**Chemical reactions**

Now let’s consider the application of our thermodynamics formalism to chemical reactions. We would like to see if we can predict how many reactions will occur when we let two chemical species interact, what heat will be given off, or absorbed, etc. Our procedure will be very similar to the one we used for the interacting gasses of the previous file.

**Modeling chemical reactions**

Let’s consider chemical reactions held under different conditions, and see how we could theoretically determine how many reactions would take place, heat given off, etc. I’ll just consider the simplest case:

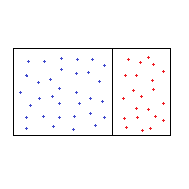


I’ll take A and B molecules to be just gasses with no interatomic structure. But then a C molecule, consisting of bonds between the A’s and B’s I’ll assume to have some potential energy, bond strength,

φ (a negative #). So UA and UB = KE, while UC = KE + φ

**Reaction under closed conditions: constant energy, volume, overall particle number**

Suppose we have a N0A and N0B of gas A and B respectively, separated by a partition of volume V0A and V0B, at temperatures T0A and T0B, respectively. When the partition is opened, and the gasses mix and equilibrate, how many particles of gas A, B, and C will there be assuming closed conditions?



Well from the particle balance, we know that:



where dξ is the # of reactions that have taken place. And so then,



From the energy balance we know that:



and where the U are related such as to conserve energy, i.e. aUa + bUb = cUc, and Qij = -Qji so that net heat transfer is zero as well. From the composite entropy balance we know that:



which means internal entropy will increase until equilibrium is established. So we need to construct an expression for the system entropy and maximize it. We have:



Note that entropy of the product gas is subtracting the bond strength term from the energy per particle. Now let’s implement the constraints: namely energy and particle number:



Of course we know U because we know the initial temperature of each of the two gasses. Differentiating w/r to UA and setting to zero we get TA = TC, and doing the same w/r to UB we get TB = TC. So all temperatures are equal as expected. And these two equations would thereby enable us to solve for UA and UB in principle (perhaps in terms of ξ). Differentiating w/r to the volumes results in them being maximized so VA = VB = VC = V. Differentiating w/r to the extent of reaction and setting to zero would give us an equation for ξ. And note that the equation would involve the Φ’s. But this would mean that we cannot really solve for ξ, unless we have experimentally determined their values. Let’s work out the result a little. The equality of temperatures equation yields:



Additionally we have U = Ua + Ub + Uc. So we can put Ua,b,c in terms of U, and

so:



and so:



Also, Va = Vb = Vc = V. So filling these in, we get:



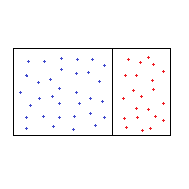
Then we’d fill in the N’s in terms of the extent of reaction,



and maximize w/r to ξ. Note that once we plug ξmax, the ξ that maximizes the entropy, into S we will have an exxpression for S(U,V,N0a,N0b), which is the equilibrium entropy for the mixture. In light of the fact that Na = N0a­ – aξ, and Nb = N0b­ – bξ, and that we know ξ, we could write this as S(U,V,Na,Nb). And if we had, say, started with a certain number of C’s, instead of zero, then we would have S(U,V,Na,Nb,Nc), right? But this seems to violate the fact that our chemical reaction restricts us to just one d.o.f. Well that’s if we fix N0a,b,c. But if we allow these to vary too, by arbitrarily adding particles when we feel like it, then dN0i ≠ 0, and so we’re back to three d.o.f.

**Reaction at constant temperature and volume and overall particle number**

Suppose we have a N0A and N0B of gas A and B respectively, separated by a partition of volume V0A and V0B, at temperatures T0A and T0B, respectively. When the partition is opened, and the gasses mix and equilibrate, how many particles of gas A, B, and C will there be assuming constant temperature conditions – i.e. that they’re put in contact with a thermal bath at temperature T?



Just as before, entropy must be maximized (but now have to include the bath). I’m going to let S, U, V, N stand for the overall characteristics of the box(es), Si, Ui, Vi, Ni (runs between A and C) be the properties of the individual gasses, and Ssys, Usys., Vsys., Nsys. stand for the composite box + bath system. So we have:



Note that Vbath and Nbath are fixed. Let’s formulate the maximum of the total entropy in terms of the degrees of freedom of the system which are entirely contained within the box. Taking the total differential we have:



And so we have that the Helmholtz free energy of the box must be minimized under these conditions. So let’s work out the consequences of this statement. Minimizing w/r to Ui we have (see couple lines above) (seems weird to have to be minimizing w/r to Ui because isn’t T constant? yes but I haven’t fully worked out the consequences of that energy conservation constraint. I took the derivative of Sbath, but haven’t yet done so on any of the Si’s, so that’s why we don’t have the constant T constraint implemented quite yet):



Minimizing w/r to volumes, will just yield that the volumes expand to fill the container. So substituting in our results so far we will have, for F:



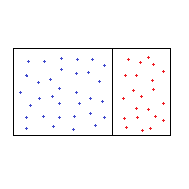
and then finally putting this in terms of the extent of reaction,



and so at this point we’d minimize w/r to ξ. Note that once we plug ξmax, the ξ that minimizes F, into F we will have an exxpression for F(T,V,N0a,N0b), which is the equilibrium free energy for the mixture. In light of the fact that Na = N0a­ – aξ, and Nb = N0b­ – bξ, and that we know ξ, we could write this as F(T,V,Na,Nb). And if we had, say, started with a certain number of C’s, instead of zero, then we would have F(T,V,Na,Nb,Nc), as argued above.

