University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 3
Homework due on Monday 26 Jan. at midnight.
Show calculations as well as answers for all problems.

1) An energy "ladder" composed of an infinite sequence of equally spaced energy levels is a model for the vibrational motions of atoms in crystals or bond vibrations in diatomic molecules.

a) The partition function for the energy ladder was given in Lecture 5 as $q = \sum_{n=0}^{\infty} e^{-n\varepsilon/k_B T} = \left(1 - e^{-\varepsilon/k_B T}\right)^{-1}$ where ε is the spacing between adjacent the energy levels, i.e. $\Delta E = E_{n+1} - E_n = \varepsilon$, n=0, 1, 2, etc. Assume $\Delta E = \varepsilon = 1.00 \times 10^{-20} J$. Calculate q at T=1K, 300K, and 2000K. Based on your answers, what percentage of particles are in the ground state at each temperature? Calculate also the internal energy and entropy per mole at each temperature assuming $Q=q^N$.

b) Using the formula $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and the expression for the partition function for the ladder, calculate the heat capacity at T=1K, 300K, and 2000K.

c) Compare your answers in parts a and b and explain this trend in heat capacity.

2) The energy ladder partition function $q = \sum_{n=0}^{\infty} e^{-n\varepsilon/k_B T} = \left(1 - e^{-\varepsilon/k_B T}\right)^{-1}$ used in problem 1 corresponds to vibration in a single dimension, as might occur for the vibration of a chemical bond in a diatomic molecule. However, in an atomic crystal (i.e. a crystal composed of a pure atomic substance like copper or silver) the atoms vibration in three dimensions. In this case the total partition function is the product of partition functions corresponding to vibrations in the X, Y and Z directions: $q_{total} = q_X q_Y q_Z$. If the X, Y, and Z vibrational motions are equivalent then $q_X = q_Y = q_Z$ and $q_{total} = q^3 = \left(1 - e^{-\varepsilon/k_B T}\right)^{-3}$. Assume $Q=q^N$.

a) Calculate the internal energy per mole for the vibration of a bond in a diatomic molecule. Assume the partition function has the form of an energy ladder: $q = \left(1 - e^{-\varepsilon/k_B T}\right)^{-1}$. Assume $\Delta E = \varepsilon = 1.00 \times 10^{-21} J$ and T=2000K. Calculate also the internal energy for the vibration of an atomic crystal assuming $q = \left(1 - e^{-\varepsilon/k_B T}\right)^{-3}$ and $\Delta E = \varepsilon = 1.00 \times 10^{-21} J$ and T=2000K. Compare your answers and explain the difference.

b) Calculate the heat capacities $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ for the vibration of a bond in a diatomic molecule and for the vibration of an atomic crystal. Use the same partition functions and physical conditions used in part a.

c) There is an empirical rule for the heat capacities of atomic crystals called the Law of Dulong and Petit, which states that as the temperature increases, the heat capacity approaches a constant. Based on your answer in part b, what is this constant? Hint: the constant has the form 3X where X is a well-known quantity.

3) Suppose we have an equilibrium between two crystalline forms A and B of the same pure element: $A \rightleftarrows B$.Within each crystal A and B the atoms vibrate and the vibrational energies are described by energy ladders as described in lecture 5 and in problems 2 and 3. We take as a very simple assumption that the difference between these two crystals is that the spacing between the energy ladders is different. Suppose the spacing between the energy levels in crystal A is $\varepsilon_A = 5.00 \times 10^{-21} J$. Assume $Q=q^N$

a) Assume for crystal form B, $\varepsilon_B = 10\varepsilon_A$. Calculate q_A, q_B, and the equilibrium constant K. Assume T=1000K

b) Repeat the calculations in part a only now assume $\varepsilon_B = 0.10\varepsilon_A$. How is the equilibrium influenced by changes in the energy level spacing? Can you explain this trend?

c) To clarify, calculate the entropy changes involved in parts a and b. Assume $N=10^{24}$. To do this use the expression for the entropy of an energy ladder given in lecture 5, and in each case calculate S_A, S_B, and then $\Delta S = S_B - S_A$.

4) Consider the helix coil transition for a tetramerN=4.

a. Calculate the average number of helical units and the fractional helicity for s=0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 assuming a non-cooperative model

b. Repeat the calculations in part a assuming a fully-cooperative model.

c. Plot your results from parts a and b. What features of these graphs differ most significantly for the two models?