



13. What's better than chemistry? Electrochemistry.



LEARNING GOALS

Learning Objectives

1. Given a balanced chemical reaction, define the reaction quotient Q
2. Describe how the reaction quotient is named the equilibrium constant when all concentrations are at equilibrium
3. Explain why the concentrations of the condensed phases are not included in the equilibrium constant
4. Balance a simple chemical reaction
5. Summarize how the Gibbs energy of mixing leads to a minimum Gibbs energy between reactants and products
6. Given a table of standard formation enthalpies and standard entropies, calculate the standard Gibbs energy for a reaction
7. From the standard Gibbs energies for reactants and products, determine the standard Gibbs energy for a reaction
8. From the standard Gibbs energy for a reaction, determine the value of the equilibrium constant
9. Given the half-cell reactions, write a balanced equation for the overall redox reaction
10. Determine the overall standard cell potential, given the standard half-cell potentials
11. Predict which electrode will be the anode and which the cathode, given the half-cell potentials
12. Relate the Gibbs energy to the cell potential, and vice-versa
13. Justify the use of the standard hydrogen electrode
14. Apply the Nernst equation to determine the cell potential at arbitrary concentrations
15. Explain both uniform and galvanic corrosion
16. Explain corrosion prevention by cathodic protection

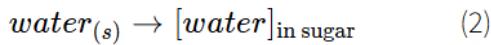
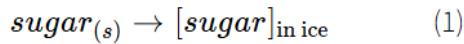


It's probably best to start at equilibrium.

Haha! I'm so funny. I mean, we really need to discuss a few things about chemical equilibrium before we can dive into electrochemistry. So, let's start with what we know; since we've just finished phase equilibria, do you recall in the water-sugar phase diagram that we said there was *essentially* no solid solubility of sugar in solid water ice, nor of water in solid sugar? If you heard me talking about it I might

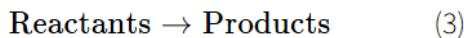


have just hesitated awkwardly. An important word was *essentially* (or my awkward hesitation) since there would actually be a tiny amount of each dissolved in the other. A few molecules of sugar will dissolve in solid water ice, for example. So, in this case we are getting a glimpse into the heart of equilibrium, because equilibrium exists in both of these cases, just very close to pure water ice and pure sugar. We could write the equations as



and in practice we'd be fine to say that the compositions (remember: in wt% sugar) were essentially $C_{\text{ice}} = 0$ wt% and $C_{\text{sugar}} = 100$. But, in this business (chemistry and materials science) even tiny concentrations can make all the difference so we need to be more precise.

Let's see if we can sort things out with a general reaction:



and let's say that for this reaction $\Delta G^\circ < 0$, meaning that the reaction is spontaneous as written, that is, it will proceed to the right. Here it will be handy to graphically illustrate the Gibbs energy as the reaction proceeds from left (reactants) to right (products).

The progress of a reaction

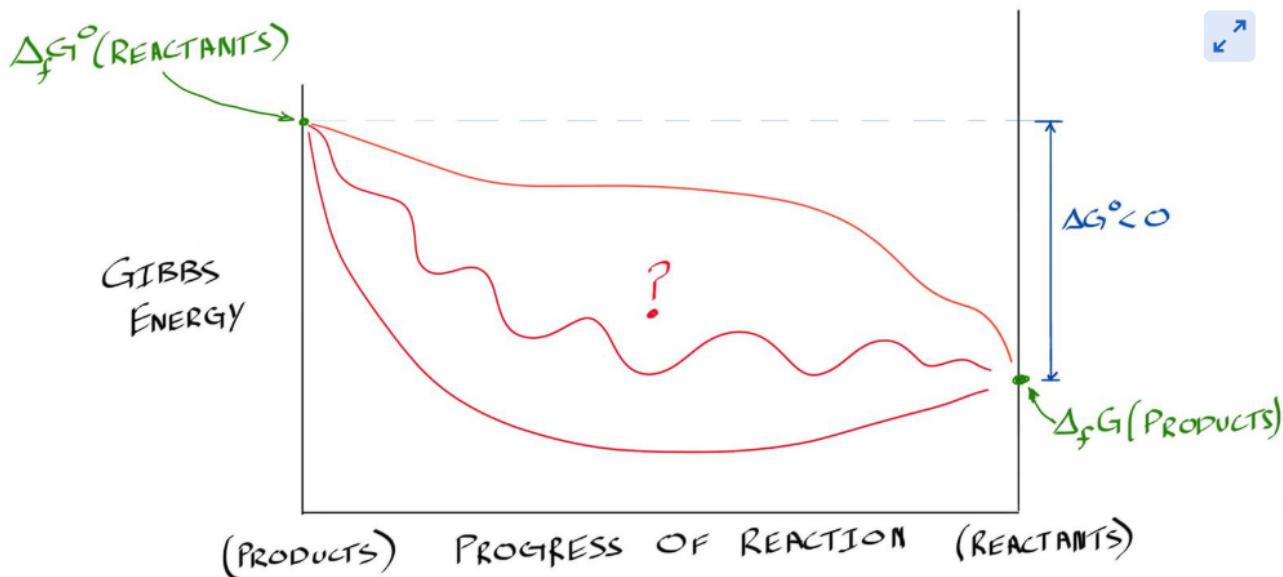


Figure 1. The Gibbs energy of a spontaneous reaction must decrease from products to reactants, but what does it look like in between?

