

Chapter 21: ELECTROCHEMISTRY

TYING IT ALL TOGETHER

$$-RT \ln K = \Delta G = -nFE^{\circ}$$

$$\text{CH 17-20} = \text{CH15} = \text{CH 21}$$

Important errata to fix.

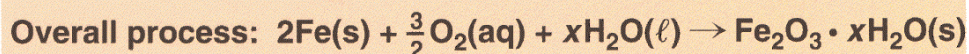
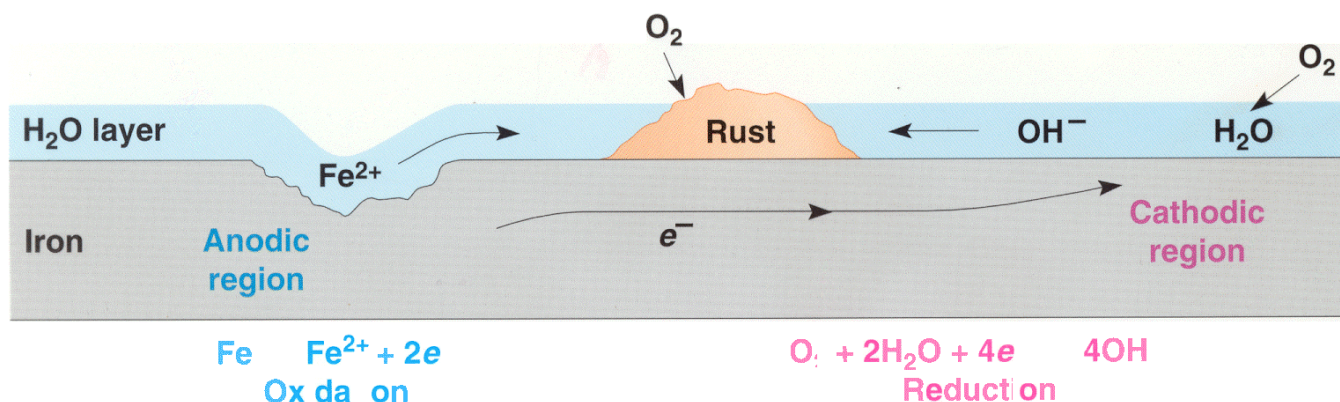
$F = 9.649 \times 10^4$ C/mole in problem on current measurement.

Beginning of section on anodes and cathodes should read: “Oh, and by convention, in a galvanic cell the positive terminal is the CATHODE and the negative terminal is the ANODE”

As we move into our final section of the course, we tackle electrochemistry which is our first real example of modern analytical chemistry. By that we mean that plenty of scientists do electrochemistry today because it is often the best way to solve certain problems in chemical analysis like understanding corrosion (rust).

Whitten/Davis/Peck, General Chemistry, 6/e

Figure 2 2



Electrochemistry is everywhere.

Electrochemistry is also important to technological advances in society because it has everything to do with creating effective forms of solar heating, making electric cars work and generally doing anything useful that involves energy storage. So the next time the rechargeable battery on your lap top computer or your camcorder or your boom box reaches equilibrium (dies), stop to think about how extraordinary the electrochemistry was that made such a battery in the first place.

Electrochemistry is physical measure
of electron movement in chemical reactions.

In looking for a context for understanding electrochemistry, recognize that all of chemistry centers around the making and breaking of chemical bonds. Chemical bonds are formed by a redistribution of electron density around nuclei. Electrochemistry has as its foundation the well-controlled delivery or measure of a source of electrons; i.e., the number of electrons delivered or produced and the work it takes to move the electrons is well known. Note that there will be many parallels between electrochemistry and acid/base chemistry. The primary distinction is the difference in currency, we now care about electrons rather than protons, but we usually ask the same questions.

acid/base

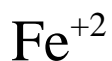
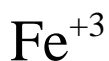


electrochemistry



Ten things to know before working electrochemistry problems:

1. Oxidation-Reduction Reactions. Every electrochemical reaction must involve a chemical system in which at least one species is being oxidized and one species is being reduced. For example



oxidizing agent reducing agent

reduction product oxidation product

In this case, as noted, there is an oxidizing agent that accepts electrons to form a reduction product (the $\text{Fe}^{+++}/\text{Fe}^{++}$ couple here) and a reducing agent that donates electrons to yield an oxidation product (the $\text{Cu}^{+}/\text{Cu}^{++}$ couple). Please review p.135-139 of Davis.

Every time you evaluate the electrochemistry of a system, identify the half reactions and where and what the electrons are doing.

Time out for a kind of problem you are expected to do on the exam:

Determining relative strengths of oxidizing and reducing agents. In working this kind of problem, note the similarities to relative acid/base strength problems. In both cases you start with a list of reactions:

acid and base strength			oxidizing and reducing agent strength		
K_a	acid dissociation rxn	K_b	E°_{red}	reduction half rxn	E°_{ox}
10^{-2}	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	10^{-12}	-0.7	$\text{Zn}^{++} + 2\text{e}^- \rightleftharpoons \text{Zn}$	+ 0.7
10^{-5}	$\text{HAc} \rightleftharpoons \text{H}^+ + \text{Ac}^-$	10^{-9}	0.0	$\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.0
10^{-9}	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	10^{-5}	+0.3	$\text{Cu}^{++} + 2\text{e}^- \rightleftharpoons \text{Cu}$	-0.3
HSO_4^- is the strongest acid, NH_3 the strongest base			Cu^{++} is strongest ox.agent, Zn is strongest red. agent		

Things to notice in comparing K to E for relative strengths:

- There are two directions for reactions: acids in the forward direction, bases in the reverse direction; reduction in the forward direction, oxidation in the reverse direction.
- There are two pairs of constants, K_a and K_b , E_{red} and E_{oxid} .
- There are some simple rules for determining strength:
 - "The larger the K_a , the stronger the acid and the weaker the conjugate base"
 - "The larger the K_b , the stronger the base and the weaker the conjugate acid."
 - "The stronger the oxidizing agent the more easily a species is reduced"
 - "The stronger the reducing agent, the more easily a species is oxidized."
- In table as written, the strongest acid is always in the upper left hand corner (HSO_4^-) and the strongest base in the lower right hand corner (NH_3). The strongest oxidizing agent (most easily reduced) is always in the lower left hand corner (Cu^{++}) and the strongest reducing agent is in the upper right hand corner (Zn).

2. Electrochemistry is not done at equilibrium. As we will learn, when you are at equilibrium, you have a dead battery ($G = 0$)--and nothing gets done with a dead battery. So most electrochemistry is done by monitoring the flow (direction and amount) of electrons as a non-equilibrium system moves toward equilibrium.

3. Physics that you should know:

a. Electrical Charge. The fundamental unit of charge, q , is measured in Coulombs. One electron has a charge of 1.602×10^{-19} Coulombs (C). Therefore, one mole of electrons has a special amount of charge

$$F = \text{Faraday (Coulombs/mole)} = q \text{ (Coulombs)} / n \text{ (moles)}$$

$$F = 9.649 \times 10^4 \text{ C/mole}$$

So electrons are our currency for electrochemical measurements in the same way that protons were our currency for acid/base reactions. A Faraday is simply an amount of charge in the same way a dozen is an amount of eggs.

