

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**

(7-23/2) L-6537

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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 α of e^α 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 cm^{-1} . Calculate rotational partition function of HCl at 25°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 ν . 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.
(ii) Entropy production in current flow. **6**
(c) What is Onsager Reciprocal Relationship ? **3**