So, what does the Gibbs energy do in between products and reactants? (Hint: it probably doesn't form the shape of a cartoon clam smiling at you - Figure 1 does look a little like that, right? It's not just me? I didn't mean it to look like that when I drew it!)

The Gibbs energy of mixing

Well, something interesting happens when the reaction progresses. There is mixing between reactants and products and this mixing, as you might expect, leads to an increase in the entropy. Since we are speaking in terms of Gibbs energy here, we could equivalently say that the mixing leads to a *decrease* in the *Gibbs energy of mixing*, as shown in Figure 2.

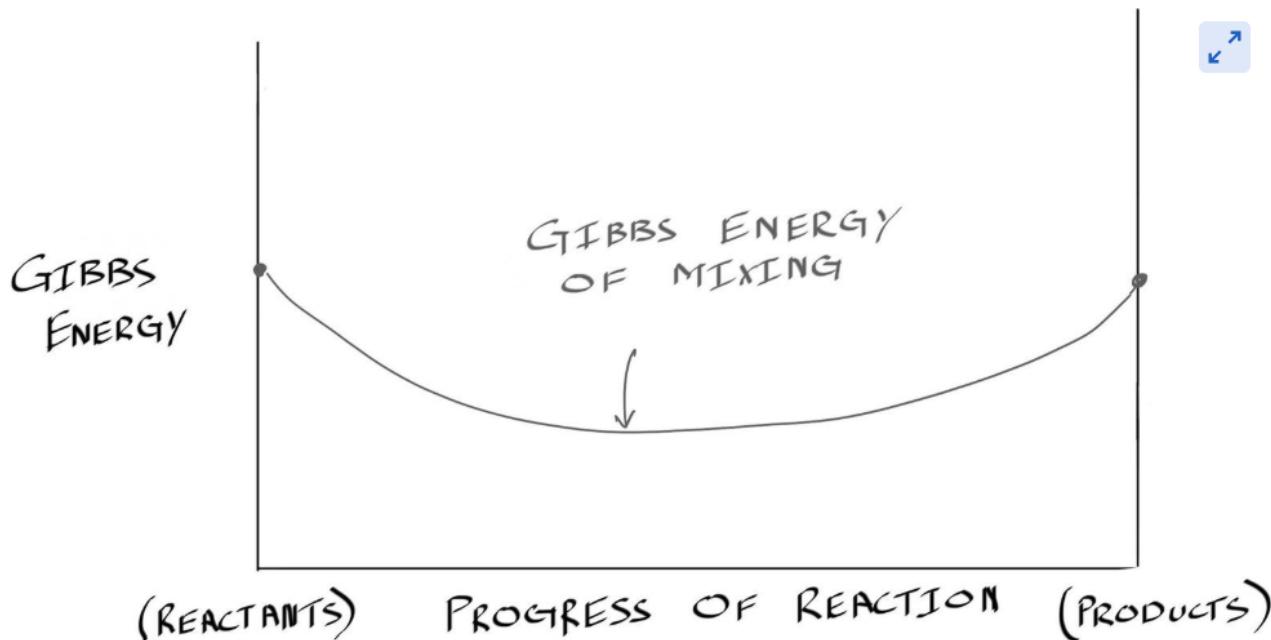
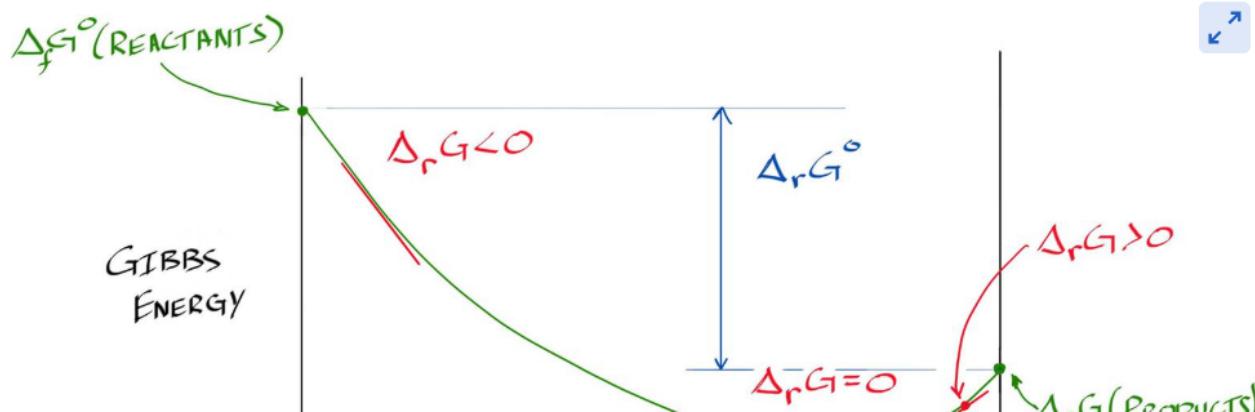


Figure 2. The Gibbs energy of mixing decreases when reactants and products mix and is at a minimum when there is maximum mixing.

