ASSIGNMENT 1: GATE 2009
CY: CHEMISTRY

EE25BTECH11039 - Manupati Manideep

1) The ^{31}P NMR spectrum of P_4S_3 consists of

a) a singlet
b) a doublet and a triplet
c) a doublet and a quartet
d) two doublets

(GATE CY-2009)

2) The geometry around the central atom in ClF_4^+ is

a) square planar b) square pyramidal c) octahedral d) trigonal bipyramidal

(GATE CY-2009)

3) The correct statement about the Cu-N bond distances in $[Cu(NH_3)_6]^{2+}$ is
a) all the bond distances are equal
b) the axial bonds are longer than the equatorial ones
c) the equatorial bonds are longer than the axial ones
d) all the bond distances are unequal (GATE CY-2009)

4) The reaction of phosgene with an excess of NH_3 produces
a) $HN = C = O$
b) $H_2N - C(Cl) = O$
c) $(H_2N)_2 C = O$
d) $(H_2N)_2 CCl_2$ (GATE CY-2009)

5) The number of metal-metal bonds in $[(C_5H_5)Fe(CO)]_2$ is

a) zero b) one c) two d) three

(GATE CY-2009)

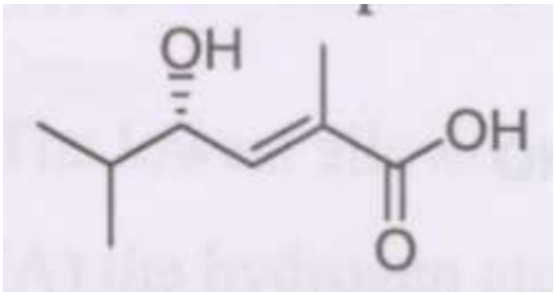
6) The coordination number of the Ba^{2+} ions in barium fluoride is 8. The coordination number of the fluoride ion is

a) 8 b) 4 c) 1 d) 2

(GATE CY-2009)

7) In the transformation of oxyhaemoglobin to deoxyhaemoglobin
a) Fe^{2+} in the low spin state changes to Fe^{2+} in the high spin state
b) Fe^{2+} in the low spin state changes to Fe^{3+} in the low spin state
c) Fe^{2+} in the high spin state changes to Fe^{2+} in the low spin state
d) Fe^{2+} in the high spin state changes to Fe^{3+} in the high spin state (GATE CY-2009)

8) For the compound

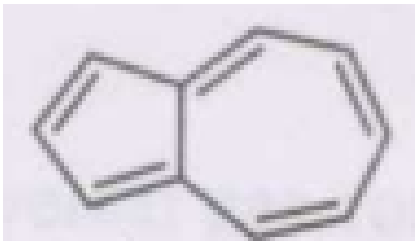


the stereochemical notations are

a) 2Z, 4R b) 2Z, 4S c) 2E, 4R d) 2E, 4S

(GATE CY-2009)

9) The compound

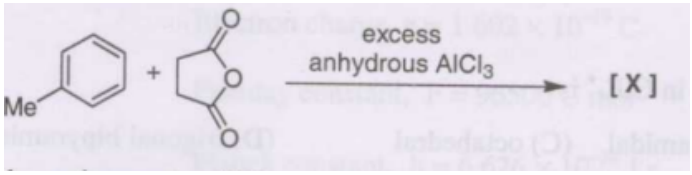


is

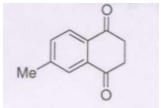
a) aromatic and has high dipole moment
b) aromatic and has no dipole moment
c) non-aromatic and has high dipole moment
d) anti-aromatic and has no dipole moment

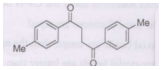
(GATE CY-2009)

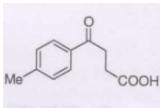
10) In the reaction

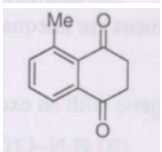


the major product X is

a) 

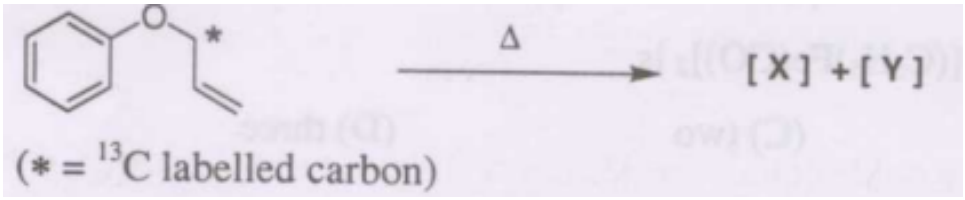
b) 

c) 

