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.

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

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'll 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 for a whole cell potential. As always, for standard conditions, Q = 1 and $\ln Q$ equals zero; that gives you $E = E°$, which we already knew anyway.

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

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Example 1. For the following reaction,

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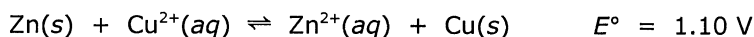
what is the cell potential (in V) when $[Zn^{2+}]$ = 0.0117 M and $[Cu^{2+}]$ = 0.0437 M?

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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.

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   Example 2. Consider the following balanced equation.

$$O_2(g) + 2 H_2O(l) + 4 Ag(s) + 4 Cl^-(aq) \rightleftharpoons 4AgCl(s) + 4 OH^-(aq)$$
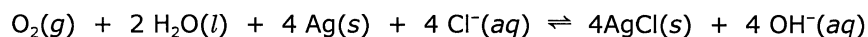
What is E (in V) for the following conditions?

$$P(O_2) = 1.66 \text{ atm} \qquad [Cl^-] = 0.0179 \text{ M} \qquad [OH^-] = 0.00215 \text{ M}$$

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   You need Nernst.

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

You need $E°$; from values in Appendix C, you can derive $E° = 0.18$ V. You need a Q expression,

$$Q = \frac{[OH^-]^4}{P(O_2) [Cl^-]^4}$$

and you need a value for n. Then, plug in.

$$E = 0.18 \text{ V} - \frac{0.0257 \text{ V}}{4} \ln \frac{(0.00215)^4}{(1.66) (0.0179)^4}$$

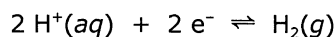$$E = 0.18 \text{ V} - \frac{0.0257 \text{ V}}{4} \ln(1.2538... \times 10^{-4})$$

$$E = 0.18 \text{ V} - \frac{0.0257 \text{ V}}{4} (-8.9841...)$$

$$E = 0.18 \text{ V} - (-0.0577 \text{ V}) = 0.24 \text{ V}$$

Again, this gives $E > E°$.

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

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   Example 3. What is the half-cell potential (in V) for

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

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

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   Nernst.

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

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

SHE is the reference, so $E^\circ_{1/2} = 0.00...$ 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 $[H^+]$, which comes to 8.7×10^{-4} M.

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

$$E_{1/2} = 0.00...\ V - \frac{0.0257\ V}{2}\ \ln(59320...)$$

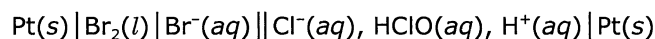$$E_{1/2} = 0.00...\ V - \frac{0.0257\ V}{2}\ (13.293...)$$

$$E_{1/2} = 0.00...\ V - 0.17\ V = -0.17\ V$$

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

Your turn. New reaction.

. . . .

Example 4. Consider the following cell.

$$Pt(s)\,|\,Br_2(l)\,|\,Br^-(aq)\,\|\,Cl^-(aq),\ HClO(aq),\ H^+(aq)\,|\,Pt(s)$$

What is E (in V) for the following conditions?

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

. . . .

You need Nernst

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

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°. (If you're not sure so far, check out Example 6 in the next Section.)

Plug your values into Nernst.

$$E = \underline{\hspace{2cm}} - \frac{0.0257\ V}{}\ \ln \underline{\hspace{4cm}}$$

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

Notice that $E < E^\circ$.

These four Examples show general applications 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.

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Example 5. Example 3 involved reduction at a hydrogen electrode with pH = 3.06 and $P(H_2) = 0.449$ atm. Now keep $P(H_2) = 0.449$ 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.

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

$$\ln Q = \frac{2}{0.0257 \text{ V}} [0.00... \text{ V} - (-0.12 \text{ V})] = 9.3385...$$

Antiln.

$$Q = e^{9.3385...} = 11367...$$

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

Re-arrange for $[H^+]$ and then pH.

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

$$[H^+] = 0.0063$$

$$pH = 2.20$$

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.

$$O_2(g) + 2 H_2O(l) + 4 Ag(s) + 4 Cl^-(aq) \rightleftharpoons 4AgCl(s) + 4 OH^-(aq)$$
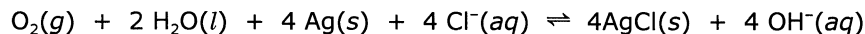
In order to increase the potential of the cell, you could

increase $P(O_2)$ or $[Cl^-]$ or both

and/or

decrease $[OH^-]$.

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 balanced 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, Q and time.