The reaction Gibbs energy

So, when we account for the Gibbs energy of mixing, along with the overall Gibbs energy change, we arrive at the so-called, *reaction Gibbs energy*, as shown in Figure 3. We can determine the direction that a reaction will proceed spontaneously from the slope of the reaction Gibbs energy curve, with negative slopes meaning the products are at a lower reaction Gibbs energy and a positive slope meaning that the reactants are at lower reaction Gibbs energy.



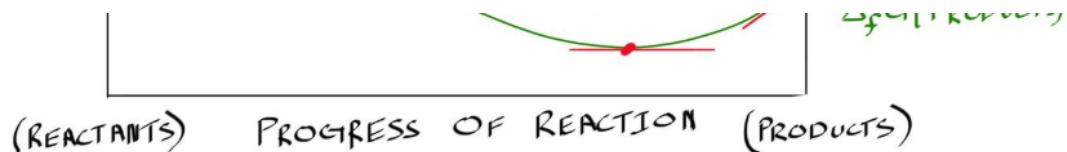


Figure 3. Reaction Gibbs energy.

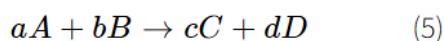
So, of course, it makes sense then that when the slope of the reaction Gibbs energy curve is zero the system is at equilibrium.

The reaction quotient

Now that we understand the reaction Gibbs energy conceptually, we can look at the mathematical relationship for the reaction Gibbs energy $\Delta_r G$

$$\Delta_r G = \Delta G^\circ + RT \ln Q \quad (4)$$

where Q is the so-called reaction quotient. The reaction quotient can be written in a few different ways, depending on whether you want to work with gas partial pressures, gas concentrations, or solution concentrations. In very general terms, if we consider a fun alphabetical reaction like this one (chemists love this stuff as much as I love the (111) plane in FCC!)



which means that we have a moles of species A (species meaning essentially an element, ion, or compound, not *species*, as in human, North Atlantic right whale, Sumatran orangutan, and red-faced spider monkey (although, if you figure out that "reaction" you should wait for your call from the Nobel committee)), b moles of species B and so on. Now we can define the reaction quotient in these same general terms as

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (6)$$

where a_i is the activity of species i and may be either the concentration or the partial pressure of a gas, although its important to note that these will yield different reaction quotients so be sure that you are consistently using one or the other in a problem. Oh, something else, the reaction quotient should be dimensionless, (that is, it has no units), so we do something sneaky and divide either the concentration by 1 M or the pressure by 1 atm and then, hey presto, no units in the activity.

Finally, we can rest (or at least be at equilibrium)

Alright, in Figure 3 we said that when a reaction is at equilibrium the reaction Gibbs energy will be zero, $\Delta_r G = 0$, and the reaction proceeds neither towards products nor towards reactants. My subtitle implies that at equilibrium everything stops, but this is not the case at all. Equilibrium means that the forward and backward reactions occur at the same rate. It's a little like when you decide to hit the brakes after

forward and reverse reactions occur at the same rate. It's a little like you decide to hit the hot tub after a tiring day of skiing and proceed to dunk yourself into the hot tub and then climb out and then dunk yourself again, over and over again. The net effect is that you are neither getting fully out of the hot tub nor getting further into it. Ah, classic chemistry humour. Be sure to watch for this one if you are ever at a chemistry conference. It works with doors and chairs just as well.

The equilibrium constant K

When a reaction is at equilibrium we give a special name to the reaction quotient and we use a new letter to represent it. As the subtitle above suggests, we call it the *equilibrium constant* and use the letter K. If we think carefully about this, we'll see that if the reaction has a negative Gibbs energy change (is spontaneous towards products) this means the numerator of the equilibrium constant will be larger than the denominator and K will be greater than 1. If a reaction favours products $\Delta G^\circ < 0$ and $K > 1$ and vice-versa if a reaction favours reactants then $\Delta G^\circ > 0$ and $K < 1$. And at equilibrium when $\Delta_r G = 0$ we can massage our equation for the reaction Gibbs energy like this

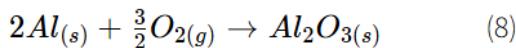
$$\Delta_r G = \Delta G^\circ + RT \ln K$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K \quad (7)$$