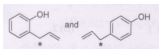
d) 

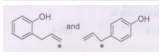
(GATE CY-2009)

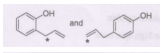
11) In the reaction

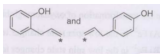


the major products X and Y are

a) 

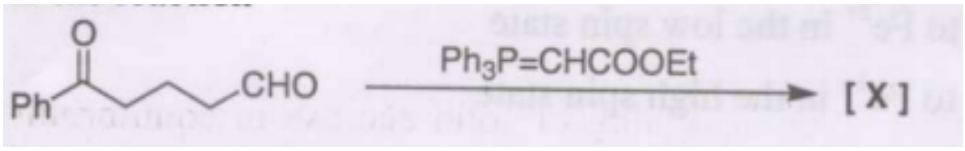
b) 

c) 

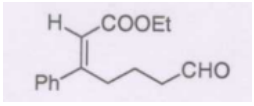
d) 

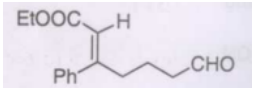
(GATE CY-2009)

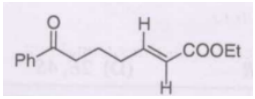
12) In the reaction

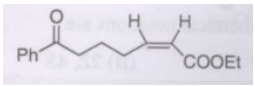


the major product X is

a) 

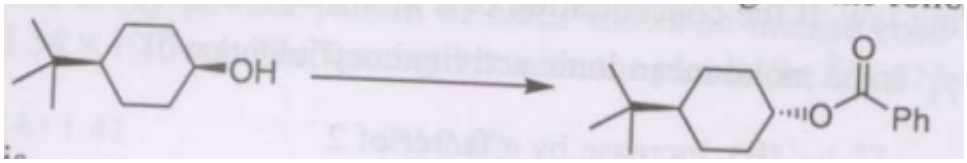
b) 

c) 

d) 

(GATE CY-2009)

13) The most suitable reagent combination to bring out the following transformation

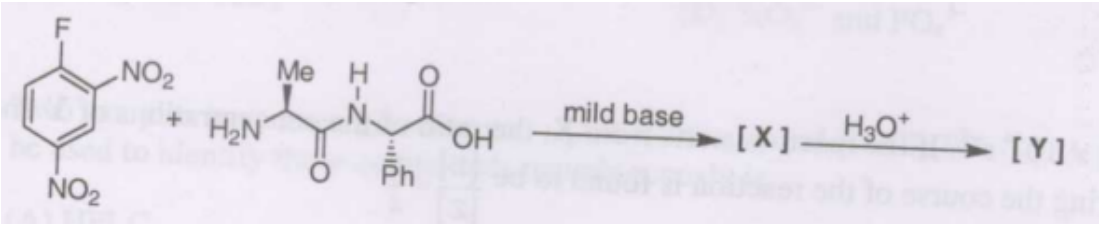


is

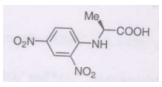
a) PhCOCl and pyridine
b) DCC and PhCOOH
c) PhBr, CO and $Pd(PPh_3)_4$
d) EtOOC-N=N-COOEt, PPh_3 and PhCOOH

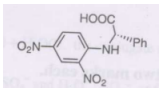
(GATE CY-2009)

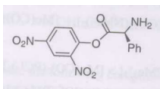
14) In the two steps reaction sequence

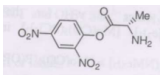


the major product Y is

a) 

b) 

c) 

d) 

(GATE CY-2009)

15) Among the following, the system that would require the least amount of thermal energy to bring its temperature to 80°C is

a) 200 g of water at $40°C$
b) 100 g of water at $20°C$
c) 150 g of water at $50°C$
d) 300 g of water at $30°C$

(GATE CY-2009)

16) Among the following, the reaction that is accompanied by a decrease in the entropy is

a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
b) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
c) $PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g)$
d) $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

(GATE CY-2009)

17) The number of degrees of freedom of a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose is

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

(GATE CY-2009)

