CALCIUM CARBONATE PHASE DIAGRAM

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.37.

We can use the Clausius-Clapeyron relation to get a rough idea of the phase diagram for the two solid forms of calcium carbonate, calcite and aragonite. Earlier, we found that one point on the phase diagram is at $T=$ 298 K and $P=3.597$ kbar. The slope of the phase boundary at this point is given by

$$\frac{dP}{dT}=\frac{S_c-S_a}{V_c-V_a} \tag{1}$$

Using the data in Schroeder's book, we have

$$\frac{dP}{dT}=\frac{92.9-88.7}{(36.93-34.15)\times 10^{-6}}=1.51\times 10^{6}\text{ Pa K}^{-1} \tag{2}$$

For temperatures near 298 K, we can assume the phase boundary is a straight line, with the equation (with the pressure in Pa)

$$P(T)-P(298) = \frac{dP}{dT}(T-298) \tag{3}$$

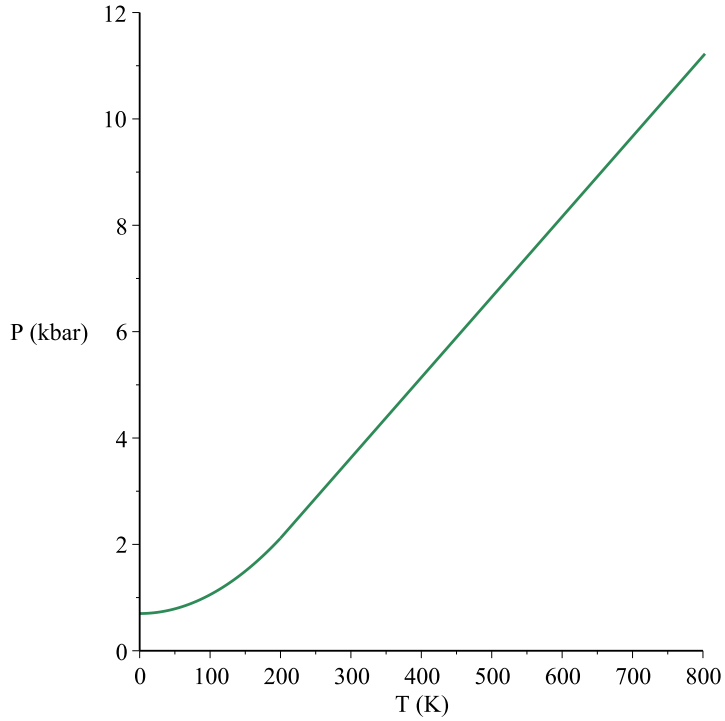
$$P = 1.51\times 10^{6}(T-298)+3.597\times 10^{8} \tag{4}$$

If we divide P by 10^8 we get the pressure in kbar.

Since we have the slope at only one point on the graph, we can't really say what the phase boundary looks like at temperatures far removed from 298 K. However, the linear relationship can't apply all the way down to $T=0$ K, since we would get a negative pressure for temperatures below

$$T=298-\frac{3.597\times 10^{8}}{1.51\times 10^{6}}=59.8\text{ K} \tag{5}$$

However, from the third law, we know that $S\to 0$ as $T\to 0$ for both phases, so the slope $\frac{dP}{dT}\to 0$ as well. From the data given, we can't really say at what pressure the phase boundary becomes horizontal, except that is must be less than 3.597 kbar. The phase diagram should look something like this:



The linear behaviour for $T > 298$ K, however, is pure speculation. Calcite is the stable form below the curve (since its Gibbs energy is lower here); aragonite is stable above it.