

Problem Set 5

issued: 10/31/05

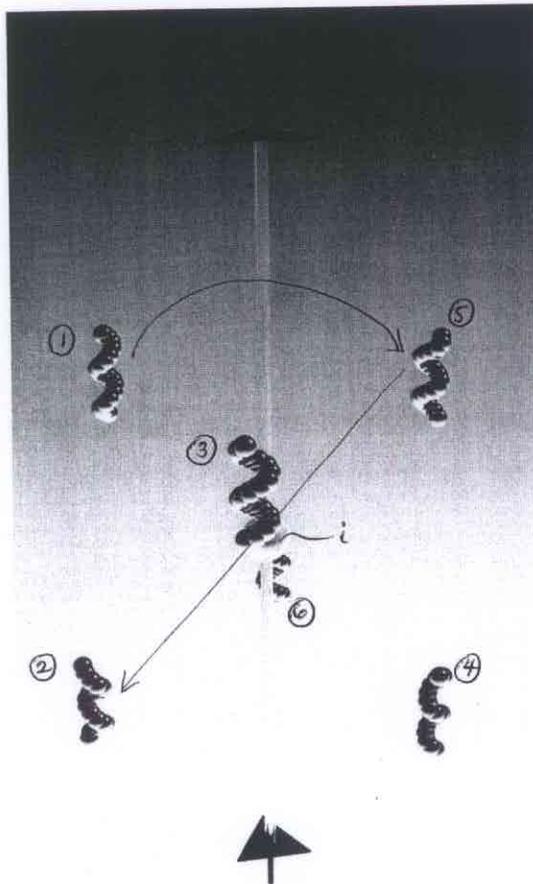
due: 11/10/05

Model solutions problems 1-4

3.012

Fall 2005

Problem 1

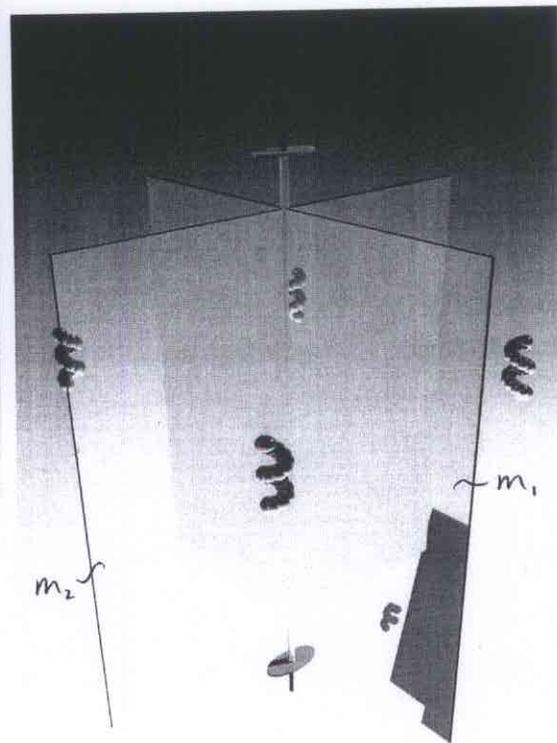


Symmetry elements

inversion - i

rotoinversion - $\bar{3}$

point group = $\bar{3}$



Symmetry elements

two mirror planes - $m_1 + m_2$

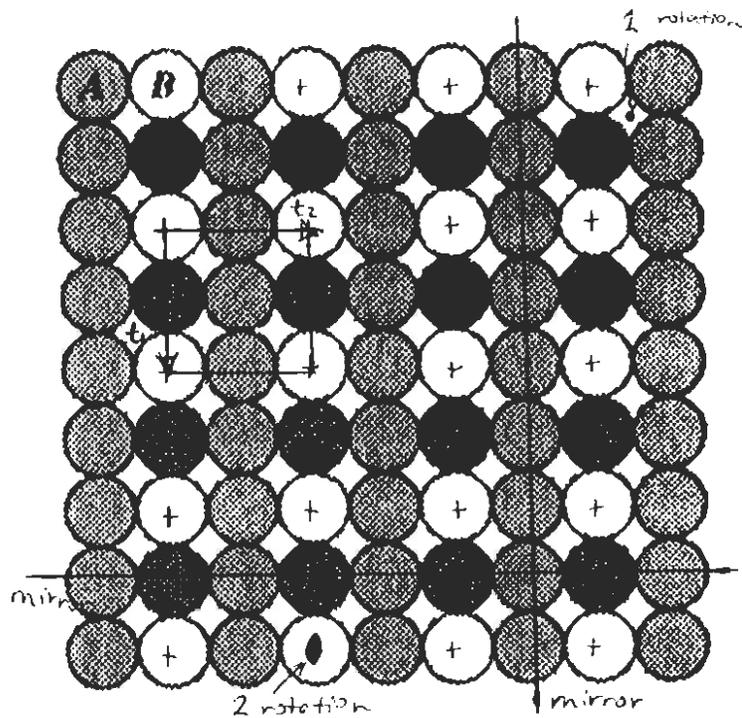
rotation - 2

point group = $2mm$

Courtesy of Marc De Graef. Used with permission.

Problem 2 - Allen-Thomas 3.5

(a) lattice points
marked by +

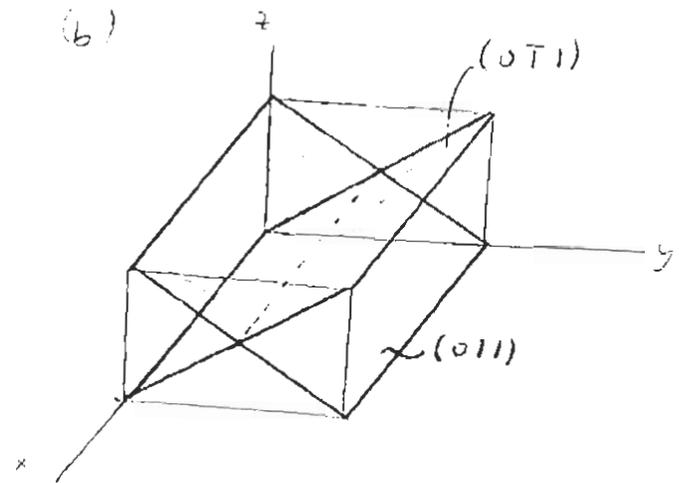
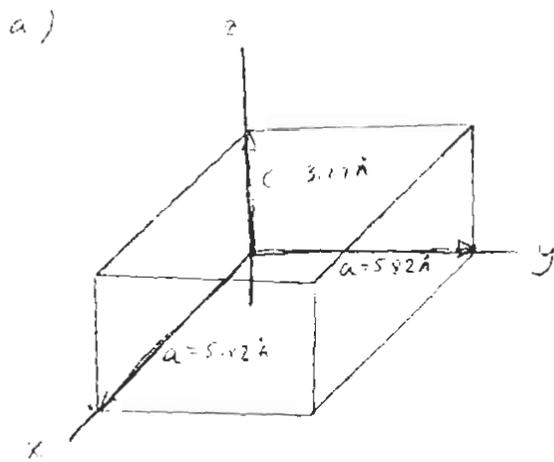


(c) There is one lattice point per primitive cell. - This is true in all primitive cells.

(d) There is one white B atom, 2 grey A atoms, and one black C atom in each unit cell.

(e) 1, 2, 2 mirrors

Problem 3 - Allen-Thomas 3.12



(c) The common direction is $[100]$.

(d) $[011] = a\hat{j} + c\hat{k}$ $[0\bar{1}1] = -a\hat{j} + c\hat{k}$
 $|[011]| = \sqrt{a^2 + c^2}$ $|[0\bar{1}1]| = \sqrt{a^2 + c^2}$

$$[011] \cdot [0\bar{1}1] = |[011]| |[0\bar{1}1]| \cos \phi = (a^2 + c^2) \cos \phi$$

and $[011] \cdot [0\bar{1}1] = -a^2 + c^2$

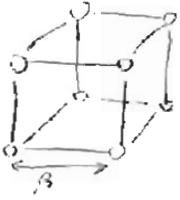
$$\Rightarrow (a^2 + c^2) \cos \phi = -a^2 + c^2$$

$$\cos \phi = \frac{-a^2 + c^2}{a^2 + c^2} = -0.542$$

$$\phi = 123^\circ$$

Problem 4

Simple cubic (s.c.)