18) The lowest allowed energy is equal to zero for

a) the hydrogen atom
b) a rigid rotor
c) a harmonic oscillator
d) a particle in a 3-dimensional box

(GATE CY-2009)

19) According to the Debye-HÃ¼ckel limiting law, if the concentration of a dilute aqueous solution of KCl is increased 4-fold, the value of $\ln \gamma_{\pm}$ ($\gamma_{\pm}$ is the molal mean ionic activity coefficient) will

a) decrease by a factor of 2
b) increase by a factor of 2
c) decrease by a factor of 4
d) increase by a factor of 4

(GATE CY-2009)

20) For the parallel first order reaction shown below

$$X \xrightarrow{k_1} Y$$
$$X \xrightarrow{k_2} Z$$

the value of k_1 is $1 \times 10^{-4} s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given time during the course of the reaction is found to be $\frac{[Y]}{[Z]} = \frac{1}{4}$. The value of k_2 is

a) $1 \times 10^{-4} s^{-1}$
b) $2.5 \times 10^{-5} s^{-1}$
c) $4 \times 10^{-4} s^{-1}$
d) $4 \times 10^{4} s^{-1}$

(GATE CY-2009)

Q.21 - Q. 60 CARRY TWO MARKS EACH.

21) The correct order of ν_{CO} for the compounds $[Mo(CO)_3(NMe_3)_3]$, $[Mo(CO)_3(POPh_3)_3]$, $[Mo(CO)_3(PMe_3)_3]$, $[Mo(CO)_3(PCPh_3)_3]$ in the IR spectrum is
a) $[Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(POPh_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(PCPh_3)_3]$
b) $[Mo(CO)_3(PCPh_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(POPh_3)_3] > [Mo(CO)_3(NMe_3)_3]$
c) $[Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(PCPh_3)_3] > [Mo(CO)_3(POPh_3)_3]$
d) $[Mo(CO)_3(POPh_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(PCPh_3)_3]$

(GATE CY-2009)

22) 2.5 g of an iron compound upon suitable treatment yielded 0.391 g of iron(III) oxide. The percentage of iron in the compound is ($atomic weight of Fe$: 55.847, O : 15.994)

a) 10.94 b) 12.15 c) 11.31 d) 9.11

(GATE CY-2009)

23) In the reaction

$$Ph_3P \xrightarrow{MeI} [X] \xrightarrow{n-BuLi} [Y]$$

the compounds X and Y, respectively, are
a) $[Ph_3P(Me)I]$; $Ph_3P = CH - CH_2 - CH_2 - CH_3$
b) $[Ph_3P(Me)]$ $[I]$; $Ph_3P = CH_2$
c) $[Ph_3P(Me)_2]$; $Ph_3P = CH_2$
d) $[Ph_3P(Me)]$ $[I]$; Ph_3P

(GATE CY-2009)

24) The ^{1}H NMR spectrum of HD consists of a

a) singlet
b) 1:1 doublet
c) 1:1:1 triplet
d) 1:2:1 triplet

(GATE CY-2009)

25) The X-ray powder pattern of NaCl shows an intense cone at $\theta = 15.87°$ using X-rays of wavelength 1.54×10^{-8} cm. The spacing between the planes $\left(in Å\right)$ of NaCl crystal is

a) 1.41 b) 2.82 c) 4.23 d) 5.63

(GATE CY-2009)

26) Among the following, the isoelectronic and isostructural pair is

a) CO_2 and SO_2
b) SO_3 and SeO_3
c) NO_2^+ and TeO_2
d) SiO_4^{4-} and PO_4^{3-}

(GATE CY-2009)

27) Two samples have been given to you: $[NiCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$. A physical method that can be used to identify these compounds unambiguously is

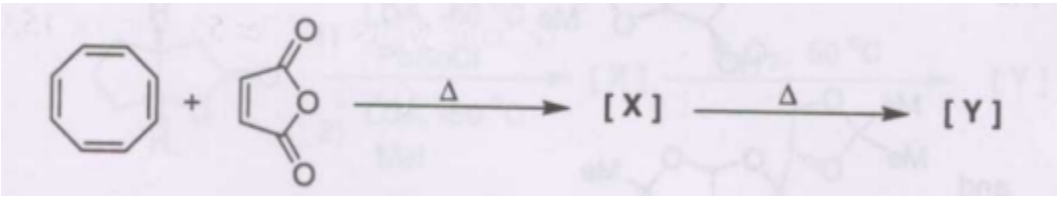
a) HPLC
b) magnetic susceptibility
c) ^{13}C NMR spectroscopy
d) MÃ¶ssbauer spectroscopy

