Chem 312 – Spring 2008
Problem Set #2
Due Monday, 18 Feb, 10:10am in class.

Question 1
How many translational, rotational and vibrational degrees of freedom are there for neon, O_2, H_2O, acetylene (C_2H_2), benzene?

Question 2
[Hint: think of this as a marbles in boxes problem with degeneracy being the relative size of the box.]
(a) Consider the placement of four indistinguishable molecules into two distinguishable energy levels with no restriction on placement. If $g_1 = 1$ and $g_2 = 1$, determine the probability of finding each distribution.
(b) How would the results change if $g_1 = 1$ and $g_2 = 3$?

Question 3
(a) Which rotational level, J = 4 or J = 5, is more highly occupied by CO molecules at 25°C? What about at -78°C or at -178°C? At what temperature will the occupation of the two levels be equal? [For the bond length of CO you may use 1.13 Å.]
(b) Determine the population ratio of the v = 0 and v = 1 states for CO at 25°C. What do you learn about the relative population of excited vibrational levels at room temperature? [For the force constant of the CO bond, you may use k = 1900 N/m. Can you calculate the bond stretch of CO in cm^{-1} from k?]

Question 4
A quantum mechanical system has two energy levels ε_0 (the ground state) and ε_1.
(a) Derive equations for the probability p_0 that the system will be in the ground state and the probability p_1 that the system will be in the higher energy state, and the partition function q for the two-state system, in terms of the energy gap, k and T.
(b) What are the probabilities at $T = 0$, $T = \infty$, and $\Delta\varepsilon = kT$? What value does the partition function have in each case?
(c) Recalculate the probabilities if the degeneracy of the ground state is three times the degeneracy of the higher energy state.
(d) Calculate the equilibrium ratio of hydrogen atoms in the $n = 2$ compared to the ground state at 1000°C. [Hint: use the Rydberg equation to find the electronic energy levels in the H atom.]

Question 5
(a) Calculate the value of the molecular translational partition function, q_{trans}, for N_2 at 298 K in a 24.8 L container (the standard volume of an ideal gas).
(b) How will the value of q_{trans} change with an increase in T, or a decrease of P?
(c) What is the value of q_{trans} for gaseous N and N_3 under the same conditions as (a)?
(d) At temperatures below which the value of q_{trans} is less than 10, the translation energy should no longer be treated classically. What is this temperature of N_2 in the same 24.8 L container from (a) when $q_{trans} = 10$?