An example: Reducing aluminum is hard (or aluminum really likes to oxidize)

Let's put all this fun stuff into action here. I find that a lot of people think that aluminum is great because it doesn't rust. This is partially true, but actually very misleading. You see, aluminum is a highly reactive metal and so it very quickly reacts with oxygen to form an aluminum oxide layer on the surface. Luckily for us, in many of the circumstances where we use aluminum this oxide layer doesn't continue to grow and instead it actually protects the underlying aluminum from further oxidation. We say that it forms a passive oxide layer on the surface. This is also important in refining aluminum and why we don't find big chunks of aluminum metal that we can mine. Let's look at the reaction for the oxidation of aluminum



and the standard reaction Gibbs energy change for this reaction can be calculated from the standard formation Gibbs energies like this:

$$\Delta_r G^\circ = \Delta_f G^\circ(Al_2O_{3(s)}) - 2\Delta_f G^\circ(Al_{(s)}) - \frac{3}{2}\Delta_f G^\circ(O_{2(g)}) \quad (9)$$

we can look up the reaction enthalpy for $Al_2O_{3(s)}$ directly from its formation enthalpy, since solid

aluminum and gas phase oxygen are both in their most stable form at 298.15 K and 1 atm. The formation enthalpy for $Al_2O_{3(s)}$ is

$$\Delta_f H^\circ(Al_2O_{3(s)}) = -1675 \frac{kJ}{mol}$$

Let's say we want to work out the formation Gibbs energy from the table of standard enthalpies and entropies, knowing that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we'll need the standard entropies for $Al_2O_{3(s)}$, $Al_{(s)}$, and $O_{2(g)}$.

$$S^\circ(Al_2O_{3(s)}) = 50.92 \frac{J}{molK}$$

$$S^\circ(Al_{(s)}) = 28.3 \frac{J}{molK}$$

$$S^\circ(O_{2(g)}) = 205.1 \frac{J}{molK}$$

and so considering the stoichiometry in equation 8, the formation entropy for $Al_2O_{3(s)}$ is

$$\Delta_f S^\circ(Al_2O_{3(s)}) = 50.92 - 2(28.3) - \frac{3}{2}(205.1) = -313 \frac{J}{molK}$$

and so the formation Gibbs energy is

$$\begin{aligned} \Delta_f G^\circ(Al_2O_{3(s)}) &= \Delta H^\circ - T\Delta S^\circ \\ &= -1675(10^3) - 298.15(-313) = -1.581(10^6) J \end{aligned}$$

This is useful for us because we can now determine the equilibrium partial pressure of oxygen that would be required to put aluminum in equilibrium with its oxide, using equation 7.

$$\Delta G^\circ = -RT \ln K$$

where $K = \frac{a_{Al_2O_{3(s)}}^{\frac{3}{2}}}{a_{Al_{(s)}}^2 \cdot P_{O_2}^{\frac{3}{2}}}$ and $a_{Al_2O_{3(s)}} = 1$ and $a_{Al_{(s)}} = 1$ since both are condensed phases (liquid or solid) and their concentrations don't change. So, we can now write

$$\Delta G^\circ = -RT \ln \frac{1}{\left(\frac{P_{O_2}^{\frac{3}{2}}}{P_{O_2}^{\frac{3}{2}}}\right)} = RT \ln \left(P_{O_2}^{\frac{3}{2}}\right)$$

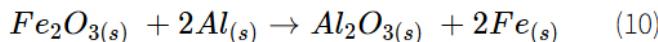
which we can massage to give

$$P_{O_2} = \left[\exp \frac{\Delta G^\circ}{RT} \right]^{\frac{2}{3}} = \left[\exp \frac{-1.581(10^6)}{8.314 \cdot 298.15} \right]^{\frac{2}{3}} = 1.8(10^{-185}) \text{ atm}$$

which is, of course, a tiny partial pressure and at any partial pressure of oxygen above this the reaction will favour $Al_2O_{3(s)}$ and we get a glimpse into why aluminum refining is challenging and energy

will favour **Al₂O₃** and we get a glimpse into why aluminum refining is challenging and energy intensive.

In fact, another way of applying this thermodynamic *desire* for aluminum to oxidize is to use aluminum to reduce another metal oxide, for example in the *thermite reaction* (also known as the *aluminothermic reduction of iron*), we use aluminum to reduce iron oxide



This reaction is extremely exothermic, so much so that it melts the iron that is produced and this reaction can be used to weld iron in locations where it is not practical to carry welding torches.