(GATE CY-2009)

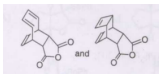
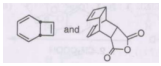
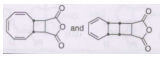
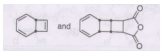
28) In the reaction $HSO_4^-(aq) + OH^-(aq) \Leftrightarrow SO_4^{2-}(aq) + H_2O(l)$, the conjugate acid-base pairs are
a) HSO_4^- and SO_4^{2-}; H_2O and OH^-
b) HSO_4^- and H_3O+; SO_4^{2-} and OH^-
c) HSO_4^- and OH^-; SO_4^{2-} and H_2O
d) HSO_4^- and OH^-; SO_4^{2-} and H_3O^+ (GATE CY-2009)

29) Designate the following complexes X, Y and Z as inert or labile:
$X = [Al(C_2O_4)_3]^{3-}$, $Y = [V(H_2O)_6]^{2+}$, $Z = [Cr(C_2O_4)_3]^{3-}$
a) X and Y are inert; Z is labile
b) X and Z are labile; Y is inert
c) X is inert; Y and Z are labile
d) X is labile; Y and Z are inert (GATE CY-2009)

30) In the reaction sequence

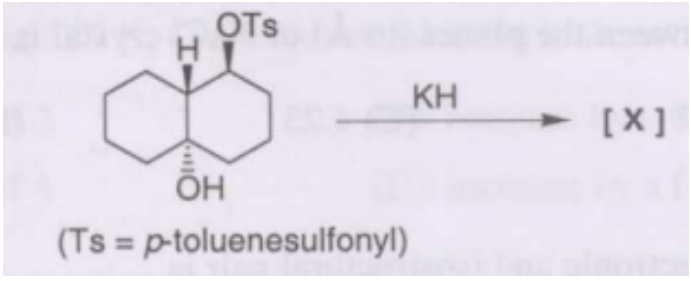


X and Y, respectively, are

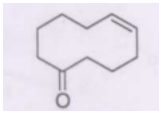
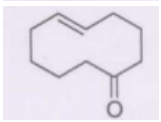
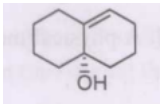
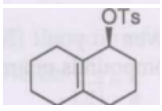
a) 
b) 
c) 
d) 

(GATE CY-2009)

31) The major product X (based on the preferred conformation) in the reaction

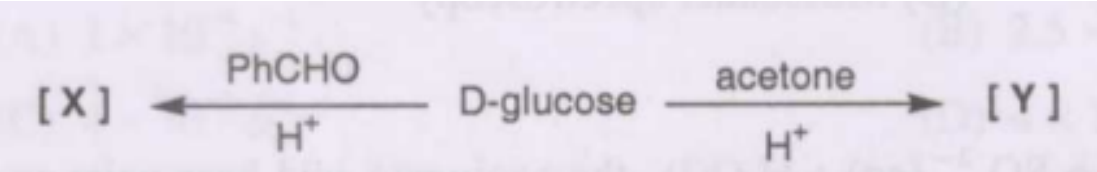


is

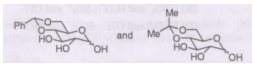
a) 
b) 
c) 
d) 

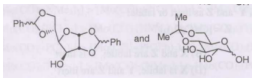
(GATE CY-2009)

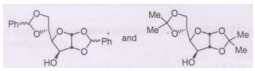
32) In the reactions

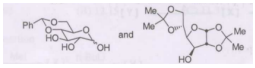


the major products X and Y, respectively, are

a) 

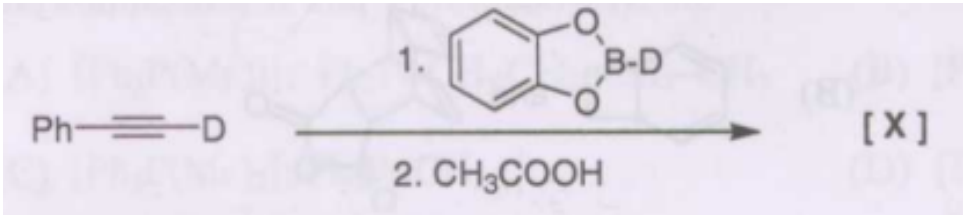
b) 

c) 

