

DIAMOND-GRAPHITE PHASE BOUNDARY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.38.

We can use the Clausius-Clapeyron relation to get a rough idea of the phase diagram for graphite and diamond. Earlier, we calculated the entropy of graphite and diamond at $T = 500$ K. The entropy of diamond was obtained by taking the heat capacity C_P as a linear function of temperature, while the entropy of graphite used the empirical relation

$$C_P = a + bT - \frac{c}{T^2} \quad (1)$$

for constants a, b and c . These gave the entropy values at $T = 500$ K as

$$S_g = 12.33 \text{ J K}^{-1} \quad (2)$$

$$S_d = 7.85 \text{ J K}^{-1} \quad (3)$$

The slope of the phase boundary at this point is given by

$$\frac{dP}{dT} = \frac{S_g - S_d}{V_g - V_d} \quad (4)$$

Using the data for the molar volumes in Schroeder's book (although these are for $T = 298$ K), we have

$$\frac{dP}{dT} = \frac{12.33 - 7.85}{(5.3 - 3.42) \times 10^{-6}} = 2.38 \times 10^6 \text{ Pa K}^{-1} \quad (5)$$

The slope of the phase boundary in Schroeder's Figure 5.17 is (reading the points at $T = 1000$ K and $T = 3500$ K):

$$\frac{dP}{dT} = \frac{100 \times 10^8 - 33 \times 10^8}{3500 - 1000} = 2.68 \times 10^6 \text{ Pa K}^{-1} \quad (6)$$

Thus the estimate 5 is a bit low.

As for why the slope is pretty much constant for high temperatures, this clearly wouldn't follow if the heat capacities continued to depend on temperature as in the empirical relations we used earlier (see above) to calculate the entropies. However, if we look at Schroeder's Figure 1.14, we see that

for solids, the heat capacities tend to level off to constant values beyond a certain temperature. Then, from the relation

$$S = \int \frac{C_P}{T} dT \quad (7)$$

the entropy would depend on $\ln T$, so wouldn't vary much for high temperatures. In that case, the difference $S_g - S_d$ would be roughly constant so, assuming the molar volumes also don't change much, the slope $\frac{dP}{dT}$ would be approximately constant.

For low temperatures, from the third law, we know that $S \rightarrow 0$ as $T \rightarrow 0$ for both phases, so the slope $\frac{dP}{dT} \rightarrow 0$ as well.