s.c. is a primitive cell.

number of lattice points = 1

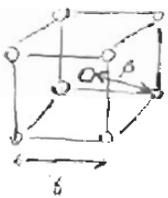
volume = V

nearest neighbor is β apart.

$$\text{volume} = \beta^3 = V$$

$$\beta = V^{1/3}$$

body centered cubic



The conventional cell (drawn here) has 2 lattice points

$$V_{\text{conventional}} = 2 V_{\text{primitive}} \Rightarrow V_{\text{conventional}} = 2 V_{\text{primitive}} = 2V$$

↑
number of lattice points

β = nearest neighbor distance

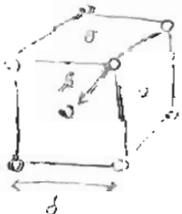
γ = conventional cell edge

$$\gamma^3 = 2V \rightarrow \gamma = (2V)^{1/3}$$

$$\beta = \frac{1}{2}(\text{cube diagonal}) = \frac{1}{2} \sqrt{\gamma^2 + \gamma^2 + \gamma^2} = \frac{\sqrt{3}}{2} \gamma$$

$$\beta = \frac{3^{1/2}}{2} (2V)^{1/3}$$

face centered cubic



The conventional cell has 4 lattice points

$$V_{\text{fcc}} = 4 V_{\text{primitive}} = 4V$$

$$\delta^3 = 4V \rightarrow \delta = (4V)^{1/3}$$

$$\beta = \frac{1}{2}(\text{face diagonal}) = \frac{1}{2} \sqrt{\delta^2 + \delta^2} = \frac{\sqrt{2}}{2} \delta = \frac{\delta}{\sqrt{2}}$$

$$\beta = \frac{(4V)^{1/3}}{\sqrt{2}}$$

s.c. : bcc : fcc

$$V^{1/3} : 1.09 V^{1/3} : 1.12 V^{1/3}$$

} fcc has nearest neighbors furthest away.

1. **Electrochemistry.**

- a. What voltage is measured across the electrodes of a Zn/Cu Daniell galvanic cell once its electrochemical reaction comes to equilibrium? (Show why).

The Nernst equation shows that the electrostatic potential on the battery derives from the free energy change occurring in the electrochemical reactions:

$$\Delta\phi = -\frac{\Delta\bar{G}_{rxn}}{2F}$$

At equilibrium, the free energy change is zero; thus, the potential drops to zero as the reactions reach completion.

- b. Engel and Reid, problem P11.13.

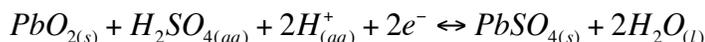
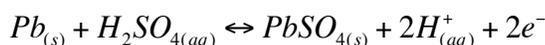
$$\Delta\bar{G}_{rxn}^o = -RT \ln K$$

$$E^o = -\frac{\Delta\bar{G}_{rxn}^o}{2F}$$

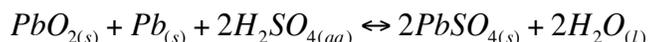
$$\Delta\bar{G}_{rxn}^o = -2FE^o = -2(96,485 \frac{C}{mole})(0.19V) = -36.7 \frac{kJ}{mole}$$

$$K = e^{-\frac{\Delta\bar{G}_{rxn}^o}{RT}} = 2.67 \times 10^6$$

2. **Thermodynamics of a car battery.** The standard lead-acid rechargeable battery used throughout the automotive industry is shown schematically below. It consists of a lead and lead oxide electrode immersed in aqueous sulfuric acid. The reactions at each electrode are:



The overall reaction for this galvanic cell is:



