Ge 212 Problem Set #6

Due Wednesday November 27, 2019

1. **Raoult’s law, Henry’s law and such**

a. Let’s say that at *T* = 0 °C benzene has a standard state saturation vapor pressure *P*obenz = 0.05 bar, whereas toluene at the same temperature has *P*otol = 0.01 bar. Assume benzene-toluene liquid solutions obey Raoult’s law for all compositions and that at these low pressures the benzene-toluene vapor is ideal. Construct and draw the Pressure-Composition phase diagram at *T* = 0°C for the benzene-toluene system, showing liquid field, liquidus curve, liquid+vapor field, vaporus curve, and vapor field.

b. Now suppose that Raoult’s law only applies to benzene in a limited range near pure benzene and that the total pressure at 0°C above a liquid solution that is 99% benzene, 1% toluene is measured to be 0.1495 bars. What is the Henry’s law coefficient for toluene?

1. Use the Gibbs-Duhem equation to prove the following proposition for a binary solution: **if** the activity of one component obeys Henry’s law (*a*1 = h1*X*1 where h1 is a constant for some particular temperature and pressure) at all values of *X*1 from 0 up to some maximum *X*1\*, **then** the activity of the other component obeys Raoult’s law (a2 = X2) for all values of X2 between 1 and 1–*X*1\*.

2. **The displaced equilibrium method for activity-composition in mixed fluid**

• At 14 kbar pressure, the reaction enstatite + magnesite = forsterite + CO2(g) (MgSiO3 + MgCO3 = Mg2SiO4 + CO2) is in equilibrium at 925°C if the vapor phase is pure CO2.

• Also at 14 kbar pressure, the same three solid phases are found to coexist at 700°C with a mixed water-carbon dioxide vapor with a CO2 mole fraction *X*CO2 = 0.03.

• Take the following values as given: for this reaction Ho = 78409 J/mol, So = 159.31 J/mol/K, and Vos = –0.0172 J/bar/mol (where this volume change refers only to the solid reactants and products; and per mol means a mole of reaction, so producing a mole of forsterite *and* a mole of CO2).

1. Write *the law of mass action* for this reaction, using unit activity at *P* and *T* as the standard state of the solids and unit fugacity at 1 bar and *T* as the standard state for the vapor, and solve this expression for *f*CO2.
2. Using the measured equilibrium at 925°C with pure vapor, calculate the *standard state fugacity of pure CO2* at 14 kbar and 925°C.
3. Now calculate the *fugacity* of CO2 in the mixed vapor phase coexisting with enstatite, magnesite, and forsterite at 14 kbar and 700 °C.
4. If I tell you that the fugacity of pure CO2 at 14 kbar and 700 °C is 172035 bars, then what is the *activity* of CO2 in this vapor?
5. Given that the mole fraction *X*CO2 = 0.03, what is the *activity coefficient* of CO2 at this composition, temperature, and pressure?

3. **Calculating standard state fugacity**

 Given the following data for the molar volume of methane at 25.0 °C:

|  |  |
| --- | --- |
| *P* (atm) | *V*(cm3/mol) |
| 0.1 | 244601.3124 |
| 0.2 | 122272.1743 |
| 0.4 | 61110.17716 |
| 0.8 | 30529.67712 |
| 1.6 | 15240.38991 |
| 3.2 | 7596.398959 |
| 6.4 | 3774.470821 |
| 12.8 | 1864.217554 |
| 25.6 | 910.9038466 |
| 51.2 | 437.8941375 |
| 102.4 | 209.3370756 |

1. Use these data to fit the coefficients of the Virial equation of state to 3rd order:

, where *A*, *B*, *C* are functions of temperature only, and so constant in this fitting exercise.

1. Calculate the standard state fugacity of CH4 (g) in atmospheres at 25.0 °C when the pressure of pure methane is 110.4 atm, using the virial equation of state and your fitted coefficients.

4. **Fugacity vs. standard state fugacity, an object lesson**

 Hirth and Kohlstedt (1996, EPSL 144:93-108) came up with the first plausible model for estimating the partition coefficient of water between olivine and basaltic melt. Here’s what they knew and what they did:

 • The concentration of OH in hydrothermally annealed olivine (that is, olivine in equilibrium with excess water vapor to which no other volatile components have been added) increases linearly with the fugacity of H2O.

 • The concentration of OH in basaltic liquid equilibrated with excess H2O vapor to which no other volatile components have been added increases as the square root of the fugacity of H2O.

 • At a pressure of 300 MPa, the concentrations of OH in water-saturated olivine and basaltic melt have both been measured and therefore at 300 MPa under water-saturated conditions the partition coefficient (concentration in olivine divided by concentration in coexisting melt, at equilibrium) is known to be 0.0004.

 • Therefore Hirth and Kohlstedt give the following equation, to be used under any conditions:

  (1)

 • Then, for example, they predict that the partition coefficient of H2O at a pressure of 2.5 GPa, where the standard state fugacity of H2O is 2.4 x 104 MPa, is 0.003. They proceed to treat this as a Henrian partition coefficient (a function of pressure and temperature only) and use it to describe the dehydration upon melting of peridotite whose olivine initially contains ~20 ppm H2O (the solubility of OH in olivine at 2.5 GPa corresponds to 1630 ppm).

1. What did they do wrong? (one big mistake, at least two little ones; but I just need the big one)
2. Give a correct expression in terms of standard state fugacity of H2O and activity of H2O. What is the expected dependence on activity of H2O? Should this system obey Henry’s law?
3. How would you do an experiment to demonstrate that Hirth and Kohlstedt’s interpretation of equation (1) is wrong?