Example: In a redox reaction involving the reduction of Fe^{+++} to Fe^{++} , a total of $9649 \times 10^3 \text{ C}$ are used up. How much Fe^{+++} was reduced?

$$(9.649 \times 10^3 \text{ C}) \left(\frac{1 \text{ mole Fe}^{+3}}{9.65 \times 10^4 \text{ C/mol}} \right) \left(\frac{55.85 \text{ g}}{1 \text{ mole Fe}} \right) = 5.585 \text{ g Fe}^{+3}$$

Note that for this reaction, a single electron is transferred from the Cu^+ to the Fe^{+++} . This is analogous to a single H^+ transfer in a monoprotic acid.

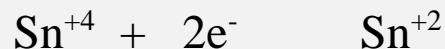
b. Add time to the equation and get CURRENT.

The measure of current as a function of time is the ampere:

One Ampere = one Coulomb/second

Having current measured as a function of time means we can talk about a rate of reaction (kinetics stuff, something we haven't considered since we started equilibrium.)

Example: What is the current measured in a circuit involving the half cell reaction



which is occurring at a rate of 4.2×10^{-3} mole/hr?

$$i = (4.24 \times 10^{-3} \text{ mole/hr}) \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) \left(\frac{2 \text{ mole e}^{-}}{1 \text{ mole Sn}^{+4}} \right) \left(\frac{9.65 \times 10^4 \text{ C}}{\text{mole}} \right) = 0.227 \text{ A}$$

By the way, what do you think about this magnitude of current? Will it kill you? Will it power a small city or a small toy?

c. What about the WORK necessary to move electrons?

In electrochemistry this is electric POTENTIAL, E , measured in Volts (V). E is the measure of the potential difference between two points. It is the physical measure of work that is done when one Coulomb of charge passes between two points. Work has the units of Joules, and with V and C also *mks* units, we have then

$$\text{Work (J)} = q E = (\text{volts})(\text{Coulombs})$$

So one Joule of work is done when one Coulomb moves across a potential gradient of one Volt.

Now don't blow this off, $w = qE$ is an extremely important concept in any kind of science associated with moving charged particles.

Example. How much work does it take to move over 2.36×10^{-3} moles of electrons across a 1.05 V potential?

$$\text{Work(J)} = (1.05\text{V})q = (1.05\text{V})(2.36 \times 10^{-3}\text{moles } e^{-})(9.65 \times 10^4\text{C/mol})$$

$$\text{Work} = 239 \text{ J}$$

By the way, is 239 J a lot or a little? Will it power a city, or a flashlight?

We just did a problem in which we used a 1.05 V potential difference. If we had wanted to do more work, we could have used a bigger potential difference; this is the idea behind purchasing a bigger battery, (a 12 V rather than a 1.5 V battery.)

d. Ohm's Law. Ohm's law will rear its head a couple of time during our discussion of electrochemistry . So it is good to remember it

$$I = \frac{E \text{ (potential)}}{R \text{ (resistance)}}$$

Ohm's law states the intuitively obvious, that as you increase the resistance in a chemical system, the current that flows will decrease.

e. And our final physics fact. The power law

$$P \text{ (Watts)} = \text{work/time} = qE/t = EI$$

The power law simply considers how much work is being done per hour.

Back to electrochemistry.

4. Types of Electrochemical Cells.

Electrochemical cells can be placed in two categories based upon thermodynamics.

- **Galvanic cells (batteries):** a spontaneous reaction occurs (E is positive)
- **Electrolytic cell:** work must be done for a reaction to occur (E is negative.)

We will discuss each of these cells at length, but obvious distinguishing features are that a galvanic cell must involve a redox couple for which G is initially negative while an electrolytic cell involves a redox couple for which G is initially positive. Note that the galvanic cell is important, because it is the definition of a battery!!

5. Tying Electrochemistry to Thermodynamics.

In electrochemistry, the quantity in which we are most interested is E , the potential energy of the system. It is the value you see on a new $E = 1.5\text{V}$ or $E = 6\text{ V}$ battery. We can relate this idea of work done in electrochemistry to the thermodynamic concept of work, free energy, through the equation:

$$\text{free energy} = G = -q E = -nFE$$

You will also remember that

$$\text{free energy} = G = -RT \ln K$$

From this equation, the following must be true about spontaneous reactions:

type of reaction	thermodynamics	electrochemistry	equilibria
spontaneous reaction	G is negative	E is positive	K is > 1
non-spontaneous reaction	G is positive	E is negative	K is < 1

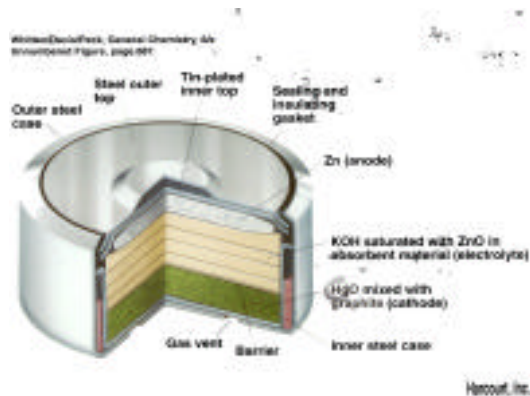
6. Galvanic Cell and Electrolytic Cels. There are two kinds of electrochemical cells, those that occur spontaneously and those that require work to occur. This is simply the consequence of having reactions that are:

spontaneous ($G < 0$ is a battery or a galvanic cell)

and reactions that are

non spontaneous ($G > 0$ is an electrolytic cell)

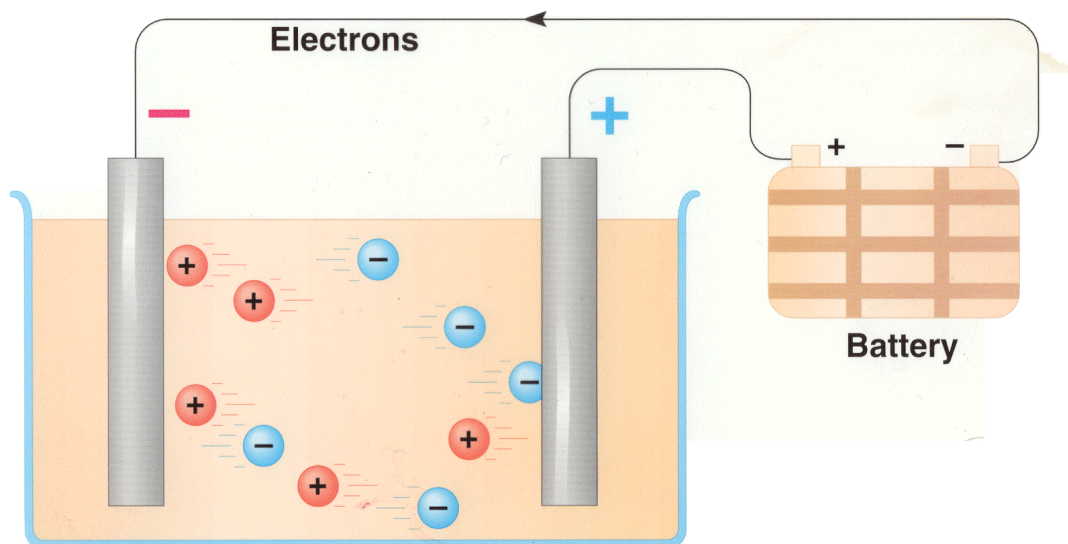
An example of a galvanic cell is shown below.



