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 $P_j = \frac{e^{-E_j/kT}}{Q}$ 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 $\frac{2}{3}\frac{E_j}{V}$. Remember that for a particle in a cubical box, $E_j = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$.

(4) For a monatomic ideal gas $Q = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N$. 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, $Q = \left(\frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}}\right)^{3N} e^{U_0/kT}$ where $\frac{h\nu}{k} = \Theta_E$ 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.