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Exam. Code : 210401
Subject Code : 4820

M.Sc. Chemistry 1st Semester

PHYSICAL CHEMISTRY–THERMODYNAMICS

Course—III

Time Allowed—3 Hours] [Maximum Marks—50

Note :— Attempt **FIVE** questions in all, selecting at least **ONE** question from each section. The **fifth** question may be attempted from any section. Non-Programmable Calculator is allowed. All questions carry equal marks.

SECTION—A

1. (a) Describe the terms : fugacity and activity. How are these related to chemical potential ? What is the physical significance of fugacity ?

   (b) Explain the following thermodynamic quantities :

   (i) Helmholtz free energy

   (ii) Gibbs free energy.

2. (a) What is meant by partial molar property ? Give methods for determining the partial molar volume.

   (b) If 3 moles of H_2, 2 moles of N_2 and 2 moles of NH_3 are mixed at constant temperature and no chemical reaction is occurring, determine the entropy change.

SECTION—B

3. (a) Using Lagrange's method of undetermined multipliers, derive an expression for Maxwell-Boltzmann Statistics.

   (b) If a system consisting of N particles has two energy levels with $g_1 = 1$, $g_2 = 2$, ($U_1 = 40$ kJ mol^{-1}, $U_2 = 60$ kJ mol^{-1}). What will be ratio of the number of particles in two energy states at 700 K temperature ?

4. (a) Give an account of the Debye-Huckel theory of strong electrolytes.

   (b) Find the ionic strength of a solution which is 0.1 molal in KCl and 0.2 molal in K_2SO_4.

SECTION—C

5. (a) Derive an expression for the molecular vibrational partition function of an ideal diatomic gas.

   (b) Using the related partition functions, determine the internal energy for a system.

6. (a) Derive an expression for the equilibrium constant of an ideal gaseous mixture in terms of the partition functions of the reactants and products.

   (b) If $C_{v,mol}$ for I_2 at 10 K is 0.9 Cal K^{-1}mol^{-1}. Determine $C_{v,mol}$ for I_2 at 15 K.

SECTION—D

7. (a) Prove the Onsager's reciprocity relation law from the principle of microscopic reversibility.

   (b) Define the following terms : flux, driving force and transport coefficient.

8. (a) Write short notes on the following :

   (i) Non-equilibrium stationary states

   (ii) Electrokinetic effects.

   (b) Derive the Gibbs relation for isolated systems.