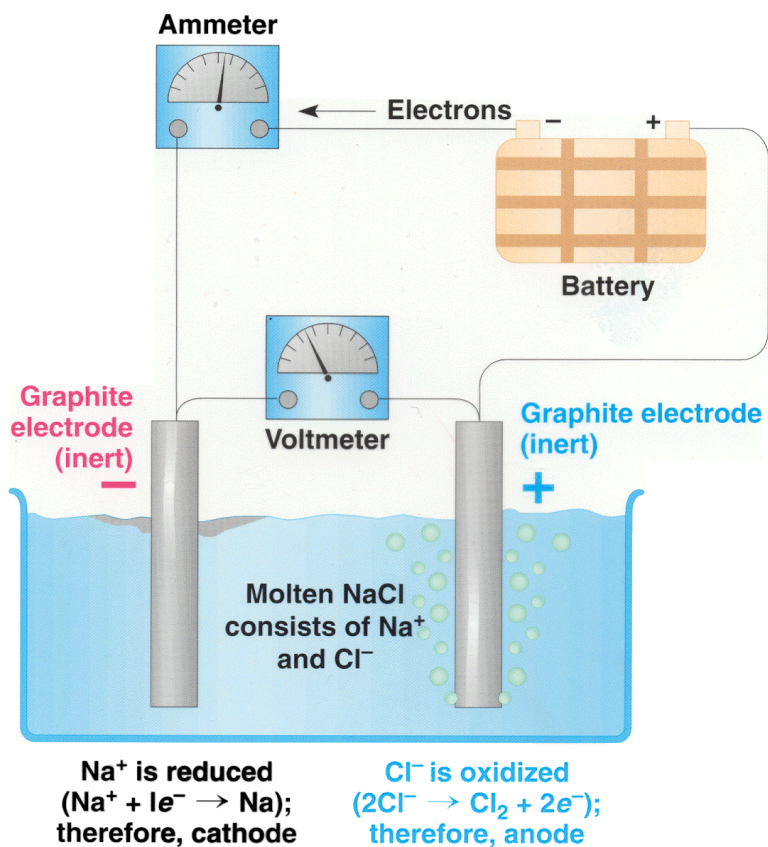
To be written as a reaction for a galvanic cell, the combined reaction must be exothermic. This means that electrons will flow spontaneously down a hill of a size particular to the reaction. As we will see, in this case, electrons slide down potential hill. Note that E is a positive value here and corresponds to a negative G (it is spontaneous).

Examples of electrolytic cells are shown below. Note that in each case, a battery (galvanic cell) is needed to make the reaction happen. This is because the reaction that you want to make happen does not occur unless you perform work to make it happen.

