# Biophysical Chemistry – CH 4403 01
## Assignment 4

## Due Friday, September 26 at 4:30 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

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

   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 (Excel is also fine), 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) Is equation 1 always accurate? Explain in plain English why or why not. (3 points)

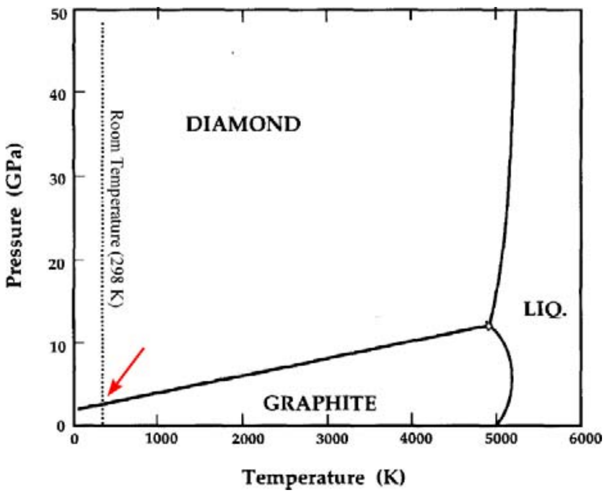
2. We will not discuss the Helmholtz energy (A) very deeply in this class, but it is a state function like enthalpy and Gibbs energy. It is defined as $A \equiv E - TS$. It be shown that, when only $pV$ work is done, the following expression applies for a change in the Helmholtz energy:

$$dA = -SdT - PdV$$

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

   b. Given that this equation is analogous to $dG = VdP - SdT$, under what conditions is $\Delta A$ equal to the non-$PV$ work that can be done by the system? (2 points)

3. Carbon can exist in several allotropes, two of which are graphite and diamond. One way to represent the different states of matter is a *phase diagram*. The phase diagram displays the most stable phases of matter as a function of pressure and temperature. The phase diagram for carbon is shown below (adapted from Bundy, *et al*. (1996) *Carbon*. 34(2): 141).



The solid lines on this graph represent the boundaries between phases (or allotropes in this case). At lower temperatures and pressures, carbon is most stable as graphite. Above 5000 K, carbon is most stable as a liquid. Each solid back line represents the boundary between the two phases where $\Delta\bar{G}^0 = 0$.

In example 3.9, your book caculates the location of one point along the line representing the graphite-diamond boundary. For 298 K, the book shows that $\Delta\bar{G}^0 = 0$ when the pressure is $1.5 \times 10^4$ bar, or 1.5 GPa (since 1 bar is 100,000 Pa). This point is indicated by the red arrow above.

In this problem, we will calculate the location of a second point on the phase diagram above. We will do this by calculating $\Delta\bar{G}^0$ along two paths: a constant pressure path (1 bar) where we increase the temperature to 1000 K, and a constant temperature path where we increase the pressure to the phase boundary.

The properties of diamond and graphite that we will need are given in the table below:

| **Property at 298K, 1 bar** | **Graphite** | **Diamond** |
|---|---|---|
| $\Delta\bar{H}^0$ (kJ mol$^{-1}$) | 0 | 1.90 |
| $\bar{S}^0$ (J mol$^{-1}$ K$^{-1}$) | 5.74 | 2.38 |
| $\Delta\bar{G}^0$ (kJ mol$^{-1}$) | 0 | 2.90 |
| $\bar{C}_p$ (J mol$^{-1}$ K$^{-1}$) | 6.12 | 8.53 |
| Density ($\rho$, gm cm$^{-3}$) | 2.26 | 3.54 |
| $\bar{V}$ (m$^3$ mol$^{-1}$) | $5.31 \times 10^{-6}$ | $3.39 \times 10^{-6}$ |

a. Using equation 1, calculate the $\Delta\bar{G}^0$ for the transition from graphite to diamond at 1000 K holding pressure constant at 1 bar. For 4 points of extra credit, you can repeat the calculations using your equations from question 1(c). Be sure to state all assumptions you've made. (3 points + 4 extra credit points)

b. Now, holding temperature constant at 1000 K, find the pressure at which graphite will spontaneously convert to diamond. Make sure your work makes sense according to the discussion above. (4 points)

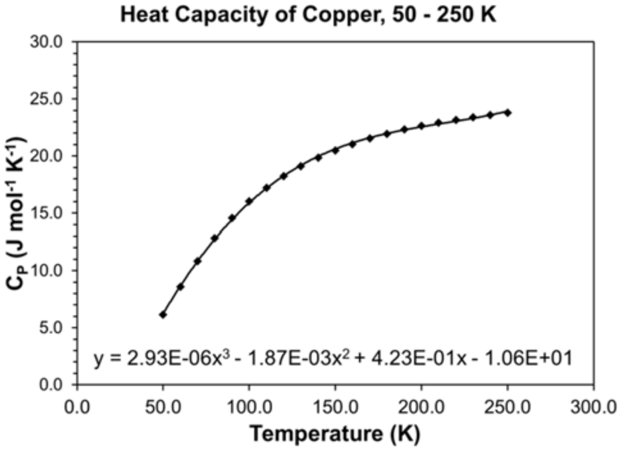
c. You will find that your answer differs slightly from the value presented in the phase diagram; it is lower than the real pressure. Why? (1 point)

We will not discuss phase diagrams in detail in this class, although in a traditional thermodynamics class they are very important. The goal of this problem is to show you how you can calculate physical properties from the thermodynamic data we have been discussing. Conversely, if you know the phase diagram, you can back-calculate properties like the difference in density, heat capacity, etc.

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. (6 points)

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

5. Consider the oxidation of $CH_4$(g) with $O_2$(g) to form $CO_2$(g) and $H_2O$(l).

a. Calculate $\Delta\bar{H}^0$, $\Delta\bar{S}^0$, and $\Delta\bar{G}^0$ for this reaction at 298 K and 1 bar. (4 points)

b. Assuming that all gaseous species are ideal gasses, calculate $\Delta\bar{G}^0$ of the reaction above at 298 K and 0.5 bar. Is the reaction spontaneous? (3 points)