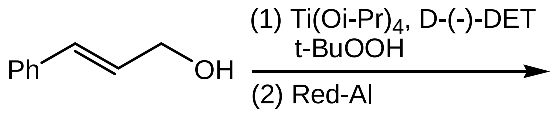
(A) 

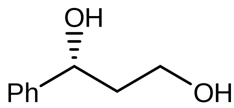
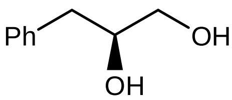
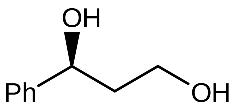
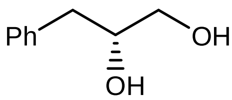
(B) 

(C) 

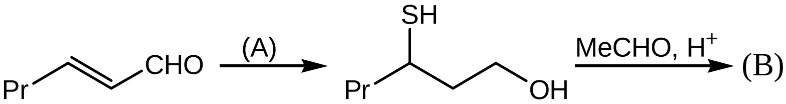
(a) A and C (b) B and C (c) only C (d) A and B

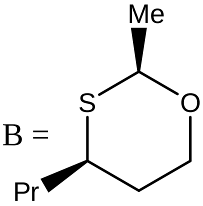
84. The major product formed in the following reaction sequence is

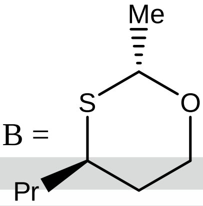


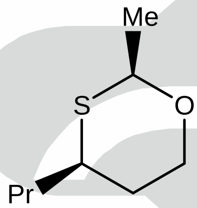
(a)  (b)  (c)  (d) 

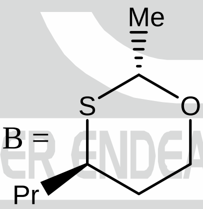
85. The reagents A and major product B in the following reaction sequence are



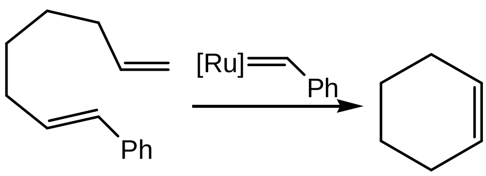
(a) A = i, $NaBH_4$; ii. H_2S, cat. piperidine, B = 

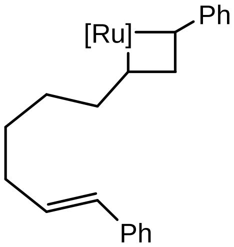
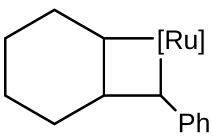
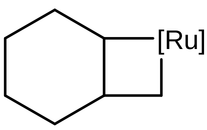
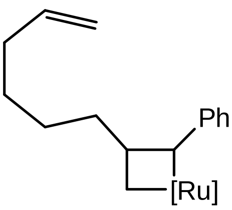
(b) A = i. H_2S, cat. piperidine, ii. $NaBH_4$, B = 

(c) A = i. H_2S, cat. piperidine, ii. $NaBH_4$, 

(d) i, $NaBH_4$; ii. H_2S, cat. piperidine B = 

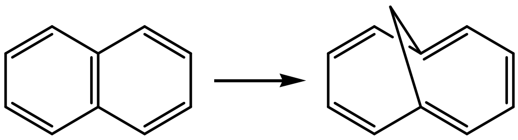
86. The intermediates involved in the follwoing reaction are




(A)

(B)

(C)

(D)

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

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



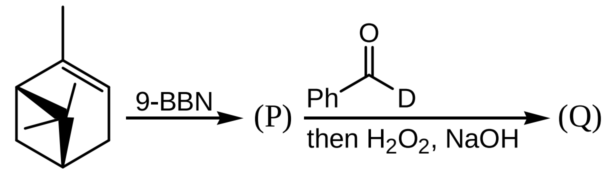
(a) (i) $CHCl_3$, NaOH; (ii) Na / liq. NH_3; (iii) DDQ; (iv) Na / liq. NH_3, EtOH

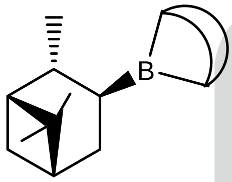
(b) (i) DDQ; (ii) Na / liq. NH_3, EtOH; (iii) $CHCl_3$, NaOH; (iv) Na / liq. NH_3

