

## Lecture 17: Electrochemistry

Electrochemistry follows the adventures of the electron



Recall that we first discussed the electron when it came up as a fundamental particle back when discussing quantum mechanics. Also recall that when learning about configurations for atoms and molecules that we obsessed over it. But as we went on to discuss thermodynamics and properties of the bulk, we put it away.

It is back now, demanding its own chapter and perhaps its own consideration in thermodynamic terms. After all, we spent six weeks on the fundamental particle called the proton and it has nothing on the electron from a reactivity perspective. How do we know this? Think about it from a charge density perspective as we compare some particles of different charge and size

Type of particle	$e^{-}$	$H^{+}$	H	$Na^{+}$
mass per particle	$8.3 \times 10^{-27}$ g	$1.6 \times 10^{-24}$ g	$1.6 \times 10^{-24}$ g	$3.7 \times 10^{-23}$ g
mass per mole	1/2000 g/mole	1 g/mole	1 g/mole	23 g/mole
charge per particle	$1.614 \times 10^{-19}$ C	$1.614 \times 10^{-19}$ C	0	$1.614 \times 10^{-19}$ C
charge per mole	$9.6 \times 10^4$ C/mole = 1 F	$9.6 \times 10^4$ C/mole = 1 F	0	$9.6 \times 10^4$ C/mole = 1 F

Note that while the mass of an electron is quite small—2000 times smaller than a proton and 50,000 times smaller than a sodium ion:

It has the same amount of charge which means that its charge density is vastly larger than any other particle.

Seeing as how we have on many occasions we have used charge density to rank reactivity, having stumbled across a particle with 2000 times the charge density of the next guy in line, we should be willing to examine it more carefully.

**Time out for charge:** Everyone understands mass—you step on scales every day to see how much you weigh and are used to buying goods “by the pound or gram.” And that is why we can talk about the mass of a mole of an atom and you just look at the periodic table and rattle off “uranium weighs 238 grams/mole.”

But charge is not so familiar. You are used to the notion of charge in the form of static electricity or getting a shock, but have no real quantitative feel for it. Until now. Very simply:

- The unit for charge is the Coulomb in the same way the unit of mass is grams.

and

- In the same way you can assign a mass to a mole of a compound—like water is 18 grams/mole, you can assign a mole of charge to something. And the best part is that a mole of charge always has exactly the same value:

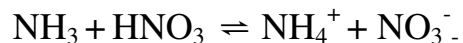
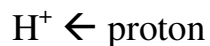
$$1 \text{ mole of charge} = 1 \text{ Faraday} = 9.6 \times 10^4 \text{ C/mole}$$

And this value is the same whether you have a mole of  $e^-$  or a mole of  $H^+$  or a mole of  $Na^+$

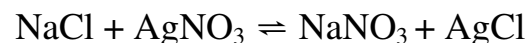
## The chemistry of the electron—oxidation/reduction reactions:

We have just finished a unit on equilibria in which we looked at reactions in which we followed the movement of a proton and reactions in which we followed the movement of cations and anions:

### Acid base reactions



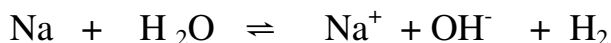
### solubility reactions



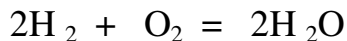
Note that in both cases, the oxidation number does not change: for example, in the acid base reaction, oxidation numbers of H = +1, N = -3 and O = -2 are assigned **for every atom on both sides of the reaction.**

In contrast, in electrochemistry we focus on reactions in which the formal oxidation number assigned to an atoms in a reaction changes. In every oxidation reduction reaction, at least one atom is oxidized (increases in oxidation number) while at least one atom is reduced (decreases in oxidation number.) For example,

0      +1 -2      +1      -2 +1      0  $\leftarrow$  note the Na atom oxidation number increases while the H atom oxidation number decreases



0      0      +1 -2       $\leftarrow$  note the H atom oxidation number increases while the O atom oxidation number decreases

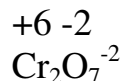


What we do in electrochemistry is follow the flow of electrons along this chemical reaction path.

**Time out—if you can't assign oxidation numbers as easily as you breathe, you will fail the electrochemistry material. So here is a refresher brought to you by your friendly neighborhood chemistry professor:**

### Assigning oxidation numbers

What do oxidation numbers tell us? Very simply, oxidation numbers tell us where the electron density is in a compound—kind of like all that work we did with quantum mechanics at the beginning of 301, but with none of the huge equations and complicated rules. So in the ion dichromate



the electrons are more densely packed around the O though than Cr and you can tell this because the more negative the oxidation number, the greater the electron density. Note surprisingly this result is consistent with everything you learned about oxygen loving electrons and metals not wanting them.

