Chapter 64　　　　　　　ECHEM, Part 4

So far, all calculations have been for standard conditions in galvanic cells. Now we deal with nonstandard conditions and the calculation of the potential for those cases. Later in the Chapter, we consider a battery of applications, which are not always galvanic.

64.1 Back in Q

In Section 46.4, we introduced the relationship for ΔG at general conditions.

$$\Delta G = \Delta G° + RT \ln Q$$

Now we develop the analogous relationship for E. If you need to, go back and review Sections 46.4 and 46.5 before getting too far along here, especially if you're rusty on the Q expressions.

Since, for standard conditions, we have

$$\Delta G° = -nFE°$$

and, for nonstandard conditions, we have

$$\Delta G = -nFE$$

and since

$$\Delta G = \Delta G° + RT \ln Q$$

then we can write the following.

$$-nFE = -nFE° + RT \ln Q$$

Dividing both sides by $-nF$ gives a very useful equation which has historically been known as the Nernst equation.

$$E = E° - \frac{RT}{nF} \ln Q$$

R and F are constants; we will also specify that $T = 298$ K for our coverage. This leads to the following result.

$$\frac{RT}{F} = \frac{(8.314 \text{ J/K}) (298 \text{ K})}{96,485 \text{ C/mol}} = 0.0257 \frac{\text{J}}{\text{C/mol}}$$

The J/C part is a volt. The mol term will eventually cancel with the mol unit in n when this is plugged into Nernst, so we can leave it out. Just remember that n in Nernst will be a number for the moles but without the mol unit. This brings us to our final working form.

$$E = E° - \frac{0.0257 \text{ V}}{n} \ln Q$$

This is now our operational version for Nernst for determining a potential at any set of conditions. This works for a half-cell potential and it works for a whole cell potential. As always, for standard conditions, $Q = 1$; at standard, $\ln Q$ equals zero and you get $E = E°$, which we already knew anyway.

Let's start in on some Examples, starting with our old standby, $Zn + Cu^{2+}$.

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Example 1. For the following reaction,

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s) \qquad E° = 1.10 \text{ V}$$
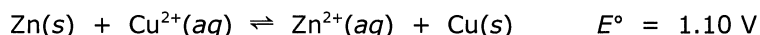
what is the potential when $[Zn^{2+}] = 0.0117$ M and $[Cu^{2+}] = 0.0437$ M?

. . . .

You will need Nernst

$$E = E° - \frac{0.0257 \text{ V}}{n} \ln Q$$

for which you need the Q expression.

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Plug it all in.

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.0117}{0.0437}$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln(0.26773...)$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} (-1.3177...)$$

$$E = 1.10 \text{ V} - (-0.0169 \text{ V}) = 1.12 \text{ V}$$

Under these conditions, $E > E°$.

This illustrates a typical Nernst-type calculation. Although Nernst is simply a plug-in equation, you do need to be sure of your $E°$, your Q expression, and the value for n. The Q expression was fairly easy in this Example but, as seen since Section 46.4, Q can get tedious.

. . . .

Example 2. Consider the following balanced equation.

$$IO_3^-(aq) + 3 H_2O_2(aq) \rightleftharpoons 3 O_2(g) + I^-(aq) + 3 H_2O(l)$$
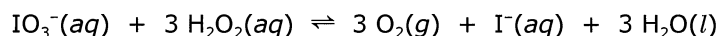
What is E for the following conditions?

$[H_2O_2] = 0.231 \text{ M}$ $[I^-] = 0.0319 \text{ M}$ $[IO_3^-] = 0.0433 \text{ M}$ $P(O_2) = 0.0182 \text{ atm}$

. . . .

You need Nernst.

$$E = E° - \frac{0.0257 \text{ V}}{n} \ln Q$$

You can get $E°$ from values in Appendix C or you can turn to Example 4 in Chapter 63; regardless, $E° = 0.38$ V.

Q is a bit involved.

$$Q = \frac{P(O_2)^3 [I^-]}{[IO_3^-] [H_2O_2]^3}$$

What's n? Once you have that, you can plug everything in.

$$E = 0.38 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln \frac{(0.0182)^3 (0.0319)}{(0.0433) (0.231)^3}$$

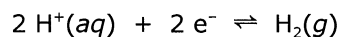$$E = 0.38 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln(0.00036031...)$$

$$E = 0.38 \text{ V} - \frac{0.0257 \text{ V}}{6} (-7.9285...)$$

$$E = 0.38 \text{ V} - (-0.0340 \text{ V}) = 0.41 \text{ V}$$

Again, this gives $E > E°$.

As noted above, Nernst also works for half-cell potentials. Let's turn a SHE into a nonstandard HE.

. . . .

Example 3. What is the half-cell potential for

$$2 H^+(aq) + 2 e^- \rightleftharpoons H_2(g)$$

at pH = 3.06 and $P(H_2) = 0.449$ atm?

. . . .

Nernst.

$$E_{1/2} = E_{1/2}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$Q = \frac{P(\text{H}_2)}{[\text{H}^+]^2}$$

SHE is the reference, so $E_{1/2}^{\circ} = 0.00\ldots$ V (exact). Notice that the equation for the half-reaction gives $n = 2$ directly. Go ahead and plug in. You will have to convert pH to $[\text{H}^+] = 8.7 \times 10^{-4}$ M.

$$E_{1/2} = 0.00\ldots \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.449}{(8.7 \times 10^{-4})^2}$$

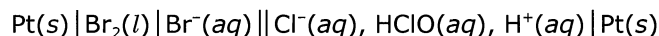$$E_{1/2} = 0.00\ldots \text{ V} - \frac{0.0257 \text{ V}}{2} \ln(593209\ldots)$$

$$E_{1/2} = 0.00\ldots \text{ V} - \frac{0.0257 \text{ V}}{2} (13.293\ldots)$$

$$E_{1/2} = 0.00\ldots \text{ V} - 0.171 \text{ V} = -0.171 \text{ V}$$

Here, $E_{1/2} < E_{1/2}^{\circ}$.

Your turn. New reaction.

. . . .

