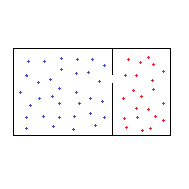
**Various Interacting Examples**

Now I’d like to consider several examples of components interacting with each other. The main interest, as before, is to work out the characteristics of the final state. Just to provide an overview of sorts, the basic methodology would be similar to what we did in the previous file. We write down the known initial conditions, as well as known final conditions. And then write down the balance equations of all the components, and solve them as far as possible in terms of left over free *state* variables **η**. Then we also plug them into the expression for the total entropy S(U,V,N;**η**) (where U, V, N are *overall* energy, volume, and particle number, which remains constant presumably) (we must assume that we can write the total entropy as a sum of composite local equilibrium entropies, which seems general enough though, as each component *will* be locally in equilibrium, when the whole system is in equilibrium). Then to determine the equilibrium arrangement, we simply maximize S w/r to **η**. This procedure is quite general in the sense that the **η** can range over quite non-equilibrium values. The **η** do have to be chosen to adequately reflect the real d.o.f. of the system though. Note this is basically identical the procedure we used to get the free energy of an ideal gas in a field.

**1a. Example**

Let’s consider equilibrium between two gasses. Let the left one be at Nb, Tb, Vb, and the other at Nr, Tr, Vr initially. And let them be adiabatically insulated. If we poke a hole in the barrier and let them diffuse through, what will be final pressure, temperature?



We’ll write balances for both species (blue gas, red gas),



Q, the energy transfer between species would be comprised of just heat I guess. Not sure how we’d break it down in this scenario. And now we fill into the composite entropy balance:



which simply says that the entropy will increase to its maximum value, subject to constraints. Assuming quasi-equilibrium for the components of the system (at least near equilibrium), we can write the entropy as, noting total conservation of energy, as is apparent from the balance equations themselves.



Maximizing w/r to Ub means that the temperatures will be the same (see that Equilibrium Systems file). as we’ll have:



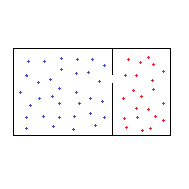
And maximizing w/r to Vb and Vr means that the gasses will expand to occupy the entire container. What will be this new temperature? We can go back to the energy balance equations and work it out. I’ll use the total energy balance. We can write the energy of each gas in terms of its temperature since it is in equilibrium both before and after the process. So the energy balance equation requires:



and the pressures will be, from the energy equation, p = NkT/V, filling in the respective N and common T and V. Then add to get total pressure. Or more formally, could use expression S(E,V,Nr,Nb) and p = T∙∂S/∂V)E,N and that S = Sr + Sb to argue that the total p = pr + pb.

**1b. Example**

Let’s reprise the last problem. Consider equilibrium between two gasses. Let the left one be at Nb, Tb, Vb, and the other at Nr, Tr, Vr initially. And let them be adiabatically insulated. If we poke a hole in the barrier and let them diffuse through, what will be final pressure, temperature?



But this time we’ll write down the balances by compartment (left = 1, right = 2).



IU, the energy transfer between compartments would be comprised of convective energy transfer (energy transfer via particle flux basically), diffusive energy transfer/work, and heat. We’ll be more explicit about such terms when we get to NETD. And now we fill into the composite entropy balance



which simply says that the entropy will increase to its maximum value, subject to constraints. Assuming quasi-equilibrium for the components of the system (at least near equilibrium), we can write the entropy as, noting total conservation of energy, as is apparent from the balance equations themselves.



Noting



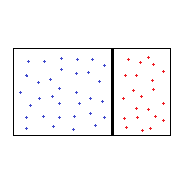
we see that maximizing S w/r to U1 means that the temperatures will be the same. And maximizing S w/r to N1r and N1b means that the chemical potentials will be the same. Employing the equality of the final temperatures in the energy balance (conservation of energy ultimately) equation gives us:



and this is the same we got last time.

**2. Example**

Let’s consider equilibrium between two gasses. Let the left one be at Nb, Tb, Vb, and the other at Nr, Tr, Vr initially. And let them be insulated from the environment, but not each other. Suppose that the barrier is simply unlatched so that it can move back and forth. What will be final pressure, temperature, volume of the gasses?



We’ll write balances for both species (red gas, blue gas), and the plate/lid thing between them:



And now we fill into the composite entropy balance:



Accounting for the energy constraint, and the fact that the volumes will expand to fill available space, we can write the total entropy as:



Maximizing w/r to Vb and Vr, we’d just have that they fill their containers so that Vb = Vℓ, say, and Vr = V - Vℓ.