So what are the rules for oxidation number: rather than try to memorize all the possible combinations, learn the following hierarchy of rules:

- Rule 0: Free elements have an oxidation number of 0. Example: Oxygen in  $\text{O}_2$  has 0 oxidation number
- Rule 1: Assigning oxidation numbers to the groups, from the left. the common formal charge on an element increases, +1, +2, +3.... From the right, skipping the noble gases, the common formal charge on an element increases, -1, -2,-3. So alkali metals are +1. Halogens are -1, etc.

Complications involving hydrides, H, and oxides, O, with other elements in compounds:

- Rule 2: Alkali metals are always +1 except for rule 0. Example Na in NaO, is +1.
- Rule 3: Hydrogen is always +1 except for rules 0 and 2. Example, H is -1 in NaH but +1 in  $\text{H}_2\text{O}$ .
- Rule 4: O is always -2 except for rules 0, 2, and 3. Example: O is -0.5 in  $\text{NaO}_2$ , but -2 in  $\text{H}_2\text{O}$ .
- Rule 5: In every redox problem you do, assign the oxidation numbers in order using rules 0- 4. There will usually only be one element left to assign by difference. Example, what is the oxidation number of P in  $\text{K}_2\text{HPO}_4$ ?

**Example of setting up problems to determine oxidation numbers for unknowns.**

What is the oxidation number for P in  $\text{K}_2\text{HPO}_4$ ?

charge on the molecule = 0 = (ox. # of K)(# of K atoms) + (ox. # of H)(# of H atoms) + (ox. # of P)(# of P atoms) + (ox. # of O)(# of O atoms)

Using rules 0 – 4 above, we can assume K is +1, H is +1 and O is -2, so sticking these values and the number of atoms in the equation above

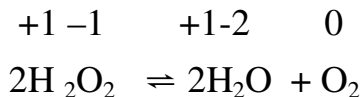
charge on the molecule = 0 = (+1)(2) + (+1)(1) + (?)(1) + (-2)(4)      so ? = ox # P = +5

You can set up this kind of equation while you are still learning oxidation numbers, but by the exam, this should be something you do in your head pretty easily.

**An Introduction to Oxidation Reduction Reactions and How to Balance Them.** Most of the cool demonstrations I show in class are redox reactions. This is either because there is a lot of energy associated with the reaction (remember the charge density of an electron) or because different oxidation states of metals have very different colors. Here are some of my favorites from class:

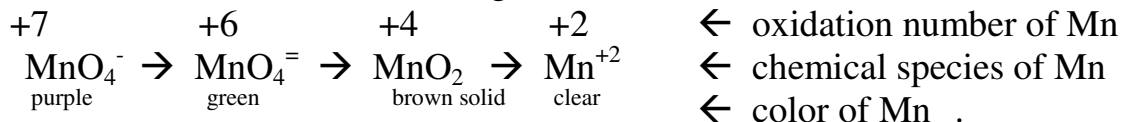
Examples:

1. I pour hydrogen peroxide in my ear to get rid of ear wax is a redox reaction:

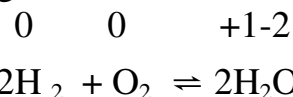


Note that the O in  $\text{H}_2\text{O}_2$  is oxidized in  $\text{O}_2$  and the O in  $\text{H}_2\text{O}_2$  is also reduced in  $\text{H}_2\text{O}$ .

2. Transition metals exhibit neat color changes and are redox reactions

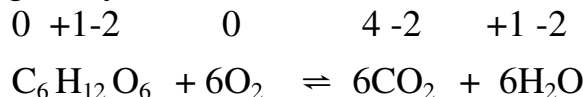


3. Exploding  $\text{H}_2$  balloons occur almost daily in class and are redox reactions



H in  $\text{H}_2$  is oxidized by 1 e and O in  $\text{O}_2$  is reduced by 2 e

4. Burning gummy bears (and all combustion reactions) are redox reactions



C in  $\text{C}_6\text{H}_{12}\text{O}_6$  is oxidized by 4 e and O in  $\text{O}_2$  is reduced by 2 e

5. Displacement reactions in which I toss sodium metal in water and head for cover are redox reactions



Na is oxidized by 1 e and H in  $\text{H}_2\text{O}$  is reduced by 1 e

## How to balance chemical reactions yourself: the quick and dirty and best way to do it!!

Did you notice that those chemical reactions above were all balanced? By that I mean that the number of atoms and the amount of charge was the same on both sides of the chemical equation and one would expect if mass and charge are to be conserved.

