Chem 534: Problem Set #2
Due in class: Tues., Sept. 15th

(1) Starting from $TdS = \sum_j E_j dP_j$ as discussed in class, show that $dS = -k \sum_j \ln P_j dP_j$, where

$$P_j = e^{-E_j / kT} \text{ and } Q = \sum_j e^{-E_j / kT}.$$  

(2) Starting from $A = -kT \ln Q$ and the Gibbs Fundamental equation for $dA$, derive the expressions

$$S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} + k \ln Q$$

$$p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

(3) Show that for a particle in a cubical box with infinitely thick walls with sides of length $L$, the pressure in quantum state $j$, $p_j$, is $\frac{2E_j}{3V}$. Remember that for a particle in a cubical box,

$$E_j = \frac{\hbar^2}{8mL^2} \left( n_x^2 + n_y^2 + n_z^2 \right).$$

(4) For a monatomic ideal gas $Q = \frac{1}{N!} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3N/2} V^N$. Derive expressions for the pressure and energy from this partition function. Also show that in general if $Q$ is of the form $f(T)V^N$ where $f(T)$ is any function of temperature alone, the ideal gas equation of state is recovered.

(5) Given the partition function of a crystal, $Q = \left( \frac{e^{-\hbar v/2kT}}{1 - e^{-\hbar v/kT}} \right)^{3N} e^{U_0/kT}$ where $\frac{\hbar v}{k} = \Theta_E$ is a constant and $U_0$ is the sublimation energy, calculate the heat capacity $C_v$ and show that at high temperatures $C_v \to 3Nk$ as $T \to \infty$ (Dulong & Petit law).

(6) Derive an expression for the fluctuation in the pressure in a canonical ensemble.