Redox Potential PhL 4.16.07

I want a clearer understanding of this chemistry topic. I do have a hazy view of it, but that does not cut the mustard.

NOTE! These notes have lots of errors, I was just starting to ponder the subject. Now correct results are presented in my Baby and Daddy Reif notes, but I decided to keep this document anyway.

Here is an opening web quote:

"Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution. Like pH, the reduction potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in much the same way that pH does not characterize the buffering capacity. "

So the claim here is that the redox potential is a property of a solution like pH. [Well OK, the half-reaction potentials are intensive, not extensive, given in volts.]

Let's digress to Chapter 14 of the Parry high-school chem book which discusses "oxidation/reduction reactions" and where I already have some notes. You can write "half-reactions" where electrons appear as either reactants or products. Like any reaction, you can perhaps look up the ΔG for a half reaction occurring in a solution, to see whether it will "go". Consider this half reaction:

$$Cu \rightarrow Cu^{+2} + 2e^{-}$$

Put Cu in water and this reaction will go until equilibrium is reached. You might define:

$$K = [e^{-}]^2 \, [\, Cu^{+2}] \, / \, [Cu]$$

as is done in the acid case Parry page 597. Can I find anything on the web that talks about such a K? No I cannot find numbers for such K's because the world does not think of it in that way. Still, there must be some value for K. The reaction will proceed until $\Delta G = 0$ [if ΔG has the right sign. Probably ΔG is the wrong sign, so Cu just stays Cu. After all, we are ionizing Cu all by itself. You need two -half reactions to have a chance.] . This gets us all involved with T and entropy and ΔH for pulling the things apart in solution, including the effects of water on the resulting ions, it is all very complicated to think about from first principles. This is "solution chemistry".

I think we can always think of ΔH as the energy given off in a reaction [not ΔG] [In general, we can set $\Delta H = \Delta E$ because volumes don't change significantly, $H = E + pV$] , and we can identify this with the voltage of our cell somehow. [Wrong guess: it turns out that ΔG makes the voltage.] If a full reaction makes 1 volt of potential, then if 1 Coulomb of electrons flow through a circuit, you have done 1 joule of work I suppose. So if you allow the reaction to go such that 1 C flows total, then you can say I think that ΔH for that amount of reaction was 1 joule. But usually we measure things not per coulomb of electrons, but per mole of reactant or per mass. Usually we see kcal/mole. A mole of electrons I guess is Av electrons. As shown on page 133 Parry, we have

1 mole of electrons = 96,500 coulombs worth of charge // number not exact!

So in our example, if we were to run our reaction with 1 volt and we moved 96,500 coulombs through the circuit, we could identify ΔH = 96,500 joules. If the reaction as shown above gives off 2 electrons, then we might claim that ΔH = 96,500/2 joules per mole of Cu that we allow to react. Then we have to convert to kcal/mole to get the usual number. We know that 1kcal = 4185 joules, so we can make the following connection:

ΔH(kcal/mole of Cu in full cell) = volts * 96,500 / 2 * (1 kcal/ 4185joule)

We have to worry about the appropriate /2 type factor depending on the reaction.

So we add the voltages of the half reactions just as we would add the ΔH's for these half reactions, but nobody every does it that way, the voltage is so much easier. The sum voltage for a full reaction is the number of joules given off when the reaction sends 1 C of electrons through a circuit. So we think maybe in terms of coulombs instead of moles when doing this stuff.

Look now at my Parry notes full reaction example. The total reaction shows V = + 0.51 volts. This means the reaction has $\Delta H > 0$ and goes as shown. [Really $\Delta G < 0$ makes it go.] This result is an absolute number. In the half reactions, you can have an arbitrary zero point.

Consider the Parry's page 333 table. Chlorine wants to exist as Cl^- and therefore wants to accept the electrons as shown. This means chlorine gas likes being reduced, it wants to be reduced, it is happy when reduced, it gives off lots of energy if you allow it to be reduced. The amount of energy it gives off is 1.36 volts per coulomb PLUS a constant that sets the zero of the scale. You might in fact be able to compute this constant from the detailed physics of the solution, but that is never necessary.

