ALUMINUM SILICATE - STABILITY OF THREE CRYSTAL STRUCTURES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.29.

We can apply a similar analysis to that for graphite and diamond to the more complex case of aluminum silicate Al_2SiO_3, which has three crystalline forms: kyanite, andalusite and sillimanite. Each is stable under some range of temperature and pressure.

Using the data in Schroeder's book, we can get some insight into the stability of these three forms by considering the Gibbs free energy. The thermodynamic potential for the Gibbs free energy is

$$dG = -S \, dT + V \, dP + \mu \, dN \tag{1}$$

First, if T and N are constant, we have

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \tag{2}$$

Ignoring compressibility, we can assume that V is constant as the pressure is increased. The molar volumes for the three forms are $V_k = 44.09 \times 10^{-6}$ m^3 for kyanite, $V_a = 51.53 \times 10^{-6}$ m^3 for andalusite and $V_s = 49.90 \times 10^{-6}$ m^3 for sillimanite. Therefore the Gibbs energies are

$$
\begin{aligned}
G_k &= G_{k0} + 44.09 \times 10^{-6} P \tag{3} \\
G_a &= G_{a0} + 51.53 \times 10^{-6} P \tag{4} \\
G_s &= G_{s0} + 49.90 \times 10^{-6} P \tag{5}
\end{aligned}
$$

The constants of integration G_{k0}, G_{a0} and G_{s0} can be found by requiring the energies to be those quoted in Schroeder for $P = 1$ bar $= 10^5$ Pa. As with our calculations for calcium carbonate, the difference in Gibbs energy between a pressure of zero and 1 bar is negligible so we can just set the constants of integration to the values quoted in Schroeder for $P = 1$ bar. We get

$$
\begin{aligned}
G_k &= -2443.88 \times 10^3 + 44.09 \times 10^{-6} P & (6)\\
G_a &= -2442.66 \times 10^3 + 51.53 \times 10^{-6} P & (7)\\
G_s &= -2440.99 \times 10^3 + 49.90 \times 10^{-6} P & (8)
\end{aligned}
$$

At $P = 0$, G_k is the lowest and since the slope of the line in the plot of G_k versus P is also the smallest, G_k will be less than both G_a and G_s at all pressures, so at a temperature of 298 K, kyanite is always the most stable form. The graph looks like this:
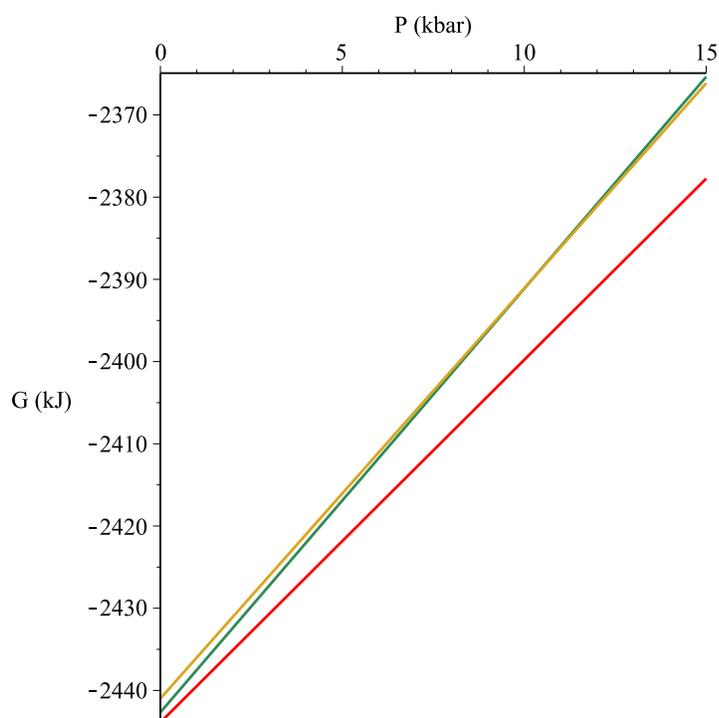
The red line is kyanite, green is andalusite and yellow is sillimanite. The latter two lines do intersect at a pressure of around 9 kbar, but kyanite is always the most stable.

At constant pressure, we can use 1 to investigate the stability of the three forms as temperature varies. We have

$$
\left(\frac{\partial G}{\partial T} \right)_{P,N} = -S \tag{9}
$$

By subtracting the two forms of this equation for two crystal types, we can get a relation for the difference in Gibbs energy between two types:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{P,N} = -\Delta S \tag{10}$$

The entropy of a substance can be written as

$$dS = \frac{dQ}{T} = C_P \frac{dT}{T} \tag{11}$$

so the total entropy as a function of temperature depends on the heat capacity C_P. If we take Schroeder's word for it that C_P at high temperatures depends only on N, then even though the raw value of S for a sample of solid increases with T, the difference between the entropy values for two substances should remain relatively constant as we increase T. We can therefore integrate 10 to get

$$\begin{aligned}
\Delta G\left(T_2\right) &= \Delta G\left(T_1\right) - \int_{T_1}^{T_2} \Delta S\left(T\right) \, dT \tag{12}\\
&= \Delta G\left(T_1\right) - \Delta S\left(T_2 - T_1\right) \tag{13}
\end{aligned}$$