Example 4. Consider the following cell.

$$\text{Pt}(s) \mid \text{Br}_2(l) \mid \text{Br}^-(aq) \parallel \text{Cl}^-(aq), \text{HClO}(aq), \text{H}^+(aq) \mid \text{Pt}(s)$$

What is E for the following conditions?

$[\text{Br}^-] = 0.0671$ M $[\text{H}^+] = 1.00 \times 10^{-4}$ M $[\text{Cl}^-] = 0.00760$ M $[\text{HClO}] = 0.206$ M

. . . .

You need Nernst

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

but you also need a fully balanced equation in order to set up a Q expression. Go ahead and work out the balanced equation.

Then find E°.

Plug your values into Nernst.

$$E = 0.41 \text{ V} - \frac{0.0257 \text{ V}}{n} \ln \underline{\hspace{8cm}}$$

Solve for E. Clue: $Q = 81941\ldots$

Notice that $E < E^{\circ}$.

These four Examples show a general plug-in for Nernst, solving for E. Variations are possible. For example, if you are given E instead of something else, then you can solve for that something else.

. . . .

Example 5. Example 3 involved reduction at a hydrogen electrode with pH = 3.06 and $P(\text{H}_2) = 0.449$ atm. Now keep $P(\text{H}_2) = 0.449$ atm but find the pH which is needed for $E_{1/2} = -0.12$ V.

. . . .

Nernst.

$$E_{1/2} = E^\circ_{1/2} - \frac{0.0257 \text{ V}}{n} \ln Q$$

In order to find pH, you need $[H^+]$ and that is within Q.

$$Q = \frac{P(H_2)}{[H^+]^2}$$

Re-arrange Nernst.

$$\ln Q = \frac{n}{0.0257 \text{ V}} [E^\circ_{1/2} - E_{1/2}] = \frac{2}{0.0257 \text{ V}} [0.00... \text{ V} - (-0.12 \text{ V})] = 9.3385...$$

Antiln.

$$Q = e^{9.3385...} = 11367... = \frac{P(H_2)}{[H^+]^2} = \frac{0.449}{[H^+]^2}$$

Re-arrange some more and solve.

$$[H^+]^2 = \frac{0.449}{11367...}$$

$$[H^+] = 0.0063$$

$$pH = 2.20$$

That's that.

Notice from the various Examples above that E can end up greater than or less than E°. This will be due to Q. A total of three outcomes are possible.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

If $Q < 1$, then $\ln Q$ is negative. You are subtracting a negative number from E°, and this will increase E such that $E > E^\circ$.

If $Q > 1$, then $\ln Q$ is positive. You are subtracting a positive number from E°, and this will decrease E such that $E < E^\circ$.

If $Q = 1$, then $\ln Q$ is zero. This gives $E = E^\circ$ even though the conditions may not be standard.

More generally, decreasing Q will increase E and increasing Q will decrease E. If you want more volts from a cell, then decrease Q. Recall that Q equals the rights over the lefts; thus, decreasing Q means decreasing the activities of the reagents on the right side of the equation and/or increasing those on the left side. Here's a simple illustration, using the equation from Example 2 earlier.

$$IO_3^-(aq) + 3 H_2O_2(aq) \rightleftharpoons 3 O_2(g) + I^-(aq) + 3 H_2O(l)$$
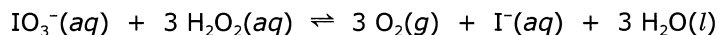
In order to increase the potential of the cell, you could

increase $[IO_3^-]$ or $[H_2O_2]$ or both

and/or

decrease $P(O_2)$ or $[I^-]$ or both.

The vice versa to this approach also applies: increasing Q means increasing the activities of the reagents on the right side of the equation and/or decreasing those on the left side. That would decrease E.

64.2 Drive

The above relationships for Q are important but there is even more significance than just this much. Keep in mind that E connects to the driving force, ΔG.

$$\Delta G = -nFE$$

F is a constant for all cases. For a particular equation, n is fixed. Only ΔG and E can change and these will change as Q changes. We can change Q by changing the activities as was done in the above Examples, but Q will also change as a reaction proceeds. For any exergonic reaction, which means for any galvanic cell, Q increases as the cell operates. Now, connect back to Section 47.2 where we talked about driving force and Q.

❝ But the driving force doesn't last forever. For any exergonic reaction, the greatest driving force (its most negative ΔG) occurs at the moment of starting the reaction. As the reaction proceeds, the driving force gets weaker (less negative ΔG) and eventually goes to zero. The driving force decreases as the reaction proceeds because the value of Q is changing. We can see this in terms of the general ΔG equation.

$$\Delta G = \Delta G° + RT \ln Q$$

Let's rewrite Q in terms of rights-over-lefts.

$$\Delta G = \Delta G° + RT \ln \frac{R}{L}$$

For an illustration, let's say we set up some reaction for which $\Delta G°$ is negative and that the initial conditions give $Q < 1$. For $Q < 1$, $\ln Q$ will also be negative. With these assumptions, the overall ΔG will be negative and the reaction is exergonic in the forward direction, L→R. Once the reaction starts and as the reaction proceeds in this direction L→R, then

> Products increase on the right and this increases the numerator of Q.
> Reactants decrease on the left and this decreases the denominator of Q.
> As a result, the value of $Q = R/L$ increases.
> The term, $RT \ln(R/L)$, increases (becomes less negative or more positive).
> This makes ΔG less negative.
> This means the driving force weakens.

