Calculating the Al_2SiO_5 Phase Diagram

mineral	ΔG°f (kJ)	ΔH°f (kJ)	$S°_{298,1}$ (J/K)	$V°_{298,1}$ (J/bar)	a (kJ/K)	b(kJ/K^2)	c (kJ K)	d (kJ $K^{-1/2}$)
and	-2440.97	-2588.77	92.70	5.153	0.2773	-6.588e-6	-1914.1	-2.2656
ky	-2442.59	-2593.13	83.50	4.414	0.2794	-7.124e-6	-2055.6	-2.2894
sil	-2438.93	-2585.89	95.50	4.986	0.2802	-6.900e-6	-1375.7	-2.3994
(all values are per mole, where applicable)								

Recall the formula for a reaction at equilibrium:

$$\Delta \overline{H}_{rxn}(298,1) + \int_{298}^{T} \Delta C_P dT + \int_{1}^{P} \Delta V dP - T\left(\Delta \overline{S}(298,1) + \int_{298}^{T} \frac{C_P}{T} dT\right) = 0 \qquad (1)$$

For this exercise, we assume that molar volume and entropy are constants. (In reality they vary with P and T, but the effects are small in this case.) Note that all the parameters but T and P are "rxn" parameters (i.e., the difference between the products and the reactants.

Your goal is to solve this equation for a number of temperature and pressure conditions, and thereby create the Al_2SiO_4 phase diagram. You must carry out this task in Excel. Here is your strategy:

1. Solve this equation analytically (i.e., without substituting in any numbers). This requires you to keep track of all the terms in a very long polynomial. It is not difficult, but requires care and focus. The result should be a polynomial with these variables: ΔH°, S, V, a, b, c, d, P, and T. All but P and T are known. Don't worry for now about whether these are "rxn" parameters or not. A fact from math that you may have forgotten is this:

   $$\int x^{-1} dx = \ln x$$

2. The formulation in equation (1) can also give a formulation for the free energy of each phase, at least in a relative sense (i.e., you cannot use it to replicate the $\Delta G°_f$ values). This allows you to do the calculation for each phase separately, and then set their free energies equal to each other. Put into excel a dummy value for T & P for now, to which you can refer in your other cells. Try 200°C and 0.3 GPa (but you'll need to switch the units to Kelvins and bars). Type in the thermodynamic data in the table, and the formula for G. I strongly recommend splitting it up among at least 5 cells (one per term in equation (1)), and them summing them to get a value for Gibbs free energy for the phase at the T&P of interest. Splitting the formulas up will allow better checking for errors. Also, if you can manage to fit it all into a single row, it will be more convenient later.
   - One useful Excel trick for complex formulas like this is to use named ranges for the constants (e.g., the molar volume of sillimanite). You highlight the cell you want to name, and then (on the Mac) go to Insert > Name >Define, or just hit [ctrl]-L. You then type a very short descriptive name for the value (e.g., "V_S"). This can then be used in later formulas to refer to that cell's value.
   - To confirm you've gotten the formulas correct, the Gibbs free energy for andalusite at 0.3 GPa and 500 Kelvins should be -2627.57 kJ/mol

3. Now you will create G-T diagrams to display the changing stabilities with variation in pressure and temperature. This is where things get much easier if you've made your formulas all on a single row, because you can then copy that row, hide everything but the inputs (T&P) and the outputs (G for

each mineral), and make plots very rapidly. You should make two plots showing the changing stability of the three minerals as illustrated by their Gibbs free energy values.

- Make a G-T plot at a pressure of 0.3 GPa over the T range [500, 1000] Kelvins. Annotate it to point out which polymorph is stable at which temperatures.
- Make a G-T plot at a pressure of 0.5 GPa over the T range [2100, 2600] Kelvins. Annotate it to point out which polymorph is stable at which temperatures. Note also which phase is the second-most stable of the three.

4. Now you will create the P-T diagram with which you are familiar. For each of a set of fixed temperatures, you will determine the pressure that forces the G_{rxn} to be zero for each polymorph pair. Your temperatures should range from 600 to 1000 Kelvins.
   - If you have separated your formulas into distinct cells (one for each of the five terms in equation (1), then you can solve for P explicitly and simply:

     $$P_{eq} = \frac{x_1 - x_2}{V_2 - V_1} + P_0 \qquad (2)$$

     where *x* signifies those four terms in equation (1) that do not include pressure, and P_0 is the STP pressure (1 bar).
   - You should create a P-T diagram showing the three reaction boundaries. Note that you can calculate the reaction boundary even where neither of the reactants are stable. This is called the "metastable" extension of the reaction.
   - Compare the slope predicted by the Clapeyron equation to the actual slope you calculate. Are they similar? identical? If not identical, think about (and comment on) why they might differ.
   - Estimate the conditions for the triple point. How precise can you be using this graph?
5. Create a better estimate for the triple point by creating a new diagram "zoomed in" on the triple point. That is, have the pressure range only over the small range of pressures where you believe the triple point exists based on the previous graph.