

**M.Sc. Examination, 2018**  
**Semester-III**  
**Chemistry(Elective)**  
**Course: CH-917**  
**Optional ( Physical Chemistry)**

**Time: Three Hours**

**Full Marks: 40**

Questions are of value as indicated in the margin.  
 Answer *any four* questions.

1. Derive the following expressions for the number of distinct microstates in case of Maxwell-Boltzmann (MB), Bose-Einstein(BE) and Fermi-Dirac(FD) distributions:

$$\Omega_{\text{MB}} = N! \prod_{i=1}^k \frac{g_i^{n_i}}{n_i!}, \quad \Omega_{\text{BE}} = \prod_{i=1}^k \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}, \quad \Omega_{\text{FD}} = \prod_{i=1}^k \frac{g_i!}{n_i! (g_i - n_i)!}. \quad 3+3+4$$

2. Derive MB, BE and FD distributions using above three expression. Hence show that  $\Omega_{\text{FD}} \approx \Omega_{\text{BE}} \approx \frac{\Omega_{\text{MB}}}{N!}$  mentioning the appropriate condition. In this context comment on the authenticity of this most probable distribution in comparison with the ensemble based method. 2+2+2+2+2

3. Define grand canonical partition function  $\Xi(v, T, \mu)$ . Derive the relation  $pv = k_B T \ln \Xi$ . Write down a relation between grand canonical and canonical partition functions. Find out the thermodynamic 'activity' from that relation? 2+4+2+2

4. a) Discuss the phenomenon of 'critical opalescence'. Show that the probability of observing a particular value  $N$  of total number of particles in grand canonical ensemble follows a Gaussian distribution. 2+3  
 b) Derive with proper arguments the most probable distribution in canonical ensemble viz.

$$P_j = \frac{\langle a_j \rangle}{\mathcal{A}} = \frac{a_j^*}{\mathcal{A}} \quad (\text{symbols have usual meaning}). \quad 5$$

5. Discuss what is Gibbs' paradox and how the paradox can be resolved. 5+5

6. a) Derive Liouville's equation and discuss its physical significance. 5+3  
 b) What do you mean by Ergodic hypothesis? When this hypothesis becomes valid? 1+1