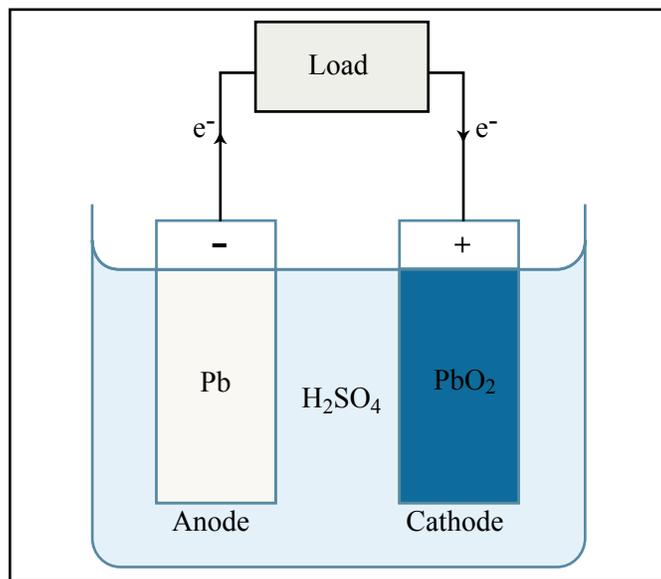


Figure by MIT OCW. After Treptow, 2002.

- a. Write an expression for the EMF of the lead acid battery as a function of physical constants, temperature, and the activities of components.

The EMF is given by the Nernst equation:

$$E = -\frac{\Delta\bar{G}_{rxn}}{2F} = -\frac{1}{2F} \left[\Delta\bar{G}_{rxn}^{\circ} + RT \ln \frac{a_{PbSO_4}^2 a_{H_2O(l)}^2}{a_{PbO_2(s)} a_{Pb(s)} a_{H_2SO_4(aq)}^2} \right]$$

Taking the standard approximation for the activities of the solid electrodes, we have:

$$E = -\frac{1}{2F} \left[\Delta\bar{G}_{rxn}^{\circ} + RT \ln \frac{a_{H_2O(l)}^2}{a_{H_2SO_4(aq)}^2} \right] = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{H_2O(l)}^2}{a_{H_2SO_4(aq)}^2}$$

- b. The standard potential of the lead-acid battery $E^{\circ} = 2.09V$ at 298 K. If the activity coefficient of 0.1 M H_2SO_4 is 0.0329 and the water present in the sulfuric acid solution can be assumed to have an activity ~ 1 , determine the voltage expected across the terminals of a battery containing 0.1 M sulfuric acid as the liquid electrolyte.

From the given information about the electrolyte, we can calculate the activity of the sulfuric acid:

$$X_{H_2SO_4(aq)} = \frac{n_{H_2SO_4(aq)}}{n_{H_2O} + n_{H_2SO_4(aq)}} = \frac{0.1}{(1L) \left(\frac{1000cm^3}{L} \right) \left(1 \frac{g}{cm^3} \right) \left(\frac{mole}{18g} \right) + 0.1} = 1.8 \times 10^{-3}$$

$$a_{H_2SO_4(aq)} = \gamma_{H_2SO_4(aq)} X_{H_2SO_4(aq)} = (0.0329)(1.8 \times 10^{-3}) = 5.9 \times 10^{-5}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{H_2O(l)}^2}{a_{H_2SO_4(aq)}^2} = 2.09V - \frac{(8.3144 \frac{J}{mole \cdot K})(298K)}{2(96,485 \frac{C}{mole})} \ln \frac{(1)}{[5.9 \times 10^{-5}]^2} = 1.84V$$

3. Stability of a closed system at constant temperature and pressure.

- a. Let's determine the shape of G (Gibbs free energy) vs. P (pressure) curves. What thermodynamic parameter(s) are related to $\left(\frac{\partial G}{\partial P}\right)_{T,n}$? From this relationship, what is the slope of G vs. P?

From the algebraic definition of dG and the combined first/second law form of dG, we have:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \dots$$

$$dG = VdP - SdT + \dots$$

The matching terms in front of the differential dP give us:

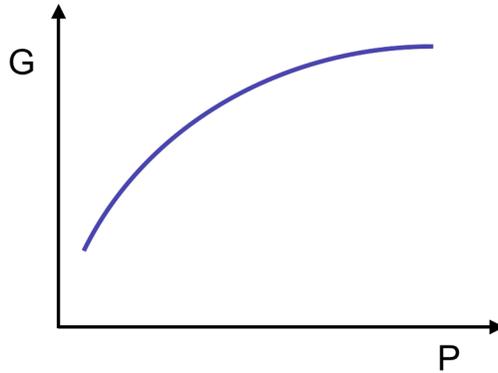
$$\left(\frac{\partial G}{\partial P}\right)_{T,n} = V$$

Because volume is always a positive quantity, the slope of G vs. P is positive.