❝ For any of the allowed processes described here, the driving force decreases as the reaction occurs. For any exergonic reaction, the greatest driving force (the 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.

Let's now look at this from a somewhat different perspective. Consider the progress of an equilibrium system 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 present illustration purposes, we specify that $\Delta G°$ is negative. We additionally specify that at least one solute or gas is present on both sides of the balanced equation and that the starting amounts of solutes and/or gases result in $Q < 1$ initially. For $Q < 1$, $\ln Q$ will be negative. Under these conditions, the 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 L→R direction, then we can note the following.

The amounts of products increase on the right and this increases the numerator of Q.
The amounts of 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).
This makes ΔG less negative.
This means the driving force weakens.

This is reflected in the diagram at right which now introduces a time component. Initially, ΔG is some negative number at time zero; this becomes less negative as time goes on. Ultimately, the system reaches $\Delta G = 0$ and there is then no net driving force. Even though there will be some amount of each reagent on the left and on the right, there is no net change in their amounts. The reaction is "done". ❞
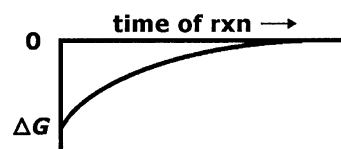
Now here we are in Chapter 64 and all of that remains applicable. Consider again the above quote, now paraphrased in a different light, replacing the driving force of ΔG with the push/pull of E. Note the parallel (even though the signs of ΔG and E are opposite):

For any of the allowed processes described here, the push/pull decreases as the reaction occurs. For any exergonic reaction, the greatest push/pull (the 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.

Let's now look at this from a somewhat different perspective. Consider the progress of an equilibrium system in terms of the general E equation.

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

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

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

For present illustration purposes, we specify that $E°$ is positive. We additionally specify that at least one solute and/or gas is present on both sides of the balanced equation and that the starting amounts of solutes and/or gases result in $Q < 1$ initially. For $Q < 1$, $\ln Q$ will be negative. Under these conditions, the 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 L→R direction, then we can note the following.

The amounts of products increase on the right and this increases the numerator of Q.
The amounts of reactants decrease on the left and this decreases the denominator of Q.
As a result, the value of Q = R/L increases.
The term, [0.0257 V/n] 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 which now introduces a time component. Initially, E is some positive number at time zero; this becomes less positive as time goes on. Ultimately, the system reaches E = 0 and there is then no net push/pull. Even though there will be some amount of each reagent on the left and on the right, there is no net change in their amounts. The reaction is "done".
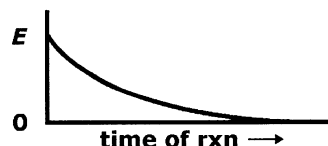
That ends the comparison to the quote from Section 47.2. It is important to keep in mind this parallel between ΔG and E.

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

$$Zn(s) \ + \ Cu^{2+}(aq) \ \rightleftharpoons \ Zn^{2+}(aq) \ + \ Cu(s) \qquad E° \ = \ 1.10 \ V$$
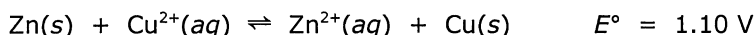
Let's say we set up a whole cell at equal concentrations of the metal cations, $[Cu^{2+}]$ = $[Zn^{2+}]$ = 0.0100 M. For purposes of convenience in this illustration, we will assume equal volumes of 1.00 L for each of the two half-cells, so that mole and molar numbers are the same. Thus, the reaction starts with 0.0100 mol each of Cu^{2+} and of Zn^{2+}. 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 0.0075 mol Cu^{2+} remaining and 0.0125 mol Zn^{2+} total; now, Q = 1.7. Plugging that into Nernst will get you E = 1.09 V. After 75% reaction, we have 0.0025 mol Cu^{2+} remaining and 0.0175 mol Zn^{2+}; 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 × 10^{37}).

Equilibrium is cell death. Although the forward and reverse reactions can occur at equilibrium as long as they are in balance, we still have ΔG = 0 and E = 0. There's no net drive and there's no push/pull remaining. 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

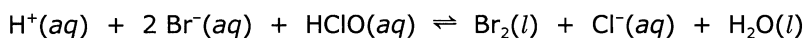$$-RT \ \ln K \ = \ -nFE°$$

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.

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

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

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   Example 6. Consider the equation from Example 4 in the prior Section, for which $E°$ = 0.41 V and n = 2.

$$H^+(aq) \; + \; 2\,Br^-(aq) \; + \; HClO(aq) \; \rightleftharpoons \; Br_2(l) \; + \; Cl^-(aq) \; + \; H_2O(l)$$

What is K for this reaction?