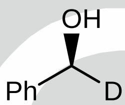
(c) (i) Na / liq. NH_3, EtOH; (ii) DDQ; (iii) $CHCl_3$, NaOH; (iv) Na / liq. NH_3

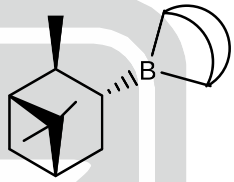
(d) (i) Na / liq. NH_3, EtOH; (ii) $CHCl_3$, NaOH; (iii) Na / liq. NH_3; (iv) DDQ

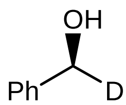
88. The major products P and Q formed in the following reaction sequence are

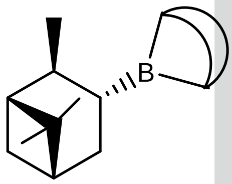


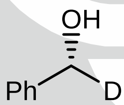
(a) P = 

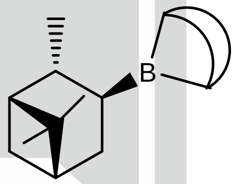
Q = 

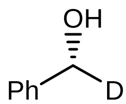
(b) P = 

Q = 

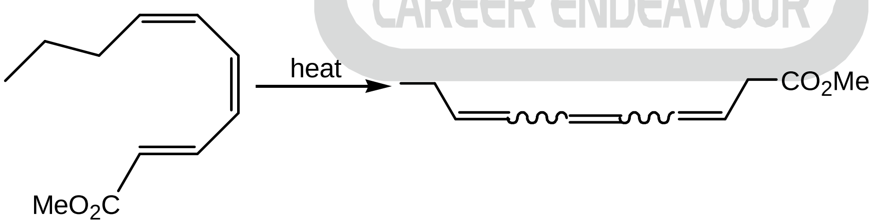
(c) P = 

Q = 

(d) P = 

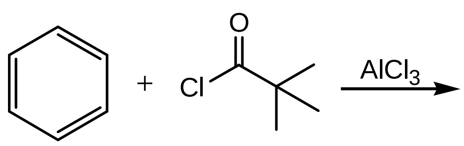
Q = 

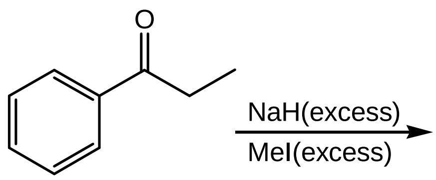
89. The stereochemistry of the double bonds in the product is

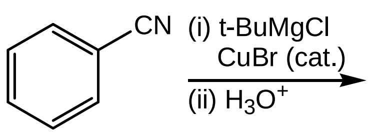


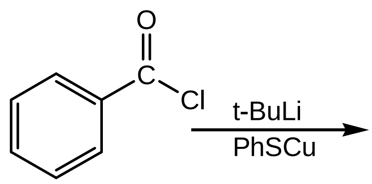
(a) 3E, 5E, 7Z (b) 3Z, 5E, 7E (c) 3E, 5Z, 7Z (d) 3Z, 5Z, 7E

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

(A) 

(B) 

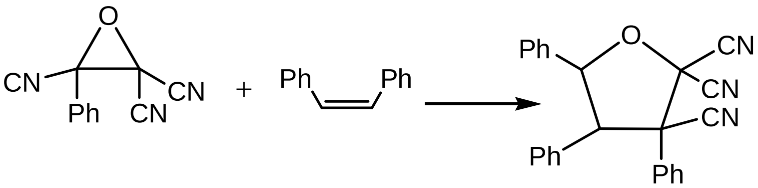
(C) 

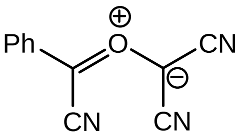
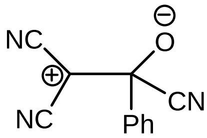
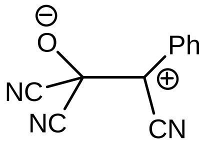
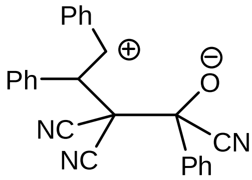
(D) 

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

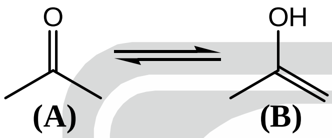
(c) only A and C (d) only B and D

91. Considering the rate law (rate = k[epoxide]) for the reaction shown below, the plausible intermediate is



(a)  (b)  (c)  (d) 

