Homework Information: The Problem Sets are based on material from class and various sources on Statistical Mechanics. There are five different categories of questions: computational $+$, computer c, concept ✓, derivation $\circ$ and math m. *A Mathematical Guide to Chemistry* Section 1.2 will be useful for recalling some summation formulas. Show all work to receive full credit for the problem. Work together, ask questions, use whiteboards and have fun with it!

1. $^+$ Consider the expression for the probability of being in state i, p_i:

$$p_i = \frac{1}{z} e^{-\varepsilon_i/kT} \tag{1}$$

(a) Show this expression is properly normalized.

(b) In our derivation of the Boltzmann distribution, we took $\varepsilon_0 = 0$. Show that the same result above is achieved even if $\varepsilon_0 \neq 0$.

2. $^\checkmark$ The partition function (z) can also be written in terms of the degeneracy of state i,

$$z = \sum_i \omega_i e^{-\beta \epsilon_i} \tag{2}$$

Recall that in this derivation we took $\epsilon_0 = 0$.

(a) Take the limit of the partition function as T approaches absolute zero.

(b) Take the limit of the partition function as T approaches infinity.

3. $^+$ Consider a box of non-interacting gas molecules: He, Ar, O_2, N_2. Write the single molecule partition function for each species, clearly showing the degrees of freedom a molecule may have (translation, rotation, vibration) and including the electronic component.

4. $^\checkmark$ (a) Write the equation for the total energy E in the microcanonical ensemble and the average energy, $\overline{E}$ in the canonical ensemble, indicating what each variable represents. Make sure to describe precisely what the different energy-related variables mean.

(b) Explain in words why the canonical ensemble energy $\overline{E}$ is normalized, while the microcanonical energy, E is not.

5. $^\circ$ Given a system at constant volume in the canonical ensemble, the mean energy, $\overline{E}$ is given by:

$$\overline{E} = U = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \tag{3}$$

(a) Determine U for the harmonic oscillator, with energy given by $E_n = (n + \frac{1}{2})h\nu$,

$$U = h\nu\left(\frac{1}{2} + \frac{1}{e^{hv/kT} - 1}\right) \tag{4}$$

(b) Then determine the heat capacity, $c_V = (\frac{\partial U}{\partial T})_V$.

(c) How would U and c_V be changed if the ground state energy was zero, i.e. $E_n = nh\nu$?

6. ° Deriving the Helmholtz free energy and entropy in the canonical ensemble.

(a) Using that $A = U - TS$, show that the internal energy can also be written in a form commonly seen in thermodynamics. Derive the following formulation of the Gibbs-Helmholtz equation:

$$U = \left(\frac{\partial(A/T)}{\partial(1/T)}\right)_V \tag{5}$$

(b) Set the result of (a) equal to the result of internal energy in the canonical ensemble:

$$U = -k\left(\frac{\partial \ln Z}{\partial(1/T)}\right)_V \tag{6}$$

Then solve for A to show that

$$A = -kT\ln Z + T\phi(V, N_1, N_2, \cdots) \tag{7}$$

(c) Finally, taking ϕ to be 0, conclude the entropy in the canonical ensemble.