Molecular and Statistical Thermodynamics CHEF415

BITS Pilani, K. K. Birla Goa Campus

Comprehensive Examination, 2022-23

Total Marks: 40 **Time: 3 hours**

Answer each question.

Q1. Consider rod-shaped molecules with moment of inertia I, and a dipole moment μ. The contribution of the rotational degrees of freedom to the Hamiltonian is

$$\hat{H}_{rot} = \frac{p_\theta^{\,2}}{2I} + \frac{p_\phi^{\,2}}{2I\sin^2\theta} - \mu E\cos\theta$$

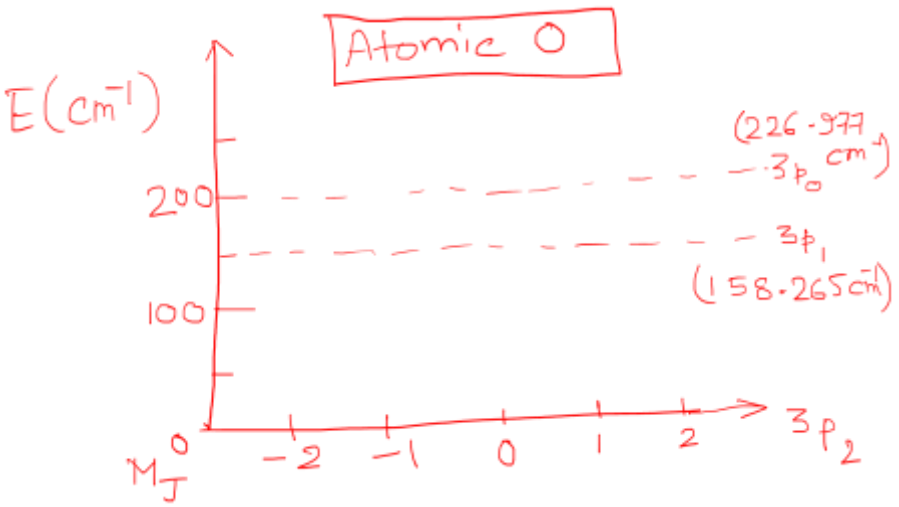
Where E is the external electric field, and (θ, φ) are polar and azimuthal angles describing the molecular orientation.

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the classical partition function.
(b) If the translation contribution is $V\lambda_T^{-3}$, calculate the free energy of the single particle.

[3 + 2 = 5 Marks]

Q2. Using canonical partition function, prove that, (a) $C_v = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}$ and (b) $U = \left(\frac{\partial (A/T)}{\partial (1/T)}\right)_{N,V}$ were A is the Helmholtz Free Energy and U is the internal Energy. **[3 + 2 = 5 Marks]**

Q3. Calculate the electronic partition function of atomic oxygen at 298.2 K. Degeneracy of each electronic term is $g_e = (2J+1)$. $q_e = \sum_{\text{All energy levels}} g_{e_i} e^{-E_i/k_B T}$ **[5 Marks]**



Q4. Calculate (a) moment of inertia, (b) reduced mass and (c) rotational energy of HCl molecule for J = 0and J = 1. Molar mass of H atom is 1 g/mol. Molar mass of Cl atom is 35 g/mol. Bond-length of H-Cl is 1.28Å. **[1 +2 + 2 = 5 Marks]**

Q5. Calculate the ratio of molecular partition function of chlorine atom and Cl_2 molecule. Molecular partition function of Cl atom has contributions from translational and electronic partition function. Molecular partition function of Cl_2 molecule has contributions from translational, rotational and vibrational partition function. **[8 Marks]**

Given data:

i) Cl atom has two states $2P_{3/2}$ and $2P_{1/2}$
ii) For $2P_{1/2}$ state, energy of Cl atom is = $1.750084299\times10^{-20}$
iii) Translational partition function for Cl_2 molecule is, $q_{trans}(Cl_2) = 2^{3/2}q_{trans}(Cl)$
iv) Bond-length of Cl_2 molecule is 1.99 Å
v) $\sigma(Cl_2) = 2$,
vi) Molar mass of Cl atom = 35.45 g/mol
vii) Vibrational frequency of Cl_2 molecule is 565 cm^{-1}. 1 cm = 2.99×10^{10} Hz.
viii) Cl_2 atom has ground state (zero state) vibrational partition function.

Q6. Calculate the absolute entropy of argon at 300K and 1 atom. Consider the Ar gas has only translational motion. Molar mass of argon is 39.948 kg/mol. R = 0.082 L atom K^{-1} mol^{-1}. **[4 Marks]**

Given data:

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V,$$

$$Q = \frac{q_{trans}^{\ N}}{N!}$$

$$S = -\frac{\partial A}{\partial T},\ A = -k_B T \ln Q$$

Q7. Calculate the wavenumber (ν) of a molecule when the molecule undergoes a transition from J_7 to J_8. **[3 Marks]**

Given data:

B = 5.77×10^{10} sec^{-1}

$\Delta E = hc\nu$

c = speed of light = 3×10^{8} m/sec

Q8. Consider a system of N particles, each of mass m, enclosed in an infinitely long cylindrical container placed in a uniform gravitational field. The system is in thermal equilibrium. Obtain expressions for the (a) classical partition function, (b) Helmholtz free energy, (c) Entropy, (d) Internal Energy and (e) Specific heat capacity at constant volume. **[2.5 + 1.5 + 1 = 5 Marks]**