Whitten/Davis/Peck, General Chemistry, 6/e
Figure 2

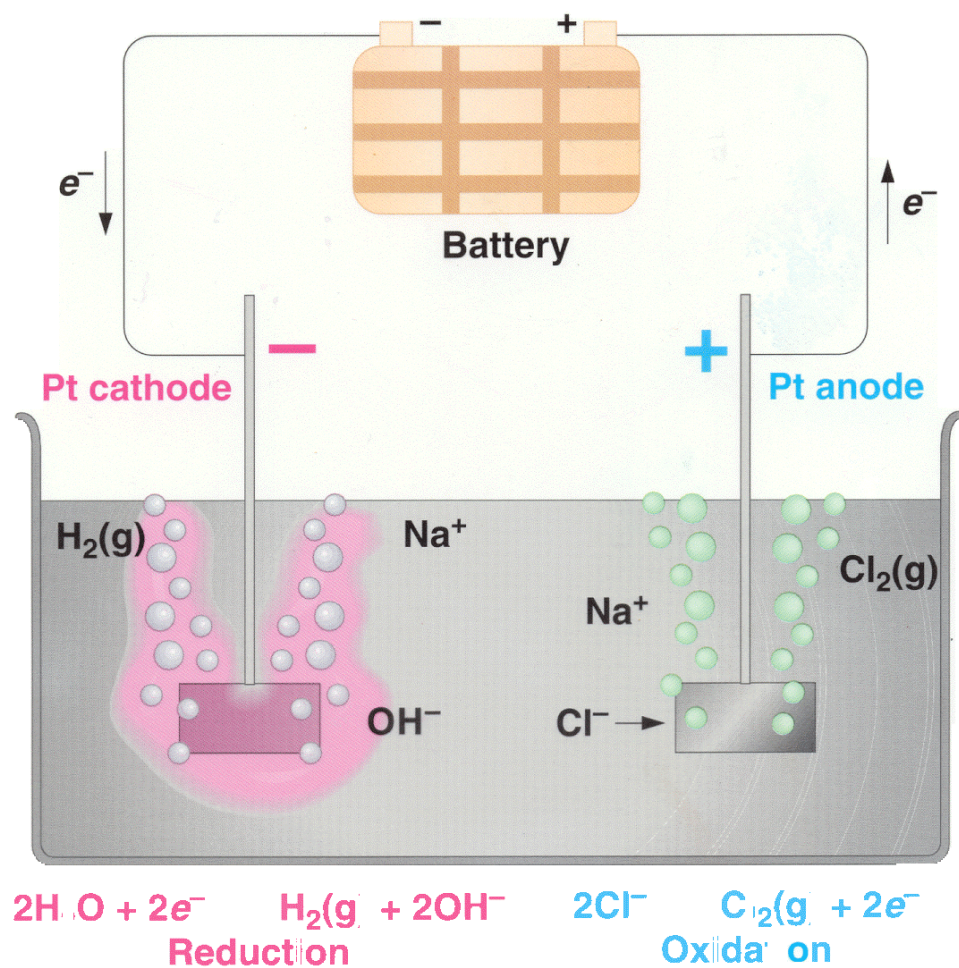


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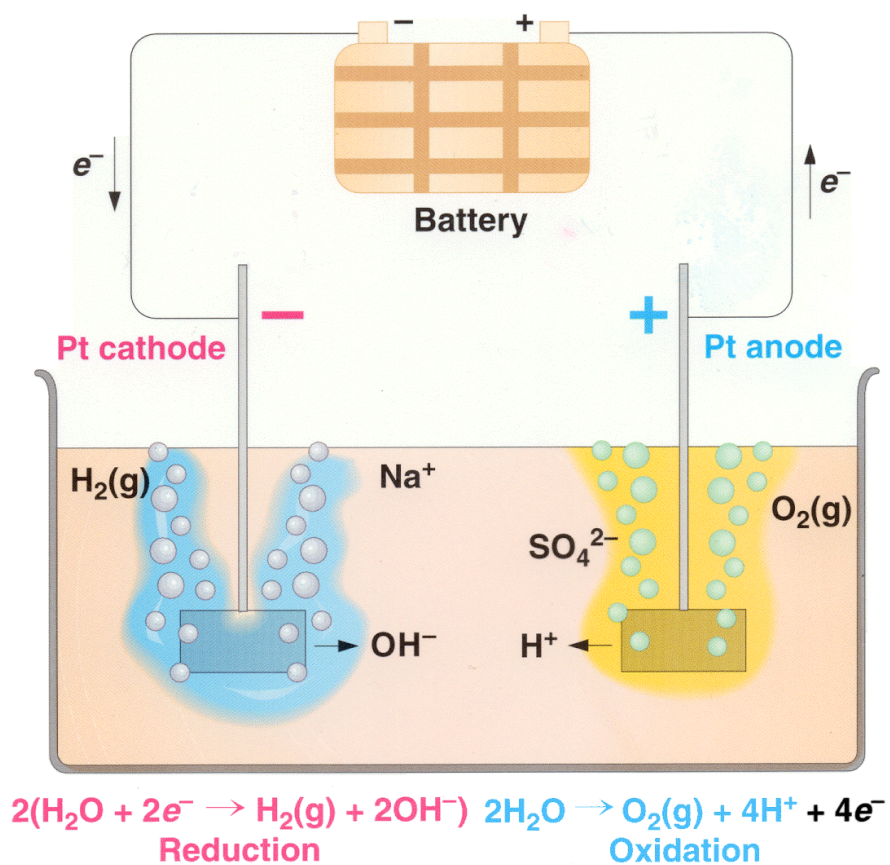


(a)

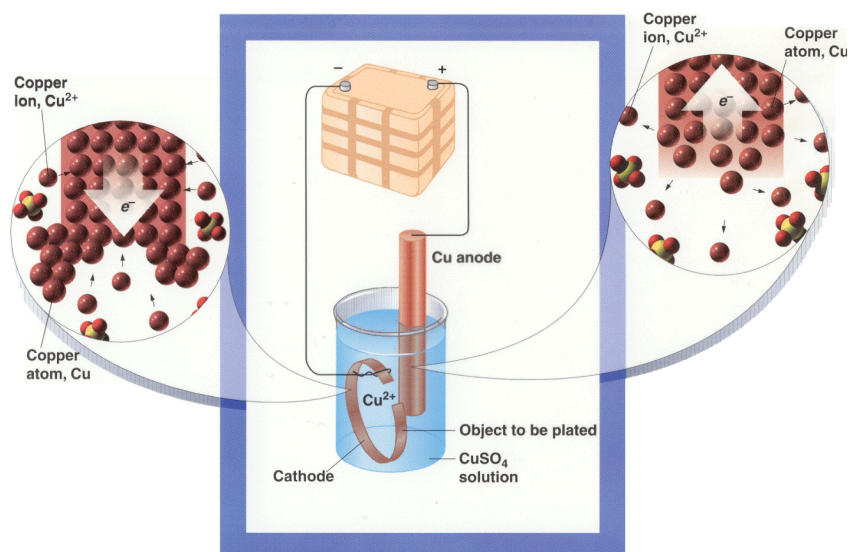
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7. ANODES AND CATHODES.

Time for a little convention. As we will see, electrochemists are not too big on adopting a convention that makes everyone happy. But one thing they can agree on is that by convention, the ANODE is defined as the electrode in the cell where OXIDATION takes place and the CATHODE is the electrode in the cell where REDUCTION takes place. Don't ask why, just accept it. Oh, and by convention, in a galvanic cell, the positively charged terminal is the cathode and the negatively charged terminal is the anode. This latter fact is subject to change without warning depending upon the type of book you read, so be cautious. But remember that anode-oxidation and cathode-reduction connection are always true.

Putting it all together to make cells:

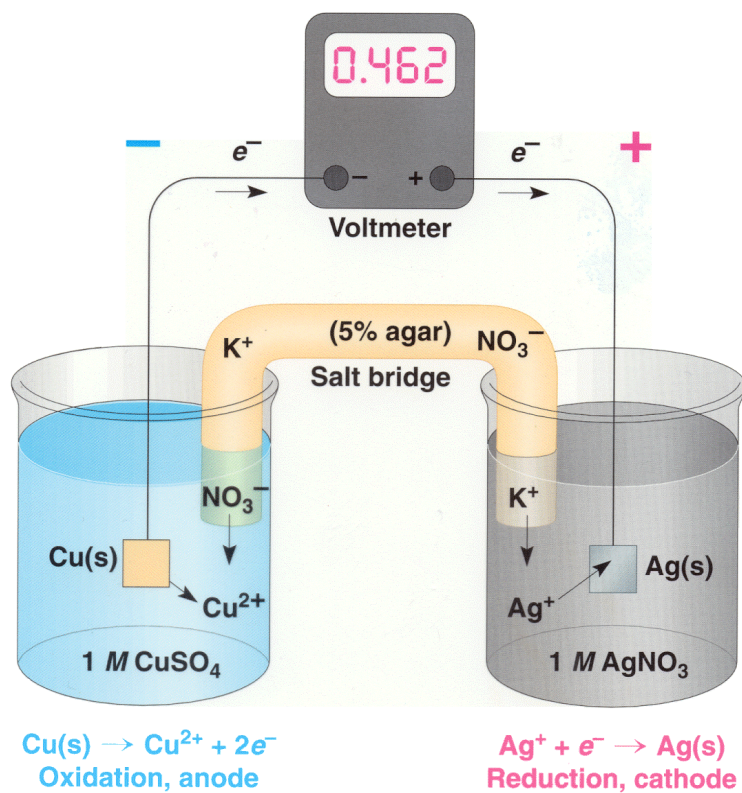
A nice summary of facts on cell construction and convention:

Electro chemical cell type	reaction type	G	E	reduction	oxidatio n	direction of e^- flow	sign at cathode	sign at anode
electrolysis	non- spontaneous	+	-	cathode	anode	e^- flow to cathode	-	+
galvanic (battery)	spontaneous	-	+	cathode	anode	e^- flow to cathode	+	-

8. Salt Bridges.

You will notice in the galvanic cell above, that there is a physical separation of the anode from the cathode that occurs because the HgO electrode consists of a solid and an insoluble paste. This sort of physical separation is typical in a battery but not in the chemistry laboratory. Instead, the electrodes usually must be placed in separate containers because otherwise the electrons would flow directly between the two electrodes and we would derive no analytical utility from the cell. However, if you isolated the two electrodes, no current flows would flow.

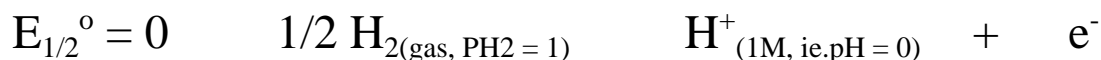
Instead, something called a **salt bridge** is often used to provide a source of supporting electrolytes that do not participate in the reaction, but do allow a completion of the circuit. A common salt bridge is a gel consisting of a saturated KCl which permits the diffusion of Cl^- to the anode and K^+ to the cathode.