**Reaction at constant temperature, pressure, and overall particle number**

Suppose we have a N0A and N0B of gas A and B respectively, separated by a partition of volume V0A and V0B, at temperatures T0A and T0B, respectively. When the partition is opened, and the gasses mix and equilibrate, how many particles of gas A, B, and C will there be assuming constant temperature and pressure conditions – i.e. that they’re put in contact with a thermal bath at temperature T, and pressure p?



I’m going to let S, U, V, N stand for the overall characteristics of the box, Si, Ui, Vi, Ni (runs between A and C) be the properties of the individual gasses, and Ssys, Usys., Vsys., Nsys. stand for the composite box + bath system. Just as before, entropy must be maximized. So we have:



Note that Nbath is fixed. So, forming the total differential to put things in terms of the changing variables, the criterion for maximum entropy turns into:



And so we have:



So we see that the Gibbs free energy is minimized under conditions of constant temperature and pressure. So let’s work out the consequences of this minimization. It works out best if we fill things in as we go. Differentiating w/r to Ui and setting to 0 we get 1 – T/Ti = 0 → Ti = T. Differentiating w/r to Vi and setting to 0 we get that the gasses will expand to fill the box: so Vi = V. After filling these in, and then differentiating w/r to V and setting equal to 0, we get that the sum of the pressures, pi will equal p.

This last part means that pi = NikT/V = (Ni/N)(NkT/V) = (Ni/N)p. Filling these results in so far we have for G:



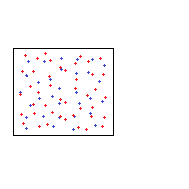
And finally, we would put all the N’s in terms of the extent of reaction:



and of course then we would differentiate w/r to ξ and set to 0 to solve for the # of reactions. Note that once we plug ξmax, the ξ that maximizes the free energy, into G we will have an exxpression for G(T,p,N0a,N0b), which is the equilibrium entropy for the mixture. In light of the fact that Na = N0a­ – aξ, and Nb = N0b­ – bξ, and that we know ξ, we could write this as G(T,p,Na,Nb). And if we had, say, started with a certain number of C’s, instead of zero, then we would have G(T,p,Na,Nb,Nc), as argued above.

**Reaction at constant temperature, and partial chemical potential + incompressibility**

Suppose we have a N0A and N0B of gas A and B respectively, in volume V, and temperature T, doing their chemical reaction thing. Let’s say that the bath holds the chemical potential of species A to μ.



And let’s also add an incompressibility constraint, namely that:



(and V is constant of course and υi is the volume of an i molecule). Just as before, entropy must be maximized. So we have:



So, forming the total differential to put things in terms of the changing variables, the criterion for maximum entropy turns into:



And so we have that a Landau free energy of the box must be minimized under these conditions. So let’s work out the consequences of this statement. Minimizing w/r to Ui we have:



So we have now:



Minimizing w/r to NA, which is now a free variable, unconstrained by the chemical reaction thing, thanks to the bath, we have:



This requires,



So we have NA in terms of VA, μ. Could write,



But we also have: VA/NA = υA → VA = NAυA →



and NA is completely fixed now. So we have:



tis a mite ugly. Continuing with the incompressibility constraint, sort of, we know that all volumes are tied to particle numbers via Vi = Niυi. So I’ll fill that:



Now we can use the constraint explicitly to write NB, say, in terms of the other guys,



So,



and last, we have NC, which, according to the chemical reaction is just cξ. So,



And then we minimize w/r to ξ. Might be concerned that knowing NA should have fixed ξ. But note that the particle balance equations will be a little different, because of the possible influx of particle A from the bath. So I think we should have:



So knowing NA doesn’t fix ξ quite. Note that once we plug ξmax, the ξ that maximizes the Landau free energy we will have an exxpression for LA(T,V,μa,N0b) (where μa = μ), which is the equilibrium entropy for the mixture. In light of the fact that Nb = N0b­ – bξ, and that we know ξ, we could write this as LA(T,V,μa,Nb). And if we had, say, started with a certain number of C’s, instead of zero, then we would have LA(T,V,μa,Nb,Nc), as argued above. We might want to write the equilibrium (i.e. minimized) Landau Free Energy of our mixture. We could say,



But I think we do have to factor in the incompressibility constraint, which says,



What is the differential formula?



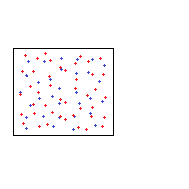
But when plug in constraint, say NC in terms of the others, we’ll necessarily invoke a dNA, which shouldn’t be here. But anyway,



Whatever.

**Reaction at constant temperature, pressure, and partial chemical potential**

Suppose we have a N0A and N0B of gas A and B respectively, in volume V, and temperature T. I guess I’ll say the box is going to be maintained at constant pressure p, temperature T, and let’s say chemical potential μA, from an external reservoir. And we’ll say of course that the particles undergo some chemical reaction.



Just as before, entropy must be maximized. So we have:



Note that Nsys(A) is fixed. So, forming the total differential to put things in terms of the changing variables, the criterion for maximum entropy turns into:



and we’d recognize this as one of the Landau ‘type’ free energies:

