2016

M.Sc. 1st Semester Examination

CHEMISTRY

PAPER—CEM-101

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(*Physical Chemistry*)

Answer *five* questions
taking *one* question from each group.

Group—A

1. (a) Find the degeneracy of the first excited state of a particle present in a cubical box of side 'a'. Consider a slight distortion of the cube by 'da' along the x-axis and hence show the possible lift of degeneracy of the above degenerate state. Comment on your result.

(b) (i) Evaluate $\langle x^3 \rangle$ for a particle in one dimensional box of length 'l' in the limit $n \to \infty$.

(ii) Write down the dimension of wave function, $\psi(x, y, z)$. 4+(3+1)

2. (a) Find out normalized eigen function $\hat{L}_z$ of operator. Show that eigen functions of $\hat{L}_z$ operator form an orthogonal set of function.

(b) Evaluate the commutator, $\left[\hat{L}_+, \hat{L}_-\right]$. (3+2)+3

Group—B

3. (a) Define 'Grand connonial ensemble'.

(b) Derive a relation which correlates between entropy and thermodynamic probability. 2+6

4. (a) Starting from the expression of thermodynamic probability (Ω) at a particular distribution (without deriva-

tion) of a microcanomical ensemble derive Boltzmann's distribution law.

$\left[\text{Given } \beta = \frac{1}{KT}\right]$

(b) Find out the condition at which inversion of population occurs. 5+3

Group—C

5. (a) Derive the expression of rotational molecular partition function for heteronuclear diatomic molecule.

(b) Calculate the translational molecular partition function for H_2 in a volume of 1 cm^3 at T = 300K.
($h = 6.62 \times 10^{-34}$ JS, $K_B = 1.38 \times 10^{-23}$ JK^{-1}) 5+3

6. (a) How does the fugacity co-efficient is determined by measuring the compressibility factor of the gas ?

(b) 5 gm moles water initially at 27°C are converted to a final state of vapour at 227°C, the conversion being affected under 1 atm. pressure. Assuming the vapour to behave ideally, compute the total change in entropy.
Given heat capacity of water = 1 cal/gm
heat capacity of water vapour = 0.4 cal/gm
Latent heat of vaporization of water = 540 cal/gm.
5+3

Group—D

7. Prove that minimum distance (critical distance) for ion-pair formation is

$$r_{min} = \frac{\lambda}{2}$$

and hence show that the fraction of ions which are associated into ion-pair

$$\theta = 4\pi ni^{\circ} \lambda^3 Q(b)$$

where $Q(b) = \int_2^b e^y y^{-4} dy$

and other terms have their usual meanings. 8

8. (a) State the Fourier series of a function, f(x) in the interval $(-\pi, \pi)$, when

(i) f(x) is an even function

(ii) f(x) is an odd function

(b) Find the constrained maxima of function $f(x, y) = e^{-x^2-y^2}$ subject to the constrained condition $x + y = 1$. 4+4

Group—E

9. (a) What is Felgett advantage in FT-IR ?

(b) Calculate to four decimal place and with units of cm^{-1}, the rotational constant 'B' for the following bonds :

(a) $^{12}C\ ^{1}H$ (b) $^{127}I - ^{127}I$

Given $m(^{12}C) = 12.000u$

$m(^{1}H) = 1.0078u$

$m(^{127}I) = 126.90u$

$r_{CH} = 1.1199A$, $r_{I_2} = 2.6663A$

Convert the B-values to units of GHz.

(c) The vibrational frequency and anharmonicity constant of an alkyl halide are 300 cm^{-1} and 0.0025 respectively. Find out the positions (in cm^{-1}) of its fundamental mode and first overtone. 2+3+3

10. (a) What is the need of another rotational quantum number 'K' for non-linear polyatomic molecules ?

(b) For a diatomic molecule AB, the energy for the rotational transition from J = 0 to J = 1 state is 3.9 cm^{-1}. Find out the energy of rotational transition from J = 3 to J = 4 state.

(c) Deduce the structure of an unknown compound with molecular formula $C_5 - H_{12}O$ using the following information obtained from its' IR spectrum

Peak Intensity	Frequency (cm^{-1})	Peak Intensity	Frequency (cm^{-1})
m	3300	m	1465
m	2900	m	1450
m	2800	m	1375

(d) Mention two major applications of Stark effect.

2+1+3+2