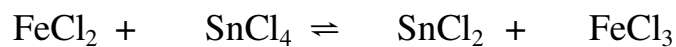
So how do you balance a reaction? Often it is by inspection—with simple acid base and solubility reactions, a little common sense is all you need.

Redox reactions are a different beast. They are hard to balance because really substantial changes in the oxidation number occurring in two paired half reactions can make for some large coefficients. And if the reaction is happening in an acid or base solution, the problem is further complicated. So I am going to show you a nice step by step method often called the change of oxidation number. It is to be preferred over the hideously complicated half reaction method that takes forever and requires a lot of redundant work. But hey, use a method that is long and complicated. I don't really care (though your exam grade might.)

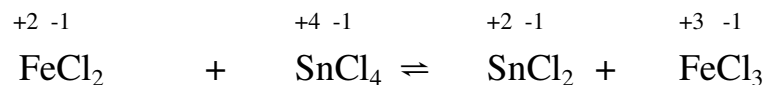
The change in oxidation number method:

1. Assign oxidation numbers to each atom in the reaction
2. Determine the number of e's for each reduction and oxidation half reaction.
3. Determine the least common multiples for the two half reactions and use these numbers to balance the reaction coefficients—at this point the number of electrons oxidized and reduced should be equal in the reaction.
4. If in acid, add one H<sub>2</sub>O to the opposite side for each deficient O. Add 2H<sup>+</sup> to the excess O side for each added H<sub>2</sub>O.
5. If in base, add 2 OH<sup>-</sup> to the opposite side for each deficient O. Add one H<sub>2</sub>O to the excess O side for every 2 OH<sup>-</sup> added

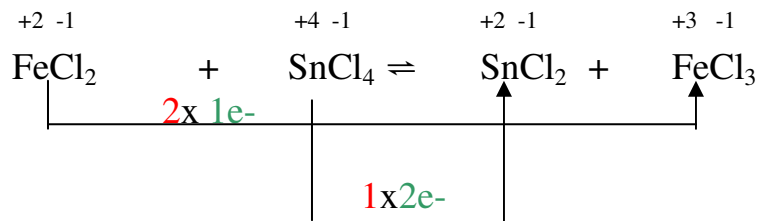
### Example 1: balancing with no acid or base



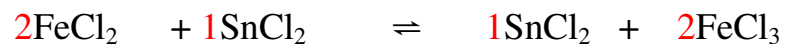
unbalanced reaction



step 1: assign oxidation numbers



step 2: determine the electrons per atom oxidized or reduced (in green)

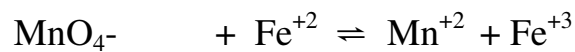


step 3: the least common multiples (1 and 2) are placed as coefficients in the reaction (in red)

The reaction is now balanced. You can check by noting that the number of atoms on each side is the same and the overall charge on each side is 0.



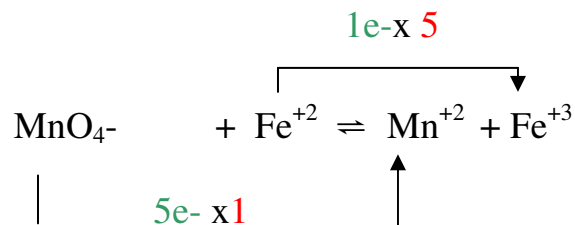
## Example 2: balancing redox reactions in acid



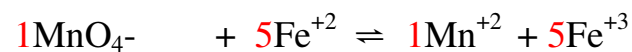
unbalanced reaction



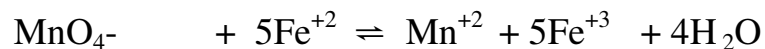
step 1: assign oxidation numbers



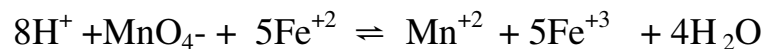
step 2: determine the electrons per atom oxidized or reduced (in green)



step 3: the least common multiples (5 and 1) are placed as coefficients in the reaction (in red)



