

Correct solution to Problem 5.1

5.1. Diamonds have been successfully prepared by submitting graphite to high pressure. Calculate the approximate minimum pressure needed using $\Delta_f G = 0$ for graphite and $\Delta_f G = +2,900 \text{ J mol}^{-1}$ for diamond. The densities of the two forms may be taken as independent of pressure and are 2.25 and 3.51 g cm^{-3} , respectively.

Solution:

As we saw in class, $\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$ (See Problem 5.15), from which we write

$$d\Delta G = \Delta V dP \text{ at constant } T.$$

Therefore,

$$\int_1^2 d\Delta G = \int_{P_1}^{P_2} \Delta V dP = \Delta G_2 - \Delta G_1 = \Delta V(P_2 - P_1) \quad (1)$$

$$P_2 = \frac{\Delta G_2 - \Delta G_1}{\Delta V} + P_1 \quad (2)$$

The initial state is graphite and the final state is diamond. Now, the ΔG 's given in the above equation are the free energy changes for the conversion of graphite to diamond, which takes $+2,900 \text{ J mol}^{-1}$ at 25°C and 1 bar pressure:

$$\Delta G = \Delta_f G_{\text{diamond}} - \Delta_f G_{\text{graphite}} = 2,900 - 0 = 2,900 \text{ J mol}^{-1}$$

Our job is to find the pressure at which the free energy change for this conversion becomes 0, so that diamond and graphite will be in equilibrium and the conversion can take place.

Therefore, our initial state corresponds to $\Delta G_1 = +2,900 \text{ J mol}^{-1}$ while the final state corresponds to $\Delta G_2 = 0$.

$$\begin{aligned} \Delta V &= 12.011 \text{ g mol}^{-1} \left(\frac{1}{3.51} - \frac{1}{2.25} \right) \frac{\text{cm}^3}{\text{g}} \times 10^{-6} \frac{\text{m}^3}{\text{cm}^3} \\ &= -1.915 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

Using Eq. (2) above,

$$\begin{aligned} P_2 &= \frac{0 - 2900 \text{ J mol}^{-1}}{-1.92 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} + 10^5 \text{ Pa} \\ &= 1.51 \times 10^9 \text{ Pa} \quad \text{or} \quad 1.51 \times 10^4 \text{ bar} \end{aligned}$$

Not part of the solution, but something you may want to know: At this pressure the system must also be at approximately 1000 K in order for the conversion rate to be high enough for the process to be practical. Thermodynamics tells us whether or not something can occur, and allows us to calculate the conditions for making something happen, but it says absolutely nothing at all about how fast or slow that process will be. Also, sorry, guys! These diamonds are really diamond “dust,” used only for industrial purposes. You still have to shell out big bucks for a decent piece of sp^3 carbon if you are planning to get married.