PROBLEM SET 3

1. The canonical partition function of an N-particle, monatomic ideal gas is given by

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}N} V^N$$

Using the definition for the chemical potential μ of a single component system,

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

find an expression for the chemical potential for a monatomic ideal gas. Then show that the same expression can be derived using the definition of the Gibbs free energy,

$$\mu = \frac{G}{N} = \frac{1}{N}(A + pV)$$

where the Helmholtz free energy $A = E - TS$.

2. In classical thermodynamics, it can be shown that the chemical potential for a one-component ideal gas as a function of temperature and pressure can be written as

$$\mu(T,P) = \mu^0(T) + k_B T \ln p$$

where $\mu^0(T)$ is the standard chemical potential. Using the canonical partition function Q, derive an expression for the standard chemical potential of a monatomic ideal gas.

3. In the limit of high temperature, the rotational partition function for a single diatomic molecule is

$$q_R = \frac{k_B T}{\sigma h c B}$$

c is the speed of light, σ is the symmetry number, and B is the rotational constant given by

$$B = \frac{h}{8\pi^2 c I}$$

where $I = \mu r^2$ is the moment of inertia, μ is the reduced mass, and r is the average internuclear distance, i.e. the bond length. What species will have the largest partition function at a given temperature: H_2, HD or D_2? Which of the species will have the largest translational partition function assuming volume and temperature are identical?

4. The partition function for an N-particle van der Waals gas is given by

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}N} (V - Nb)^N e^{aN^2/Vk_BT}$$

where *a* and *b* are the van der Waals constants. Derive an expression for the enthalpy of the vdW gas.

5. In this problem we will use the entropy formula for an ideal gas to recover a familiar thermodynamic relationship for the entropy change of a compression (or expansion) process.

a) Find an expression for the entropy of a monatomic ideal gas.

b) Show that for a monatomic ideal gas undergoing a pressure change at constant temperature, the entropy change $\Delta S = S(T, p_2) - S(T, p_1)$ is given by

$$\Delta S = N k_B \ln \frac{p_1}{p_2}$$