This is reflected in the diagram at right. Initially, ΔG is some negative number at time zero; this becomes less negative as time goes on. Ultimately, the system reaches $\Delta G = 0$ which is equilibrium; at this point $Q = K$...
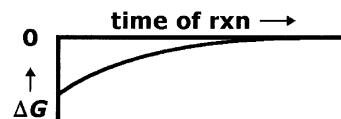
The natural drive for every process is toward $\Delta G = 0$ because, at this point, there are no further gains in entropy to be realized; thus, the driving force is zero. At equilibrium, the reaction is "done". This is the <u>net</u> stopping point overall, but it is NOT a point of total inactivity. The forward and reverse directions can still happen but they are equal and in balance. ❞

Now here we are in Chapter 64 and all of that remains very applicable. Consider again the above quote, now paraphrased in a different light, replacing driving force and ΔG with the push/pull of E. Note the parallel (even though the signs of ΔG and E are opposite):

> But the push/pull doesn't last forever. For any exergonic reaction, the greatest push/pull (its most positive E) occurs at the moment of starting the reaction. As the reaction proceeds, the push/pull gets weaker (less positive E) and eventually goes to zero. The push/pull decreases as the reaction proceeds because the value of Q is changing. We can see this in terms of the general E equation.

$$E = E° - \frac{0.0257 \text{ V}}{n} \ln Q$$

Let's rewrite Q in terms of rights-over-lefts.

$$E = E° - \frac{0.0257 \text{ V}}{n} \ln \frac{R}{L}$$

For an illustration, let's assume that $E°$ is positive and that the initial conditions give $Q < 1$. For $Q < 1$, $\ln Q$ will also be negative. With these assumptions, the overall E will be positive and the reaction is exergonic in the forward direction, L→R. Once the reaction starts and as the reaction proceeds in this direction L→R, then

> Products increase on the right and this increases the numerator of Q.
> Reactants decrease on the left and this decreases the denominator of Q.
> As a result, the value of $Q = R/L$ increases.
> The term, $\ln(R/L)$, increases (becomes less negative).
> This makes E less positive.
> This means the push/pull weakens.

This is reflected in the diagram at right. Initially, E is some positive number at time zero; this becomes less positive as time goes on. Ultimately, the system reaches $E = 0$ which is then equilibrium; at this point $Q = K$.
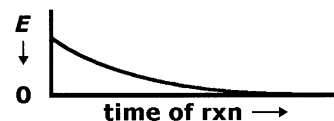
The natural push/pull for every process is toward $E = 0$ because, at this point, there are no further gains in entropy to be realized; thus, the push/pull is zero. At equilibrium, the reaction is "done". This is the <u>net</u> stopping point overall, but it is NOT a point of total inactivity. The forward and reverse directions can still happen but they are equal and in balance.

That ends the comparison to the quote from Section 47.2. It is important to keep in mind this parallel between ΔG and E.

By the way, this is what gets you a dead battery. To illustrate, we bring back our 1800's battery.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s) \qquad E° = 1.10 \text{ V}$$
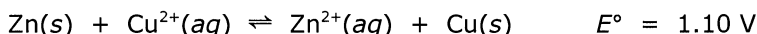
Let's say we set up a whole cell at equal conditions, $[Cu^{2+}] = [Zn^{2+}] = 0.00100$ M. For purposes of convenience in this illustration, we will assume equal volumes of 1.00 L for each of the two half-cells, so that moles and molars are the same numbers. This also gives an equal number of 0.00100 mol of Cu^{2+} and of Zn^{2+} to start the reaction. Now let the cell run for a while. The moles of Cu^{2+} decrease while the moles of Zn^{2+} increase, in a 1:1 manner as given by the balanced equation. Correspondingly, the molarities also change in a 1:1 manner: $[Cu^{2+}]$ decreases while $[Zn^{2+}]$ increases by the same amount. After 25% reaction, we have 0.00075 mol Cu^{2+} remaining and 0.00125 mol Zn^{2+} total; now, $Q = 1.7$. Plugging that into Nernst will get you $E = 1.09$ V. After 75% reaction, we have 0.00025 mol Cu^{2+} remaining and 0.00175 mol Zn^{2+} total; $Q = 7.0$ and $E = 1.07$ V. As the reaction continues, Q continues to increase and E continues to decrease. The system is going to equilibrium (which is completely to the right in this case, $K = 1.81 \times 10^{37}$, as noted in Section 63.1).

Equilibrium is cell death. Although the forward and reverse reactions can occur at equilibrium as long as they are in balance, we still have $\Delta G = 0$ and $E = 0$. There's no drive and there's no push/pull left. In actual practice, you typically change a battery well before its chemical reaction hits equilibrium, because the remaining volts are no longer enough to do the desired job. When the flashlight is too dimly lit, it's time for a change even though there may still be some juice left. The reaction may not be done, but its practical usefulness has ceased.

Speaking of equilibrium, we can bring K into the picture. From Section 47.1, we have

$$\Delta G° = -RT \ln K$$

which we can combine with

$$\Delta G° = -nFE°$$

to get

$$-RT \ln K = -nFE°$$

which re-arranges to the following.
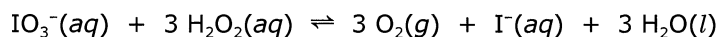
$$E° = \frac{RT}{nF} \ln K$$

As was done for Nernst at 25 °C, RT/F becomes 0.0257 V.

$$E° = \frac{0.0257 \text{ V}}{n} \ln K$$

This now allows for a direct conversion between $E°$ and K if needed.
. . . .

Example 6. Consider again the equation from Example 2.

$$IO_3^-(aq) + 3 H_2O_2(aq) \rightleftharpoons 3 O_2(g) + I^-(aq) + 3 H_2O(l)$$

What is K for this reaction?
. . . .

Use the $E°/K$ equation from above.

$$E° = \frac{0.0257 \text{ V}}{n} \ln K$$

Re-arrange.

$$K = e^{nE°/(0.0257 \text{ V})}$$

In Example 2 we had $E° = 0.38$ V and $n = 6$. Plug in.

$$\frac{nE°}{0.0257 \text{ V}} = \frac{6 (0.38 \text{ V})}{0.0257 \text{ V}} = 88.715...$$

$$K = e^{88.715...} = 3.4 \times 10^{38}$$

That is another astronomical K which is common of many echem reactions. You need a very small $nE°$ term in order to get a moderate K value.

Alright, at this time we are going to change direction a bit and put some of that drive to work. Most of the discussion so far has involved general principles of exergonic, galvanic processes. Now we get into some real life usage.

