BioE 103 Fall 2018
Exam 1: Entropy and Energy
Sept. 24, 2018
Take Home Regrade Due Oct. 1, 2018

Constants: $k_B = 1.38 \times 10^{-23}$ J·K^{-1}; $R = 8.31$ J·K^{-1}·mol^{-1}; $N_A = 6.02 \times 10^{23}$; $q_e = -1.6 \times 10^{-19}$ C; $\frac{1}{4\pi\epsilon_0} = 9.0 \times 10^9$ Nm^2 /C^2

Units: J = m^2 kg s^{-2} = N·m **Conversions:** 1 kcal = 4180 kJ; 1 rad = 57deg

Formulas: $dS = \frac{dQ}{T}$ $dU = dQ + dW$ $dW = PdV$

$$P(M,N) = W(M,N)p^N(1-p)^{M-N} \qquad W(M,N) = \frac{M!}{N!(M-N)!} \qquad lnN! \approx NlnN - N$$

$$S = -k_b lnW \qquad S = -k_b lnW(M,N) = -k_b Nln\left(\frac{M}{N}\right)$$

$$E_{Intramolecular} = \sum_i^{\#Bonds} k_b\left(b_i - b_o\right)^2 + \sum_i^{\#Angles} k_\theta\left(\theta_i - \theta_o\right)^2 + \sum_i^{\#dihedrals} k_\chi\left[1 + \cos\left(n\chi - \delta\right)\right] + \sum_i^{\#atoms}\sum_{i<j}^{\#atoms}\left\{\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]\right\}$$

A. Multiple choice (5 pts each)

1. Choose the substance with the greater entropy in each of the following pairs at 298K

(a) H_2O(l), H_2O(g); (b) N_2 (0.1atm); N_2 (1atm);

(c) ethanol (C_2H_5OH)(aq); ethane C_2H_6(aq); (d) N_2O_4(g); 2NO_2(g)

2. If a covalent bond vibrational excitation is ~25kJ/mole, is it significantly populated at 298K?

(a) yes (b) maybe

(c) no (d) all of the above

3. Constant pressure heat capacity of an ideal gas, Cp is greater than constant volume Cv because

(a) more heat is required due to loss of pV work (b) more heat is required due to gain of pV work

(c) there are no energy interactions (d) all of the above

4. Molecular interactions are classified as short-ranged when the power law exponent of r^{-n} is

(a) $n < 3$ (b) $n < 2$

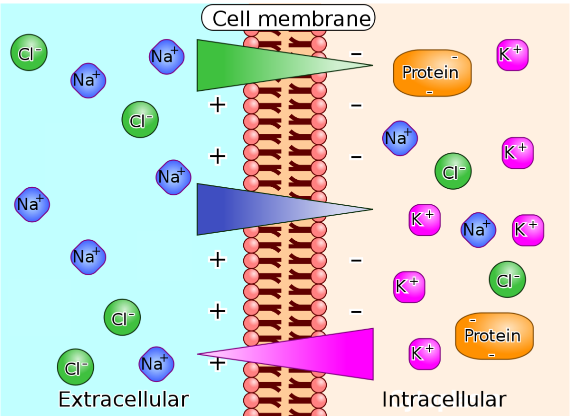
(c) $n > 3$ (d) $n > 4$

5. Which state function(s) predict spontaneous change for a stretched DNA polymer under physiological condition?

(a) $dU<0$ (b) $dS>0$

(c) $dH<0$ (d) all of the above

B. Longer problems (25 pts each)



6. Probability in cell biology. Osmosis through semi-permeable membranes (such as those that enclose cells) is a process mediated by entropy. Imagine a simplified scenario in which 1000 molecules of chemical K^+ and 500 molecules of chemical Cl^- are dilute solutes (among others) coexisting in an aqueous cell environment surrounded by a semi-permeable membrane. Outside the membrane is an aqueous environment which contains no molecules of K^+ and 1500 molecules of Cl^-. The membrane is permeable to K^+, but not to Cl^-. You may assume that K^+ and Cl^- are ideal, i.e., that they do not interact with each other or anything else in this environment.

(a) What is the difference in entropy (ΔS) between the initial state described above and a state in which 100 of the K^+ molecules had moved to the outside of the membrane? Show your work.

(b) Why can we neglect the entropic contribution of the Cl^- for the calculation in part a? Explain.