Splitting up oxidation and reduction

The aluminothermic reduction of iron reaction (Reaction 10) is a nice stepping stone to transition into the business that this chapter is supposed to be about: electrochemistry! You see, as the name implies, iron is being *reduced*. This means that iron is gaining electrons (perhaps you've heard that LEO the lion says, "GER," reminding us that we **Lose Electrons in Oxidation and Gain Electrons in Reduction**). We can write out just the most simple thing that is happening to iron in the reaction



and similarly we can write the simplest thing that is happening to aluminum



Hey, consider this fun little nugget: Al has atomic number 12, so has 12 electrons and electron configuration $1s^2 s^2 2p^6 3s^2 3p^1$ and it loses the three outermost electrons, namely $3s^2 3p^1$ so that it now looks like Ne ($1s^2 s^2 2p^6$) Did you hear that? The pieces falling into place? Okay, perhaps that was already obvious to you, but I still think its neat.

The above reduction and oxidation reactions are an example of what we sometimes call together *redox* (**reduction-oxidation**) reactions and we call the individual reactions half-reactions, as a way of reminding ourselves that they won't proceed on their own. That is, the electrons won't just spontaneously pop off aluminum, or be sitting around the pool halls of River City ^① waiting for Fe^{3+} to come along. You see, the electrons need to come from somewhere and have somewhere to go. They're like good kids that way: they don't loiter.

Enter Luigi Galvani and Alessandro Volta

So, if we wanted to have these redox reactions proceed and perhaps even be able to control them or use them for something productive, we could set them up carefully in a solution and allow the

electrons to move through a wire. This is the basis for a Galvanic cell or Voltaic cell.ⁱ

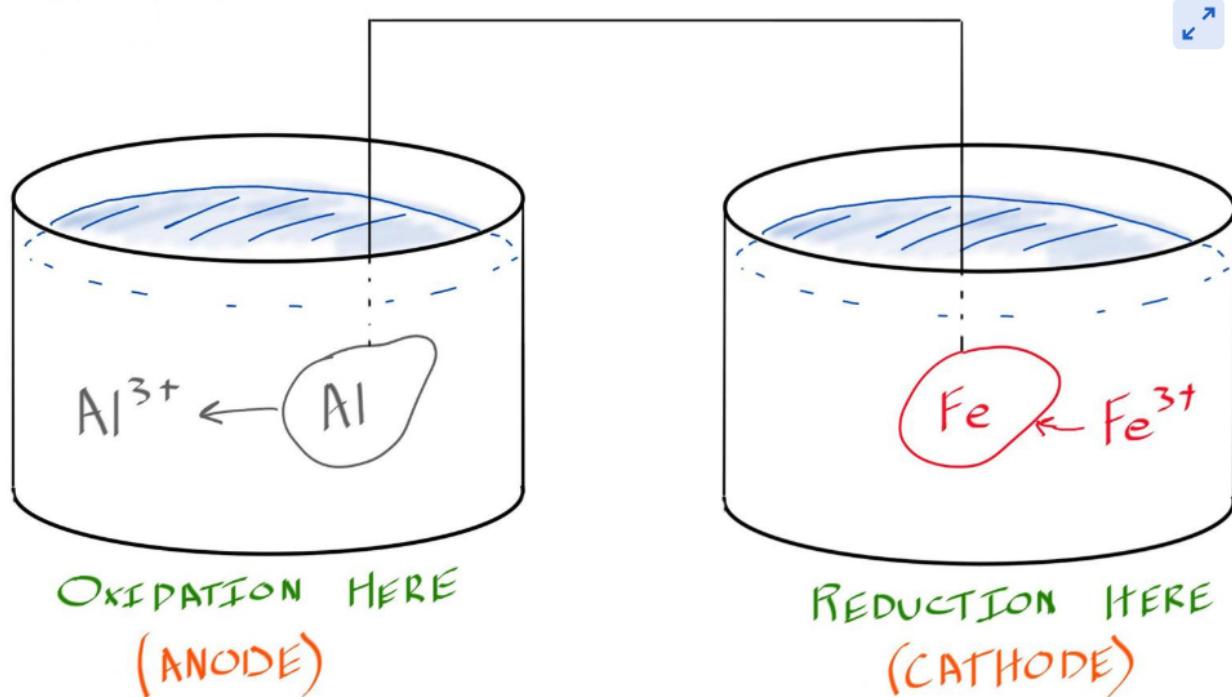
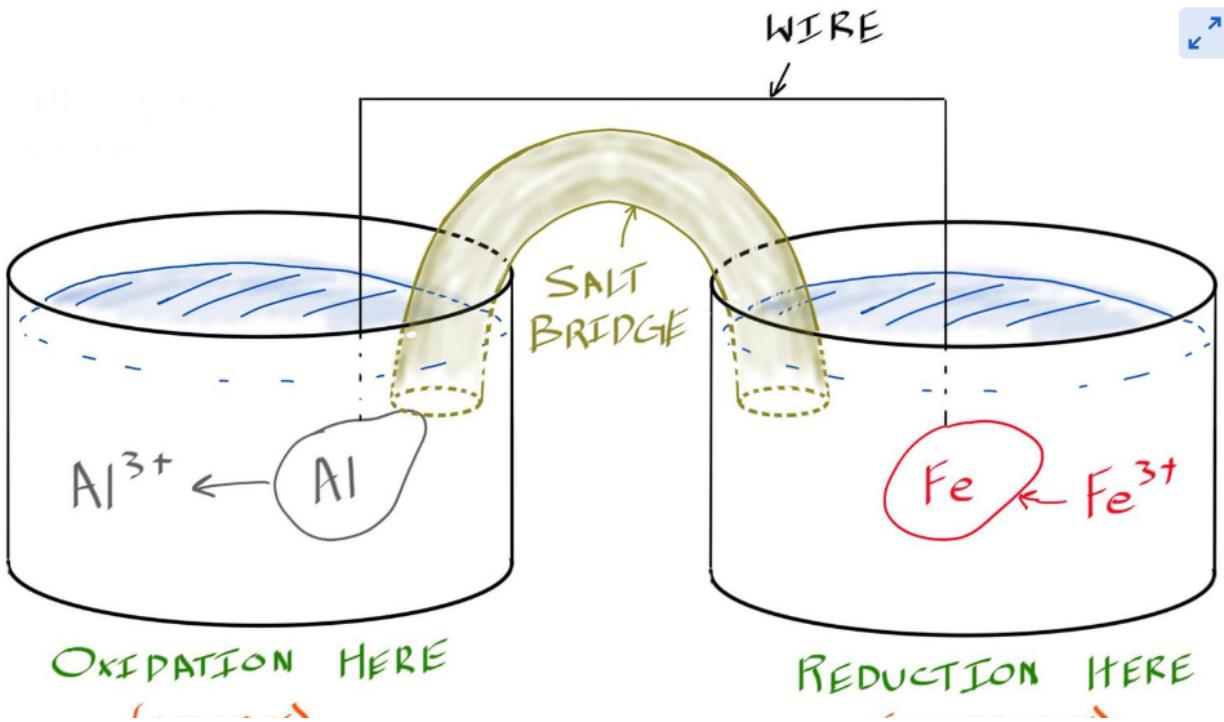