64.3 Batteries and fuel cells

Batteries are an essential part of modern human society and are used in a massive number of devices. The majority applications are based on portability of the power supply, which simply means the ability to move around without needing to stay plugged into a utility power line or a generator of some sort. Some battery applications are stationary, however, such as for emergency backup power when there is an interruption in line service, or remote power applications in places where there are no utility power sources.

As previously noted (Section 62.1), batteries can be composed of a single cell or they can be composed of multiple cells. Each cell constitutes an exergonic electrochemical reaction. There are single-use type batteries which are discarded after their useful lifetime; these are called primary batteries. There are also rechargeable batteries which can be used and recharged and used and recharged, etc., through a number of cycles; these are called secondary batteries. The usage part for the secondary battery is exergonic (galvanic), but the recharge part of the cycle is endergonic (electrolytic). For recharging, you send in electrical energy in order to reverse the chemical reaction which normally drives the cell; this reversal restores the reactants which are needed for the exergonic direction.

Commonly familiar batteries cover a range of sizes and shapes from the very small button batteries of hearing aids up to bulky and heavy vehicle batteries. Less common and less familiar batteries even extend beyond this range. There is also a wide breadth of chemical reactions and conditions which are involved in the various types of batteries, and these give the battery their designation of type, such as alkaline, nicad, silver, lithium, etc. Although most of our discussion of galvanic cells so far have involved aqueous solutions in separate half-cells, battery configurations have a much broader range of design. They all have an anode and a cathode and they all have some electrolyte solution or medium between them to allow ion flow. Some use pastes for the electrolyte instead of simple solutions. Some cannot have water present at all and they have an electrolyte solution which is completely nonaqueous. Most configurations require physical separation of the half-cells, as we have seen for a basic cell design with a salt bridge. In a battery, there is a membrane barrier called a separator between the two half-cells; this separator allows for ion flow and so it serves the purpose of a salt bridge. On the other hand, some batteries, such as the lead-acid battery, do not require physical separation of the half-cells, for reasons to be seen below.

While many people might regard a battery as a fairly trivial device, there is a huge amount of technology in batteries, and the modern and future demands of society continue to push this technology even further. Let's discuss several types of batteries, starting with those of primary importance.

The common, cylindrical primary cells which power many toys, flashlights, etc. around the world are usually either of classical zinc-carbon type or of alkaline type. Sizes vary from AAA through D, with bigger sizes carrying more capacity which means they can deliver more electrons at a suitable voltage. In more recent years, an even smaller AAAA size has come into use. Both the zinc-carbon and the alkaline types use the oxidation of Zn(s) (as anode) and the reduction of MnO_2(s) (with graphite as inert cathode). The general layout of the innards is shown at right for the classical zinc-carbon type. The zinc metal
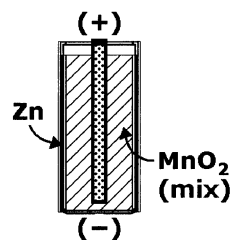
serves as a can and it makes direct contact with the (–) pole of the battery at bottom. It is typically covered on the outside by a protective wrap. A separator separates the Zn(s) from the anode compartment. The MnO_2(s) is present as a slurry with powdered graphite and an aqueous solution of electrolyte; this mix is in contact with the central graphite electrode. The graphite electrode is capped by a metal terminal for the (+) pole of the battery at the top. The half-reactions for the early zinc-carbon cell are the following.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$
$$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$$
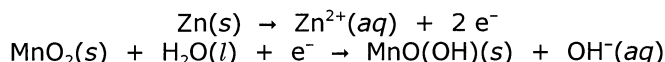
The electrolyte paste contains NH_4Cl and some $ZnCl_2$ and it is slightly acidic. The NH_4Cl reacts with OH^- to form NH_3 which reacts with Zn^{2+} to form a complex, $Zn(NH_3)_2Cl_2$. A later version of this battery does not include the NH_4Cl and has more $ZnCl_2$. Both versions are still in use. Alkaline batteries are a later variation; the cathode half-reaction is the same as above, but the anode reaction is the following.

$$Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\,e^-$$
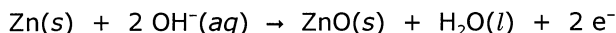
Zinc powder is used in this battery. Consistent with its name, the alkaline battery has an electrolyte with a high KOH concentration. The alkaline battery is a more substantial refinement of the prior zinc-carbon batteries. (Of course, the price increases with each refinement.) All of these batteries are rated for ~1.5 V service. If you combine six very small cells of this type into one package, you get the standard 9 V battery.

By the way, voltages for batteries are rated voltages for their intended uses. The rated voltages are not their open circuit (thermodynamic) voltage. As noted in Section 62.3, voltage decreases with more current drawn from an echem device, so a battery typically operates at less than its open circuit voltage. Furthermore, the voltage decreases with more use. The goal is to have a consistent voltage, but this is not possible over a wide range of conditions. These aspects are but a small part of the technological design of batteries.

Button or coin batteries have evolved over recent decades into a plethora of sizes and chemistries. By nature, these are for lower demand devices than standard AAA-through-D cells. (Motors in toys and incandescent lights in flashlights have larger current demands than small audio devices, LED displays, calculators, etc.) A typical watch or calculator battery is of silver type and a typical construction is shown

at left. The Zn(s) is now finely divided and is typically present as an alloy; for many years, the alloy was with mercury but newer designs have eliminated the mercury content. A separator divides the zinc from the Ag_2O cathode compartment. The electrolyte is again strongly basic, either NaOH or KOH. Metal caps at top and at bottom (insulated by a gasket) provide for electrical contacts. The half-reactions are the following.