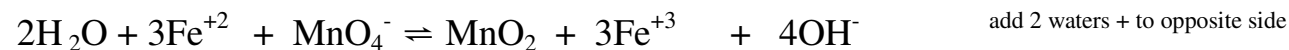
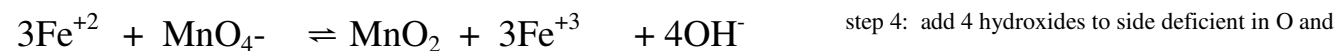
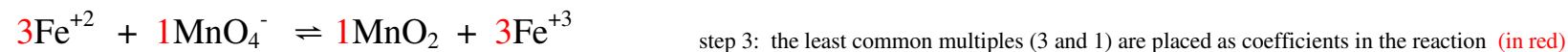
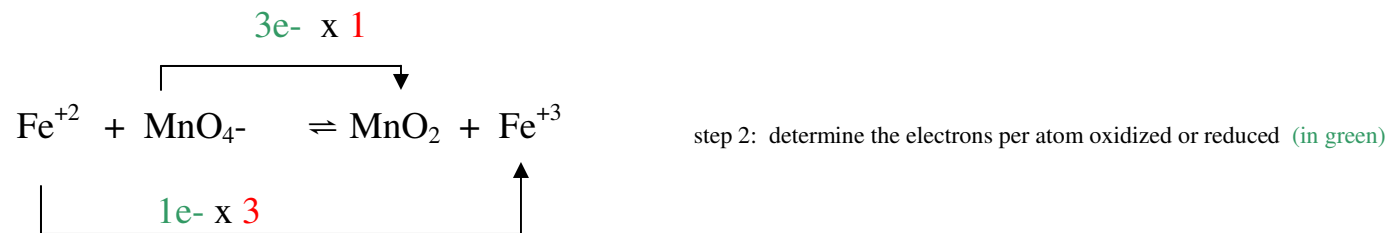
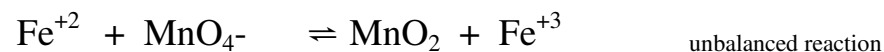
step 4: add 4 waters to side deficient in O and



and add 8H<sup>+</sup> to opposite side

The reaction is balanced. You can check by noting that the number of atoms on each side is the same and the overall charge on each side is +17.

### Example 3: balancing redox reactions in base



The reaction is balanced. You can check by noting that the number of atoms on each side is the same and the overall charge on each side is +5.

## The important place you find these redox reactions: batteries:

As we finish up redox reactions, note that the ones we are interested in are those that make useful things like batteries. In fact, a battery is simply a couple of redox half reactions that can be put together so that  $E$  is positive and some work can be done. So as you consider the electrochemical cell conventions below, understand that they are useful in helping to describe the following kinds of famous batteries:

### **Famous modern batteries use a variety of chemicals to power their reactions. Typical battery chemistries include:**

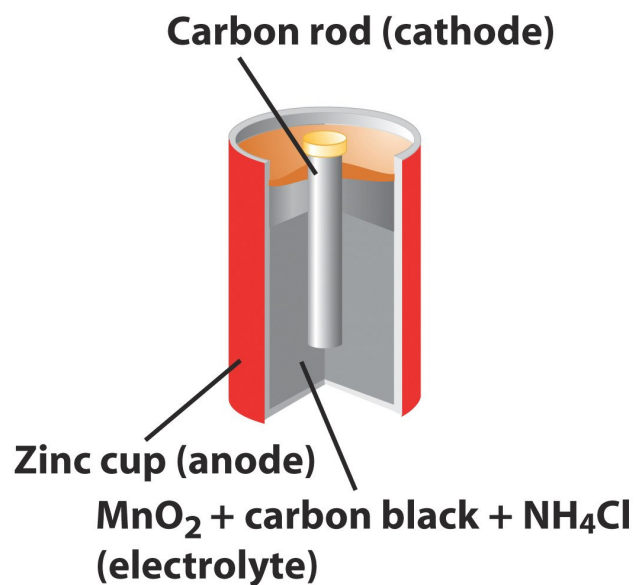
- Zinc-carbon battery - Also known as a standard carbon battery. Zinc-carbon chemistry is used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them that serves as the electrolyte.
- Alkaline battery - Used in common Duracell and Energizer batteries. The electrodes are zinc and manganese-oxide, with an alkaline electrolyte.
- Lithium photo battery - Lithium, lithium-iodide and lead-iodide, used in cameras because of its ability to supply power surges.
- Lead-acid battery - Used in automobiles. The electrodes are made of lead and lead-oxide with a strong acidic electrolyte. Rechargeable.
- Nickel-cadmium battery - Uses nickel-hydroxide and cadmium electrodes, with potassium-hydroxide as the electrolyte. Rechargeable.
- Nickel-metal hydride battery - Rapidly replacing nickel-cadmium because it does not suffer from memory effect. Rechargeable.
- Lithium-ion battery - Very good power-to-weight ratio, often found in high-end laptop computers and cell phones. Rechargeable.
- Zinc-air battery - Lightweight, rechargeable.
- Zinc-mercury oxide battery - Often used in hearing-aid batteries.
- Silver-zinc battery - Used in aeronautical applications because the power-to-weight ratio is good.
- Metal Chloride battery - Used in electric vehicles.