Figure 4. A galvanic cell. Note that there is still no place for the electrons to go really so only a little bit happens. A small amount of aluminum goes into solution as cations, leaving a net negative charge on the anode and a little bit of iron cation leaves the solution and enters the cathode, giving it a net positive charge. This sets up a voltage, or cell potential.

The galvanic cell illustrated in Figure 4 won't do much apart from establishing a voltage difference or *cell potential*. The reason that not too much happens is that there is no place for the ions and electrons to go. To solve this we can add a tube of gelled electrolyte, called a *salt bridge*, as shown in Figure 5.



(ANODE)

(CATHODE)

Figure 5. A galvanic cell, this time with a salt bridge added to maintain charge neutrality and permit the flow of ions and electrons.

Now that we've made the ions and electrons happy, so-to-speak, and they're not all crowded around each electrode we can measure the voltage of the cell and even use the cell to do useful work, or run it in reverse, to recharge a cell, or operate an electroplating operation, say. Now, as you can see in Figure 6, we can measure the voltage of this cell, but what cell voltages, or potentials represent changes, much like we had for enthalpy and Gibbs energy, and we don't concern ourselves with trying to define their absolute values.

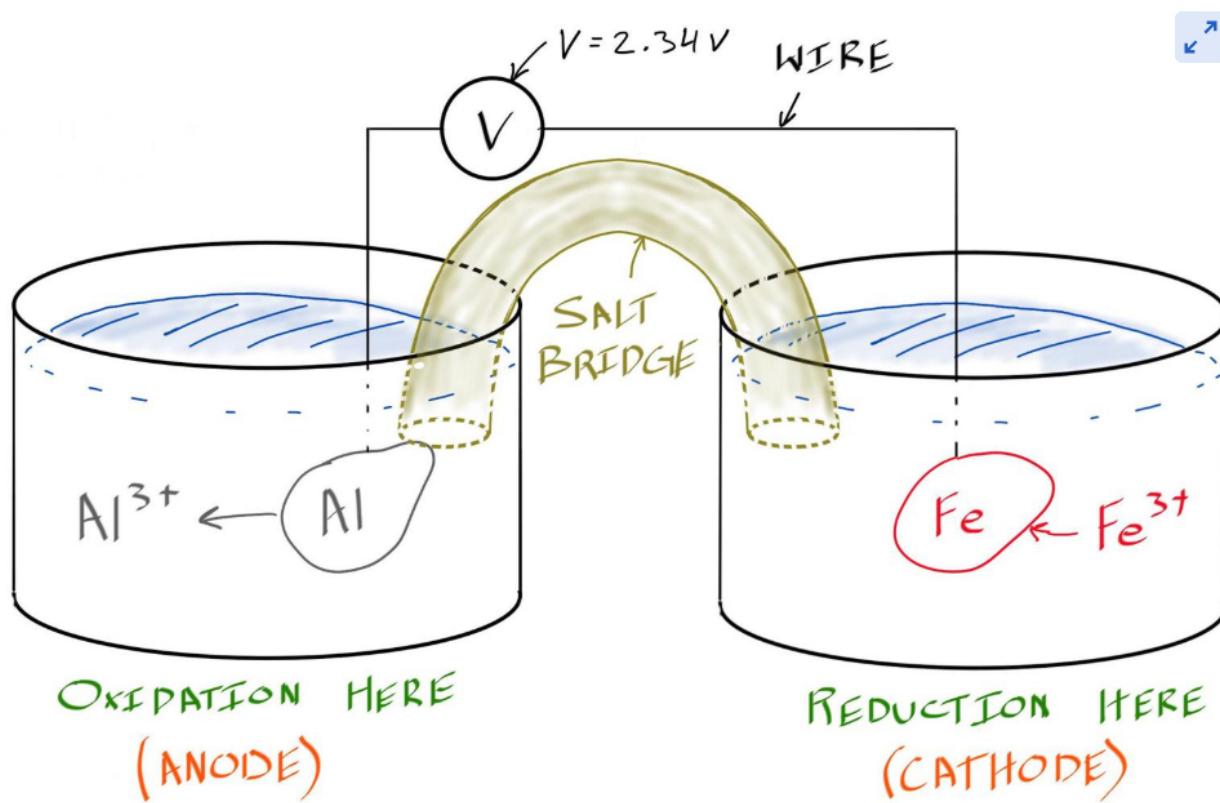
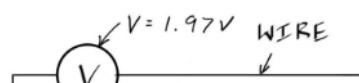