$$Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\,e^-$$
$$Ag_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Ag(s) + 2\,OH^-(aq)$$
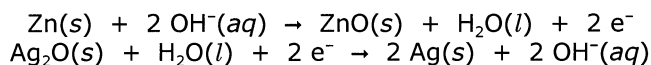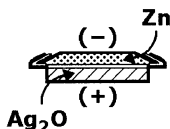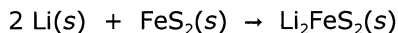
This cell gives 1.55 V, and very reliably so. The cost of silver limits its applications to small sizes and small devices although large versions can be found in specialized applications.
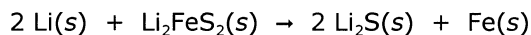
Lithium primary batteries have become quite common and they are available in cylindrical or button versions. Lithium primary batteries use Li(s) as anode. There are two especially important features of the use of lithium as a battery component: Li(s) is a very strong reducing agent so that higher voltages are possible for a single cell, and, lithium has a very low density which means the cells are much lighter than other types of cells. The latter matters more greatly as the battery size increases. As a very strong and very reactive reducing agent, however, there are additional issues for lithium cells; for example, Li(s) reacts directly with water, so these are nonaqueous systems. Various materials are available for the cathode, and cells up to and exceeding 3 V are available depending on the choice of cathode. For example, Li(s) batteries which use MnO_2(s) as cathode are rated ~3 V and these are common in the button format. Batteries with FeS_2(s) as cathode are rated 1.5 V and these are common in cylindrical format to compete with the traditional 1.5 V market. The overall cell reaction with the MnO_2(s) cathode is the following.

$$Li(s) + MnO_2(s) \rightarrow LiMnO_2(s)$$
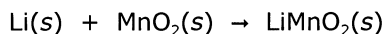
For a cell using the FeS_2 cathode, two reactions are possible.

$$2\,Li(s) + FeS_2(s) \rightarrow Li_2FeS_2(s)$$

$$2 \, \text{Li}(s) \; + \; \text{Li}_2\text{FeS}_2(s) \; \rightarrow \; 2 \, \text{Li}_2\text{S}(s) \; + \; \text{Fe}(s)$$
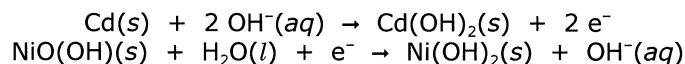
By the way, FeS_2 is not iron(IV) sulfide, although it may look like that from the formula. The anion is actually the disulfide ion, S_2^{2-}, so the compound is iron(II) disulfide.

Feeling drained? Time for a recharge.

Secondary batteries allow for recharging whereas primary batteries do not. Many people often wonder why you can't just apply enough voltage and recharge any battery, including primaries. Well, there are practical limitations to doing this based on the chemical reaction involved or on the physical design of the battery. It's actually quite dangerous to try this with some batteries, since they can leak or explode. If you want to recharge, stick with a battery which is designed for that. Even the rechargeables have some limitations to the number of cycles which they can undergo because some undesired reaction occurs slowly over time; that can lead to loss or degradation of reactants or physical components. Nevertheless, rechargeables commonly can handle hundreds of charge/discharge cycles, and some can do over a thousand. By the way, it takes a proper amount of time to recharge a battery. You can't just send in as many volts and amps as you want, expecting to recharge it faster. There are serious limitations to this, most of which involve ion flow. Those ions are moving as fast as they safely can; they have to find their way through a solution and/or a separator and/or a paste or some other muck, and some have farther to go than others. In addition to ion flow, overcharging can lead to generation of $\text{H}_2(g)$ and or $\text{O}_2(g)$. If you push the system harder with more volts, some rechargeable batteries can overheat, leak and/or explode. Rechargers recharge at an intended rate for a given type of battery; these are designed to balance various factors such as battery design and integrity, as well as the consumer's impatience in wanting it done stat. Don't exceed the recommended rate. And don't use different types of batteries in a recharger which was designed for some other type.

Nicad (NiCd) batteries were one of the first, reliable, rechargeable batteries to achieve widespread use in common devices. The monikers nicad and NiCd relate to the $\text{Ni}(s)$ cathode and $\text{Cd}(s)$ anode which are used in the cells. The half-reactions are the following.
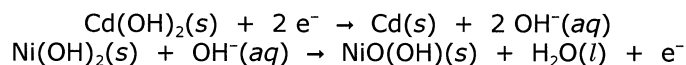
$$\text{Cd}(s) \; + \; 2 \, \text{OH}^-(aq) \; \rightarrow \; \text{Cd(OH)}_2(s) \; + \; 2 \, e^-$$
$$\text{NiO(OH)}(s) \; + \; \text{H}_2\text{O}(l) \; + \; e^- \; \rightarrow \; \text{Ni(OH)}_2(s) \; + \; \text{OH}^-(aq)$$

Despite good performance and widespread usage, the presence of Cd and Cd(OH)_2 in these cells was always a concern due to the toxicity of cadmium and its compounds; these cells constitute health and environmental hazards after use and disposal. The Cd was eventually replaced by a metal hydride anode to give the nickel metal hydride batteries, NiMH or just NMH. The term "metal hydride" can encompass many things; for battery applications, it refers to the product of the absorption of hydrogen into a metal or alloy which results in individual hydrogen atoms mixing in with the metal atoms of the network solid. Those hydrogens are formally the redox active component; the metal itself does not form ions and dissolve in the process. The anode reaction is the following, where M is generic for the metal network.

$$\text{MH}(s) \; + \; \text{OH}^-(aq) \; \rightarrow \; \text{M}(s) \; + \; \text{H}_2\text{O}(l) \; + \; e^-$$
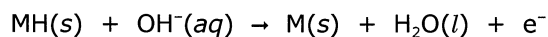
The actual identity of M can vary and mixtures (such as La and Ni) are typically used. The cathode reaction for the NiMH cell is the same as for the NiCd cell above. Both the NiCd and the NiMH cells are rated for ~ 1.2 V. These 1.2 V batteries often work in a device which is rated 1.5 V, but that's because the usual 1.5 V carbon zinc and alkaline batteries typically drop to 1.2 V and lower during their useful lifetime. Nevertheless, some 1.5 V devices will not function properly with NiCd or NiMH batteries.