We will have a separate lecture on famous batteries to end our presentation on electrochemistry, but for now, sit back and offer your thanks to the chemists and engineers who have made your life a walk in the park (with a dozen batteries on your person.)

## Electrochemical cell convention.

Regardless of how we draw the picture of an electrochemical cell:

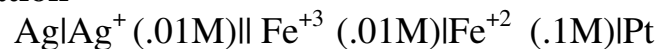
As a battery



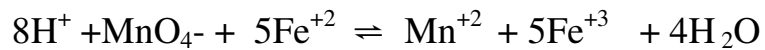
As a couple of isolated beakers



As cell notation



Or as a chemical reaction



Electrochemical cells consist of the same simple parts—a couple of half reactions and a way to isolate the systems to allow current to flow across a voltage drop. When you think about it, the only difference between the hydrogen balloon that I explode in class, and the hydrogen car of the future, is that someone has done a good job of packaging the reaction so that you can control the work done (the electrons that move) by how much you put your pedal to the metal.

So what are the conventions used in describing the parts of an electrochemical cell. For this course, you will need to be able to distinguish:

- The magnitude and sign of the electrochemical cell potential (in other words, whether the cell has  $E(+)$  or  $E(-)$ )
- Where oxidation and reduction occur
- Electrode name (cathode and anode)
- Electrode sign (+ and -)
- Electron flow direction

To begin assigning cell convention and to perform any kind of electrochemical cell calculation, you have to know whether you have a cell that is spontaneous or a cell that is non-spontaneous (this brings back memories of thermo, which is quite appropriate as we will see shortly).

If an electrochemical cell is spontaneous, we can say the following about it and mean the same thing:

$E = (+)$  for a spontaneous reaction and  $\Delta G$  is  $-$  and  $K > 1$

These cells are called battery, voltaic, galvanic

If an electrochemical cell is non-spontaneous, we can say the following about it and mean the same thing:

$E = (-)$  for a non-spontaneous reaction so  $\Delta G$  is  $+$  and  $K < 1$

These cells are called electrolytic or electrolysis cells

All cells do share common features:

- Two  $\frac{1}{2}$  cells are involved, one oxidation and one reduction
- Electron flow through the external wire to the cathode in both cells
- Oxidation is at the anode and reduction is at cathode in both cells

The only distinction between the two kinds of cells is the sign convention:

- In battery a cathode  $+$ , anode  $-$
- In electrolysis: cathode  $-$ , anode  $+$

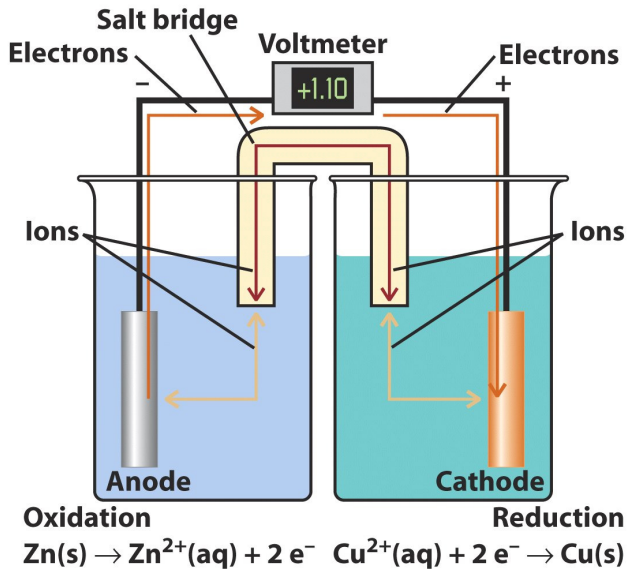
(When I am in WalMart I always remember that the  $+$  on the battery I see is the cathode and everything follows from that)

So let's put these ideas for cell convention in a table and memorize it for some easy points on tests.

electrochemical cell type	reaction type	$\Delta G$	$E$	reduction	oxidation	direction of e flow	sign at cathode	sign at anode
<b>electrolysis</b>	non-spontaneous	$+$	$-$	cathode	anode	e- flow to cathode	$-$	$+$
<b>galvanic (battery)</b>	spontaneous	$-$	$+$	cathode	anode	e- flow to cathode	$+$	$-$

## Example: Identifying Cell Conventions.

So let's apply this set of conventions to the nice copper-zinc battery below. Create a list of all the things you can say about this picture:



Things you can say about the picture of the cell:

- It is a battery because  $E$  is positive (which means the reaction is spontaneous)
- The zinc is oxidized at the anode which is written as the leftmost electrode
- The copper is plated onto the cathodic electrode
- The Sign of the anode is  $-$  and the sign of the cathode is  $+$
- The electrons are flowing through the external circuit to the cathode
- A salt bridge is being used to complete the circuit
- The potential difference is a large one (1.1V) which suggests this might be a good battery—if only we could get the voltage up to 1.5V (wait till next lecture.)