Consider this simpler situation:

$2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$ volts

If this reaction were in a plasma instead of a water solution, you would say that the reaction gives off twice the ionization potential of hydrogen, adjusted for the molecular stability correction. But in solution, it is not so simple. Both the H^+ and the e^- would be hydrated and that makes a correction. I suspect that the details of how an electron exists in a water solution is not very well known. The best web search is for "solvated electrons" and you end up with blocked PDF papers.

When you measure full-cell reaction potentials at 1 mole, your measurement incorporates all the complexities of the way the electron and the ion is hydrated in the solution.

Conclusion: in the page 333 table, the top entries want to accept electrons with enthusiasm, so the non-electron reactant on the left wants to accept electrons and thus wants to be reduced. So you would say that chlorine has a "high reducing power" as indicated by its large positive Eo value. [I think this is wrong. Something with high reducing power is something wants to reduce something else??]

I don't yet have a connection between the inorganic high-school concept of half reactions and the stuff used in biological reactions. The wiki page does say:

"**Standard Reduction potential** (also known as **redox potential**, **oxidation / reduction potential** or **ORP**) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced."

So Parry page 333 shows that chlorine gas has a high affinity for electrons and so the half-reaction has a large positive "reduction potential" (notice that you maybe use one word or the other). If you are talking about accepting electrons as chlorine gas wants to do, you say chlorine has a high "reduction potential" meaning it wants to accept electrons, it wants to be reduced. Let us continue in Wiki:

"**Reduction potential** is measured in volts (V), millivolts (mV), or Eh (1Eh = 1mV). Because the true or absolute potentials are difficult to accurately measure, reduction potentials are defined relative to the standard hydrogen electrode (SHE) which is arbitrarily given a potential of 0.00 volts. **Standard reduction potential** (E^0), is measured under standard conditions: 25°C, a 1 M concentration for each ion participating in the reaction, a partial pressure of 1 atm for each gas that is part of the reaction, and metals in their pure state. Historically, many countries, including the United States, used **standard oxidation potentials** rather than reduction potentials in their calculations. These are simply the negative of standard reduction potentials, so it is not a major problem in practice. However, because these can also be referred to as "redox potentials", the terms "reduction potentials" and "oxidation potentials" are preferred by the IUPAC. The two may be explicitly distinguished in symbols as E_r^0 and E_o^0."

So this shows the confusion in the various names for the potentials that people use, but it is only in polarity, not in scale (so far). The E^o in Parry is in fact a "reduction potential" and this is made clear in his appendix 7 on page 598. Notice in this Parry table this entry:

$1/2O_2 + 2H+ + 2e- \rightarrow H_2O$ $\qquad E^o = +1.23$ volts $\qquad$ SHE

This is pretty high on the list and suggests that this half reaction has a very high reduction potential. But the Watson book shows this at 820 mV, so they just use a different zero point? Or is it due to different molarities?

The SHE reference means that standard hydrogen electrode, but SCE is more practical.

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Pause to consider information here: http://en.wikipedia.org/wiki/Nernst_equation

We know from Reif that if your system A is in contact with a thermal reservoir, you can say:

$$P_r = C \exp(-\beta E_r)$$

where r labels some "state" of system A. Now, consider this reaction:

$Cl + e- \rightarrow Cl-$

and we think of the two sides of this equation as two "states" of System A. The two states have different energy, and the difference is 1.36 electron volts from our Parry table, apart from a certain "zero" issue, if

we have a 1 molar solution for [Cl-]. So the relative probabilities of these two states are given by the factor as

$$\text{Prob(Cl + e-)/Prob(Cl-)} = \exp(-\beta\varepsilon_1 + \beta\varepsilon_0)$$

where ε_1 is our energy difference expressed as in Perry, and ε_0 is the unknown zero point of the energy scale. Note that $\beta\varepsilon_1$ is positive, so the Cl- state is favored, ignoring the scale issue. Now it seems awfully reasonable to say this:

$$\text{Prob(Cl + e-)/Prob(Cl-)} = [Cl] / [Cl^-]$$

Then we have shown that

$$[Cl] / [Cl^-] = \exp(-\beta\varepsilon_1 + \beta\varepsilon_0) \quad \Rightarrow \ln([Cl] / [Cl^-]) = -\beta\varepsilon_1 + \beta\varepsilon_0$$

then $\varepsilon_1 = \varepsilon_0 - kT \ln([Cl] / [Cl^-])$ [// So we get Nernst from Boltzmann!]