(c) How many molecules of K^+ would have to escape the membrane for the system to be at equilibrium?

(d) **Extra Credit (5 pts).** Cell membranes are permeable to water and to certain solutes. Using your understanding of the laws of thermodynamics, explain what will happen to cells if they are put into pure distilled water (i.e. water that is missing ions such as K^+ and Cl^-)

7. Protein Folding. For the folding of a 100 residue protein, containing 6 glycines and 4 prolines, at 300K, consider the following assumptions.

- When unfolded, each residue except the glycine and proline residues can take on 3 conformations of equal energy; glycine can take on 4 conformations; proline can take on only 1 conformation.
- The conformation of the folded state has every residue in a single unique conformation.
- Assume water molecules have 6 possible configurations when surrounding the polar sidechains otherwise they have only 2 possible configurations around non-polar groups.
- All hydrophobic sidechains are buried in the folded state with no water around them.
- Assume water-protein interaction energy is zero.

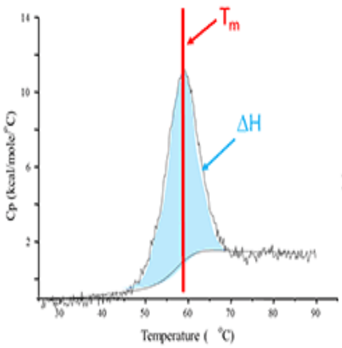
(a) Calculate the entropy for components only involving the protein ($\Delta S_{protein}$), i.e. no water. Does the protein entropy favor folding or unfolding?

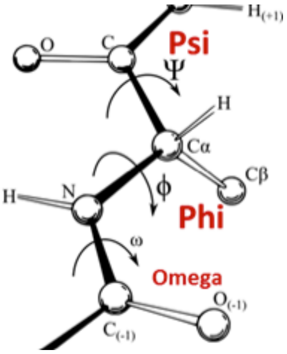
(b) Calculate the change in entropy for water interacting with one polar residue, $\Delta S_{polar,H2O}$. Show your work. Does $\Delta S_{polar,H2O}$ favor folding over non-folding?

(c) Calculate the change in entropy for water interacting with one non-polar group, $\Delta S_{non\text{-}polar,H2O}$. Show your work. Does $\Delta S_{non\text{-}polar,H2O}$ favor folding over non-folding?

(d) **Extra credit (5 pts).** How many of the 100 residues of the protein should be hydrophobic and hydrophilic to favor the folded state over the unfolded state?

8. Protein Heat Capacity. The variation in the constant pressure heat capacity, C_P, of a protein as a function of temperature is known as the melting curve, where at the melting temperature T_m, C_P measures the relative populations of the folded and unfolded proteins in water at 50% each. We would like to use C_P measurements to understand what energetic interactions are disrupted in the folded protein to create the unfolded state. For each type of interaction (b-e), will it contribute to change in heat capacity from 300K-370K?





(a) The folding to unfolding event occurs over a range of 25-70C. What is the value of k_bT at the two temperature end points T_i and T_f?

(b) Assume a C-H bond of alanine is broken when it goes from its equilibrium value of 1 Å to 2 Å, which causes a change in hybridization such that the associated bond angle goes from 109° to 180°. How much energy in the form of heat is needed to break the C-H bond and change the hybridization in units of k_bT (assume T_f) if k_b=2000 kj/mol/Å^2 and k_θ=125 kj/mol/rad^2

(c) The ϕ, ψ angles determine the preferences for secondary structure such as α–helices and β–sheets and random coils (let $\chi = 60$, n=3 and δ=0), while rotation of ω of the peptide bond is stiffer and is trans as opposed to cis (χ=180, n=2, and δ=0). If $k_\chi = 0.125$ kj/mole for ϕ, ψ and $k_\chi = 12.5$ kj/mole for ω, how much heat is needed to unfold the secondary structure and induce a cis conformation for the peptide bond?

(d) The protein has two ion pairs (both are arginine---aspartic acid), one which sits in the protein interior and one at the surface. Estimate how much energy is needed to dissociate the two ion pairs? (Remember your units with $1/4\pi\epsilon_0$)

(e) **Extra credit (5 pts).** Evaluate the energy for breaking the Lennard-Jones interaction of two alanine side chains using order of magnitude estimates of the size of the side chains and assuming a reasonable energy scale.