More problems from Dill: 8.8, 8.12, 8.13
(Problem Set 4, part 2)

8.8) Computing enthalpy and entropy with a temperature dependent heat capacity.
The heat capacity for liquid n-butane depends on temperature: $C_P(T) = a + bT$, where
a=100LK^{-1}mol^{-1} and b=0.1067JK^{-2}mol^{-1}, from its freezing temperature Tf=140K to
Tb=270K, its boiling temperature.

(a) Compute ΔH for heating liquid butane from TA=170K to TB=270K.

$$\Delta H = \int_{T1}^{T2} C_p dT = \int_{170}^{270} a\,dT + \int_{170}^{270} bT\,dT = a\Delta T + \frac{bT^2}{2}\bigg|_{T1}^{T2} =$$

$$a(270K - 170K) + \frac{b}{2}[(270K)^2 - (170K)^2] = 12.35\frac{kJ}{mol}$$

(b) Compute ΔS for the same process.

$$\Delta S = \int_{T1}^{T2}\frac{C_P}{T}dT = \int_{T1}^{T2}\left(\frac{a}{T} + b\right)dT = a\ln\left(\frac{T2}{T1}\right) + b\Delta T =$$

$$\left(100\frac{J}{Kmol}\right)\ln\left(\frac{270K}{170K}\right) + \left(0.1067\frac{J}{K^2 mol}\right)(100K) = 56.93\frac{J}{Kmol}$$

8.12) ΔS for an adiabatic expansion of a gas. In an adiabatic quasi-static expansion of
an ideal gas, how do you reconcile the following two facts: (1) the increase in volume
should lead to an increase in entropy, but (2) in an adiabatic process, δq=0 so there
should be no change in entropy (since $dS = \frac{\delta q}{T} = 0$)?

The reason there is not a contradiction here is that the first statement is not the whole
story. Entropy is not only a function of volume but also of temperature. It is true that if
we increase the volume of a gas at constant temperature, the entropy should increase.
However, this would not be a quasi-static, adiabatic process. In a process where δq=0,
there is a simultaneous reduction in temperature which decreases the entropy enough to
compensate for the entropy increase induced by the volume change. Mathematically we
can observe this phenomenon as follows, and observe how these volume and temperature
changes relate such that $dS = 0$. Expand the differential entropy element dS in terms of its
partials and integrate:

$$\int dS = \int\left[\left(\frac{dS}{dT}\right)_V dT + \left(\frac{dS}{dV}\right)_T dV\right] = \int\frac{P}{T}dV + \int\frac{C_V}{T}dT$$

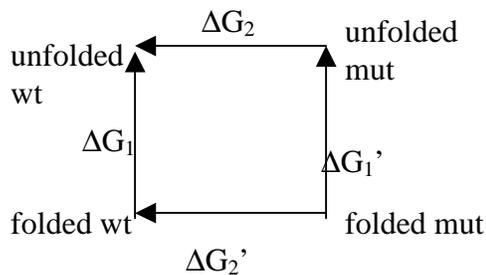$$= \int_{V1}^{V2}\frac{Nk}{V}dV + \int_{T1}^{T2}\frac{C_V}{T}dT = Nk\ln\frac{V2}{V1} + C_V\ln\frac{T2}{T1} = 0$$

8.13) A thermodynamics cycle for mutations in protein folding. Suppose that you can
measure the stability of a wild-type protein, ΔG_1 = Gfolded – Gunfolded, the free energy

difference between folded and unfolded states. A mutant of that protein has a single amino acid replacement. Design a thermodynamic cycle that will help you find the free energy difference $\Delta G_2 = G_{\text{unfolded, mutant}} - G_{\text{unfolded, wildtype}}$, the effect of the mutation on the unfolded state.

Before you see the solution, assume the following information as well, and try this problem! (It's a pretty easy problem, they just left out some crucial information.) (1) Assume you can also measure $\Delta G_1' = G_{\text{folded, mutant}} - G_{\text{unfolded, mutant}}$. This isn't too unreasonable considering that you can do it for the wildtype. (2) ALSO assume that you can *estimate* $\Delta G_2' = G_{\text{folded, mutant}} - G_{\text{folded, wildtype}}$ by computer simulation. You need this information to solve this problem. Make sure you understand WHY this information is needed!

We know that G is a state function, so it does not depend on the path you use to get from state-to-state. If you have measured how much energy it takes to get from state 1 to 2 along one path, then you can use this energy again to figure out the components of another path. (As long as you have enough information to get your unknowns!)

$\Delta G_{1\,+}\,\Delta G_2' = \Delta G_1'\,_+ \Delta G_2$ so:
$\Delta G_2 = \Delta G_1 - \Delta G_1' + \Delta G_2'$