2017

M.Sc.

1st Semester Examination

CHEMISTRY

PAPER—CEM-101

Subject Code—24

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)

Group—A

Answer any *one* question of the followings.

1. (a) Spherical Harmonics, $\left\{Y_l^m(\theta, \phi)\right\}$ are the eigen functions of $\hat{L}^2$ and $\hat{L}_z$ operator. Use operator algebra to show, $-l \leq m \leq l$. (Symbols have their usual significances)

(b) A system is known to be in a state described by the wavefunction,

$$\psi(\theta, \phi) = \frac{1}{\sqrt{30}}\left[5Y_4^0 + Y_6^0 - 2Y_6^3\right]$$

where Y_l^m are the spherical Harmonics. Find the probability of getting the particle in the states with $l = 6$ and $l = 4$. 6+4

2. (a) A particle of mass 'm' is moving in a one dimensional box. The potential, V of the particle has the following form.

$$V = 0 \text{ when } -a/2 < x < a/2$$

$$= \infty \text{ when } x \leq -a/2 \text{ and } x \geq a/2$$

Deduce the expression of energy and eigen functions of the particle.

(b) A particle of mass 'm' confined in a box of length 'L'. Assume $\Delta x = L$ and $\Delta p_{min} = \left\langle p^2 \right\rangle^{1/2}$. Use uncertainty principle to obtain the estimate of the energy of particle. Find which one of the following is correct.

(i) $\frac{h^2}{8mL^2}$ (ii) $\frac{h^2}{8mL^2}$ (iii) $\frac{h^2}{32mL^2}$ (iv) $\frac{h^2}{2mL^2}$ 6+4

Group—B

Answer any *one* question of the followings.

3. (a) Derive the expression for the molar entropy of a perfect monoatomic gas.

(b) The molar heat capacity of butane can be expressed by,

$$\overline{C}_P / R = 0.05641 + \left(0.04631 K^{-1}\right)T$$

$$- \left(2.39 \times 10^{-5} K^{-2}\right)T^2 + \left(4.807 \times 10^{-9} K^{-3}\right)T^3$$

over the temperature range $300K \leq T \leq 1500K$. Calculate ΔS if one mole of butane is heated from 300K to 1000K at constant temperature. 7+3

4. (a) Obtain an expression for the thermodynamic probability distribution of particles described by antisymmetric wave functions and arrive at the appropriate quantum statistical distribution law.

(b) Calculate the rotational partition function for F_2 at 25°C, given that $I = 32.5 \times 10^{-47}$ kgm^2. 7+3

Group—C

Answer any *one* question of the followings.

5. (a) The following data were obtained from the vibrational fine structure in the vibronic spectrum of a diatomic molecule : $W_e = 512\ cm^{-1}$ $W_eX_e = 8\ cm^{-1}$. Find out the dissociation energy of the molecule.

(b) How does the population of a state vary with the corresponding quantum number at a particular temperature ?

(c) What are the advantages of Fourier transformation technology ?

(d) The vibrational frequency and anharmonicity constant of an alkali halide molecule are 300 cm^{-1} and 0.0025 respectively. Find out the positions of the fundamental and first overtone band. 3+2+2+3

6. (a) What is the selection rule for vibrational Raman spectra under harmonic approximation ?

(b) The rotational constant for $H^{35}Cl$ is observed to be 10.5909 cm^{-1}. What are the values of $\bar{B}$ for $H^{37}Cl$ and $^2D^{35}Cl$?

(c) Find out the population of the first rotational energy level of a microwave active molecule at 27°C whose characteristic $2\overline{B}$ value is 4.0 cm^{-1}.

(d) Write down the expression for rotational energy of a symmetric top molecule (no derivation required) considering all kinds of rotation and distortion during rotation.

2+3+3+2

Group—D

Answer any *five* questions of the followings.

7. (a) "The entropy of acetone is higher than the entropy of trimethylene oxide." — Justify.

(b) What is the Gibbs Paradox in the entropy of mixing of ideal gases and how did Gibbs resolve it ?

(c) Graphically show the variation (no explanation required, only label properly) of population of rotational energy levels of a molecule at two different temperatures.

(d) What are hot bands ?

(e) Suppose L^2 is measured for a rigid rotator and the value is found to be $12\hbar^2$. Now if L_z is measured at the sametime, what will be the possible value of L_z ?

(f) The operator $S_{\pm}$ are defined by $S_{\pm} = S_x \pm iS_y$. S_x and S_y are the component of spin angular momentum operator. Evaluate the commutator $[S_z, S_+]$.

(g) Give the number of normal vibrational modes of SO_2, C_2F_2 and CCl_4. 5×2