Now differentiating w/r to Ub, we have:



We’ll call the new temperature T. And differentiating w/r to Vℓ, we have:



and finally w/r to Pℓ,



And now since the gasses are in equilibrium before and after we can write the total energy conservation equation as:



And the entropy balance result states:



And we can also use conservation of volume,



This gives us our last equation that we can use to get the final temperature and volume of our gas. So we’re done! What would happen if we just plugged the balance equations into the entropy equation, after having presumed the gas volume expands to fill the container?



Setting forces and currents to zero (in equilibrium) gives us:



If we also apply the entropy balance to each individual compartment, we’d have:

which itself additionally requires:

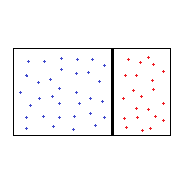


And in conjunction with the global balance requires:



**3. Example**

Let’s consider equilibrium between two gasses. Let the left one be at Nb, Tb, Vb, and the other at Nr, Tr, Vr initially. And let them be adiabatically insulated. Suppose that the barrier is simply unlatched so that it can move back and forth. What will be final pressure, temperature, volume of the gasses assuming they cannot exchange heat?



We’ll write balances for both species (red gas, blue gas), and the plate/lid thing between them:



And now we fill into the composite entropy balance:



Accounting for the energy constraint, and the fact that the volumes will expand to fill available space, we can write the total entropy as:



Maximizing w/r to Vb and Vr, we’d just have that they fill their containers so that Vb = Vℓ, say, and Vr = V - Vℓ.



Now differentiate w/r to Vℓ, mindful of the fact that, like above, it’s correlated with Ub, and Ur. But, as mentioned before, maximizing over the phase space allowed by physical constraints and our balance equations is somewhat tricky. So in *this* case, on approach to equilibrium, Ub *won’t* be independent of Vℓ because of the gas energy balance equation (before, the Q term made these two independent). So maximizing with respect to these variables, using the generic form of S(U,V,N) we would get:



So interestingly, we don’t precisely get equality of the pressures from the entropy balance. We do get that the lid will stop moving though, and this is tantamount to πr = πb, or if in equilibrium, that:



And now since the gasses are in equilibrium before and after we can write the total energy conservation equation as:



And the pressure equality condition result states:



And the sum of the volume balance equations also gives:



But this isn’t enough! We need one more equation, like the temperature equality condition we had last time. So we would have to assume something about the process of coming to equilibrium – probably that it was quasi-equilibrium the *entire* time. Then we could use the isentropic equation of state to relate volumes and pressures.



for both compartments. We can make a more general assumption when we get to NETD.

**4. Example**

A diathermic cylinder is inside a water bath at a constant temperature T0 = 10oC . Inside it, a diathermic piston separates two chambers with 1mol of gas in each of them, with a Helmholtz free energy F(V,T) =−nRTln(V−nb)+J(T), where J(T) is some function that depends only on temperature T. Initially, one gas occupies a volume V1(0)=1ℓ and the other a volume V2(0)=2ℓ. Find the internal energy U(V,T) of the system of both gases, considering J(T) as a known function.



This will be minimized w/r to V1. In other words – their pressures will be equal. So we’d do,



So then,



The internal energy would be:



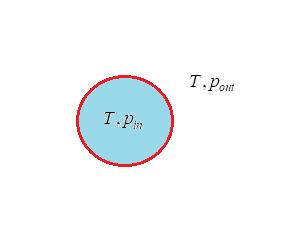
So,



Yeah.

**A Surface Tension Example**

Say we have an elastic balloon full of air at pressure pin, at temperature T, within an air environment also at temperature T, and pressure pout. Would like to know what the volume, V, of the balloon will be, supposing we know its elasticity or something.



So the energy of a balloon is:



Should have Free energy of the system minimized. So,



Minimizing w/r to V, the independent variable, we’d have:



We can assume the pressure of the outside is not appreciably affected by the volume of the balloon. So that pout is the same regardless of V. In that case we would have:



Could solve for V. But I’ll leave it like this. In the context of a cell in an aqueous environment, I think the γ∂A/∂V = ∂Eballoon/∂V guy is called the cell’s osmotic pressure? Can simplify this a little, perhaps,



This is called Young-Laplace’s equation?

