Chemistry 163C   Problem Set #3
Due Thursday, 4/24 at the beginning of class

1)   The efficiency of a code or alphabet is given by the Shannon information measure
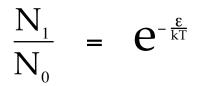
$$I = -\sum_{i=1}^{N} p_i \ln p_i$$

where p_i is the probability of a typical message containing the ith character.   For example, in the English language, the p_i values correspond to the probabilities of occurrence associated with various letters of the alphabet.   Use the method of Lagrange multipliers to maximize I subject to the constraint

$$\sum_{i=1}^{N} p_i = 1$$

to develop an expression for p_i. Your result should show that the most efficient code is one in which all characters arise with equal probability. Is this the case for English?

2)   For a two level system with nondegenerate levels, we know that the relative populations of the two states follows:

$$\frac{N_1}{N_0} = e^{-\frac{\varepsilon}{kT}}$$

Rearrange this equation and solve for T and then plot T vs N_1/N_0 from 0 to 2. What happens when $N_1 = N_2$? What temperature describes a "population inversion" where the excited state is more populated than the ground state?

3)   Consider a three level system of energies 0, ε, and 2ε. The second level is doubly degenerate.   a) Write down the molecular partition function. b) Develop an expression for the probability of occupying the middle level.   c) Sketch this probability from T = 0 to T → ∞. d) What value does the probability reach at T→ ∞? Briefly explain this result.

From Engel & Reid 3rd Edition, Chapter 14, Problems: 1, 3, 5, 9, 10, 13, 15, 26, 27, 31, 36, 39