When the above reactions have proceeded far enough and the batteries are depleted, they are placed into a recharger which sends in electrical energy to reverse the above reactions. This is now an electrolysis. Rechargers commonly operate at several tenths of a volt greater than the rated use voltage for each cell. Let me make a technical point here with some terminology. When you recharge a battery, you are reversing the reaction of the cell; this reverses the roles of the anode and cathode. For example, when you reverse the half-reactions of the NiCd cell, you get

$$\text{Cd(OH)}_2(s) \; + \; 2 \, e^- \; \rightarrow \; \text{Cd}(s) \; + \; 2 \, \text{OH}^-(aq)$$
$$\text{Ni(OH)}_2(s) \; + \; \text{OH}^-(aq) \; \rightarrow \; \text{NiO(OH)}(s) \; + \; \text{H}_2\text{O}(l) \; + \; e^-$$

and now the cadmium half-cell is the cathode and the nickel half-cell is the anode. Be careful with this role reversal for anode and cathode. The terms anode and cathode as used below for other examples of secondary batteries will refer specifically to the galvanic use (discharge).

Lithium ion batteries have been strong performers in the secondary battery market in recent years and their uses will likely increase. Note that there is a distinction between a lithium battery and a lithium

ion battery; the latter does not use elemental Li(s). Although Li(s) is used in primary cells (above), there are technical problems with reducing Li$^+$ back to Li metal during a recharge and these problems preclude the widespread use of Li(s) in secondary batteries. (These are much more prone to catastrophic failure, including fire.) Lithium ion cells use Li$^+$ but not in a direct redox role; they are instead a vital part of the ion flow within the cell. Various combinations of anode and cathode materials are again available, and we will only consider one combination here.

A typical anode material involves graphite. As described in Section 38.4, C(*graphite*) is a two-dimensional network of sheets lying on top of each other, with the sheets held by IFs (dispersion). This 2D sheet structure permits things to get in between the layers, and that can include metals. When graphite reacts with an alkali metal, the alkali metal reduces the graphite and the resulting metal ions go in between the sheets, spreading the sheets apart a bit. The general sheet structure of the reduced graphite is maintained, but now there are additional electrons delocalized within each sheet which came from the alkali metal. You can actually do this reaction to varying extents, meaning there can be varying numbers of carbon atoms per added electron. We will represent this generically by C_x^-, which means one electron has been added to a graphite sheet for every x number of carbon atoms. In the case of lithium, we represent this as LiC$_x$ which means there is one Li$^+$ ion for every x number of carbon atoms. These LiC$_x$ materials are yet very strong reducing agents, although not as strong as Li metal. Nevertheless, these are still high voltage devices and they must still be nonaqueous. A key feature is that LiC$_x$ is far more reliable as a rechargeable cell component than is elemental Li(s). During use, the anode reaction is the following.

$$LiC_x \rightarrow Li^+ + x\,C(\textit{graphite}) + e^-$$

The graphite sheet loses electrons; at the same time, Li$^+$ ions leave from between the graphite layers and become part of the ion flow through the nonaqueous medium.

A typical cathode material is composed of Li$_y$CoO$_2$ with $y < 1$ but y can vary. This is another network solid which is composed of layers, although a bit differently from graphite layers. Cobalt and oxygen ions make up the layers and each layer is now 2 - 3 atoms thick; Li$^+$ ions reside in between those layers. Some of the cobalts have oxidation number 3 and some have 4, and the latter makes this material a very strong oxidizing agent. Formally, we can look at this material as a mix of LiCoO$_2$ and CoO$_2$, and the reduction occurs for the CoO$_2$.

$$CoO_2 + e^- + Li^+ \rightarrow LiCoO_2$$
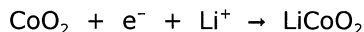
Li$^+$ ions are taken up by the solid during the process. Thus and overall, during operation of the whole cell, Li$^+$ ions are released at the anode (from LiC$_x$) and taken up by the cathode (to form LiCoO$_2$), hence the name lithium ion battery. There is also a lithium salt serving as the electrolyte in the nonaqueous solvent. Since these are still high energy and high hazard devices, a typical battery pack contains sensors and a microcomputer to help prevent a catastrophic failure.

For our final example here of secondary batteries, we turn to the long-standing, traditional workhorse: the lead-acid battery used in automobiles, other vehicles, and other applications. We'll detail this a bit more and illustrate some of the other aspects which can be involved.

A typical car battery is composed of six cells. The whole reaction for each cell is the following.

$$Pb(s) + PbO_2(s) + 2\,H^+(aq) + 2\,HSO_4^-(aq) \rightleftharpoons 2\,PbSO_4(s) + 2\,H_2O(l)$$
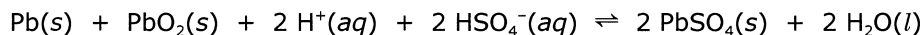
This is called a lead-acid battery because Pb(s), PbO$_2$(s) and PbSO$_4$(s) are the redox components and these react in the presence of sulfuric acid (H$^+$ + HSO$_4^-$). The concentration of sulfuric acid is ~4.7 M, so this is a very corrosive solution. The actual potential of each cell is rated ~2.1 V. The electrodes for both cells are usually a lead alloy, made in such a way as to have a highly porous structure. The anode reaction is the following.

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$$

The oxidation of lead metal produces insoluble lead(II) sulfate, which sticks to the electrode surface and pores. The cathode reaction is the following.

$$2\,e^- + PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) \rightarrow PbSO_4(s) + 2\,H_2O(l)$$

The reduction of lead(IV) oxide also produces lead(II) sulfate, which again sticks to the electrode surface and pores.