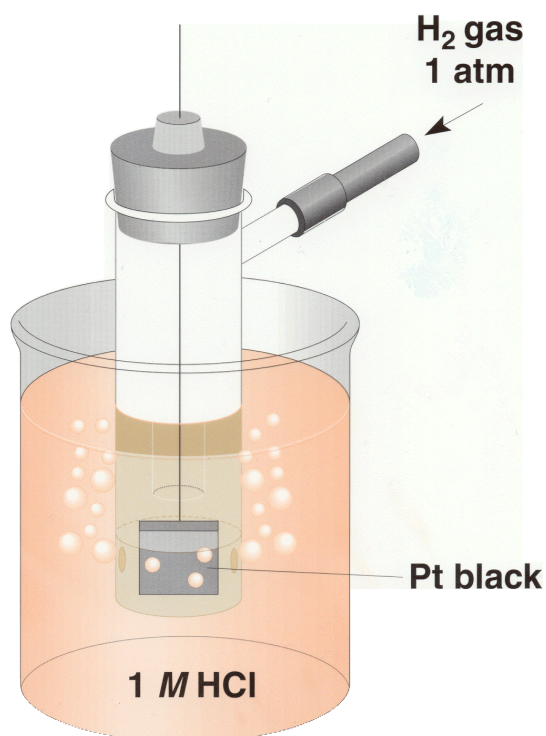


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9. Standard Potentials.

You will recall from our brief detour into physics that you need the difference between TWO potentials to do work. A single half cell reaction is only a figment of your imagination (or an incorrect answer on an exam.) The only value of interest to us is this difference, this CHANGE IN POTENTIAL. Now here is the problem, do you know how many half cell reactions there are in the world? Well a lot, since absolutely every chemical reaction can be described as an oxidation or reduction. So what do we do? We create a STANDARD REFERENCE POTENTIAL (E°) to which we arbitrarily assign a number. Then all the other half cell reactions can be compared to the reference and through that reference, to each other. Let's let our STANDARD REFERENCE POTENTIAL for a half cell reaction be equal to 0 V, so we can do the math in our head. Now, let's choose a half cell to be our reference AGAINST WHICH ALL OTHERS THINGS ARE MEASURED!!! Let's choose THE STANDARD HYDROGEN ELECTRODE (SHE).





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Now looking at this half cell, it doesn't seem to have a lot going for it. To build one you need to have a gas bulb filled with an explosive gas, AND a solution that is at $\text{pH} = 0$. But we don't get to pick, it was already chosen for us. Fortunately we don't have to use this half cell in the lab, we just use it to make the table of standard half cell reactions. In the lab we will use something else as a reference cell, like a STANDARD CALOMEL ELECTRODE (SCE) and we will simply note the difference between the SCE and the SHE when we do our calculations.

10. TABLES OF STANDARD HALF CELL REACTIONS. Let's go in the lab, pull out a standard hydrogen electrode, and hook it up in a cell like the one below.



Now let's hook up all the half cell reactions in the world and obtain standard reference potentials (E°). A couple of things to consider.

First, electrochemistry is just thermodynamics, and you may recall from thermodynamics that things like concentration and temperature matter, so we need some standard concentrations and a standard temperature. How about:

- all reactants and products must be at 1 atm or 1M
- remember to record the temperature, because we can use thermodynamics to correct to a standard temperature like 298K.

One more thing. We need to either write our half reactions as either oxidations or reductions. (We can't switch back and forth or we get our signs mixed up.) Now this may seem no big deal to you, but it sure was worth fighting over among electrochemists. We are going to take the easy out, and use what is in APPENDIX J of Davis, starting on page A-27: REDUCTION POTENTIALS. This means the electrons will appear on the left side of the equation. Anyway, here it is, our very abbreviated table:

TABLE 21-2 *Standard Aqueous Reduction Potentials in Aqueous Solution at 25°C*

Element	Reduction Half-Reaction	Standard Reduction Potential E° , volts
Li	$\text{Li}^+ + e^- \longrightarrow \text{Li}$	-3.045
K	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
Cr	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
H_2	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000 (reference electrode)
Cu	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337
I_2	$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-$	+0.535
Hg	$\text{Hg}^{2+} + 2e^- \longrightarrow \text{Hg}$	+0.789
Ag	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.799
Br_2	$\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-$	+1.08
Cl_2	$\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$	+1.360
Au	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.50
F_2	$\text{F}_2 + 2e^- \longrightarrow 2\text{F}^-$	+2.87

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Notice in my small table that the SHE sits pretty much in the middle of things. Half of the reactions when written as reductions are spontaneous (E° is positive) and half are not spontaneous (E° is negative).

There is a much bigger collection of standard reduction potentials in Davis, Appendix J. Spend some time looking at them and making sense out of what you see from everyday life. Also, look at the bounds for this table. Does it make sense that Li and F_2 half reactions exhibit the largest absolute magnitudes?

11. Using the Tables of Standard Reduction Potentials.

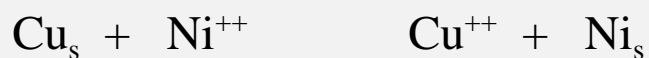
The whole purpose of the reduction potential tables was to avoid writing an exponentially increasing number of reactions between every new half cell reaction and every half cell reaction we already knew. So how do we put two half cell reactions together using the SHE?

By convention:

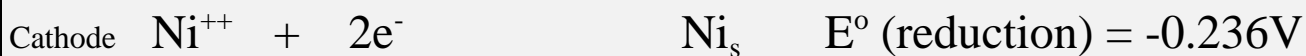
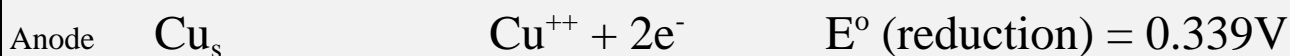
$$E^{\circ}_{(\text{net})} = E^{\circ}_{(\text{cathode})} - E^{\circ}_{(\text{anode})}$$

Use this equation exactly as written, inserting values directly from the table of standard reductions. DON'T switch signs in the half cell reaction and then use this equation or you will mess up.

Example: Given below is an electrochemical cell reaction. Is the reaction spontaneous as written?



