**Polymers/Alloys**

**Homogenous Mixture Free Energy**

So we want to construct the Free Energy of a two component mixture: A and B.



First we’ll consider an expression for the energy. Say we have NA, A molecules and NB, B molecules, for a total of N = NA + NB molecules. The molecules have two options, they can bond with themselves, or they can bond with the other type. Let’s say EA is the bond energy between two A molecules, EB is the bond energy between two B molecules, and EAB is the bond energy between an A and B molecule. Also define cA = NA/N, and cB = NB/N. And assume that the number of particles a given molecule can interact with is proportional to that other molecule’s concentration, with proportionality factor Z. Then the total energy would be:



But actually, we’ve double counted, since, with respect to the A’s alone, we counted the interaction of say A1 with A2 and also A2 with A1, whereas there can be only one interaction between them. Similarly with the B’s. And likewise for the AB interaction, we counted the interaction of say A1 with B2, and B2 with A1, whereas there is only one interaction between them. So really,



Now putting entirely in terms of concentration:



Now let’s call cA simply c, and then cB = 1-c. Or let’s not. Then we have:



and we can write this as:



So we have:



Now let’s consider the entropy. Entropy is:



Ω is the total number of distinct ways you can arrange the particles. The number of ways you can arrange N particles, regardless of whether the arrangement is distinct or not, is N!. But to get the number of *distinct* arrangements, we have to divide out the number of arrangements of A particles amongst themselves (because they are all of the same type, and hence, identical from an entropy perspective), which is NA!, and we have to divide out the number of arrangements of B particles amongst themselves (for same reason), which is NB!. And so we get Ω = N!/(NA!NB!). So,



Now use Stirling’s approximation: lnN! ≈ NlnN – N. Actually just lnN! ≈ NlnN suffices:



Then in terms of concentrations…



So we have, in terms of just cA = c (or not, because in retrospect, I can’t keep the term meanings straight w/o the subscripts):



Putting it all together, we have:



Then define: χ = Z(EAB – EA/2 – EB/2)/kT. So then we’d write this as:



But still, everything here is a constant, presumably, including cA, and so there is nothing to minimize yet. Looks like we’re leaving out translational kinetic energy and entropy, i.e., the E and S associated with momentum.

**Inhomogeneous Mixture Free Energy**

Now suppose that the system could exist in two phases, phase 1 and phase 2 (or just one of either). Often times, the way this works is as follows, if i remember correctly. At a given temperature, if we start with say low concentration of A, then A will bond with A, and B with B, and AA’s and BB’s will homogeneously distribute themselves throughout the container. As we increase A concentration, we’ll eventually get phase separation where we have two different regions (i guess this requires the two phases to be immiscible?) whereby one is higher in A concentration and the other lower in A concentration. Actually I don’t know anything about this, ‘cause I don’t know how this relates to the interspecies AB interaction, but it is crucial somehow. Anyway, let the following concentrations be defined:



Further let,



Then for instance, the overall concentration of A, i.e., cA would be:



OK so then it seems that the total free energy of this phase separated thing is the free energy of each phase, which would be:



So, more concisely,



But recall that cA is fixed. And so only two of the three variables, cA(1), cA(2), and x1, are actually independent. So we typically choose cA(1) and cA(2). Now solve for x1 in terms of these variables, then:



and then of course,



These are called the Lever Rules:



So then we could write Ftotal as:



Equilibrium is determined by minimizing Ftotal w/r to these two independent variables. So we must compute,



So working this out,



And,



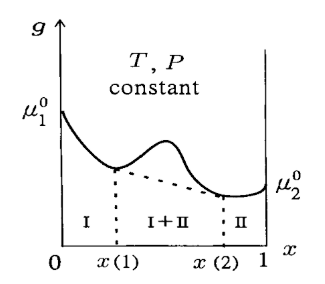
So our two conditions are, succinctly,



Now μ1(cA(1)) is the slope of f1(cA(1)), and μ2(cA(2)) is the slope of f2(cA(2)). So our equation implies that these two slopes must match. But then since they also equal [f1(cA(1)) – f­2(cA(2))]/(cA(1) – cA(2)), this means that the slopes (i.e., the tangent lines) must also lie on a common line. Now observe that f1 and f2 are the same *function* (and so are the chemical potentials therefore). So let f be the single phase free energy function. Then we have:



So we just plot f(c), and see which two concentrations cA(1) and cA(2) on that graph simultaneously have the same slope, and lie on the secant line connecting them (graph’s x’s are my c’s I think/hope).



There is more we can conclude, though, and that is that at this temperature T, any concentration concentration c, between cA(1) and cA(2), we will get this phase separation. And for c’s less than cA(1), we’ll get a homogeneous phase (1), and for c’s greater than cA(2), we will get just homogeneous phase (2). Don’t understand this part.

**Another way**

Trying to relate to the standard way of doing things…our total F can be written as a sum of the F’s of the two phases.



The functions F1 and F2 have the same form. Particles are connected via constraints:



And so we can write:



So the independent variables are: NA1 and NA2. Differentiating w/r to these and setting equal to zero, we have:



and,



But then, if we use a little care in writing out the free energy, we’ll see, moreover, what the form of these chemical potentials is. Note from way up there that we can write:



and putting these four variables in terms of the independent d.o.f., NA(1) and NB(1) we have:



We’ll need derivatives of all of these w/r to NA(1), and NB(1). These are:



and,



So now repeat the differentiation thing:



and then the other is:



So our two equations are:



If we subtract them, we get:



and if we plug this into the second equation, we get:



So our results are:



**Example**

An alloy consists of 70% metal A and 30% metal B by mass. At a certain temperature, the alloy is in a two-phase region containing phases α and β. The α phase has a composition of 60% A and 40% B, while the β phase has a composition of 90% A and 10% B, all by mass. The densities of the α and β phases are 8 g/cm3 and 6 g/cm3, respectively. Calculate the volume fractions of the α and β phases in the alloy at this temperature.

So going back to the lever rule,



I think we can consider all the numbers and number fractions to be mass fractions rather than numbers and number fractions. So let’s work this out, switching 1 to α and 2 to β.



Then, to get the volume fractions we can do:



and,



Reassuringly, these add up to 1.