**A brief aside: Electrochemical Shorthand for lazy people like your professor (and all other chemists)**

No one likes to draw cells. So they use electrochemical shorthand and substitute the following symbols and convention to represent the pretty beakers.

$\parallel \leftarrow$  saltbridge

$| \leftarrow$  phase change

$\text{Cu}|\text{Cu}^{+2} \leftarrow$  Half Cell

Also, by convention, the anode is always written first on the left side

Put all this together and written succinctly below is a zinc-copper battery

$\text{Zn}|\text{Zn}^{+2} \parallel \text{Cu}^{+2}|\text{Cu} \leftarrow$  shorthand for battery we just drew.

We can even add concentrations

$\text{Ag}|\text{Ag}^+ (.01\text{M}) \parallel \text{Fe}^{+3} (.01\text{M})|\text{Fe}^{+2} (.1\text{M})|\text{Pt}$

Is a battery in which oxidation takes place at the silver electrode, reduction take place on a piece of platinum wire for  $\text{Fe}^{+3}$ , and the starting concentrations are as written.



## Let's get Quantitative with Electrochemistry.

Electrochemistry is just another way of describing thermodynamics. The kinds of things we found useful in thermodynamics, like understanding whether a reaction happens, or the extent of the reaction, can be determined with electrochemistry. Proof of this statement comes from comparing the simple relationship between  $K$  from equilibria,  $\Delta G$  from thermodynamics and now,  $E$  for electrochemistry in the equations below

$$-RT \ln K = \Delta G = -nFE$$

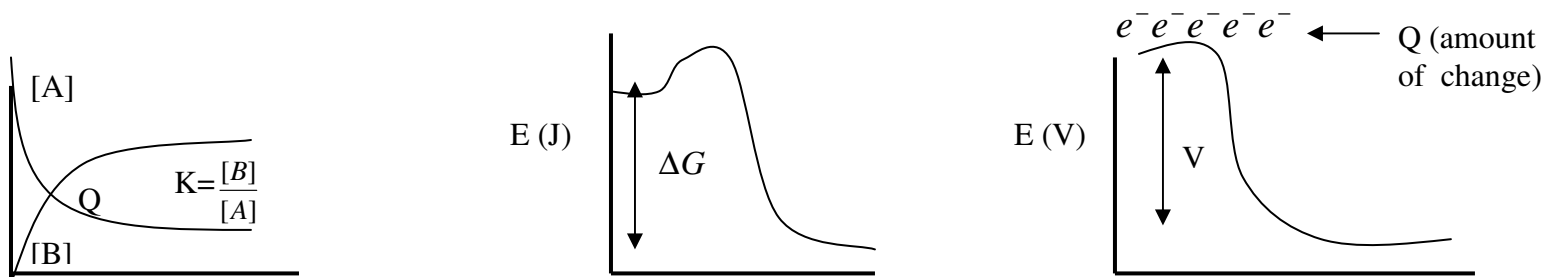
Note that the units of each equation are a measure of energy change in a chemical reaction. It is kind of neat to see all the ways that we have defined energy this spring

gases	=	gases	=	work	=	heat	=	electrochemistry
$P\Delta V$	=	$\Delta nRT$	=	$w$	=	$\Delta H$	=	$qE$
units of J		units of J		units of J		units of J		units of J

and realize that it is just the way we account for the energy change that is different:

- In thermodynamics we keep track of energy as measured in Joules
- In equilibria we keep track of the ratio of concentrations
- In electrochemistry we keep track of the electrochemical potential for a population of electrons

The three graphs below provide another way to view the similarity between  $K$ ,  $\Delta G$  and  $E$

