Chemistry 163C Problem Set #6
Due Thursday, 5/15 at the beginning of class

1) Integer spin particles follow Bose-Einstein statistics where there is no limit on the number of particles that occupy a particular quantum state. The number of ways of distributing n_i particles over a level of degeneracy g_i follows:

$$w_i = \frac{(n_i + g_i - 1)!}{(n_i)!\,(g_i - 1)!} \qquad \text{Eq. 1}$$

(see Eq. 12.10 in our book) and the total statistical weight considering all levels is:

$$W_{BE} = \prod_i w_i \qquad \text{Eq. 2}$$

a) Work out all possible arrangements for two particles distributed over three degenerate states and show that the number of arrangements is correctly given by w_i in Equation 1. b) Next, use the method of Lagrange multipliers along with appropriate constraints on N and E to maximize W_{BE} and show that

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1} \qquad \text{Eq. 3}$$

where $-\mu/kT = \alpha$. c) Set $\mu = 0$, and let $T \rightarrow 0$ to show that all particles go to the ground state, hence, no Pauli Exclusion. d) Note that our final expression for n_i, given by Equation 3, is very similar to the Planck distribution for Black Body radiation (replace ε_i with photon energy hc/λ). Why might this be so?

2) Think of collection of atoms adsorbed to a surface, but with mobility along the surface, as a two-dimensional gas. a) Develop a 2D translational partition function following the same strategy used in class for 3D. b) Calculate the internal energy U. c) Calculate the internal energy based on equipartition. Does this match your answer in b? d) Develop and expression for the entropy S. For a fixed number of atoms, does S increase or decrease with increasing surface area? Does your answer make sense?

3) The equilibrium constant for the gas phase isotope exchange reaction below is approximately four as indicated:

$${}^{35}Cl_2 + {}^{37}Cl_2 \; \text{<------>} \; 2\,{}^{35}Cl^{37}Cl \qquad K \approx 4$$

Use stat mech to determine why this is so. Note that there is no appreciable difference in the ground state energies and further the vibrational energy spacings are almost equivalent for all species. Hint: set up your general expression and use physical reasoning to cancel terms.

From Engel & Reid 3rd Edition, Chapter 15, Problems: 30, 31 32, 39, 47