Figure 6. A simple galvanic cell between aluminum and iron, showing the cell voltage

Measuring (and tabulating) cell voltages

Another way to look at this is to imagine that you only knew the distance from your hotel to the fruit market. That would be fine as long as you only ever travelled between your hotel and the fruit market. Later you want to go to the bakery, but you only know the distance from the library to the bakery. You won't be able to estimate the time to walk from your home to the bakery. What you really need is a list of the distances from your hotel to the bakery, the library, the fruit market, and the hardware store (because that's always handy).



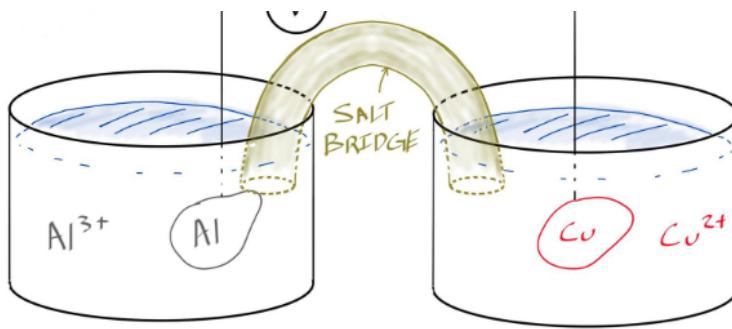


Figure 7. The aluminum copper cell has a voltage of 1.97 V.

Then you could even work out how long it would take to get from the bakery to the hardware store (assuming there was only a single linear route between all these places; well, you get my point here.)

Heading back to our galvanic cells, say the hotel in our analogy was copper, the bakery was aluminum, and the hardware store was iron; individually we'd have the voltage for the Al-Cu cell (Figure 7) and for the Cu-Fe cell (Figure 8) and we could then add them together to get the voltage for the Al-Fe cell (Figure 6).

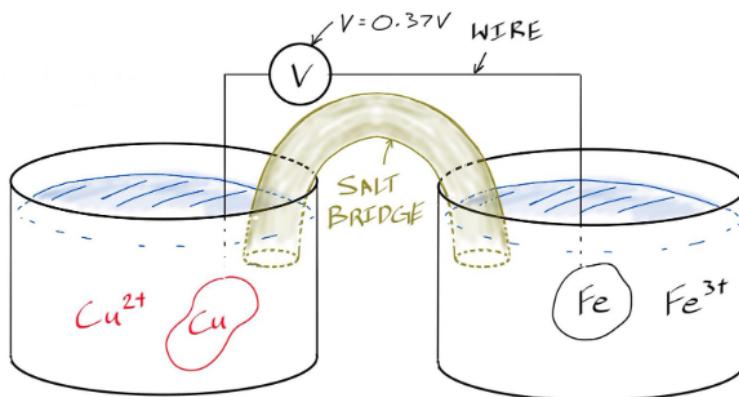


Figure 8. The copper-iron cell has a voltage of 0.37 V.

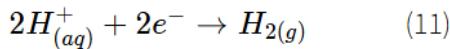
Describing the cells this way, in words, gets a little tedious, and is also somewhat imprecise.

