**Biophysical Chemistry – CH 4404 01**
**Assignment 3**

**Due Friday, September 12 (by 4:00 pm)**

Please complete the answers to this assignment on a separate page (or pages), showing your work and sources (if you referred elsewhere for constants, enthalpies, etc.).

1. State the second law of thermodynamics in three different ways. You can use an equation for one of your restatements. It's okay to use the Internet, but cite your sources. (3 points)

2. Empirically, we know that hot air rises. The upper floors of a building are warmer than the lower floors, and the lower density of hot air creates a buoyancy effect that pushes it up. In this problem, we will answer the following question: Given that warm air rises, why are the mountains cold?

   (a) Suppose a gust of wind **rapidly** blows 1 liter of an ideal gas (the system) from a valley to a mountaintop. At sea level, the temperature is 25 $^0$C, and the pressure is 1 bar. At the top of the mountain, the atmospheric pressure is 0.85 bar. What assumptions can you make about the gas as it travels from the valley to the mountaintop? (Hint: if the transformation is **rapid** what type of transformation might be a good model?) (2 points)

   (b) Given your assumptions in part (a), calculate the volume and temperature of the gas as it blows from the valley to the mountain. (3 points)

   (c) Given your results from (a) and (b), if warm air rises, why are the mountains cold? (1 point)

3. In the first week of class, we discussed the idea of protein folding: Under normal conditions, proteins adopt a folded, compact form (the native state). But it is possible for proteins to "unfold" and adopt a random, disordered form. This unfolded form is thought to behave similarly to a piece of spaghetti, with few (if any) intra-molecular interactions, and no regular secondary or tertiary structure:

   F(olded) → U(nfolded)

   (a) Using PyMOL, open the PDB file 2OED. This file shows the coordinates for a small protein called GB3. Render the file as a cartoon diagram. As you can see, GB3 contains four strands, numbered 1 through 4 starting from the N-terminal end of the protein. It also contains a single alpha helix. If you had to choose an "unfolding pathway" for GB3, what would you devise? In other words, what parts of GB3 would unfold first, and why? (There's no single correct answer here, just take a look and see what you can come up with.) (1 points)

   (b) Intuitively, the entropy of GB3 would be much higher in the unfolded state than in the folded state. Yet in solution, it is observed that the folded state is favored, and unfolding

is not spontaneous. Give a thermodynamic explanation for why this might be (*Hint:* Think about the system vs. the surroundings; for more help see pp. 62-65 of your book.) (3 points)

(c) Which would you expect to have the higher heat capacity: N or U? Why? (3 points)

*Note:* Chapter 3, question 19 is closely related to this question. You do not need to do question 19 for homework (the answers are in the appendix), but future homework questions will pertain to protein folding, and the experience may prove useful.

4. Tinoco chapter 3, question 6. For part (a), think about the highest temperature that liquid water can attain. (6 points)

5. Tinoco chapter 3, question 20. Part (a) asks you to determine the starting materials you would need if you were determining the enthalpy of formation for formic acid from first principles. You may wish to examine Examples 2.8 and 2.9. You do not have to calculate the enthalpy of formation, but you can for extra credit. (8 points + 3 extra credit points)

6. Tinoco chapter 3, question 22. (4 points)

7. Tinoco chapter 3, question 24. (6 points)

8. Tinoco chapter 3, question 26. (10 points) Two quick notes:

   (i) Note for parts (d) and (e), you should assume that the question is talking about the *change* in each of the quantities (ie. $\Delta U$, $\Delta H$, $\Delta S$, $\Delta p$, etc.).
   (ii) For part (e), assume that the relevant quantities are for the *system*, i.e. the change in internal energy (U) *for the system*, or the change in enthalpy *for the system*.