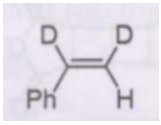
d) 

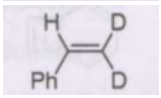
(GATE CY-2009)

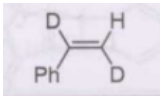
33) In the reaction

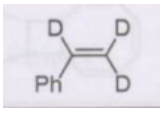


the major product X is

a) 

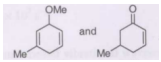
b) 

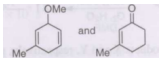
c) 

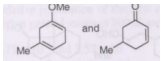
d) 

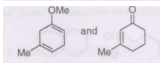
(GATE CY-2009)

34) Reaction of m-methylanisole with lithium in liquid ammonia and t-butyl alcohol at −33°C generates compound X as the major product. Treatment of the compound X with dilute sulphuric acid produces compound Y as the major product. The compounds X and Y, respectively, are

a) 

b) 

c) 

d) 

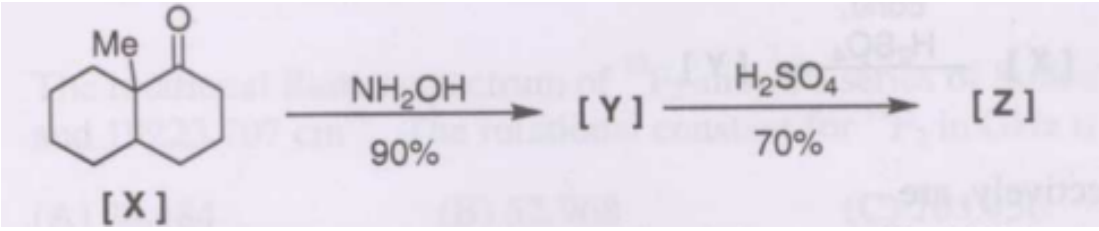
(GATE CY-2009)

35) The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are

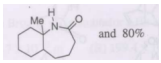
a) 3, 4 and 2 b) 3, 3 and 2 c) 4, 4 and 2 d) 3, 4 and 4

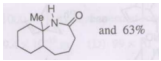
(GATE CY-2009)

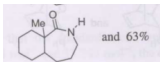
36) In the reaction sequence

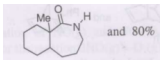


the structure of the major product Z and the overall yield for its formation from the ketone X, are

a) 

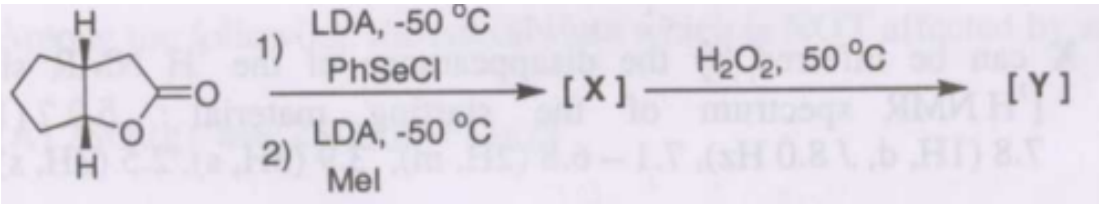
b) 

c) 

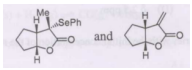
d) 

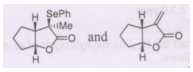
(GATE CY-2009)

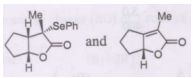
37) In the reaction sequence

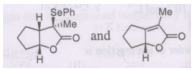


the major products X and Y, respectively, are

a) 

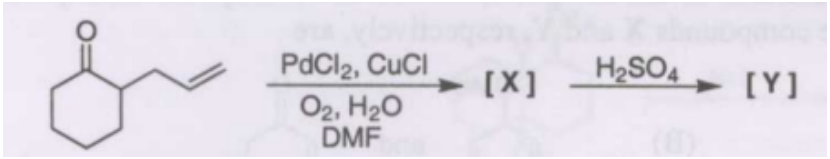
b) 

c) 

