

Roll No. ....

Total Pages : 03

**LMDQ/D-23**

**6537**

PHYSICAL CHEMISTRY SPECIAL-II  
CHEM-305

Time : Three Hours]

[Maximum Marks : 60

**Note** : Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks. Calculator is allowed for solving numerical only.

**Section A**

1. (a) What do you mean by phase space, representative point and ensembles ? **4**
- (b) Using Lagrange's method of undetermined multipliers derive an expression for Maxwell-Boltzmann Statistics. **8**
2. (a) Differentiate microcanonical, canonical and grand canonical ensembles. **3**
- (b) Derive a relation for Maxwell distribution law of velocities from Boltzmann distribution expression. **7**
- (c) Particles to be distinguished in 2 boxes such that box 1 contains 30 particles and box 2 contains 26 particles. Find the number of ways of distribution. **2**

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### Section B

3. (a) Derive an expression for B.E statistics showing its deviation from ideal gas when  $B > 1$ . **5**
- (b) Why is He more degenerate than Hydrogen for B.E statistics ? **3**
- (c) Describe the case of degeneration for Fermi Dirac system when  $\alpha$  of  $e^\alpha$  is positive. **4**
4. (a) Illustrate thermionic emission of electron from metals for F.D statistics. **9**
- (b) Comment on the degeneracy of classical and quantum mechanical objects. **3**

### Section C

5. (a) Derive an expression for translational partition function of gas and also derive Sackur Tetrode equation. **8**
- (b) The rotational constant of gaseous HCl, determined from microwave spectroscopy is  $10 \text{ cm}^{-1}$ . Calculate rotational partition function of HCl at  $25^\circ\text{C}$ . **2**
- (c) What do you understand by characteristic vibrational temperature ? **2**
6. (a) Derive an expression of relationship of internal energy of system in terms of partition function and absolute temperature. **6**

- (b) What are the postulates of statistical thermodynamics ? What is significance of Boltzmann constant ? **3**
- (c) The vibrational frequency of a homonuclear diatomic molecule is  $\nu$ . Calculate the temperature at which the population of the first excited state will be half that of the ground state. **3**

### Section D

7. (a) Derive a relationship between Partition function and equilibrium constant. How is this relationship helpful in understanding Activated complex theory ? **5**
- (b) Determine pre exponential and steric factor for the system :
- Atom + Linear molecule  $\rightleftharpoons$  Linear molecule  
Linear molecule + Linear molecule  $\rightleftharpoons$  Nonlinear molecule **7**
8. (a) What are the forces and fluxes in irreversible Thermodynamics ? How are they related ? Explain with examples. **3**
- (b) Derive an expression for :
- (i) Entropy production in matter flow. **6**
- (ii) Entropy production in current flow. **6**
- (c) What is Onsager Reciprocal Relationship ? **3**