- b. Now, what about the curvature of G vs. P: What thermodynamic parameters are related to $\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n}$, and what can you say about the curvature of G vs. P, based on your knowledge of property requirements for stability? Draw a qualitative sketch of what G vs. P must look like using your information from (a) and (b).

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} = \left(\frac{\partial V}{\partial P}\right)_{T,n} = -\kappa_T V$$

where κ_T is the isothermal compressibility. Because κ_T is always positive for stability, the curvature of G vs. P is negative. Combining these two results, we have for G vs. P, qualitatively:



- c. What are the two inequalities that must be satisfied by the Gibbs free energy for a system to be at a stable equilibrium with respect to fluctuations in temperature (all other variables held constant) or pressure (all other variables held constant)?

To guarantee stable equilibrium, we need:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} = -\left(\frac{\partial S}{\partial T}\right)_{P,n} = -\frac{C_p}{T} \leq 0$$

We know from stability considerations for internal energy that heat capacities are positive, and temperature must be positive. Thus, the second derivative with respect to temperature must be negative. Note that this inequality can be predicted without relying on the prior proof of positive C_p values by relating the stability requirements for internal energy to those of Gibbs free energy (using Legendre transformation relationships)—this is discussed in the reading from Callen. For fluctuations in pressure:

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} = \left(\frac{\partial V}{\partial P}\right)_{T,n} = -\kappa_T V \leq 0$$

...where the inequality is again set by the required positivity of compressibility (as we have already shown using internal energy considerations) and volume, or alternatively, by relating the stability requirement for Gibbs free energy to the requirements on internal energy via Legendre transformation relations.

You may be confused by the requirement that the curvature of the Gibbs free energy with respect to temperature is negative, given that we must **minimize** G for equilibrium. Recall that we minimize Gibbs free energy at **constant** temperature and pressure: thus, in calculations we are minimizing G with respect to **other** extensive parameters of the system (e.g., moles of a certain component in one phase or another).

- d. For the system to be stable against arbitrary simultaneous fluctuations in both temperature and pressure, what inequality must the second derivative of Gibbs free energy, d^2G satisfy?

NOTE: Parts (d) and (e) were not graded for credit. We did not cover in lecture the subtlety in determining the sign of the inequality in this problem. However, here is the solution:

We know that under conditions of constant temperature and pressure, the Gibbs free energy is minimized. Minimization would require:

$$\left(d^2G\right)_{T,P} \geq 0$$

Recall that when T and P are constant, the terms we would include in the inequality above would be partial derivatives with respect to extensive variables like the number of moles of a given component in a given phase— i.e., we minimize the Gibbs free energy with respect to the distribution of chemical species among different phases present in the system.

Now, considering the general case where fluctuations in temperature or pressure are allowed to occur, we have:

$$d^2G = \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} dT^2 + \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} dP^2 + 2\left(\frac{\partial^2 G}{\partial T \partial P}\right) dT dP \leq 0$$

...assuming the simple case of a system where n is fixed (no partial derivatives with respect to n needed). This inequality arises because thermodynamic functions are always concave functions of their intensive variables, and convex functions (the first inequality above) of the extensive variables. This is determined by the Legendre transformation used to change variables from (S,V,n) in internal energy to (T,P,n) in Gibbs free energy. The mathematics of this transformation are discussed in the text by Callen.