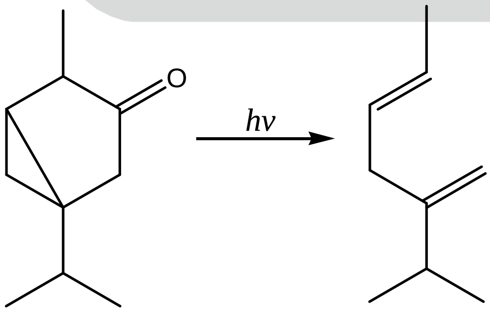
92. Given below are the bond dissociation energy (BDE; $kJmol^{-1}$) values. Based on the data, the correct statement about the following equilibrium is



Bond	BDE $(kJmol^{-1})$	Bond	BDE $(kJmol^{-1})$
O – H	–460	C – C	–360
C – H	–420	C = O	–760
C – O	–380	C = C	–630

(a) A is more stable than B by 70 kJ mol^{-1} (b) A is more stable than B by 130 kJ mol^{-1}
(c) B is more stable than A by 70 kJ mol^{-1} (d) B is more stable than A by 130 kJ mol^{-1}

93. The following transformation involves

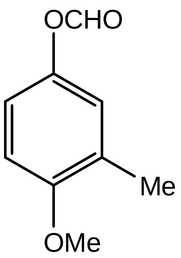


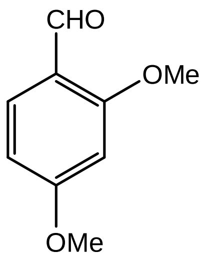
(a) i) Norrish type-II; ii) fragmentation of a cyclopropyl diradical
(b) i) Norrish type-I; ii) fragmentation of a cyclopropyl diradical
(c) i) Norrish type-I; ii) di-π-methane rearrangement
(d) i) Norrish type-II; ii) di-π-methane rearrangement

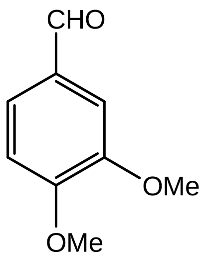
94. The correct structure that corresponds to the spectroscopic data given below is

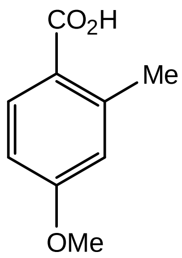
IR $\left(cm^{-1}\right)$: 2720, 1710

^{1}H NMR : δ9.80(s, 1H), 7.50(dd, J = 8.0, 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 6.90(d, J = 8.0 Hz, 1H), 3.90(s, 3H), 3.80(s, 3H)

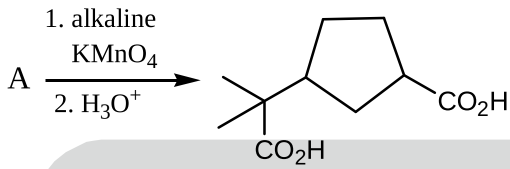
(a) 

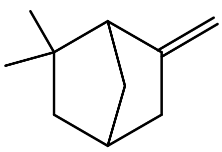
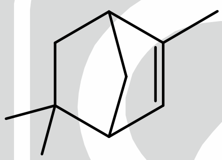
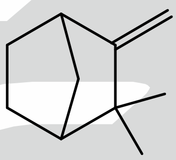
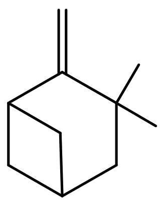
(b) 

(c) 

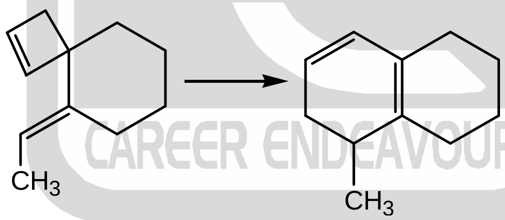
(d) 

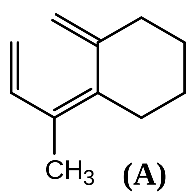
95. Structure of A, based on the following reaction, is

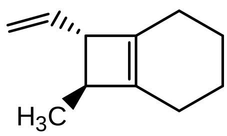


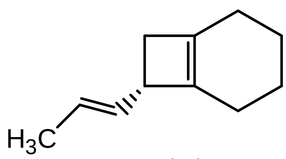
(a) 
(b) 
(c) 
(d) 