All redox components are insoluble solids and they all adhere to the electrodes themselves. The adhesion is critical, since it keeps the redox materials in close proximity to the Pb electrodes and available for reaction. Other batteries can involve solids but the solids may precipitate elsewhere in the cell. Furthermore for the lead-acid battery, there is no significant amount of $Pb^{2+}(aq)$, so there are no soluble redox ions which can migrate from one electrode to another. Because of this characteristic, there is no need to physically separate the half-cells, so there is no need for a salt bridge or any kind of separator membrane. This is a HUGE advantage because salt bridges and separators impede current flow and they decrease the operating voltage. Now, the cathode and the anode are spaced closely together (but not touching) in each cell with only an acid solution containing a high concentration of ions between them; the acid solution allows for an extremely high current flow. In this way, the lead-acid battery can deliver a lot of amps and that is its job when starting your car, even though the voltage drops considerably while doing so. Once your engine is running, the engine turns the alternator which sends electrical energy back into the battery in order to recharge it electrolytically.
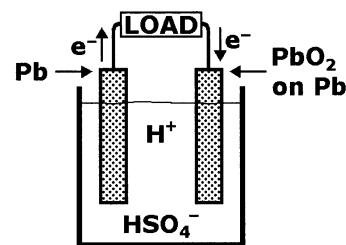
The lead-acid battery has been a very good workhorse doing what it has needed to do for many decades, and a modern lead-acid battery is much improved over those of not many decades ago. Nevertheless, it does have major disadvantages which are tempering its present uses and will limit its future. Yes, it effectively delivers a lot of amps on demand for a brief period of time in order to start your car, even in cold weather. Your starter could be pulling 100, 200, or even more amps when you turn the key. That's a lot of current by typical standards and that is why the cables attached to your battery are so thick. Compare that to the 100-W household lamp bulb of Section 62.3 which pulls a mere 0.83 A, albeit at 120 V. Many small homes are only rated for 100 A service, so your battery is delivering more current than such a home is using. Of course, the battery can only do this for a brief period. A lead-acid battery can also undergo an extremely large number of charge/recharge cycles, even more than other rechargeable batteries of any size. Due to supply, demand and development over many years, the lead-acid battery is also relatively cheap for its capability.

But it's still based on lead and it still requires a lot of strong acid. The latter is a significant hazard in handling these batteries, since the acid can leak out over time. Sulfuric acid does not evaporate at normal temperatures; if you have any liquid residue on the top of your car battery which does not dry out, it's likely to be sulfuric acid and it can chemically burn you. It's also probably eating your battery posts and connectors, giving them an off-white growth or even green/bluish if it's eating into the copper connections. Be careful anytime you are around one.

As with any aqueous battery, overcharging can lead to the production of some $H_2(g)$ which can ignite with a spark. Fortunately, modern batteries are much less prone to this than those of years ago but it's still possible. But this is a common problem for many rechargeable batteries anyway.
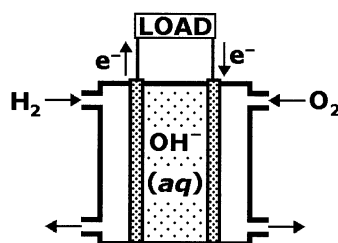
Serious drawbacks remain with the use of lead and lead compounds due to health and environmental concerns, along with the density. The majority of the environmental concerns are addressed by recycling efforts, but there are still releases. The density, especially of the lead itself, makes these batteries very heavy. An electric car powered by these types of batteries would consume a large amount of energy just to carry the batteries around. Although some electric vehicles do use these, this is not a good, long term solution on the big scale. The NiMH batteries have been powering vehicles for some years now, especially in hybrid vehicles. Lithium ion batteries are more recent players on the vehicle scale.

The survey of batteries here illustrates only a small portion of the diversity of types and chemistries available. While batteries have been everywhere doing all sorts of things for over a hundred years, the search for better continues. A fuel cell is an extension of the battery concept. A primary battery starts with some amount of reactants which are then depleted during use; the battery is then discarded. A secondary battery starts with some amount of reactants which are then depleted during use; the battery is then recharged to restore the amounts of reactants. In a fuel cell, a fresh supply of reactants is constantly fed into the battery; the fuel cell continues running unless the supply is cut off. Thus, the fuel cell is not a closed package like a battery; instead, the fuel cell is an open system with new materials continually coming in and exhaust products continually going out. Fuel cells typically use a combustion reaction to generate electricity. Fundamentally, combustion reactions are redox reactions and they tend to be high energy reactions. In a fuel cell, much of the chemical energy of the combustion is converted to electrical energy directly; as such, these can be very efficient. This contrasts sharply with electricity

from a typical combustion-based utility; these convert chemical energy to heat and then to mechanical energy and then to electrical energy, with losses at each step.

By far, the most-used fuel in fuel cell applications is $H_2(g)$. The development of these fuel cells received tremendous impetus from the space program over 4 - 5 decades due to the need for large electrical capacity and light weight. Space vehicles routinely carry H_2 and O_2 as cryogenic liquids which are therefore very compact; this, however, is not available to a typical earth-bound application which must store these as gases at high pressures. Nevertheless, the uses of fuel cells have extended into other markets such as backup power sources and service in remote locations, where fuel cells are often preferred over stationary battery systems. Additional uses are growing and are projected, and there is interest in the vehicle market if the hydrogen portability issue can be resolved. Ironically and unfortunately, the largest source of H_2 produced industrially is from fossil fuels, and several tons of CO_2 are released for every ton of H_2 produced. Thus, this does not eliminate the problems associated with fossil fuel combustion. At least not yet.

Although there are other fuels used in lesser applications, we look only at the H_2/O_2 fuel cell. Even here, there are many different designs for different sets of conditions. The present description is for one of the oldest, the alkaline fuel cell (AFC), and a basic setup is shown at left. The gases enter from separate sides and come into contact with the electrodes, which are porous conductors or some composite design involving membranes. The central area is a strongly basic aqueous solution. The overall reaction is simple combustion

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(l)$$
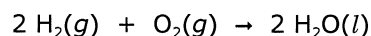
whose anode and cathode half-reactions are the following.

$$H_2(g)\ +\ 2\ OH^-(aq)\ \rightarrow\ 2\ H_2O(l)\ +\ 2\ e^-$$
$$O_2(g)\ +\ 2\ H_2O(l)\ +\ 4\ e^-\ \rightarrow\ 4\ OH^-(aq)$$
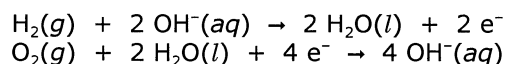
The H_2 enters the fuel cell and permeates into the electrode. Electrons are removed and these are channeled into the external circuit. The remaining H^+ ions migrate through, reaching the basic solution where they are neutralized to form H_2O. On the other side, O_2 enters the fuel cell and permeates into its electrode. Electrons from the external circuit reduce the O_2 and the ions migrate into the basic solution where they combine with water to form OH^- ions. As seen by the overall equation, H_2O is produced; over time, this would dilute the OH^- solution considerably. In some systems, some water is vented as $H_2O(g)$ in the exhaust gas of the cell while, in other systems, the alkaline solution is continuously recycled through the cell and the water is partly evaporated while outside the cell. In a closed vehicle such as a space vehicle, the exhaust water is collected, treated, and used for drinking water.