- e. Write out the expression for d^2G and show that the stability requirement on d^2G is equivalent to the condensed expression:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)\left(\frac{\partial^2 G}{\partial P^2}\right) - \left(\frac{\partial^2 G}{\partial T \partial P}\right)^2 \geq 0$$

The stability requirement:

$$d^2G = \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} dT^2 + \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} dP^2 + 2\left(\frac{\partial^2 G}{\partial T \partial P}\right) dT dP \leq 0$$

Is algebraically identical to:

$$\frac{1}{\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n}} \left\{ \left[\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} dT + \left(\frac{\partial^2 G}{\partial T \partial P}\right) dP \right]^2 + \left[\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} - \left(\frac{\partial^2 G}{\partial T \partial P}\right)^2 \right] dP^2 \right\} \leq 0$$

Multiplying both sides of the inequality by $\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n}$ simplifies this expression to:

$$\left[\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} dT + \left(\frac{\partial^2 G}{\partial T \partial P}\right) dP \right]^2 + \left[\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n} - \left(\frac{\partial^2 G}{\partial T \partial P}\right)^2 \right] dP^2 \geq 0$$

Note the change in direction of the inequality because we have multiplied both sides by a negative quantity. The first term in brackets in this expression is always positive because it is squared. Thus in order to satisfy the inequality, we need only:

$$\left(\frac{\partial^2 G}{\partial T^2}\right) \left(\frac{\partial^2 G}{\partial P^2}\right) - \left(\frac{\partial^2 G}{\partial T \partial P}\right)^2 \geq 0$$

4. **Understanding single-component phase diagrams.** The phase diagram of carbon is shown below, along with some physical data for two different forms of carbon, diamond and graphite. Use this data to answer the questions below.

- a. The phase boundary between diamond and graphite at $T = 298 \text{ K}$ occurs at $P = 14,300 \text{ atm}$. What is the free energy change to transform 1 mole of graphite to diamond at this temperature and pressure?

At the phase boundary, diamond and graphite are in equilibrium:

$$\Delta \bar{G}_{\text{graphite} \rightarrow \text{diamond}} = \bar{G}_{\text{diamond}} - \bar{G}_{\text{graphite}} = 0$$

$$\therefore \bar{G}_{\text{diamond}} = \bar{G}_{\text{graphite}}$$

- b. Recall that $\left(\frac{\partial G}{\partial P}\right)_{T,n} = V$, and thus $\left(\frac{\partial \Delta G}{\partial P}\right)_{T,n} = \Delta V$ for a process where volume change occurs. Calculate the free energy change to transform 1 mole of graphite to diamond at 298 K, assuming the volume change in transforming from graphite to diamond is approximately independent of pressure at this temperature.

The difference in molar volumes of graphite and diamond at 298 K and 1 atm is related to the change in free energy with pressure:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_{T,n} = \Delta V$$

$$\left(\frac{\partial \Delta G_{\text{graphite} \rightarrow \text{diamond}}}{\partial P}\right)_{T,n} = \Delta V = V_{\text{diamond}} - V_{\text{graphite}}$$

We can calculate ΔV from the given density data:

$$V_{\text{diamond}} = \left(\frac{\text{cm}^3}{3.515 \text{ g}}\right)\left(\frac{12 \text{ g}}{\text{mole}}\right) = 3.41 \frac{\text{cm}^3}{\text{mole}}$$

$$V_{\text{graphite}} = \left(\frac{\text{cm}^3}{2.22 \text{ g}}\right)\left(\frac{12 \text{ g}}{\text{mole}}\right) = 5.41 \frac{\text{cm}^3}{\text{mole}}$$

$$V_{\text{diamond}} - V_{\text{graphite}} = -1.99 \frac{\text{cm}^3}{\text{mole}}$$

If ΔV is approximately independent of pressure, then we can rearrange this expression and integrate:

$$\left(\frac{\partial \Delta G_{\text{graphite} \rightarrow \text{diamond}}}{\partial P}\right)_{T,n} = \Delta V$$

$$d\Delta G_{\text{graphite} \rightarrow \text{diamond}} = \Delta V dP$$

$$\int d\Delta G_{\text{graphite} \rightarrow \text{diamond}} = \Delta V \int_{1 \text{ atm}}^{14,300 \text{ atm}} dP'$$

$$\Delta G_{\text{graphite} \rightarrow \text{diamond}}(T = 298 \text{ K}, P = 14,300 \text{ atm}) - \Delta G_{\text{graphite} \rightarrow \text{diamond}}(T = 298 \text{ K}, P = 1 \text{ atm}) = \Delta V(14,300 \text{ atm} - 1 \text{ atm})$$

$$0 - \Delta G_{\text{graphite} \rightarrow \text{diamond}}(T = 298 \text{ K}, P = 1 \text{ atm}) = \Delta V(14,300 \text{ atm} - 1 \text{ atm})$$