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





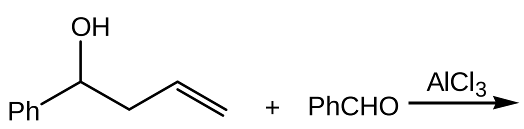
(A)


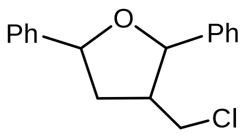
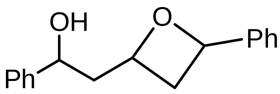
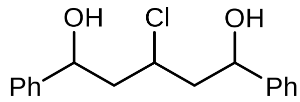
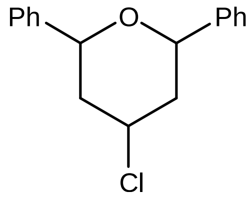
(B)


(C)

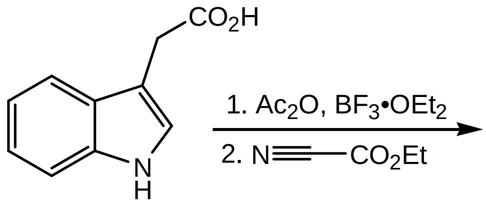
(a) A and C (b) B and C (c) only A (d) only B

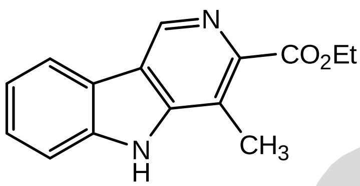
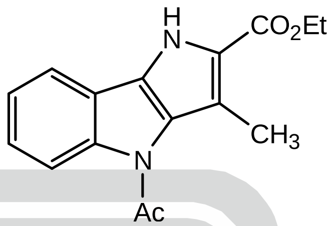
97. The major product formed in the following reaction is

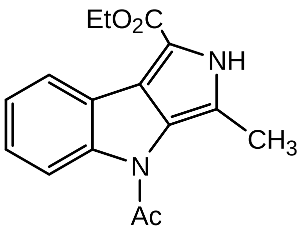
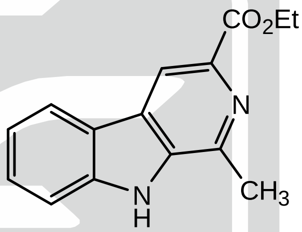


(a)  (b)  (c)  (d) 

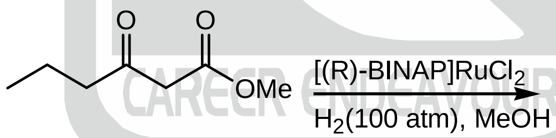
98. The major product formed in the following reaction is

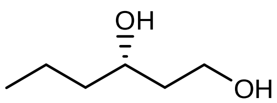
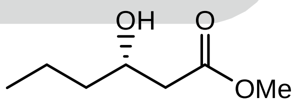


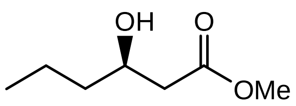
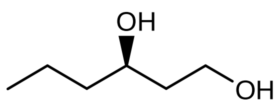
(a)  (b) 

(c)  (d) 

99. The major product formed in the following reaction is



(a)  (b) 

(c)  (d) 

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

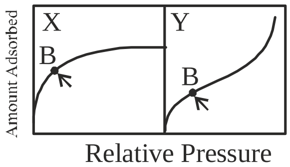
Column-P	**Column-Q**
(A) Ethyl acetate	(I) Two singlets in ^{1}H NMR
(B) 2-chloropentane	(II) Peak intensity at M:(M + 2) is 3:1 in El-MS
(C) 1, 2-dibromo-2-methylpropane	(III) Absorption band at 1740 cm^{-1} in IR

(a) A-III, B-I, C-II (b) A-I, B-III, C-II (c) A-II, B-III, C-I (d) A-III, B-II, C-I

101. 1 mole of $^{16}O_2$ and 1 mole of $^{18}O_2$ 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 $^{16}O_2$ is 300K what is the temperature of $^{18}O_2$ in K?