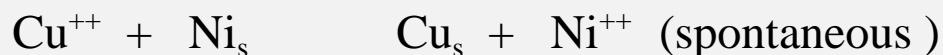
Break it down into the half cell reactions:

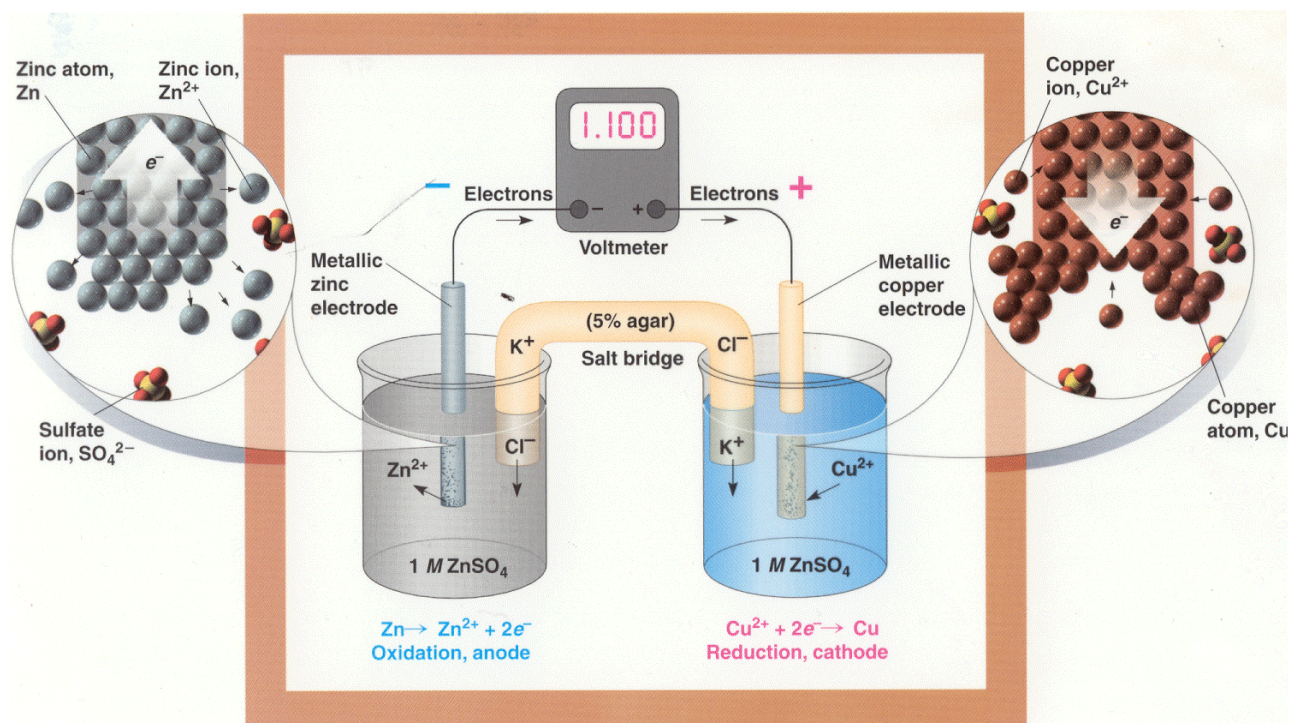


Now use the equation

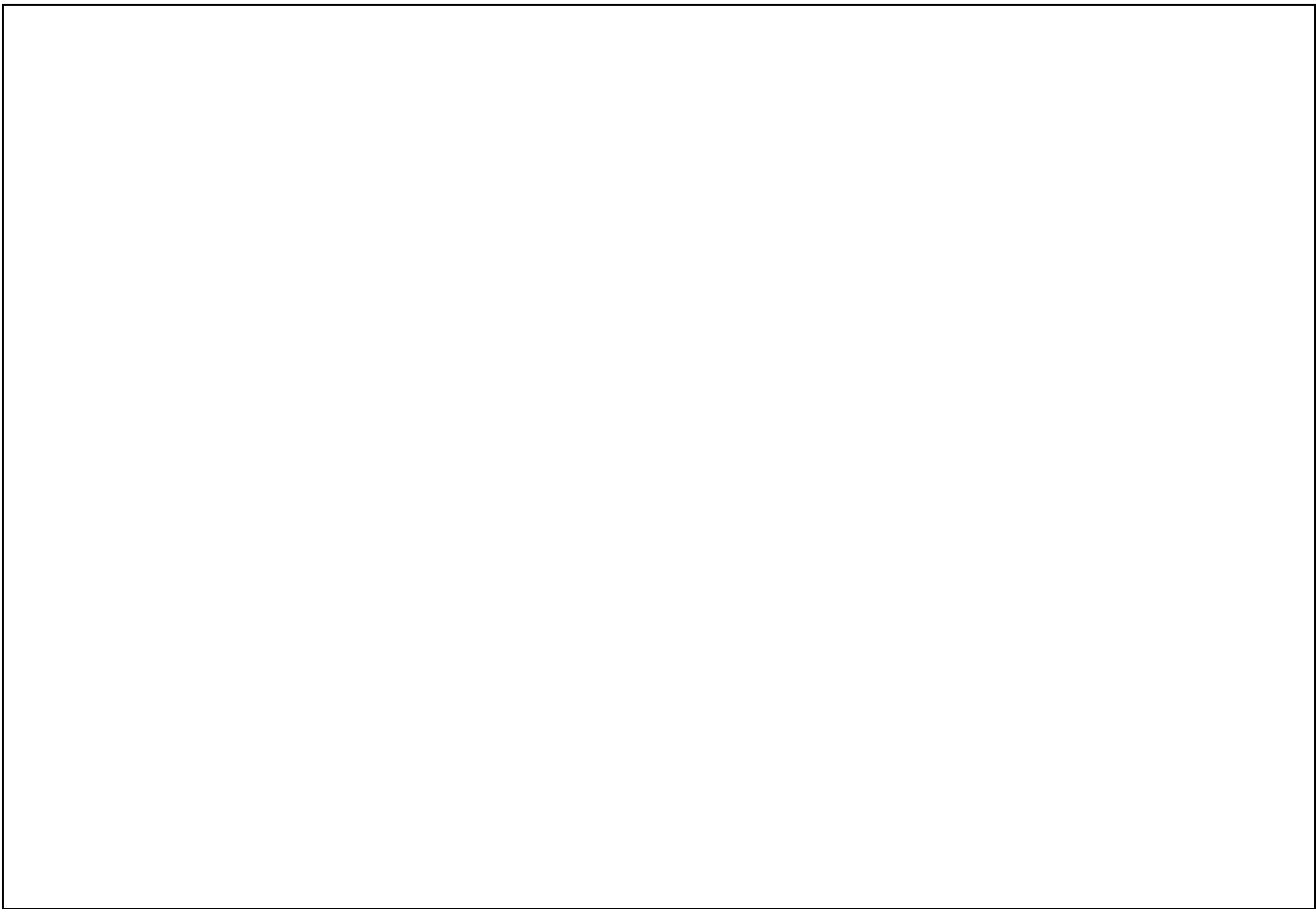
$$E^\circ = \underset{\text{cathode}}{(-0.236\text{V})} - \underset{\text{anode}}{(0.339\text{V})} = \underset{\text{net}}{-0.575}$$

Note that AS WRITTEN, this reaction is not spontaneous. However we can reverse the reaction and $E^\circ = +0.575$ and the reaction is spontaneous.





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12. COMPLICATION: THE NERNST EQUATION

If electrochemistry was simply a matter of calculating E° values, life would be easy. But it is not. Do you really think that if we put together a nickel and copper cell and measured the potential, it would be 0.575? If you do, you are probably the same sort of person who believes that the pH of a 0.01M HCl solution is 2 (Go measure it, it is not.) In fact, there are a lot of complications to solution chemistry that need to be addressed if we are going to get a reasonable quantitative handle on the actual potential of an electrochemical cell. We need to deal with CONCENTRATION and how it affects E . We will borrow what we learned back in thermodynamics about relating G to G° through Q

$$G = G^\circ + RT \ln Q$$

You may have noticed that batteries go dead. This means that even when they read 1.5V on the label, the battery's potential to do work is no longer 1.5V. Why is this? The problem is, we aren't accounting for concentration changes in the electrochemical cell. Remember that electrochemistry is just thermodynamics, and thermodynamics always considers relative concentrations. So clearly we will have to add corrections for concentrations to our equation for E .