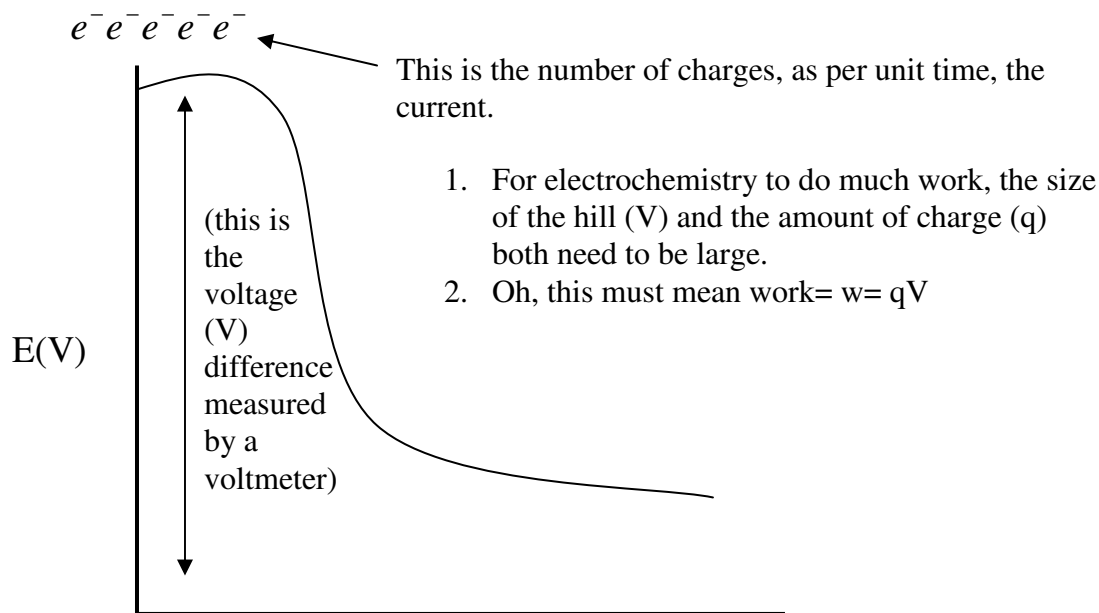


**Deep though number 1 on why you should love electrochemistry:** Note that these simple relationships allow us to convert from thermodynamics in one form to another. For example, if you have a value of  $\Delta G$  from a table of thermodynamic constants you can calculate  $K$ . Or if you have a voltmeter that measures  $V$  from a cell reaction, you can obtain  $\Delta G$  values to put in a table.

And unlike thermo or equilibria for which you have to use complicated devices like spectrometers or bomb calorimeters to find values of  $K$  or  $\Delta G$ , all you need to find electrochemical potentials,  $E(V)$ , is a voltmeter you can buy at Radio Shack for \$10!!

### A comment on the electrochemistry plot above and why it is so profoundly important conceptually

Everyone gets energy and how it describes extent of reaction. Everyone gets concentration and how it describes extent of reaction. Few intuitively get electrochemistry ( $qE$ ) and why it describes the extent of reaction. SO spend some time looking at this plot below and appreciate that it is the combination of the amount of electrons, and the potential hill they fall down, that define work. Think of it this way, some people say that it is the current that kills, and others say that it is the voltage that kills. Actually it is both. The amount of  $e^-$  determines the current per unit time, and must obviously be larger to give someone a shock. At the same time, the size of the hill that must be traveled down matters as well. Hence the work that is done in a chemical system is equal to the produce of  $q$  and  $E$ .



## Calculating Cell Potential: Table of Standard Reduction Potentials and the Standard Hydrogen Electrode

You have begun to see examples of half cell reactions being put together to make cell potentials. Above we saw a cell potential of 1.1V for zinc and copper. Could we create a table of all the possible electrochemical cells?

Sure but we would have millions and millions of cell reactions. Is there a simpler way to do this? What about using a standard to which all half cell reactions are compared?

For example, just for kicks let's choose a cell reaction like

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  and decide to give it a reference voltage of 0V. Let's even call it a **Standard Hydrogen Electrode (SHE)**. We can even choose a set of standard conditions, like a standard temperature (298K) and concentrations (1M or 1atm.)

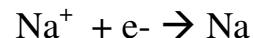
Now, let's remember from thermodynamics that Hess said we didn't have to care about the path that a reaction took, it was only how things started and ended that mattered. This means that if every half cell is referenced to the standard hydrogen electrode we can put them in a single table and directly compare them to each other after subtracting out the SHE potential (which is 0V, what a good idea for a voltage to subtract.)

Presented below is the Standard Reduction Potential Table. Note that by convention, all the half reactions are written as reductions. Also note that all are compared to the SHE and there is a voltage range of from -3V to +3V.