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

102. Which of the following statement/s corresponding to the accompanying figures displaying isotherms is/are corect?



(A) Figure X represents an isotherm of type II and point B shows near complete coverage of the surface

(B) Figure Y represents an isotherm of type II and point B shows near complete coverage of the surface

(C) Figure X represents an isotherm of type I and point B shows near complete coverage of the surface

(D) Figure Y represents an isotherm of type III and point B shows beginning of the multilayer formation.

(a) Only statement D is correct
(b) Statements C and D are correct
(c) Statements B and C are correct
(d) Statements A and B are correct.

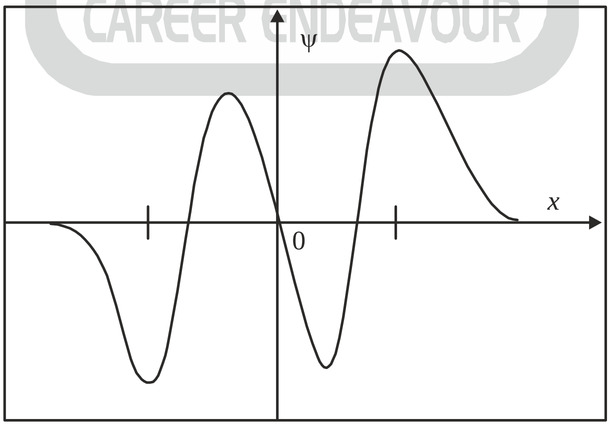
103. The partition function for a gas is given by

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

The internal energy of the gas is

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

104. 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, $E_0 = \frac{1}{2}\hbar\omega$)



(a) $\frac{7E_0}{k}$
(b) $\sqrt{\frac{14E_0}{k}}$
(c) $\frac{14E_0}{k}$
(d) $\sqrt{\frac{7E_0}{k}}$

105. For a C–H bond with a stretching frequency 3000 cm^{-1}, what is the expected isotope (deuterium) effect k_H/k_D at 298 K for a full bond homolysis? Given: h = 6.63×10^{-34} Js, c= 3×10^{10} cm/s, k_B = 1.38×10^{-23} J/K.

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

106. 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 10μM (in a cuvette of path length 2 cm) is 0.59, the number of tryptophan residues in the protein must be

[Given: $\varepsilon_{280}(\text{Tyrosine}) = 1500\ M^{-1}cm^{-1}$; $\varepsilon_{280}(\text{Tryptophan}) = 5000\ M^{-1}cm^{-1}$]

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

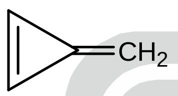
107. What is the cell potential (in V) at 298K and 1 bar for the following cell?

$Zn(s)|ZnBr_2(aq, 0.20\ mol/kg)||AgBr(s)|Ag(s)|Cu$

(Given: $E^0_{Zn^{+2}/Zn} = -0.762\,V$, $E^0_{AgBr/Ag} = +0.730\,V$ and assuming $\gamma_\pm$ of $ZnBr_2$ solution = 0.462)?

(a) 0.298 (b) 2.198 (c) 0.531 (d) 1.566

108. 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 ethyelene is $E = \alpha + \beta$]

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

109. 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 $H = \frac{1}{2\ell_x}(L_x^2 + L_y^2) + \frac{1}{2\ell_z}L_z^2$, the eigenvalues for the levels with quantum numbers $\ell = 1, m_\ell = 1$ and $\ell = 1, m_\ell = 0$ 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 $\hbar^2$

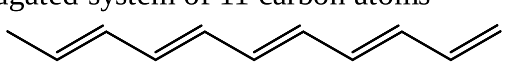
110. The molecular weight of polyethene determined in five individual experiments is given below:

Experiment No.	Molecular weight (g/mol)
1	10000
2	11000
3	9000
4	10500
5	11500

The standard deviations in the above measurements is closest to

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

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



Assume the average C-C bond length to be 1.5Å and treat the system as a 1-dimensional 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) $\frac{7}{225}\frac{k}{h}$

112. 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) $nRT\left(x_A \ln x_A + x_B \ln x_B\right)$ (b) $nRT\left(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B\right)$