This is where the Nernst equation comes in. The Nernst equation accounts for the concentration of electroactive species in an electrochemical cell; i.e., the Nernst equation turns E° into E , the actual cell potential. It is easily obtained by combining the above equation with the one on p.131 that relates E to G .

For a reaction: $aA + ne^- \rightleftharpoons bB$ $Q = \frac{[B]^b}{[A]^a}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[B]^b}{[A]^a}$$

R = ideal gas constant
 T = temperature
 n = # of e^-
 F = Faraday

Here, Q has the same form as an equilibrium constant in that it is equal to products over reactants, but the difference is that Q is used when NOT AT EQUILIBRIUM. (In other words, Q applied back when you added NaOH to your titration flask and things were kind of pink just before the solution went clear.)

It is important to note from the Nernst equation that when $Q = 1$, then $\ln Q = 0$ and $E = E^\circ$. This makes sense, because remember that E° is the standard potential and by definition occurs when all our concentrations are 1 M. If you stick the number 1 into every concentration in Q , obviously you end up with the $\ln Q$ term going away.

A more practical form of the Nernst assumes that $T = 25^\circ\text{C}$ and uses $\log_{\text{base } 10}$. In this case a Nernst equation half cell reaction is

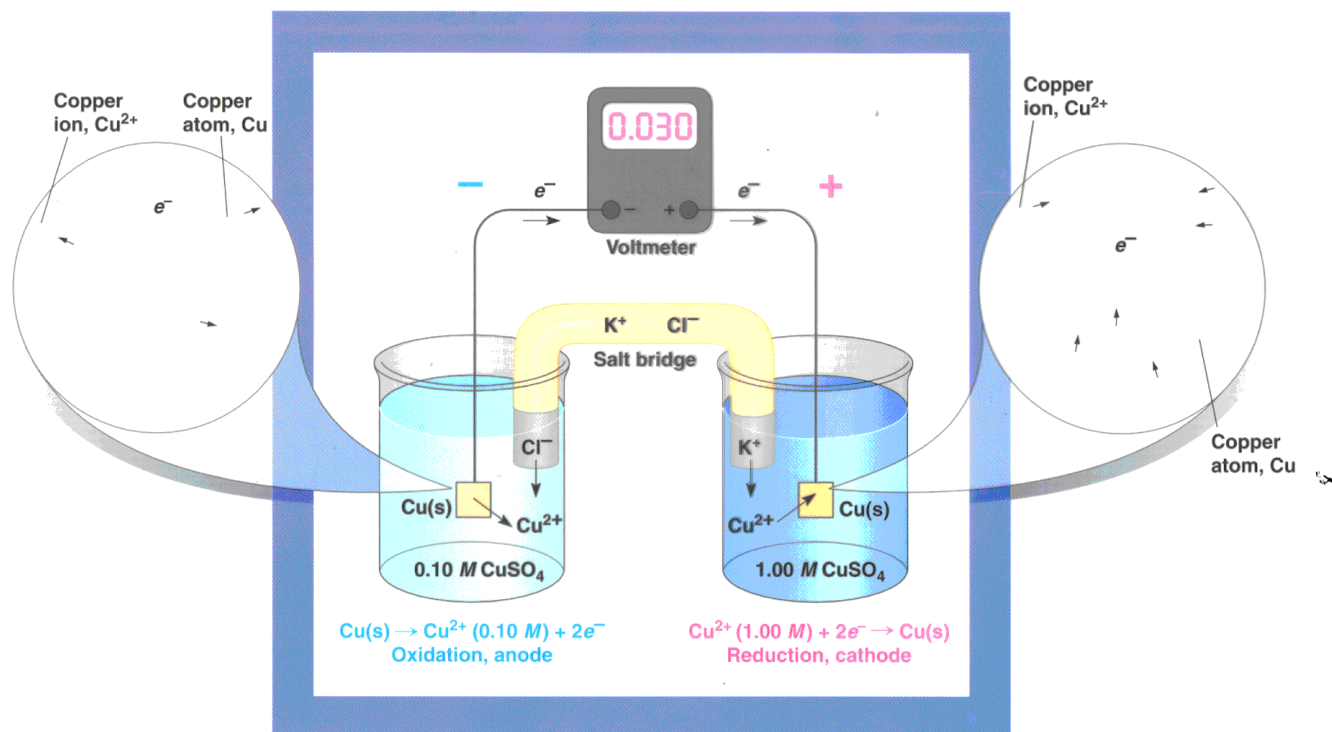
$$E_{1/2} = E_{1/2}^\circ - \frac{0.05916}{n} \log Q$$

and for the cell reaction

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.05916}{n} \log Q$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

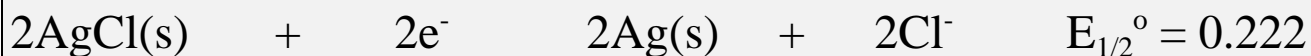
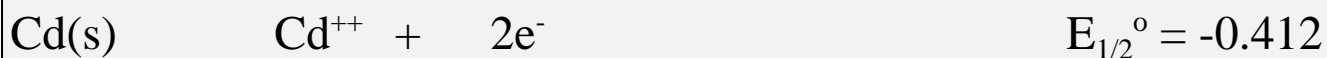
where Q is the reaction quotient for the balanced redox reaction. Here n is the number of electrons in the balanced reaction.



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EXAMPLE OF NERNST EQUATION.

For the two half cell reactions,



which give a cell reaction



the Nernst equation is

$$E_{\text{cell}} = 0.624 - \frac{0.05916}{2} \log [\text{Cl}^-]^2 [\text{Cd}^{++}]$$

And if we use our earlier cell reaction with the CdCl_2 concentration = 0.167M then

$$E_{\text{cell}} = 0.624\text{V} - \frac{0.05916}{2} \log [0.0334]^2 [0.0167]$$

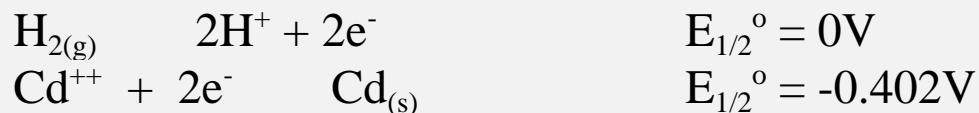
$$E_{\text{cell}} = 0.764\text{V}$$

Note that as written, by lowering the CdCl_2 concentration from 1M, we were able to make the reaction MORE EXOTHERMIC.