We can decide to put these half cells together then to find the voltages for a cell potential. The equation we will use is

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \text{or} \quad E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}}$$

Example: What is the standard cell potential for a battery formed by the following half reactions:



Note that the half reactions are +1.69V and -2.71V respectively. And if we put them together to form a battery (a positive E value), then the Au half reaction must be the cathode and the sodium half reaction the anode:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 1.69 - (-2.71) = 4.4\text{V} \text{ which is a pretty hefty battery.}$$

**TABLE 12.1** Standard Potentials at 25°C\*

Species	Reduction half-reaction	$E^\circ$ (V)
<b>Oxidized form is strongly oxidizing</b>		
$F_2/F^-$	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	+2.87
$Au^+/Au$	$Au^+(aq) + e^- \longrightarrow Au(s)$	+1.69
$Ce^{4+}/Ce^{3+}$	$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-, H^+/Mn^{2+}, H_2O$	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	+1.51
$Cl_2/Cl^-$	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}, H^+/Cr^{3+}, H_2O$	$Cr_2O_7^{2-} + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	+1.33
$O_2, H^+/H_2O$	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	+1.23; +0.82 at pH = 7
$Br_2/Br^-$	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	+1.09
$NO_3^-, H^+/NO, H_2O$	$NO_3^-(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(l)$	+0.96
$Ag^+/Ag$	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}/Fe^{2+}$	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$I_2/I^-$	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	+0.54
$O_2, H_2O/OH^-$	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	+0.40; +0.82 at pH = 7
$Cu^{2+}/Cu$	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag, Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$H^+/H_2$	$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0, by definition
$Fe^{3+}/Fe$	$Fe^{3+}(aq) + 3 e^- \longrightarrow Fe(s)$	-0.04
$O_2, H_2O/HO_2^-, OH^-$	$O_2(g) + H_2O(l) + 2 e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	-0.08
$Pb^{2+}/Pb$	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13
$Sn^{2+}/Sn$	$Sn^{2+}(aq) + 2 e^- \longrightarrow Sn(s)$	-0.14
$Fe^{2+}/Fe$	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.44
$Zn^{2+}/Zn$	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76
$H_2O/H_2, OH^-$	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83; -0.42 at pH = 7
$Al^{3+}/Al$	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66
$Mg^{2+}/Mg$	$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.36
$Na^+/Na$	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$K^+/K$	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
$Li^+/Li$	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
<b>Reduced form is strongly reducing</b>		

\*For a more extensive table, see Appendix 2B.

## A final deep thought to tie Electrochemistry to Equilibria: Strong oxidizing and reducing agents

Electrochemistry is thermodynamics and equilibria is thermodynamics so I bet the ideas we develop for electrochemistry look like the ideas for acid and bases. For example, remember how we ranked acid and base strength from the  $K_a$  and  $K_b$ . Also remember the simple relationship between  $K_a$  and  $K_b$  using  $K_w$ .

Acid strength increased as  $K_a$  increased. Basic strength increased when  $K_b$  increased. So in the chart below:  $\text{HSO}_4^-$  is the strongest acid and  $\text{NH}_4^+$  is the weakest acid.  $\text{NH}_3$  is the strongest base and  $\text{SO}_4^{2-}$  is the weakest base.

### Acid/Base Strength

	$K_a$	Dissociation reactio	$K_b$	
Strongest acid	$10^{-2}$	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$10^{-12}$	← Weakest base
	$10^{-5}$	$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{COOH}^-$	$10^{-9}$	
Weakest acid	$10^{-9}$	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	$10^{-5}$	← Strongest base

**Oxidation/Reduction Strength.** We can create similar rankings of oxidation and reduction strength using the half cell reactions. The question now, is, what is most easily reduced or what is most easily oxidized? The answer. The easiest is always the most positive value in the same way that acids and bases are strongest (dissociate easiest) with the largest K values.

Note other similarities in the table below. There is an  $E_{\text{ox}}$  value that is related to  $E_{\text{red}}$  in this case by an opposite sign. Also note that the  $E_{\text{ox}}$  reaction is for the reverse reaction that is not actually written.

In this table, the strong reactants are the most positive ones.  $\text{Cu}^{++}$  is the strongest oxidizing agent because it is most easily reduced. Zn is the strongest reducing agent because it is most easily oxidized.

	$E_{\text{red}}$	$\frac{1}{2}$ Reaction, reduction	$E_{\text{ox}}$	
Weakest oxidizing agent $\rightarrow$ (hardest to reduce)	-0.7	$\text{Zn}^{++} + 2\text{e}^- \rightleftharpoons \text{Zn}$	+0.7	$\leftarrow$ Strongest reducing agent (easiest to oxidize)
	0	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0	
Strongest oxidizing agent $\rightarrow$ (easiest to reduce)	+0.3	$\text{Cu}^{++} + 2\text{e}^- \rightleftharpoons \text{Cu}$	-0.3	$\leftarrow$ Weakest reducing agent (hardest to oxidize)

Example: What are the strongest and weakest oxidizing and reducing agents in the large table of reduction potentials?

Answer: Just as with the smaller table above, look to the diagonal corners. The most positive value is the strongest oxidizing agent,  $\text{F}_2$ . The most positive reducing agent (most easy to oxidize) is for the most negative reaction and its reverse reaction that is not written: Li.