**More Chemical Reactions**

Now like to consider more extensive chemical reactions, especially as applied to chemical batteries. Implicit in the analysis is determining the chemical potential of a species dissolved in another. So let’s consider this for a bit,

**Chemical potential of species in mixture**

Let’s suppose we have two species, A and B. And let’s say that A is dissolved in B, or perhaps they can form a sort of bound state, C, which can be described by the chemical reaction: aA + bB = cC. Let N0A be the initial # of A, and N0B be the initial # of B, and φ be the (negative) bond strength. Then what will be the final #’s of A, B, C if conditions are constant temperature and pressure? And so then what will be the chemical potential of either species A or B in this mixture? Well we know that the Gibb’s free energy will be minimized, and



but subject to constraint that pA + pB + pC = p. Now the Gibb’s free energy of an ideal gas with bond strength (-)φ is:



So we have:



but we have that pi = NikT/V = (Ni/N)NkT/V = (Ni/N)p. So we can write this as:



Then we have to minimize w/r to particle #’s. According to the conservation equations we have

NA = N0A­ – aξ

NB = N0B – bξ

NC = cξ

and we’d get:



This is too complicated in general. But maybe I’ll hazard a Taylor series expansion in ξ. So I’ll assume that there are just a few reactions. Then,



and then,



and,



which simplifies a little to:



A quick plot seems to legitimate keeping only up to this order if ξ is small. Take derivative and set to 0,



Simplifying,



Even this is too complicated I think. But if I solve for ξ then I get:



OK so yeah too hard. But I wonder if this is even a correct description? I’m implicitly assuming that μA = ∂G/∂N0A)N0B. But it seems more like ‘canon’ that μA = ∂G/∂NA)NB. And this is problematic since a chemical reaction doesn’t allow one species # to be held fixed if the other can vary. So this might mean that I shouldn’t be allowing a chemical reaction in the first place, at least in the present context of a solvent dissolved in a solute? Dunno. So let’s look at some simpler descriptions. The expression for the chemical potential of an ideal gas is:



now if the gas is part of a mixture of gasses, then the chemical potential would be:



As before we could write this pressure as pi = (Ni/N)p. So then we’d have:



where xi = Ni/N. By analogy, the chemical potential of an ideal solution is defined to have the same xi dependence:



where μ0(T,p) would be the chemical potential of the pure substance at that temperature and overall pressure. Real solutions approximately obey this formula when xi ~ 1. But when xi << 1, we can still use this equation, but with a different reference state. Solutions for which this equation is true over the entire range are called *ideal* solutions. We can write the chemical potential of a species in a real solution as:

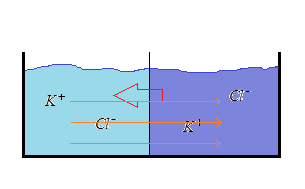


γi is called the activity coefficient, and naturally it goes to 1 as xk → 1. Together γkxk is called the *activity* ak. And so we could write:



**Membrane potential difference**

Consider a container with a semi-permeable (to K+ ion) membrane separating two different concentrations of KCl.



K+ ion will flow to the left to equalize its chemical potential. As a consequence, positive charge will build up on the left, creating a potential difference. Eventually enough positive charge will build up so that flow stops. We’d like to calculate what the potential difference will be. Well at equilibrium we must have the Gibbs potential maximized w/r to free parameters. We can write it as:



where C is the capacitance of the solution and the last term is the interaction potential energy between the two sides – I think it is best to model it as charging a capacitor, since each side will be equally and oppositely charged, and each side will probably be at the same potential too, since ionic solutions are good conductors so we use the formula PE = Q2/2C. OK, well the chemical reactions is:



and so we have:



Maximizing then, we have:



where in the last line we use ΔV = Q/C. And this would simplify to the following, taking into account the equality of the ‘pure’ part of the chemical potentials on either side, we could write the potential difference as:



**Concentration Cell**

Suppose we want to turn this into a battery. This would be called a concentration cell, and we could make it like this. Suppose we have the same set-up but use a different solution – this time CuCl2. And we will use a copper anode and cathode. The membrane would be permeable to Cl-, but not Cu2+.



