M.Sc. 4th Semester Examination, 2021

CHEMISTRY

(Physical Chemistry Special)

Paper: CHEM 403E

Course ID: 41453

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* of the following questions: 2×5 = 10

   a) Write down the Boltzmann distribution law in classical mechanics.

   b) Prove that the molar entropy of CO at 0K will be Rln2.

   c) Write down the expression of rotational partition function of an ideal non-linear polyatomic gas. Define the terms.

   d) Calculate the possible arrangements of 2 particles in 3 states using Maxwell-Boltzmann statistics.

   e) Define phase integral in classical mechanics. Explain the parameters.

   f) Show that the characteristic rotational temperature of an ideal diatomic gas has the dimension of temperature.

   g) Write down the expression of degeneracy of a Fermi-Dirac gas within the energy interval between ε and $\varepsilon+d\varepsilon$. Define the parameters involved.

2. Answer *any four* of the following questions: 5×4 = 20

   a) From the energy distribution for an ideal gas obeying Maxwell-Boltzmann distribution, calculate the total internal energy and specific heat of the gas. 5

   b) A system has two energy levels in thermal equilibrium with a heat reservoir at 600K. The energy difference between two levels is 0.2 eV. Find (i) the probability that the system is in the higher energy level and (ii) the temperature at which the probability will be equal to 0.25. 2+3 = 5

c) Show that for a canonical ensemble the relative fluctuation in energy with respect to mean fluctuation will be, 5

$$\frac{(\partial\overline{U}^{2})^{\frac{1}{2}}}{\overline{U}} = \frac{(KT^{2}C_{V})^{\frac{1}{2}}}{\overline{U}}$$

d) For an ideal gaseous system, relate the equilibrium constant of a chemical reaction to the partition function of the species involved in the reaction. 5

e) Determine the translational partition function for argon gas kept at a temperature 273K and occupying volume of 2.24×10^{-2} m^3. 5

f) Considering the motion of a free particle, establish the relation between the volume in phase space in classical mechanics and the number of quantum states in quantum mechanics. 5

3. Answer *any one* of the following questions: 10×1 = 10

a) (i) Three identical, indistinguishable particles are placed into a system of four energy levels with energies 1, 2, 3 and 4 *eV*, respectively. Find the average number of particles, occupying each energy level, if those particles are (i) bosons and (ii) fermions with total energy of the system is 6 *eV*.

(ii) Justify the following:

A) At room temperature the number of molecules present at higher vibrational state is negligible.

B) A gas of high molecular weight implies high molar entropy.

(iii) What do you mean by 'phase space' in classical statistical mechanics?

4+(2+2)+2 = 10

b) (i) Derive the equation, which represents the most probable distribution of the indistinguishable particles among various energy levels obeying Bose-Einstein statistics. Show that under special circumstances it reduces to the Boltzmann distribution law.

(ii) The Fermi energy for lithium is 4.72 *eV* at 0K. Calculate the number of conduction electrons per unit volume in lithium. (h = 6.63×10^{-34} J.s, m = 9.11×10^{-31} kg). (4+2)+4 = 10