Ge 212 Problem Set 7

Due Wednesday November 29, 2017

1. Consider the component space CaO-MgO-Al2O3-SiO2. Let us concern ourselves only with the following phases and their stoichiometric constituents (or *phase components*): olivine [ol] (Mg2SiO4ol), orthopyroxene [opx] (Mg2Si2O6opx (en) - MgAl2SiO6opx (MgTs)), clinopyroxene [cpx] (CaMgSi2O6cpx (di) - CaAl2SiO6cpx (CaTs)), spinel [sp] (MgAl2O4sp), anorthite [an] (CaAl2Si2O8an). Assuming heterogeneous equilibrium, there are six intensive variables for this system: a valid choice of an independent set might be *T*, *P*, and the chemical potentials of the four oxide components. One way to look at the usefulness of thermodynamics in understanding how this system can behave is to find the equations that allow us to solve for 6-*f* of these variables if we specify *f* of them.
   1. Let us start by writing equations that give the chemical potential of each of the 7 phase components in terms of the chemical potentials of the 4 oxide components.
   2. There are 7 phase components and 4 system components, so the phase components must not be linearly independent. Can you find three independent chemical reactions among phase components that express this linear dependence, and also give the corresponding statements of equality of the chemical potentials of these phase components?
   3. What is the variance *f* of the assemblage ol+opx+cpx+sp+an?
   4. Let us use the Gibbs-Duhem equations for each of these five phases to express the interdependence of the six intensive variables. Write the five Gibbs-Duhem equations (in intensive terms and using the phase components; add the new variables *Xen* and *Xdi* to describe the pyroxene compositions).
   5. Substitute the relations between the chemical potentials of the phases and of the system components (i.e, the four oxides) to put the set of Gibbs-Duhem equations in terms of the system components.
   6. Now put this into matrix form **Ax** = **b** where **b** is the vector of molar volumes of the minerals times d*P* and **x** is the vector of the total differentials of the other five intensive variables. This is something you could solve to find the family of five-phase equilibrium points by matrix inversion if you knew the entropies and volumes of the phases, the activity-composition relations of the solid solutions, and the mineral compositions at one (*P*, *T*) point where the five phases coexist.
   7. For instance, say you have a starting point where the five phases coexist and you know *P*, *T*, *Xen* and *Xdi*. You also know the entropies and volumes of the pure phases as functions of (*P*, *T*); the standard state entropies and volumes of the pyroxene end members as functions of (*P, T*); and you use the strictly regular binary solution model for each pyroxene solid solution with *P*- and *T*-independent excess parameters *W*opx and *W*cpx. So, you have everything you need to evaluate and solve the system of equations in (f) to get the changes d*T* and d for the four oxide components, given some small pressure increment d*P*. Great – now give me an explicit equation for d*Xen* in terms of things you know (start from the expression for the chemical potential of en in the opx solid solution).
   8. You could also get an expression for d*Xen* starting from the expression for the chemical potential of MgTs in the opx solid solution. Can you show that this gives the same answer (hint, you’ll need expressions for the volume and entropy of strictly regular binary solid solutions).
   9. Why is the system of equations derived in part (f) better than the Clausius-Clapeyron equation?

2. a. For an expanded binary strictly regular solution (that is, a c-component solution with one excess parameter for every pair of components),

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(where *Wij* = *Wji* and *Wii* = 0). Derive an expression for the chemical potential of a component of this solution, i(*X1*,…,*Xc*). I know of two ways to do this, pick your favorite: multiply by N to get an expression for extensive G, so you can apply the definition i = (∂*G*/∂*N*i)P,T,Nj≠i. Or use the expanded Darken equation,

(that is, evaluate the derivative along a pseudobinary through the ith end member and the composition of interest, which keeps the ratios of all other mole fractions constant).

b. Say I want to describe a binary solution by



Can you find the corresponding expression for  and then recover this chemical potential expression from it? If not (*hint, hint*), what is wrong here?

1. The (original) Redlich-Kwong (RK) equation of state is

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The a and b parameters are given in terms of measurements of the critical pressure Pc and critical temperature Tc:

a = 0.4275 R2 Tc2.5 / Pc

b = 0.0866 R Tc / Pc.

The critical pressure and temperature for CO2 are 73.87 bars and 31.01 °C.

• Solve for a, b, and the critical molar volume of CO2 (hint, the correct density of critical CO2 is 468 kg/m3).

• According to the van der Waals equation of state, Zc = PcVc/RTc = 3/8; how different is the compressibility factor at the critical point of the Redlich-Kwong model of CO2?

• Now use the RK equation with your fitted parameters to calculate the volume of pure CO2 (a numerical search is recommended!) at P = 200 bars and T = 600 K. The measured value is 243.82 cm3/mol = 24.382 J/bar/mol; how well does the RK equation do under these conditions?