The entropy values quoted in Schroeder's book for 1 mole at $T = 298$ K and $P = 1$ bar are $S_k = 83.81$ J K^{-1}, $S_a = 93.22$ J K^{-1} and $S_s = 96.11$ J K^{-1} so using the Gibbs energy values from above, we get (with energies in kJ):

$$\begin{aligned}
\Delta G_{ka} &= G_k - G_a - \left(S_k - S_a\right)\left(T - 298\right) \tag{14}\\
&= -1.22 + 9.41 \times 10^{-3}\left(T - 298\right) \tag{15}\\
\Delta G_{ks} &= -2.89 + 12.30 \times 10^{-3}\left(T - 298\right) \tag{16}\\
\Delta G_{as} &= \Delta G_{ks} - \Delta G_{ka} \tag{17}\\
&= -1.67 + 2.89 \times 10^{-3}\left(T - 298\right) \tag{18}
\end{aligned}$$

If we plot these three lines, we get
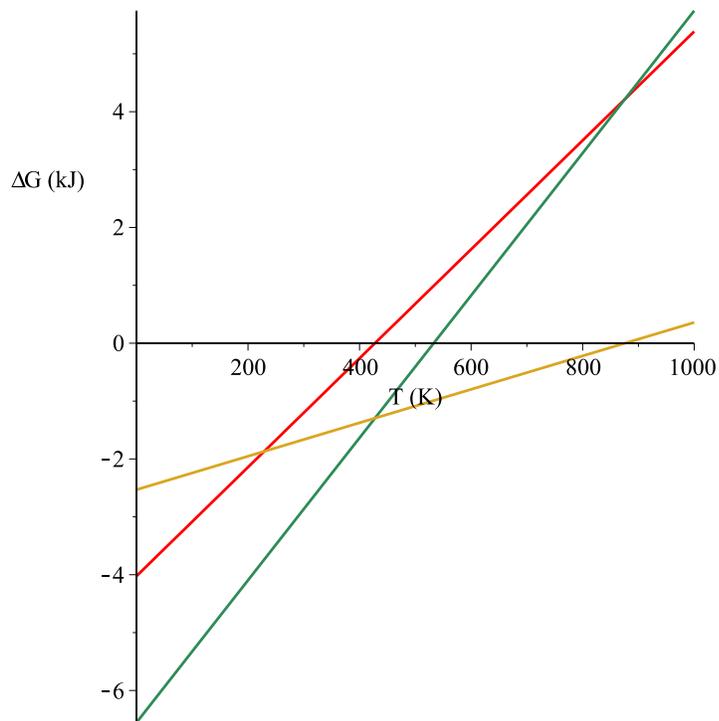
Here, ΔG_{ka} is red, ΔG_{ks} is green and ΔG_{as} is yellow. To use this graph to determine the temperature range for which each structure is the most stable, we observe that the most stable form has the lowest value of G at that temperature. For kyanite to be the most stable, for example, we must have $G_k < G_a$ and $G_k < G_s$. Therefore, $\Delta G_{ka} = G_k - G_a < 0$ and $\Delta G_{ks} = G_k - G_s < 0$. Looking at the graph, these conditions are true if both the red and green lines are below the T axis, which occurs when T is less than the point where the red line crosses the T axis, which is where $\Delta G_{ka} = 0$. From 15 this occurs at $T = 427.6$ K.

For andalusite to be stable, we must have $G_a < G_k$ and $G_a < G_s$, which means $\Delta G_{ka} > 0$ and $\Delta G_{as} < 0$. Thus the red line must be above the T axis and the yellow line must be below the T axis. The minimum T satisfying these conditions is $T = 427.6$ K that we found above. The maximum T is where the yellow line crosses the T axis, which occurs when $\Delta G_{as} = 0$, at $T = 875.9$ K.

For sillimanite to be stable, we must have $G_s < G_k$ and $G_s < G_a$, which means $\Delta G_{ks} > 0$ and $\Delta G_{as} > 0$. Thus both the green and yellow lines must be above the T axis, which is true for $T > 875.9$ K. To summarize: kyanite is stable for $T < 427.6$ K, andalusite is stable for 427.6 K $< T < 875.9$ K and sillimanite is stable for $T > 875.9$ K.

How accurate is the assumption that ΔS (the difference in entropy between two states of the substance) is actually a constant over a wide range of temperature? From 11 for one state, we can integrate:

$$S(T_2) = S(T_1) + C_P \int_{T_1}^{T_2} \frac{dT}{T} \tag{19}$$

$$= S(T_1) + C_P \ln \frac{T_2}{T_1} \tag{20}$$

Thus ΔS between two states, i and j is obtained by subtracting one equation of this type from the other:

$$\Delta S_{ij}(T_2) = \Delta S_{ij}(T_1) + \left(C_{Pi} - C_{Pj}\right) \ln \frac{T_2}{T_1} \tag{21}$$

ΔS_{ij} will be constant if the two states have equal heat capacities. From the data in Schroeder's book, $C_{Pk} = 121.71$ J K^{-1}, $C_{Pa} = 122.72$ J K^{-1} and $C_{Ps} = 124.52$ J K^{-1}. Using a reference temperature of $T_1 = 298$ K, the log factor over the range of temperatures over which the state changes occur varies from $\ln \frac{427.6}{298} = 0.361$ to $\ln \frac{875.9}{298} = 1.08$. The largest difference in heat capacity is $C_{Ps} - C_{Pk} = 2.81$, so we can expect the last term in 21 to be in the vicinity of 1 J K^{-1}. The entropy differences used in 15 and following equations are between around 2 and 12 J K^{-1} so actual value of ΔS could be in error by a fair bit. Of course, we've also used the heat capacities for $T = 298$ K and assumed that they don't vary over the temperature range, so we'd really need to correct *that* error as well.

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