

CHEM 482, sec 0102. Homework #1

Due date: Wed, February 18, 2004, 10am

A printed or hand-written homework (no electronic versions please) is due no later than 10am Wed, February 18, 2004. It can be handed in during the class (after the lecture). If you are unable to come to the class, please bring it to my office at any other time before the deadline.

1. (5 points) A macromolecule has three conformations, T_0 , T_1 , and T_2 , which are characterized by Gibbs free energies of -1.7 kJ/mol, 0 kJ/mol, and 2.9 kJ/mol.

(a) Calculate the fraction of the molecules in each conformation at 25°C .

(b) At what temperature will the ratio of these fractions be 3:2:1 ?

2. (10 points) Consider ligand binding to a protein molecule containing 3 independent binding sites (let's call them A, B, and C), with the equilibrium (association) constants k_A , k_B , and k_C . Using the concept of partitioning between various ligand-bound states of the protein, derive an expression for the average number of ligands bound per protein as a function of the free ligand concentration. Derive a relationship between the macroscopic (stoichiometric formulation) and microscopic equilibrium constants.

3. (5 points) Consider a molecule with the energy levels $\epsilon_0, \epsilon_1, \epsilon_2, \dots$. The molecular partition function is $q = \sum_i e^{-\epsilon_i/kT}$. It is convenient to set the energy of the ground state to

0, so that the energy levels become $0, \epsilon_1 - \epsilon_0, \epsilon_2 - \epsilon_0, \dots$, and the resulting partition function is $q_o = \sum_i e^{-(\epsilon_i - \epsilon_0)/kT} = 1 + e^{-(\epsilon_1 - \epsilon_0)/kT} + e^{-(\epsilon_2 - \epsilon_0)/kT} + \dots$. This latter expression differs from the

original one by a temperature-dependent factor $e^{\epsilon_0/kT}$: $q_o = q e^{\epsilon_0/kT}$. Would the presence of this factor (its derivative over T is not zero) affect the results that we obtained for (1) the number of particles in a given state, (2) the total energy and (3) the entropy of a system of N molecules. Explain why or why not. Show your derivations.