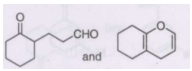
d) 

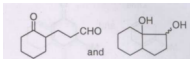
(GATE CY-2009)

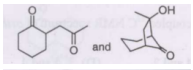
38) In the reaction sequence

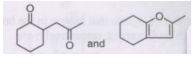


the major products X and Y, respectively, are

a) 

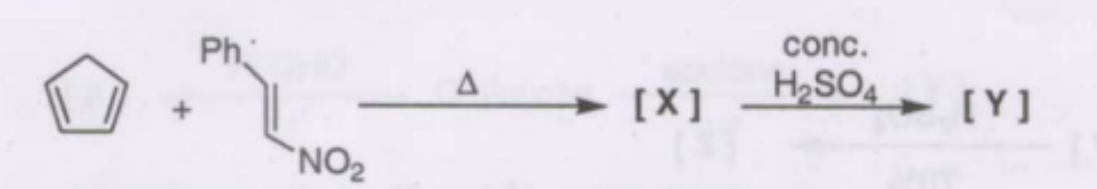
b) 

c) 

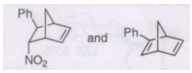
d) 

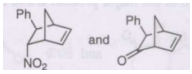
(GATE CY-2009)

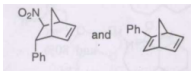
39) In the reaction sequence

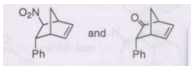


the major products X and Y, respectively, are

a) 

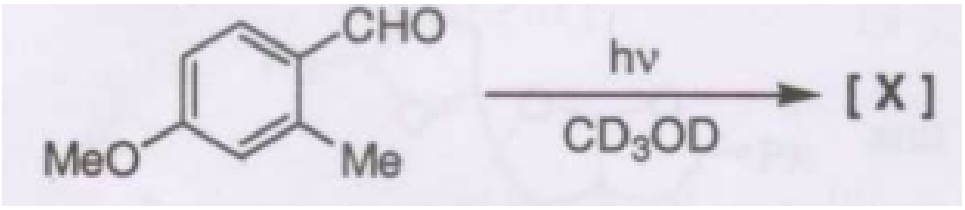
b) 

c) 

d) 

(GATE CY-2009)

40) In the photochemical reaction



formation of the compound X can be inferred by the disappearance of the ^{1}H NMR signal at
(^{1}H NMR spectrum of the starting material: $\delta 9.7\,(1H, s)\,, 7.8\,(1H, d, J 8.0 Hz)\,, 7.1 - 6.8\,(2H, m)\,, 3.9\,(3H, s)\,, 2.5$

a) δ 9.7 ppm
b) δ 7.8 ppm
c) δ 3.9 ppm
d) δ 2.5 ppm

(GATE CY-2009)

41) The half-life ($t_{1/2}$) for the hydrolysis of an ester varies with the initial concentration of the reactant ($[E]_0$) as follows:

$[E]_0 / 10^{-2}$ mol L^{-1}	5.0	4.0	3.0
$t_{1/2}/s$	240	300	400

The order of the reaction is

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

(GATE CY-2009)

42) The fluorescence lifetime of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is

a) 1×10^8 s^{-1}
b) 1×10^7 s^{-1}
c) 1×10^6 s^{-1}
d) 9×10^7 s^{-1}

(GATE CY-2009)

43) The fundamental vibrational wavenumbers for H_2 and I_2 are 4403.2 cm^{-1} and 214.5 cm^{-1}, respectively. The relative population of the first excited vibrational states of these two molecules compared to their respective ground states at 300 K are, respectively:

a) 6.75×10^{-10} and 3.57×10^{-1}
b) 6.75×10^{-10} and 3.57×10^{-1}
c) 3.57×10^{-1} and 6.75×10^{-1}
d) 3.57×10^{-1} and 6.75×10^{-1}

(GATE CY-2009)

44) The degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy is

a) 3 b) 6 c) 1 d) 4

(GATE CY-2009)

45) The rotational Raman spectrum of $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.218 cm^{-1} and 19223.707 cm^{-1}. The rotational constant for $^{19}F_2$ in GHz is

a) 26.484 b) 52.968 c) 105.936 d) 3.541

(GATE CY-2009)