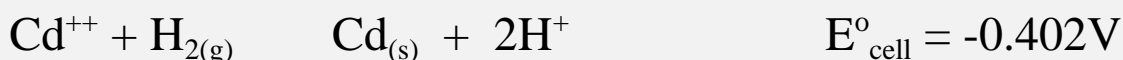
ANOTHER EXAMPLE OF THE NERNST REACTION.

This one is fun because you get to apply some of what you've learned about acid base chemistry!!

For the two half cell reactions,



which give a cell reaction



the Nernst equation is

$$E_{\text{cell}} = -0.402\text{V} - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2}{[\text{Cd}^{++}]\text{P}_{\text{H}_2}}$$

Now according to the Nernst equation, if all the concentrations were unity (in this case it would mean the pH = 0), then the reaction is not spontaneous. But is it possible to make this reaction spontaneous? According to LeChatlier we can do so by altering the concentrations. What if we left $\text{P}_{\text{H}_2} = [\text{Cd}^{++}] = 1$, what would the pH have to be to make the reaction spontaneous? Mathematically, this means we want to find the pH when E goes from negative to positive:

$$0 = -0.402\text{V} - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2}{(1)(1)}$$

Now solve for H^+ and you get

$$[\text{H}^+] = 1.6 \times 10^{-7} \text{ M or pH} = 6.8$$

So this is an example of a reaction that does not occur in acidic solution but is spontaneous at physiological pH and has a large driving force in base!! This is a startling example of how easily we can manipulate the balance of materials in a chemical system to observe very different types of chemistry. It is also why body pH is so important to all you medical types.

The Dead Battery: What happens at equilibrium.

Galvanic cells (batteries) work when a reaction is NOT at equilibrium. But in a battery, reactants decrease, products increase and then we reach a point where nothing happens. This place is of course, EQUILIBRIUM. While it is the case that EQUILIBRIUM is just one special case for an electrochemical cell, it is an important case at a boundary.

$$\text{when } Q \rightarrow K \quad E_{\text{cell}} \rightarrow 0$$

At that point we can substitute K into the Nernst equation and do a little rearranging

$$0 = E^{\circ} - \frac{0.05916}{n} \log K_{25}$$

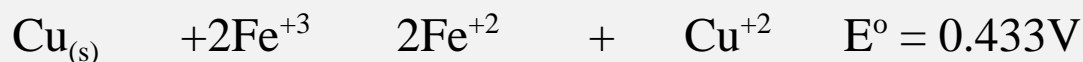
$$E^{\circ} = \frac{0.05916}{n} \log K_{25}$$

$$K_{\text{eq}} = 10^{nE/0.05916}$$

WOW!!! An equation that allows us to use an electrochemical cell to measure equilibrium constants. I'm sure many of you were wondering how we made all those tables of K values, for the most part they were developed from electrochemical measurements of dead batteries!!

Example of a dead battery as an equilibrium problem.

Given the following cell reaction:



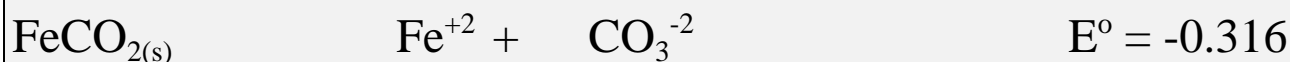
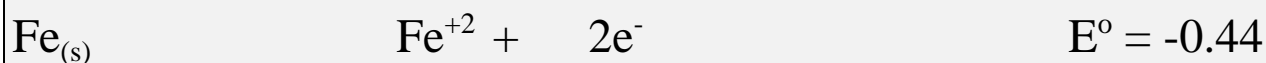
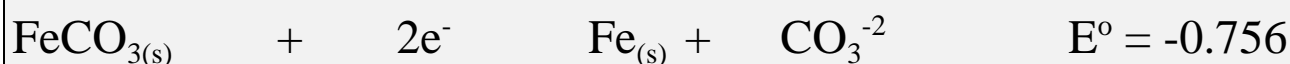
What is the equilibrium constant for the reaction?

$$K_{eq} = 10^{(2)(0.433)/0.05916} = 4 \times 10^{14}$$

Note that when E° is positive, K is greater than 1.

Another example:

Combine the two half cell reactions:



what we have is a K_{sp} equilibrium for FeCO_3 .

$$K_{eq} = K_{sp} = 10^{2(-0.316)/0.05916} = 2 \times 10^{-11}$$

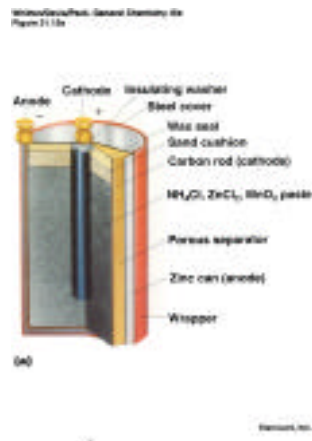
Note that as expected, our K_{sp} is a very small number. This occurs when E° is negative.

Let's think for a second about the magnitude of the relationship between E° and K ? Can you come up with a rule of thumb for how to estimate what K is given a particular E° ?

Quick, E° is 1.3, what is K_{eq} . Quick, $E^\circ = -2.4$, what is K_{eq} ?

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

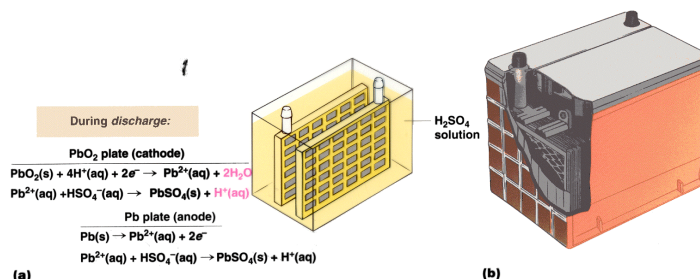
- Zinc-carbon battery - Also known as a standard carbon battery. Zinc-carbon chemistry is used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them that serves as the electrolyte.



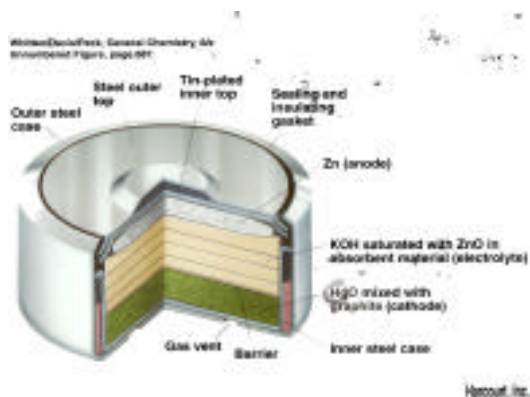
- Alkaline battery - Used in common Duracell and Energizer batteries. The electrodes are zinc and manganese-oxide, with an alkaline electrolyte.
- Lithium photo battery - Lithium, lithium-iodide and lead-iodide, used in cameras because of its ability to supply power surges.
- Nickel-cadmium battery - 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 the memory effect that nickel-cadmiums do. 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.
- Lead-acid battery - Used in automobiles. The electrodes are made of lead and lead-oxide with a strong acidic electrolyte. Rechargeable.

Whitten/Davis/Peck, General Chemistry, 6/e
Figure 21.16



- 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.