Biophysical Chemistry – CH 4404 01
Assignment 4

Due Friday, September 27 at 5:00 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. In the last assignment, we discussed protein folding. Recall that this reaction can be represented by:

   $$N \rightarrow U \text{ (at } T_1\text{)}$$

   Where N is the native state, and U is the unfolded state. In class, we determined that if $\Delta\bar{H}^0(T_1)$ and $\Delta\bar{S}^0(T_1)$ are known, an approximation for the Gibbs energy at a different temperature T_2 is

   $$\Delta\bar{G}^0(T_2) = \Delta\bar{H}^0(T_1) - T_2\Delta\bar{S}^0(T_1) \tag{1}$$

   Equation (1) assumes that enthalpy and entropy do not change as a function of temperature. In this problem, we will determine the limitations of that approximation.

   (a) If $\bar{C}_P(N)$ and $\bar{C}_P(U)$ are both known and constant over the interval $[T_2, T_1]$, write an expression for the entropy $\Delta\bar{S}^0(T_2)$ in terms of the known parameters of the system. As a reminder, the other known parameters are T_1, $\Delta\bar{S}^0(T_1)$, and $\Delta\bar{H}^0(T_1)$, and we derived an expression in class for $\Delta\bar{S}^0(T_2) - \Delta\bar{S}^0(T_1)$. In your final result, you should express the difference in heat capacities as $\Delta\bar{C}_P = \bar{C}_P(U) - \bar{C}_P(N)$. (3 points)

   (b) Write an analogous expression to part (a) for the enthalpy $\Delta\bar{H}^0(T_2)$. (3 points)

   (c) Using your answers for (a) and (b), write an expression for $\Delta\bar{G}^0(T_2)$. It is always true that

   $$\Delta\bar{G}^0(T_2) = \Delta\bar{H}^0(T_2) - T_2\Delta\bar{S}^0(T_2)$$

   Thus, your answer for part (c) involves taking your answers from parts (a) and (b) and simplifying some algebra. Your expression should be in terms of the known enthalpy and entropy change (at T_1), the change in heat capacities $\Delta\bar{C}_P$, the starting temperature T_1, and the ending temperature T_2. How does your expression differ from eq. 1 above? (3 points)

   (d) A protein unfolding at 298 K has typical values of 168 kcal mol^{-1} for $\Delta\bar{H}^0$, 0.55 kcal mol^{-1} K^{-1} for $\Delta\bar{S}^0$ and a $\Delta\bar{C}_P$ of 5.0 kcal mol^{-1} K^{-1}. Using your favorite plotting software, plot the expression for $\Delta\bar{G}^0(T_2)$ you developed in part (c) vs. temperature from 200 K to 400 K (at increments of 5 K). On the same graph, plot the simplified expression from above (eq. 1). (3 points)

(e) What does your plot tell you about the accuracy of eq. 1? (3 points)

2. The following expression applies for a change in Gibbs energy when only P-V work is present:

$$dG = VdP - SdT$$

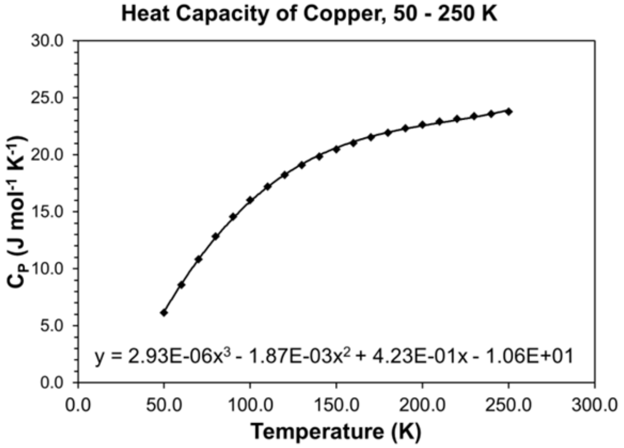
Based on our discussion of multidimensional calculus, write equations for S and V in terms of partial derivatives of G. (3 points)

3. Tinoco chapter 3, question 12. (6 points)

4. Throughout the class, we've assumed that heat capacity is constant as a function of temperature, and this has allowed us to simplify many integrals. In practice, this assumption does not hold, especially over large temperature differences. In this problem, we will examine the behavior of a real material. We will consider the entropy change versus temperature when pressure is constant:

$$\bar{S}(T_1) - \bar{S}(T_2) = \int_{T_1}^{T_2} \frac{\bar{C}_p(T)}{T} dT \approx \bar{C}_p \ln \frac{T_2}{T_1}$$

In the expression above, the approximation on the far right assumes that heat capacity is constant, whereas the integral expression makes no such assumption. The $\bar{C}_P$ vs. T curve for solid copper is given below, along with third-order polynomial approximation to the experimental data.



a. The heat capacity at 150 K is 20.50 J mol^{-1} K^{-1}. Assuming that the heat capacity is constant at this value, calculate $\Delta\bar{S}$ as the temperature is raised from 100 K to 200 K. (4 points)

b. Using the polynomial approximation calculate the $\Delta\bar{S}$ over the same temperature range taking into account the temperature dependence of $\bar{C}_P$. Compare your answer with part (a). This is one of the few questions in this class where you will have to perform an integral. (8 points)

c. Looking at the curve, do you think the approximation in part (a) would become better or worse at higher temperatures? (3 points)

5. Tinoco chapter 4, question 7, part (a). (6 points)

6. Assuming that all species are ideal gasses, how would the free energy change you calculated in question 5 change if the pressure were lowered to 0.5 atm (at the same temperature)? (3 points)