46) The de Broglie wavelength for a He atom travelling at 1000 ms^{-1} (typical speed at room temperature) is

a) 99.7×10^{-12} m
b) 199.4×10^{-12} m
c) 199.4×10^{-10} m
d) 99.7×10^{-10} m

(GATE CY-2009)

47) Given that the standard molar enthalpies of formation of $NO(g)$ and $NO_2(g)$ are, respectively, 90.3 kJ mol^{-1} and 33.2 kJ mol^{-1}, the enthalpy change for the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is

a) 16.6 kJ b) -57.1 kJ c) -114.2 kJ d) 57.1 kJ

(GATE CY-2009)

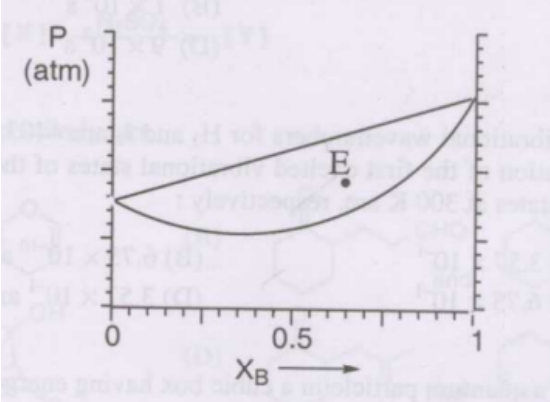
48) Among the following, the equilibrium which is NOT affected by an increase in pressure is
a) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
b) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
c) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
d) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ (GATE CY-2009)

49) The free energy change (ΔG) of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm is

a) RTln2 b) -2RT c) -RTln2 d) 2RT

(GATE CY-2009)

50) Two liquids B and C form an ideal solution. In the figure below, the vapour pressure P of this solution is shown as a function of the mole fraction, X_B, of component B.



Given a state of this vapour-liquid mixture whose overall composition corresponds to point E in the figure, the mole fraction of B in the vapour phase is approximately

a) 0.25
b) 0.53
c) 0.65
d) 0.80

(GATE CY-2009)

Common Data Questions

Common Data for Questions 51 and 52:

Treatment of $W(CO)_6$ with 1 equivalent of Na(C_5H_5) in THF solution gives the ionic compound M. Reaction of M with glacial acetic acid results in product N. The ^{1}H NMR spectrum of N displays two singlets of relative intensity 5:1. When N is heated, hydrogen gas is evolved and O is produced. O may also be prepared by refluxing $W(CO)_6$ with cyclopentadiene and H_2 is also produced. Treatment of O with an equivalent of Br_2 produces P. (Use the 18 electron rule as your guide).

51) The compounds M and N, respectively, are

a) $[(C_5H_5)W(CO)_3]Na$ and $[(C_5H_5)W(CO)_3H]$
b) $[(C_5H_5)W(CO)_4]Na$ and $[(C_5H_5)W(CO)_3H]$
c) $[(C_5H_5)W(CO)_3]Na$ and $[(C_5H_5)W(CO)_4H]$
d) $[(C_5H_5)W(CO)_4]Na$ and $[(C_5H_5)W(CO)_4H]$

(GATE CY-2009)

52) The compounds O and P, respectively, are

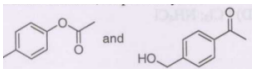
a) $[(C_5H_5)W(CO)_3]_2$ and $[(C_5H_5)W(CO)_3Br]$
b) $[(C_5H_5)W(CO)_4]_2$ and $[(C_5H_5)W(CO)_3Br(THF)]$
c) $[(C_5H_5)W(CO)_3(THF)]_2$ and $[(C_5H_5)W(CO)_3Br]$
d) $[(C_5H_5)W(CO)_3]_2$ and $[(C_5H_5)W(CO)_3Br(THF)]$

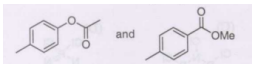
(GATE CY-2009)

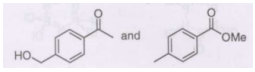
Common Data for Questions 53 and 54:

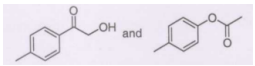
An organic compound X ($C_9H_{10}O$) exhibited the following spectral data.
IR: 1680 cm^{-1}
^{1}H NMR: δ 7.8 (2 H, d, J 7.5 Hz), 7.2 (2 H, d, J 7.5 Hz), 2.7 (3 H, s) and 2.4 (3 H, s)
Compound X on treatment with m-chloroperbenzoic acid produced two isomeric compounds Y (*major*) and Z (*minor*).