You see, the electrolyte present at each electrode is important, so we have a shorthand for writing cells, like this: **anode|anode electrolyte||cathode electrolyte|cathode**. So, more efficiently this time, we can summarize Figures 6, 7, and 8 like this: **$Al|Al^{3+}||Cu^{2+}|Cu: 1.97\text{ V}$** , **$Cu|Cu^{2+}||Fe^{3+}|Fe: 0.37\text{ V}$** , **$Al|Al^{3+}||Fe^{3+}|Fe: 2.34\text{ V}$** .

The standard hydrogen electrode

Did you notice that $1.97 + 0.37 = 2.34$? So now the question becomes, "is the hotel the best place for our reference location?" If we live in the hotel it makes a lot of sense, but if we live somewhere else then another location would make more sense. In the world of electrochemistry this *reference electrode* is a very important question and if you speak with an electrochemist they will tell you that you can't properly explain this point in anything less than 11 hours of lectures. I'll try my best to

explain it here in a sentence. Actually, I'll just tell you and you'll have to trust me. We use something called the standard hydrogen electrode (SHE)



and we write this cell out in shorthand as $Pt_{(s)}|H_{2(g,1\text{ atm})}|H_{(1M)}^+$. So the SHE is like our standard state for half-cell reactions and just like we tabulated standard enthalpies, we can tabulate standard reduction potentials (the convention is to write them as reduction reactions, and the potential of the reverse, oxidation reaction has the opposite sign). A few common half-cell reactions along with their corresponding standard reduction potentials are shown in Table 1. Note that the reduction potential for the SHE is listed and has a standard reduction potential of 0V and that all other reactions are relative to this.

Reduction Reaction	E° (V)
$Li_{(aq)}^+ + e^- \rightarrow Li_{(s)}$	- 3.045
$Zn_{(aq)}^{2+} + 2e^- \rightarrow Zn_{(s)}$	- 0.763
$Fe_{(aq)}^{2+} + 2e^- \rightarrow Fe_{(s)}$	- 0.44
$2H_{(aq)}^+ + 2e^- \rightarrow H_{2(g)}$	0.000
$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)}$	+ 0.337
$Pt_{(aq)}^{2+} + 2e^- \rightarrow Pt_{(s)}$	+ 1.2

Table 1. Standard reduction potentials for a few half-cell reactions.

Work done by an electrochemical cell

Now that we have a standard to measure cell voltages against (the SHE) and we can therefore determine the standard voltage of any given cell, given the standard reduction potentials, we are actually in a position to determine the work done by a cell. Let's work it out dimensionally first to ensure it makes sense. I'll put the dimensions into square brackets like this [*hamster*].^① Say we knew the number of electrons transferred n [*#electrons*] and the charge on each electron (fundamental charge e) [$\frac{C}{electron}$], and the energy per electron transferred (cell potential E°) [$V = \frac{J}{C}$], we could determine the energy per electron and if we multiplied by Avagadro's number N_A we could get the energy per mol:

$$W = n \cdot e \cdot N_A \cdot (-E^\circ)$$
 (12)

noting that the negative sign on the standard cell potential is due to the sign convention for the polarity of the electrodes.

And, tying things back to our earlier thermodynamics, specifically the Gibbs energy, we know that the

Gibbs energy is the isothermal work done at equilibrium, so

$$\Delta G = W$$

$$\Delta G = -n \cdot e \cdot N_A \cdot (E) \quad (13)$$

and since $e \cdot N_A$ comes up fairly often in this field we could simplify things by assigning it another letter, say F . Okay, that's already been done and its called the Faraday constant $F = 96,485 \frac{J}{V \cdot mol}$, so

$$\Delta G^\circ = -n \cdot F \cdot (E^\circ) \quad (14)$$

And this tells us that half-cells with more positive E° have more negative ΔG and will be reduced more readily, or *are more cathodic*. Similarly, half-cells that have more negative E° are more readily oxidized or *are more anodic*. Referring to Table 1 you'll note that platinum is less *inclined* to oxidize than lithium, for example, or that if iron is put in contact with zinc, it is the zinc that will corrode rather than the iron, since the reduction potential for zinc is more negative than that of iron. This is precisely the fact that is exploited with galvanized steel or with anodic protection of the hull of some boats.



The Nernst equation

Hopefully you recall equation 4 for the reaction Gibbs energy, from the start of this chapter $\Delta_r G = \Delta G^\circ + RT \ln Q$. Now, if substitute equation 13 into this equation and massage it a little we can work out the cell potential at other concentrations, away from equilibrium, and at other temperatures

$$-nFE = -nFE^\circ + RT \ln Q$$

or

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (15)$$

Equation 15 is known as the Nernst equation and one of the things it shows us is that we can apply a voltage to drive a non-spontaneous reaction. This is the basis for aluminum refining, which is very energy intensive and is also where we started this whole journey!

