

# Diamond and Graphite: Calculating a Simple Phase Diagram

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## Standard state properties for diamond and graphite (at room temp/pressure = 1bar = 1 atm, 298K)

<u>formula</u>	<u>mineral</u>	<u>E° kJ/mol</u>	<u>V° cm<sup>3</sup>/mol</u>	<u>S° J/mol•K</u>
C	diamond	2.900	3.417	2.38
C	graphite	0	5.298	5.74

E = internal energy; V = volume; S = entropy

### Background

For this exercise, we assume that molar volume and entropy are constants. (In reality they vary with P and T, but the effects are small.) With this assumption, the Gibbs free energy of any phase at pressure (P) and temperature (T) can be calculated as

$$G = E + PV - TS$$

E (internal energy/mol), V (volume/mol), and S (entropy/mol) are constants, so G varies linearly with P and T.

Recall that the phase (or assemblage) with least Gibbs free energy is most stable. Looking at the above equation, we see that at high pressure Gibbs free energy is minimized for phases with low volumes. In other words, the denser phases are stable at high pressure.

We can make a similar observation about stability and temperature. Because of the negative sign in front of the TS term, the phase with greatest entropy (S) will be the one most stable at high temperature! (It will have the lowest Gibbs free energy.)

For any reaction, the Gibbs free energy of reaction, internal energy of reaction, volume of reaction, and entropy of reaction can be calculated by subtracting values for reactants from values for products:

$$\begin{aligned}\Delta G_{\text{rxn}} &= G_{\text{products}} - G_{\text{reactants}} \\ \Delta E_{\text{rxn}} &= E_{\text{products}} - E_{\text{reactants}} \\ \Delta V_{\text{rxn}} &= V_{\text{products}} - V_{\text{reactants}} \\ \Delta S_{\text{rxn}} &= S_{\text{products}} - S_{\text{reactants}}\end{aligned}$$

At equilibrium:

$$\Delta G_{\text{rxn}} = 0 = \Delta E_{\text{rxn}} + P\Delta V_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

This is the equation of a line in PT space.

### Problems

Use the data in the table at the top of the page.

1. Calculate the Gibbs free energy of graphite and diamond at room temperature and pressure.<sup>1</sup> Which of the two is the stable phase?

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<sup>1</sup>For this calculation and for others later on, be sure to get the units right. You will need the conversion factor that 1J = 10 cc-bar.

Consider the reaction diamond = graphite

2. Calculate  $\Delta E$ ,  $\Delta V$ , and  $\Delta S$  for the reaction.

3. Given the results from questions 1 and 2, sketch a schematic P-T phase diagram showing how reaction (1) plots. Label both sides of the reaction.

4. We don't have to be schematic, however. We know that when reaction (1) is at equilibrium:

$$0 = \Delta G_{rxn} = \Delta E_{rxn} + (P \times \Delta V_{rxn}) \times (0.1 \text{ J/bar-cm}^3) - T \times \Delta S_{rxn}$$

This is the equation of a straight line. Plot it on the phase diagram below.

(Be sure to note that the vertical axis is in Kbars, not bars. Note the conversion factor because  $1 \text{ cm}^3 = 0.1 \text{ J/bar.}$ )

Label both sides of the reaction.

Note that the Clausius-Clapeyron equation says the slope of the reaction line is

$$dP/dT = \Delta S_{rxn} / \Delta V_{rxn}$$

You do not have to use this relationship but it might be useful.

