University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

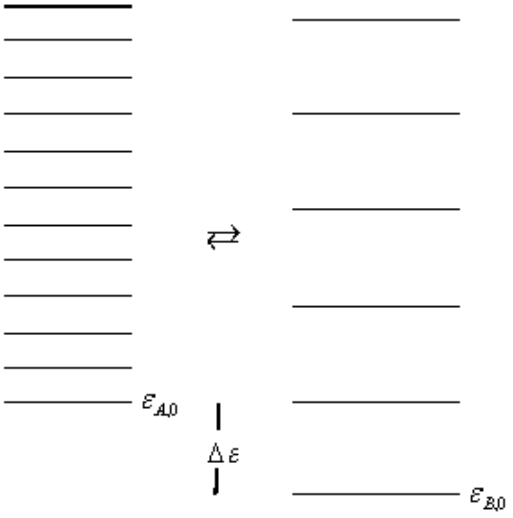
Homework Assignment 4

Due at midnight onTuesday 2/03/15. Show calculations as well as answers.
Note: This homework set contains material from pretty much the entire first half of the course. It is good practice for the midterm exam on 6 Feb.

1) Consider the equilibrium between molecule A and molecule B, pictured at the right. We represent the energies of molecule A and molecule B as energy ladders. As shown in the diagram, the ground state energies are related by

$$\varepsilon_{B,0} + \Delta\varepsilon = \varepsilon_{A,0}$$

For energy ladder A the spacing between energy levels is ε_A and for energy ladder B the spacing between energy levels is ε_B



a) Using energy ladder expressions for the partition functions, write out the expression for the equilibrium constant in terms of ε_A, ε_B, $\Delta\varepsilon$, and T. The constant k_B will also be in the expression. Hint: see Lecture 8.

b) Using your result in part a, calculate the equilibrium constant at T=10K. Calculate also the standard molar Gibbs energy change ΔG^o. Does the equilibrium lie toward A or B in this case? Calculate the standard molar enthalpy ΔH^o, and the standard molar entropy ΔS^o and determine whether the equilibrium is determined mainly by the enthalpy change or the entropy change. Assume $\Delta\varepsilon=1.00\text{x}10^{-20}$J. Also assume $\varepsilon_B = 1.00\times10^{-20}\,J$ and $\varepsilon_A = 1.00\times10^{-21}\,J$.

c) Raise the temperature to T=1000K and repeat the calculation. Is A or B favored now, and is this due mainly to the entropy term or the enthalpy term?

2) For a polypeptide composed of N monomers that undergo C to H transitions non-cooperatively, the structural state of each monomer can be treated as a two level system. The energy of the C structure will be $\varepsilon_C = 0$ and the energy of the H structure will be

$\varepsilon_H = \varepsilon$. Then the partition function for a single monomer is $q = 1 + e^{-\varepsilon/k_B T} = 1 + s$, where $s = e^{-\varepsilon/k_B T}$ The partition function for a polypeptide composed of N distinguishable monomers is $Q = \left(1 + e^{-\varepsilon/k_B T}\right)^N = \left(1 + s\right)^N$.

a) Calculate the Internal Energy U divided by T i.e. $\frac{U}{T}$ for this peptide if N=100. and s=0.500. Hint: Use the expression for the internal energy of a two level system and substitute $\varepsilon = -k_B T \ln s$

b) Using your result from part a, calculate the entropy S for this peptide if N=100. and s=0.500.

c) Suppose s changes from 0.500 to 1.50. Calculate the change in helical fraction Δf_H, and the change in entropy ΔS when one mole of proteins, each composed of 100 monomers, has this change in helical fraction. Explain these changes.

3) As shown in Lecture 9 , the Zipper model has a simple equation for the partition function that can be used to determine helicity f_H: $q = q_0 \left(1 + \sigma \sum_{k=1}^{N} \left(N - k + 1\right) s^k\right)$ where the term N-k+1 is the number of way you can arrange k contiguous H monomers in a peptide chain N monomers long.

a) From the partition function equation given above for the zipper model, it is easily shown that the probability of observing a helical sequence of length k in a peptide N monomers long is:

$$p_k = \frac{q_0 \sigma}{q}\left(N - k + 1\right) s^k$$

For N=30, s=1.0, and σ=0.0001, determine the relative probability of observing a helical sequence of length k=10 versus k=25. Repeat the calculation for s=5.0. Explain these results.

b) For N=30 and s=1.5, and σ=0.001, what is the most probable helical length k in a protein with N monomers? What is the most probable helical length k if s changes to 5? Explain these results. Hint: Determine the maximum probability k by differentiating the expression for p_k with respect to k. Then solve $\frac{\partial p_k}{\partial k} = 0$ for k*, the k for which the probability is maximum.

c) In Lecture 9, we reviewed various ways to determine the fractional helicity f_H using the Zpper model. Using the information provided in Lecture 9, determine q and f_H for N=30, s=1.5, σ=0.001. Assume q_0=1. Hint: Use the closed form expressions for q in equation 9.12 and for f_H in 9.13. How can these expressions be simplified to make your calculations easier?

4) In the lecture notes we did not obtain a general expression for the partition function for the Bragg-Zimm model. As explained in Lecture 10, the Bragg-Zimm partition function is calculated using a 2x2 matrix $\tilde{M} = \begin{pmatrix} 1 & \sigma s \\ 1 & s \end{pmatrix}$. To obtain the partition function for a peptide N monomers long we use the expression: $\frac{q}{q_0} = \begin{pmatrix} 1, & 0 \end{pmatrix} \tilde{M}^N \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ where (1, 0) is a row vector with elements 1 and 0 and $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ is a column vector.

a) Using statistical matrix approach, obtain the partition function for a Bragg-Zimm trimer (N=3).

b) Using your expression for a Bragg-Zimm trimer from part a, calculate the fractional helicity f_H for s=1.00 and σ=0.001.

5) As shown in lecture 10, for very large values of N, there is a simple form for the Bragg-Zimm partition function: $\ln q \approx N \ln \lambda_1$, where $\lambda_1 = \frac{1 + s + \sqrt{(1-s)^2 + 4\alpha s}}{2}$.

a) Assuming N=10000, s=1, and σ=0.001, calculate λ_1.

b) Calculate the average number of helical monomers $\langle n \rangle$ and the fractional helicity f_H assuming, N=10000, s=1.0, σ=0.001

6) For a protein with four ligand binding sites the general expression for the binding polynomial Q is: $Q = [P]\left(1 + 4k_1[L] + 6k_1k_2[L]^2 + 4k_1k_2k_3[L]^3 + k_1k_2k_3k_4[L]^4\right)$ where the microscopic equilibrium constants k_1, k_2, k_3, and k_4 correspond to equilibria between the ligand L and the four partially filled or completely filled polymers.

a) In lecture we showed that if $k_1=k_2=k_3=k_4=k$ we obtain the expression for non-cooperative binding. Assuming non-cooperative binding calculate the average number of sites bound $\langle \nu \rangle$ for k=100 and [L]=0.01M. Repeat for k=100, [L]=0.001M and k=100 [L]=0.0001M.

b) Repeat the calculation in part a only now assume fully cooperative binding. Explain any differences in your results for part a and b.