We set the free energy change for the transformation at 298K P = 14,300 atm to zero because this (T, P) lies on the diamond/graphite phase boundary, indicating that the two phases are in equilibrium under these conditions. Finally:

$$\Delta G_{\text{graphite} \rightarrow \text{diamond}}(T = 298 \text{ K}, P = 1 \text{ atm}) = (1.99 \frac{\text{cm}^3}{\text{mole}})\left(\frac{\text{L}}{1000 \text{ cm}^3}\right)(14,299 \text{ atm})\left(\frac{8.3144 \frac{\text{J}}{\text{mole} \cdot \text{K}}}{0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mole} \cdot \text{K}}}\right) = 2,883 \frac{\text{J}}{\text{mole}}$$

As expected, because the transformation of graphite to diamond is not stable at 1 atm 298 K, the free energy change is positive.

- c. Using the information provided in the phase diagram, draw a qualitatively correct diagram G vs. T of the molar free energies of all relevant phases of carbon at a fixed pressure of 1×10^5 atm over the temperature range 1000-5000 K.

We approximately determine the positions of the coexistence curves where phase transitions occur:

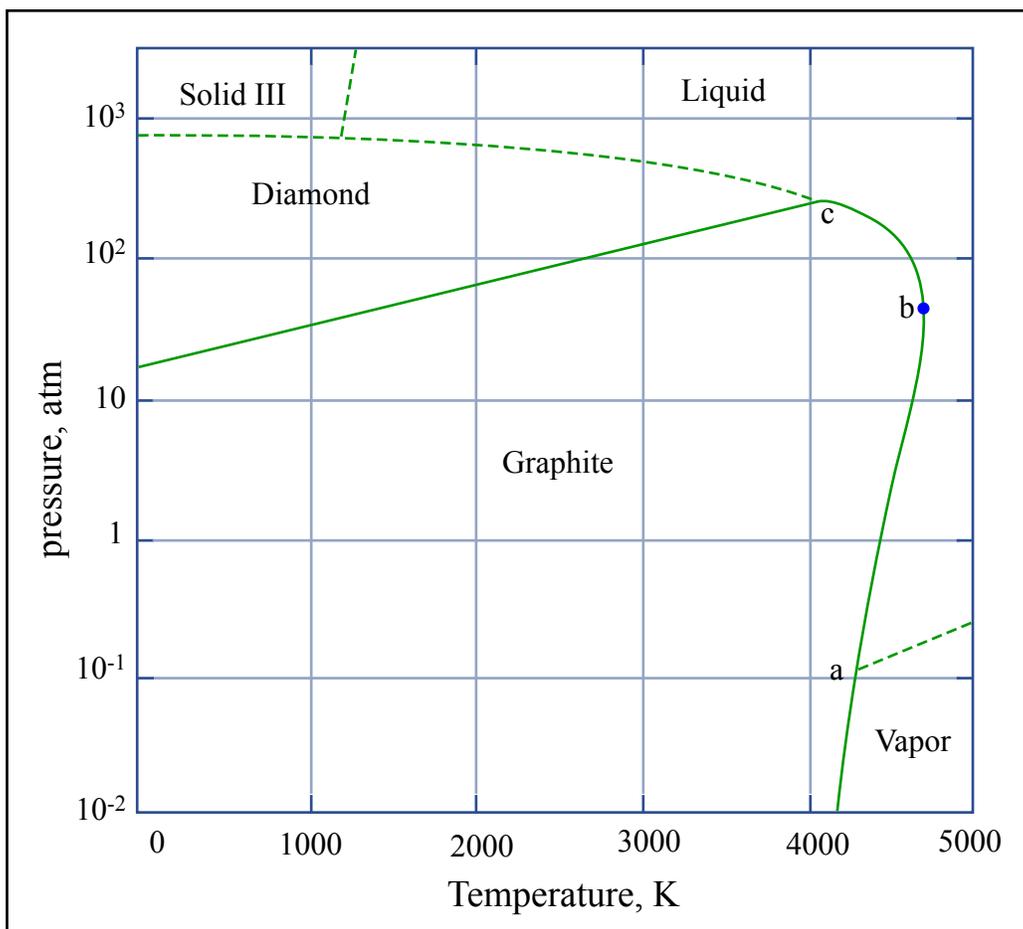
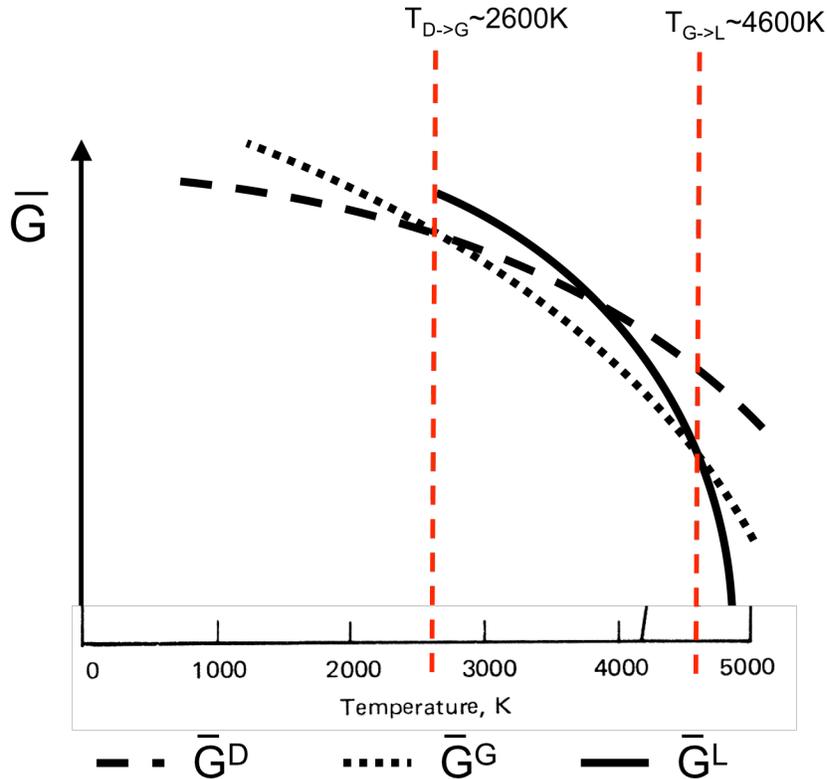


