P.G. Semester-IV Examination, 2023

CHEMISTRY

Course ID : 41453 **Course Code : CHEM-403E**

Course Title : Physical Chemistry Special

Time : 2 Hours Full Marks : 40

The figures in the right-hand margin indicate 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) Write down the expression of rotational partition function of an ideal non-linear polyatomic gas. Define the terms therein.

   c) Calculate the possible arrangements of 3 particles in 4 states using Maxwell-Boltzmann statistics.

   d) Calculate the translational partition function of H_2 molecule confined in a 2000 cm^3 vessel at 273K.

   e) The partition function of a system having three different energy levels is, $\left(1+e^{-\beta E}\right)^2$. Find out the energies of three levels along with their degeneracies.

   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 having two energy levels is in thermal equilibrium with a heat reservoir at 600 K. 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 functions of the species involved in the reaction. 5

e) How many ways can two fermions be placed in a 3-fold degenerate energy level? The Fermi velocity of electron in a metal is 0.7×10^6 m s^{-1}. Calculate the Fermi temperature. 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: $10 \times 1 = 10$

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) For lithium, the Fermi energy is 5.72 eV at 0 K. Calculate the number of conduction electrons per unit volume in lithium, $\left(h = 6.63 \times 10^{-34} \text{J.s} \, m = 9.11 \times 10^{-31} \text{kg}\right)$.

$(4+2)+4=10$

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