GRAPHITE AND DIAMOND

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.24 - 5.27.

Two of the main forms of elemental carbon are graphite and diamond. We can get some insight into the stability of these two forms by considering the Gibbs free energy. From the thermodynamic potential for the Gibbs free energy

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

we have

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

Using data given in Schroeder's book, the molar volume of graphite is $V_g = 5.31 \times 10^{-6}$ m^3 and of diamond is $V_d = 3.42 \times 10^{-6}$ m^3. If we ignore compression effects over a wide range of pressures, we can integrate 2 to get a linear relationshipe between G and P. If we take the Gibbs energy of graphite to be $G_g = 0$ at $T = 298$ K and $P = 10^5$ Pa then for diamond under the same conditions we have $G_d = 2900$ J, so the relations are (for one mole of carbon atoms):

$$
\begin{aligned}
G_g &= V_g P = 5.31 \times 10^{-6} P \tag{3} \\
G_d &= V_d P = 2900 + 3.42 \times 10^{-6} P \tag{4}
\end{aligned}
$$

As the diamond line starts above the graphite line but has a smaller slope, it will intersect the graphite line at a pressure P_{gd} determined by

$$
\begin{aligned}
5.31 \times 10^{-6} P_{gd} &= 2900 + 3.42 \times 10^{-6} P_{gd} \tag{5} \\
P_{gd} &= 1.534 \times 10^9 \text{ Pa} \tag{6} \\
&= 15.34 \text{ kbar} \tag{7}
\end{aligned}
$$

using the conversion 10^5 Pa $= 1$ bar.

If we include the effect of compressibility, things get a bit more complicated. The isothermal compressibility of graphite (given by Schroeder) is about

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = 3 \times 10^{-6}\ \text{bar}^{-1} = 3 \times 10^{-11}\ \text{Pa}^{-1} \tag{8}$$

Assuming κ_T is constant over the range of pressures we're considering, we can integrate this to get

$$\frac{dV}{V} = -\kappa_T dP \tag{9}$$

$$\ln\frac{V}{V_0} = \kappa_T\left(P_0 - P\right) \tag{10}$$

where V_0 and P_0 are some reference volume and pressure, which we can take as the molar volume and a pressure of 1 bar.

Thus the volume is a function of the pressure:

$$V = V_0 e^{\kappa_T P_0} e^{-\kappa_T P} \tag{11}$$

For graphite, this gives

$$V_g = \left(5.31 \times 10^{-6}\right) e^{3 \times 10^{-6}} e^{-\kappa_T P} \tag{12}$$

$$\approx 5.31 \times 10^{-6} e^{-3 \times 10^{-11} P} \tag{13}$$

since $e^{3 \times 10^{-6}} \approx 1$. The Gibbs energy for graphite can then be found from 2 as

$$G_g = -\frac{5.31 \times 10^{-6}}{3 \times 10^{-11}} e^{-3 \times 10^{-11} P} + G_0 \tag{14}$$

$$= -1.77 \times 10^5 e^{-3 \times 10^{-11} P} + G_0 \tag{15}$$

The integration constant G_0 can be found from the condition that $G_g\left(10^5\ \text{Pa}\right) = 0$, so $G_0 = 1.77 \times 10^5$ J and we get

$$G_g = 1.77 \times 10^5 \left(1 - e^{-3 \times 10^{-11} P}\right) \tag{16}$$

As κ_T for diamond is about ten times smaller than κ_T for graphite, we can approximate G_d by the same straight line that we used above. The pressure at which diamond becomes more stable than graphite is found by equating G_g and G_d as before, although this time we get a transcendental equation (with P found both in an exponent and as a linear factor), so we can solve the equation numerically using Maple:

$$1.77 \times 10^5 \left(1 - e^{-3 \times 10^{-11} P_{gd}}\right) = 2900 + 3.42 \times 10^{-6} P_{gd} \quad (17)$$

$$P_{gd} = 1.647 \times 10^9 \text{ Pa} \quad (18)$$

$$= 16.47 \text{ kbar} \quad (19)$$

The Gibbs energies look like this, with the blue curve being graphite and the red curve being diamond:
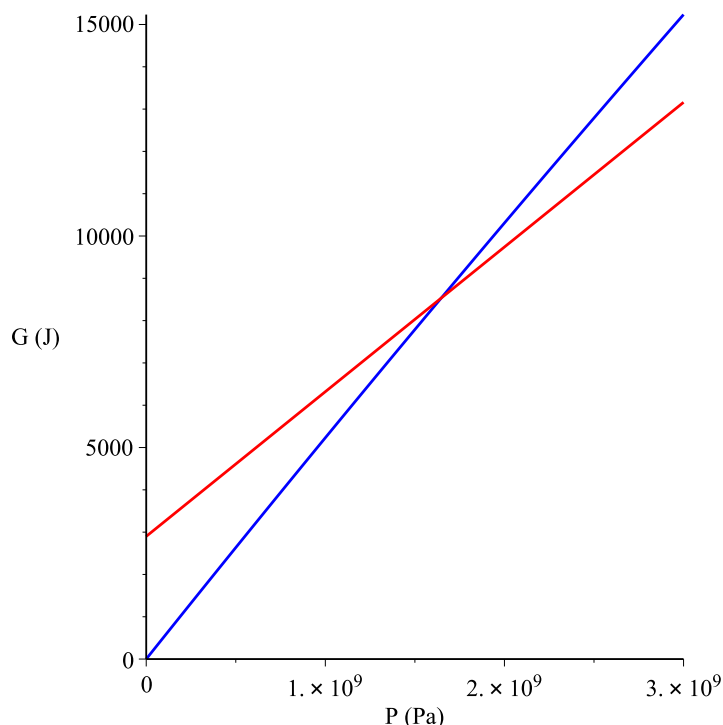
The blue curve is actually slightly concanve downwards, as can be seen by plotting it for higher pressures, but in the pressure range here, it's approximately linear. The red curve is actually a straight line.

There are a couple of rather odd features about the graphite-diamond transition. First, from the Gibbs energy plot, we see that graphite is actually the more stable form at atmospheric pressure and temperature, so that should mean that diamonds will spontaneously degrade into graphite over time. Fortunately for owners of diamonds, this process takes a very long time (although it should also be noted that diamonds, being carbon, *do* burn, so don't throw your wedding ring into a fire!).

Another odd fact is that because of its more ordered crystal structure, diamond has a lower entropy than graphite (for 1 mole, the values are $S_d = 2.38 \text{ J K}^{-1}$ and $S_g = 5.74 \text{ J K}^{-1}$). Schroeder asks us to explain how

the conversion of graphite to diamond at high pressure can result in an over-all increase of the environment's entropy. It's not clear to me why this should be, though perhaps because $G_d < G_g$ at high pressure, the energy transferred away from the graphite into the environment causes an overall increase in entropy. Comments welcome.

Finally, geochemists use a bizarre unit of volume equal to kJ kbar^{-1}. The conversion to the more standard cubic metre is given by

$$1 \text{ kJ kbar}^{-1} = 1 \text{ J bar}^{-1} = 10^{-5} \text{ J Pa}^{-1} = 10^{-5} \text{ m}^3 \tag{20}$$

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