Figure by MIT OCW.

Then the free energy vs. T diagram is, qualitatively:



The slopes must increase in the order of diamond < graphite < liquid, in keeping with the steadily increasing entropy of higher-temperature phases.

- d. Does liquid carbon have a greater molar volume than graphite at the melting point of graphite at 1 atm pressure? Does liquid carbon have a greater molar volume than graphite at the melting point of graphite at 100 atm? Show why.

As discussed in lecture, the difference in molar volumes between two phases determines the sign on the slope of coexistence curves on P vs. T phase diagrams for single component materials, via the Clausius-Clapeyron equation:

$$\left. \frac{dP}{dT} \right|_{\text{coexistence}} = \frac{\Delta \bar{S}_{\text{trans}}}{\Delta \bar{V}_{\text{trans}}}$$

...because the sign on the entropy change at any phase transition moving from the low temperature phase to the high temperature phase is positive. Looking at the phase diagram, the slope dP/dT at $P = 1$ atm is positive for the graphite/liquid phase transition, while at $P = 100$ atm, the slope is negative. Thus, the molar volume of liquid carbon is greater than graphite at 1 atm, but less than graphite at the higher pressure.

(Gaskell)

$$\rho_{\text{graphite}}(298K) = 2.22 \frac{\text{g}}{\text{cm}^3}$$

$$\rho_{\text{diamond}}(298K) = 3.515 \frac{\text{g}}{\text{cm}^3}$$

Modified from Gaskell, Introduction to Metallurgical Thermodynamics (Hemisphere, New York, 1981)
Ch. 7 p. 185