With this, we close the discussion of batteries and fuel cells. Hopefully, you can see some of the diversity of designs and some of the good and the bad which are inherent to them. All of these are redox, electrochemical devices. Again, these are high tech devices and improvements continue to be intensely explored. A major ultimate goal nowadays is widespread use of an electric car, but even rechargeable batteries still get their energy from the electricity generated from fossil fuel combustion at most utility sources. Thus, these are definitely not zero pollution devices although the marketeers will tell you otherwise.

Problems

1. True or false.
   a. For a given cell, if $Q > 1$, then $E > E°$.
   b. For any cell, a more positive E constitutes a greater drive for a reaction to occur.
   c. A battery uses an endergonic chemical reaction to provide electricity.
   d. Recharging a secondary battery constitutes an electrolytic process.
   e. When an automotive battery turns an engine, the energy is provided by the oxidation of lead and reduction of lead(IV) oxide.
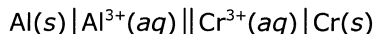   f. Fuel cells generate electricity via combustion.

2. Consider a galvanic cell using the following reaction.

    $$H_2(g) + Br_2(l) \rightarrow 2\,H^+(aq) + 2\,Br^-(aq)$$
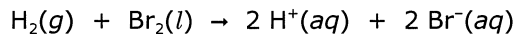
    The cell is operated at the following conditions.

    $P(H_2) = 0.603$ atm   12.4 g Br_2 $[H^+] = 0.0115$ M $[Br^-] = 0.0240$ M
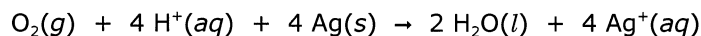
    a. What is $E°$ (in V)?

    b. What is the value of n?

    c. What is E (in V) for the given conditions?

3. Consider the following cell.

    $$Al(s)\,|\,Al^{3+}(aq)\,||\,Cr^{3+}(aq)\,|\,Cr(s)$$

    The cell is operated at the following conditions.

    $[Al^{3+}] = 0.0192$ M $[Cr^{3+}] = 0.00306$ M

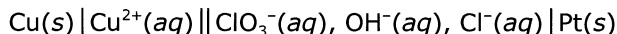   a. What is $E°$ (in V)?

    b. What is the value of n?

    c. What is E (in V) for the given conditions?

4. Consider the following balanced equation.

    $$O_2(g) + 4\,H^+(aq) + 4\,Ag(s) \rightarrow 2\,H_2O(l) + 4\,Ag^+(aq)$$

    The cell is operated at the following conditions.

    $P(O_2) = 0.413$ atm   pH $= 3.64$ $[Ag^+] = 0.0240$ M

   a. What is $E°$ (in V)?

    b. What is E (in V) for the given conditions?

    c. What is the value of K?

5. Consider the following cell.

    $$Cu(s)\,|\,Cu^{2+}(aq)\,||\,ClO_3^-(aq),\ OH^-(aq),\ Cl^-(aq)\,|\,Pt(s)$$

    The cell is operated at the following conditions.

    $[Cu^{2+}] = 0.00627$ M $[ClO_3^-] = 0.00874$ M $[Cl^-] = 0.00362$ M $[OH^-] = 0.00851$ M

    a. What is $E°$ (in V)?

    b. What is E (in V) for the given conditions?

    c. What is the value of K?

6. A galvanic cell is comprised of SHE as the anode and a Ag^+/Ag cathode. If the cell voltage is 0.69 V, what is $[Ag^+]$ (in M)? (SHE stays standard.)

7. Consider a cell running the following reaction at standard conditions.
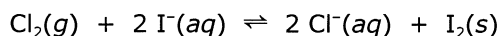
    $$Cl_2(g) + 2\,I^-(aq) \rightleftharpoons 2\,Cl^-(aq) + I_2(s)$$

    For each of the following changes, does E of the cell increase, decrease or stay the same?

    a. Decrease the pressure of Cl_2.

    b. Increase $[I^-]$.

    c. Decrease $[Cl^-]$.

    d. Increase the amount of I_2.

8. Consider a cell running the following reaction at standard conditions.
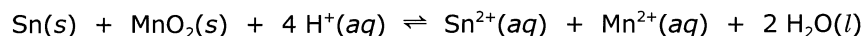
    $$Sn(s) + MnO_2(s) + 4 H^+(aq) \rightleftharpoons Sn^{2+}(aq) + Mn^{2+}(aq) + 2 H_2O(l)$$

    For each of the following changes, does E of the cell increase, decrease or stay the same?

    a. Increase the amount of MnO_2.

    b. Decrease the pH in the cathode compartment.

    c. Increase $[Sn^{2+}]$.

    d. Decrease $[Mn^{2+}]$.

    e. Dilute the cathode solution ten-fold.

9. Consider the following cell.

    $$Pt(s)|NO(g)|NO_3^-(aq), H^+(aq)||SeO_4^{2-}(aq), H^+(aq), H_2SeO_3(aq)|Pt(s)$$

    For each of the following changes, does E of the cell increase, decrease or stay the same?

    a. Increase the pressure of NO.

    b. Increase the pH in the anode compartment.

    c. Increase $[SeO_4^{2-}]$.

    d. Dilute the cathode solution ten-fold.

10. The reaction in each cell of a typical car battery is the following.

    $$Pb(s) + PbO_2(s) + 2 H^+(aq) + 2 HSO_4^-(aq) \rightleftharpoons 2 PbSO_4(s) + 2 H_2O(l)$$

    The actual conditions involve a high concentration of sulfuric acid, and each cell is rated ~2.1 V. Using free energies of formation, calculate $\Delta G°$ (in kJ) and $E°$ (in V) for the reaction.