Then the concentration gradient would spur migration of Cl- ions to the left. Then the Cu atoms in the left rod will oxidize (leave off 2e- on the copper rod, become Cu2+) and dissolve into the solution, binding with the excess Cl-. This surplus of electrons in the copper rod will now migrate onto the other rod on the right. The excess Cu2+ ions in solution will then reduce (absorb the 2e- on the copper rod), turn into regular copper solid and bind to the rod. And then the process will continue. Note the copper rod on the left will become depleted (i.e. will dissolve) and the copper rod on the right will become larger. And the concentrations of CuCℓ2 will eventually equalize. We can infer the effective potential generated by the cell by placing a potential difference (the battery) in series with it, and tuning it to stop all current, and therefore all chemical reactions.



We can write the total Gibbs energy as:



And then we’ll maximize w/r to free variables to see what the values of the various N’s will be given a certain ψL, ψR. And then we would demand that the N’s are unchanged from their original values and see what ψL and ψR correspond to this criterion. OK let’s write down the chemical reactions taking place:



And so we have:



Filling these equations into the Gibbs potential we can write:



And so then differentiating w/r to each variable and setting to zero we get the equations (note that the extra terms cancel in the second and fourth equations):



It seems that we could solve for the potential difference with the first equation. But we’ll work it out in terms of the Cl- ion’s chemical potential. So it seems rather that he does this…solve for the potential difference with the third:



and then solve for the electron chemical potentials with the second and fourth equations, to get:



Then it seems we say that the copper chemical potentials are equal, and so have that:



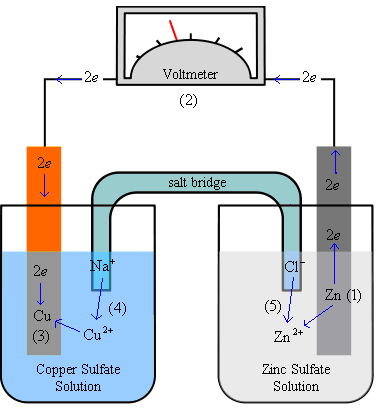
Putting chemical potentials in terms of activities: μ = μ0 + RT ln(a), we can write:



So that’s our answer!

**Wet Cell**

Now we move on to a more general type of battery. A prototypical ‘wet’ cell battery is shown below,



It consists of a Zn electrode (the + terminal) (grey colored bar) in a zinc sulfate solution, a Cu electrode (the – terminal) (copper colored bar) in a copper sulfate solution, and salt bridge. The bridge can be any salt, NaCl, KCl, etc. (1) There is a tendency for Zn atoms in the electrode to jump into the solution as ions, leaving behind 2e- in the electrode. This puts an excess of solitary Zn2+ ions in the solution and leaves behind 2e- in the electrode. (2) These aggregated electrons then push themselves through the metal wire/circuit into the  electrode. (3) These excess electrons in the Cu electrode attract Cu2+ ions in the copper sulfate () solution which join them and turn into Cu, and adhere to the Cu electrode; one would say that the Cu2+ ions ‘plate’ onto the Cu electrode. This leaves excess sulfate in the solution, which gives the solution a net negative charge. At this point the salt bridge (perhaps NaCl?) comes to the rescue. (4) Na2+ leaches out of the salt bridge into the and neutralizes the excess and forming NaSO4 presumably, but this leaves the salt bridge with a net negative charge. (5) Then on the others side of the salt bridge, Cl2- leaches out into the solution restoring neutrality to the salt bridge, and then neutralizes the excess Zn2+ ions, forming ZnCl2, restoring neutrality to the solution. Then the process starts over with (1).

We’d like to determine the potential difference generated by such reactions. And it works the same way as above. Since it was the reactions at the electrodes that mattered, I’ll just write the reactions there, as well as the one where the electrons transfer from left to right, get their affinities and set to 0.



And so we must have:



And in terms of the bare chemical potentials and electric potentials we will have (and note the cancellation of the potential terms when the reaction only involves one side):



Then solving for the potential difference we have:



So we have:



and we could put this in terms of the activities as before.