(c) $nRT\left(x_A \ln \gamma_A + x_B \ln \gamma_B\right)$ (d) $nRT\xi x_A x_B$

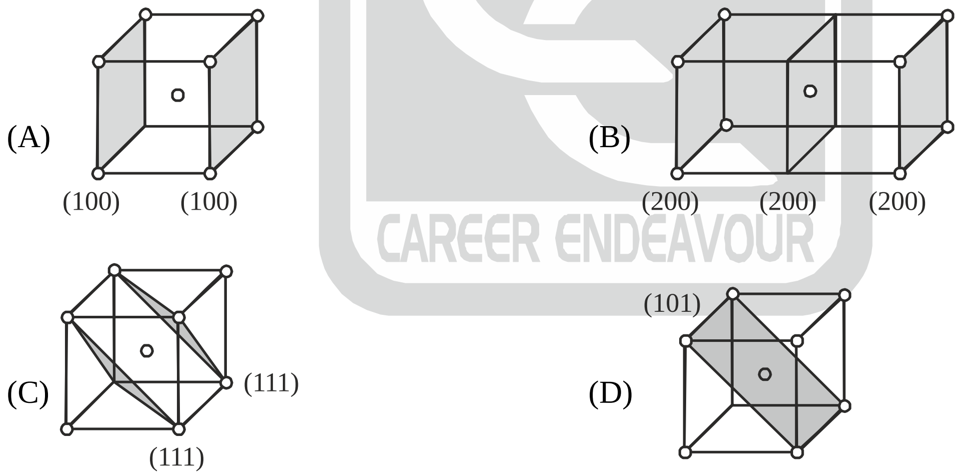
113. The effective rate constants for a gaseous unimolecular reaction:
$A \rightarrow P$ following the Lindemann-Hinshelwood mechanism are $1.70\times10^{-3}s^{-1}$ and 2.20×10^{-4} s^{-1} at [A] = 4.37×10^{-4} mol dm^{-3} and 1.00×10^{-5} mol dm^{-3}, respectively. The rate constant for the activation step in the mechanism is approximately equal to (in $dm^3mol^{-1}s^{-1}$)

(a) 12.3 (b) 49.4 (c) 6.1 (c) 24.7

114. Six distinguishable particles are distributed over 3 non-degenerate levels, of energies $0, \varepsilon$ and 2ε. The most probable value for the total energy is

(a) 5ε (b) 7ε (c) 8ε (d) 6ε

115. 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) A and D (b) A and C (c) B and C (d) C and D

116. Carbonic anhydrase (2.5×10^{-9} 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 mol dm^{-3} 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 $dm^3mol^{-1}s^{-1}$) is

(a) 4×10^5 (b) 10^6 (c) 10^7 (d) 10^4

117. 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-Huckel constant = 0.509 at 298K; log 0.884 = –0.05)
(a) –1.554 (b) –1.395 (c) –0.777 (d) –0.389

118. The predicated rate law, using the steady approximation, for the reaction

$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$$

following the possible mechanism is

$$H^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HI \quad \textit{rapid equilibrium}$$
$$HI + H_2O_2 \xrightarrow{k_2} H_2O + HOI \quad \textit{slow}$$
$$HOI + I^- \xrightarrow{k_3} I_2 + OH^- \quad \textit{fast}$$
$$OH^- + H^+ \xrightarrow{k_4} H_2O \quad \textit{fast}$$

is

(a) $\dfrac{k_1k_2\left[H^+\right]\left[I^-\right]\left[H_2O_2\right]}{k_{-1}+k_2\left[H_2O_2\right]}$ (b) $k_2\left[HI\right]\left[H_2O_2\right]$

(c) $k_1k_{-1}k_2\left[HI\right]\left[H_2O_2\right]$ (d) $\dfrac{k_2k_1}{k_{-1}k_4}\left[H^+\right]\left[I^-\right]\left[H_2O_2\right]$

119. The vibrational energy of the n[th] state of HCl is approximately given as

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

The vibrational quantum number, n_{max}, beyond which HCl undergoes dissociation is
(a) 29 (b) 59 (c) 119 (d) 19

120. The state of an electron in a hydrogenic atom is given by the un-normalised wavefunction.

$$\Phi = \left\{Y_{10}(\theta,\phi) + \frac{1}{\sqrt{2}}Y_{11}(\theta,\phi)\right\}R(r)$$

where $Y_{\ell m}(\theta,\phi)$ are spherical harmonics and $R(r)$ is the radial function. The probability that a measurement of L_z will give an eigenvalue of $\hbar$ is

(a) 1/2 (b) $\dfrac{1}{\sqrt{2}}$ (c) 1/3 (d) $\dfrac{1}{\sqrt{3}}$

❍❍❍