Now if we define the chemical potential to have the oppose sign of ε and call if μ, then we get

$$\mu_1 = \mu_0 + kT \ln([Cl] / [Cl^-])$$

Notice that μ's have dimensions of energy. [This is the difference in the chemical potential of the two species.] If we divide by electric charge e, we get units of volts and we get

$$E_1 = E_0 + (kT/e) \ln([Cl] / [Cl^-])$$

where E is an electric potential you might measure with a voltmeter if you could make just a half cell reaction. This last two equations appear on the web page just quoted.

What about the second derivation shown there? It starts off like this:

$S(A) = S^0(A) - k \ln[A]$ as the entropy of species A single molecule

Again I have to appeal to my "reaction volume" idea V_A to justify this claim. Given the above, it is then easy to show that

$\Delta S_{reaction} = \Delta S^0_{reaction} - k \ln Q$ where Q is the "usual thing" with little exponents as needed.

How, we know that G = H - TS and with reservoir on T and p situation we have $\Delta G = \Delta H - T\Delta S$, but then we get $\Delta G = \{ \Delta H - T\Delta S^0_{reaction} \} + kT \ln Q$ which we call $\Delta G^0 + kT \ln Q$. Finally, author identifies the ΔG with the μ chemical potential we used above, and ends up with the same Nernst equation.

This says it is ΔG which causes the current to flow, not ΔH. How do I explain that fact? In Reif's two phase situation, I accepted that equilibrium meant $g_1 = g_2$, free energy per molecule on the two sides. The larger the difference if you are out of eq, then the larger the voltage.

I found a site which claims that really the chemical potential μ_1 is what Reif called g_1 , the free energy of a single molecule.

Then the question is: how does this relate to the voltmeter? Why can we connect the voltage with the free energy change? Why is this not $\Delta E = \Delta H$? For one thing, even at eq, there is still a non-zero ΔH for the reaction, but the voltage is certainly going to go away. Here is a quote:

"The free energy change for a process represents the maximum amount of non-*PV* work that can be extracted from it. In the case of an electrochemical cell, this work is due to the flow of electrons through the potential difference between the two electrodes. Note, however, that as the rate of electron flow (i.e., the current) increases, the potential difference must decrease; if we short-circuit the cell by connecting the two electrodes with a conductor having negligible resistance, the potential difference is zero and no work will be done. The full amount of work can be realized only if the cell operates at an infinitessimal rate; that is, reversibly"

I like this quote, but I want to know **WHY it is true.** A statement like that needs a derivation.

OK, here is something from a reasonable location

http://www.chem.arizona.edu/~salzmanr/480a/480ants/ageq&max/ageq&max.html

Here then is my derivation:

$dU = dQ + dW$ = heat added + work done on system , causes increase in system energy U

$dQ = TdS$ = add small heat to a system, that increases its entropy as this shows, more states.

Also, $dW = -pdV + dW_{other}$ / where dW_{other} might include work done pushing electrons thru a circuit

Then we get

$dU = TdS - pdV + dW_{other}$

Now, define $G = U - TS + pV$ This is H - TS

Then $dG = dU - TdS - SdT + pdV + VdP$

$= (TdS - pdV + dW_{other}) - TdS - SdT + pdV + VdP$

$= dW_{other} - SdT + VdP$

Now if we work with a reservoir of T and P, we set $dT = 0$ and $dP = 0$ and we get:

$dG = dW_{other}$

This says that the free energy is equal to the work that a system can do (other than pdV type work) provided the system works in a reversible smooth process. Where did this last assumption come in?