53) Compounds Y and Z, respectively, are

a) 

b) 

c) 

d) 

(GATE CY-2009)

54) Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because

a) Y produces 4-methylphenol and Z is unaffected
b) Y produces 4-methylphenol and Z produces 4-methylbenzoic acid
c) Y is unaffected and Z produces 4-methylbenzoic acid
d) Y is unaffected and Z produces 4-methylphenol (GATE CY-2009)

Common Data for Questions 55 and 56:

Character table for the point group C_{2v} is given below.

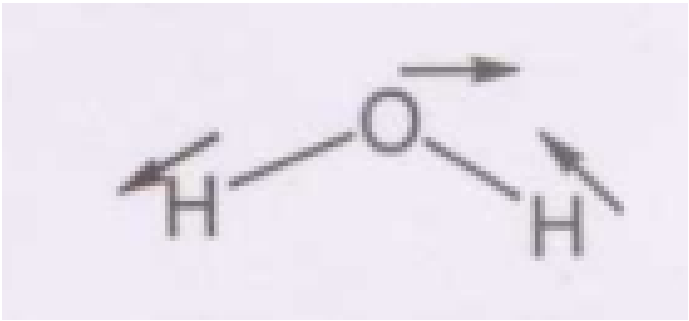
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

55) The reducible representation corresponding to the three translational degrees of freedom, Γ_{tr}, is

a) $3, 1, 1, 1$ b) $3, -1, 1, 1$ c) $3, -1, -1, -1$ d) $3, 1, -1, -1$

(GATE CY-2009)

56) The asymmetric stretching mode of the H_2O is shown below. The molecular plane is yz and the symmetry axis of H_2O is z.



This vibration transforms as the irreducible representation

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

(GATE CY-2009)

Linked Answer Questions

Statement for Linked Questions 57 and 58:

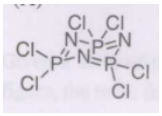
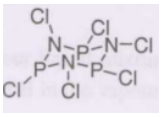
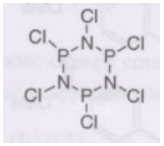
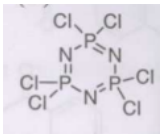
Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120-150 °C using appropriate solvents.

57) The reactants X and Y, respectively, are

a) PCl_5, NH_3
b) PCl_3, NH_3
c) PCl_5, NH_4Cl
d) PCl_3, NH_4Cl

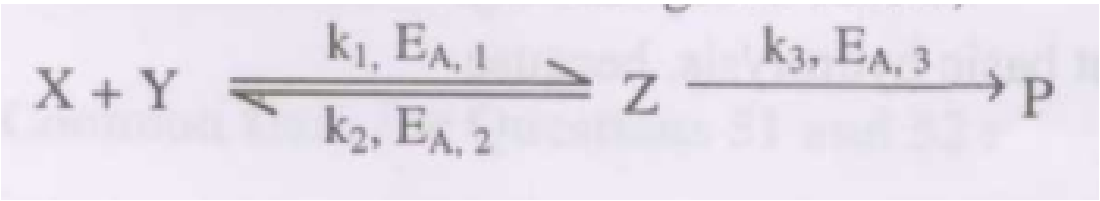
(GATE CY-2009)

58) The structure of triphosphazene is

a) 
b) 
c) 
d) 

(GATE CY-2009)

Statement for Linked Questions 59 and 60:
In the reaction mechanism given below,



'k's represent rate constants, 'E_A's represent activation energies, and $k_2 \gg k_3$.

59) The overall rate constant (k_{overall}) for the formation of P can be expressed as
a) k_1k_3/k_2
b) k_1
c) $k_1/(k_2 + k_3)$
d) $k_1/(k_2 - k_3)$

(GATE CY-2009)

60) The overall activation energy ($E_{A,\text{overall}}$) for the formation of P can be expressed as
a) $\dfrac{E_{A,1} \cdot E_{A,3}}{E_{A,2}}$
b) $E_{A,1}$
c) $E_{A,1} + E_{A,3} - E_{A,2}$
d) $\dfrac{E_{A,1}}{E_{A,2} + E_{A,3}}$

(GATE CY-2009)

END OF THE QUESTION PAPER