POSTGRADUATE FOURTH SEMESTER EXAMINATION, 2022

CHEMISTRY

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

Physical Chemistry Special

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: $2\times5 = 10$

a) Write down the expression of thermal de-Broglie wavelength of a particle of mass m at temperature T, and find out its dimension.

b) Four distinguishable molecules are distributed in energy levels E_1 and E_2 with degeneracy of 2 and 3, respectively. Find out the number of microstates with 3 molecules in energy level E_1 and one in energy level E_2.

c) Write down the Boltzmann distribution in classical mechanics and explain the terms therein.

d) Express Helmholtz free energy in terms of partition function for a system of non-interacting classical particles having two energy levels with energies ε and 2ε. Assume 4-fold degeneracy of lower level and 2-fold degeneracy of upper level.

e) Calculate the translational partition function of the H_2 molecule confined in a 1000 cm^3 vessel at 273 K.

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

g) Prove that the molar entropy at 0 K of CO would be R ln2.

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

a) For Fermi-Dirac distribution function (f), show that, $-\partial f/\partial E$ is maximum at the Fermi level. 5

b) How many ways two fermions can adjust in a 3-fold degenerate energy level? The Fermi velocity of the electron in a metal is 0.7×10^6 m/s. Calculate the Fermi temperature. 2+3 = 5

c) i) Calculate the fraction of N_2(g) molecules in the v = 0 and v = 1 vibrational states at 300 K. [θ_v of N_2(g) = 3374 K].

ii) Derive the equation of state associated with the partition function,

$$q = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-nb)^N e^{\beta a N^2/V}$$, where 'a' and 'b' are constants. 2+3 = 5

d) Derive the expression of pressure of a perfect Bose-Einstein gas. 5

e) Write down the expression of Bose temperature for a perfect Bose-Einstein gas and define the parameters. The Bose condensation occurs in liquid ^4He kept at ambient pressure at 2.17 K. At which temperature will Bose condensation occur in ^4He gas, the density of which is 1000 times smaller than that of liquid ^4He? 2+3 = 5

f) Establish the relation between grand canonical partition function and canonical partition function for non-interacting identical particles. 5

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

a) Consider two indistinguishable particles are placed in a 3-fold degenerate energy level. How many ways the particles can be placed, if they are (i) bosons and (ii) fermions? Show schematically all the possible distributions for both the cases.

b) Calculate the rotational partition function of HCl at 25 °C. The rotational constant of HCl is 10.59 cm^{-1}.

c) Considering the motion of a free particle, derive the relation between the volume in phase space and the number of quantum states. 4+2+4 = 10

b) (i) Derive the expression of total number of particles in terms of translational partition function for a perfect Bose gas.

(ii) Calculate the Fermi energy ε_{F_0} of a free electron as a function of volume V. Hence calculate the specific heat at constant volume C_V, if V = 10 $cm^3 mol^{-1}$.

5+(3+2) = 10

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