. . . .

Use the $E°/K$ equation from above.

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

Re-arrange.

$$K \; = \; e^{nE°/(0.0257 \text{ V})}$$

Plug in.

$$\frac{nE°}{0.0257 \text{ V}} \; = \; \frac{2\,(0.41 \text{ V})}{0.0257 \text{ V}} \; = \; 31.906...$$

$$K \; = \; e^{31.906...} \; = \; 7.2 \times 10^{13}$$

That is another large K which is common for 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 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, large and small. Many of the historical applications were started before electrical grids were established (which is still true in some areas), or were based (and still are) on portability of the power supply, which simply means the ability to move around without staying plugged into a utility power line or a generator of some sort. Electric vehicles are a major application of a portable electrical system. Besides mobile applications, however, the use of large, stationary battery systems have also increased in recent decades, extending into energy storage systems which can back up the grid for emergencies or for smoothing the variations in energy provided by some sources such as solar, tides or wind.

As previously noted (Section 62.1), batteries can be composed of a single cell or they can be composed of multiple cells. There are single-use batteries which are discarded (or recycled) after their useful lifetime; these are called primary batteries. There are rechargeable batteries which can be used and recharged and used and recharged, etc., etc., through a number of cycles; these are called secondary batteries. The usage part for the secondary battery is galvanic, but the recharge part of the cycle is 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 galvanic direction.

Common and familiar batteries cover a range of sizes and shapes from the small button batteries of hearing aids up to large vehicle batteries. Less common batteries extend the range further. 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 zinc-carbon, alkaline, silver oxide, lithium, NiCd, NMH, etc. Although most of our discussion of galvanic cells so far have involved aqueous solutions in separate half-cells, battery configurations have a broad range of design. They all have an anode and a cathode and they all have some electrolyte solution or other medium between them to allow ion flow. Many use pastes for the electrolyte instead of homogeneous solutions; some even use solids to conduct ion flow. Some cannot have water present and they have an electrolyte solution which is nonaqueous (and flammable). 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. Of course, the job of the battery is to provide electron flow to an external circuit, but you can't have external electron flow without internal ion flow.

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

The common, cylindrical primary cells which have powered many toys, flashlights, etc. around the world for many decades are usually of classical zinc-carbon type or of alkaline type. Sizes vary from AAAA through D, with bigger sizes carrying more capacity which means they can deliver more electrons at a suitable voltage. 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 the 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 in 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. Representative half-reactions for the early zinc-carbon cell are the following.


$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$
$$2\ MnO_2(s) + H_2O(l) + 2\ e^- \rightarrow Mn_2O_3(s) + 2\ OH^-(aq)$$
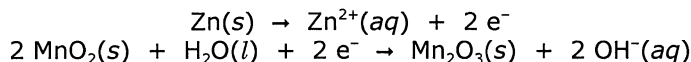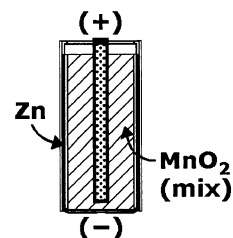
The electrolyte paste contains NH_4Cl and/or $ZnCl_2$ and is slightly acidic. The NH_4Cl reacts with OH^- to form NH_3 which reacts with Zn^{2+} to form a complex, such as $Zn(NH_3)_2Cl_2$. A later version of this battery does not include the NH_4Cl and has more $ZnCl_2$. Both versions still find considerable use but they have been on the wane for years, losing ground to alkaline batteries. In alkaline batteries, the cathode half-reaction is the same as above, but the anode half-reaction is the following.

$$Zn(s) + 2\ OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\ e^-$$
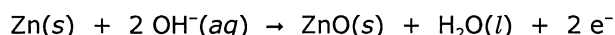
Zinc powder is used in this battery. Consistent with its name, the alkaline battery has an electrolyte with a high KOH concentration. The alkaline battery is a more substantial refinement of the prior zinc-carbon battery. All of these batteries are rated for ~1.5 V service. If you combine six small cells 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 being drawn from an echem device, so a battery operates at less than its open circuit voltage. Furthermore, the voltage decreases over time with more use, or even without more use due to shelf-life. A goal is to have a consistent voltage, but this is not always 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 compared to the types of devices which use standard AAA-through-D cells. While there are some alkaline button batteries, many button batteries are of silver oxide type or of lithium type. A typical construction is shown at left for a silver oxide battery. The Ag_2O serves as cathode while the anode is again Zn, which is now finely divided. A separator divides the zinc anode compartment 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.

$$Zn(s) + 2\ OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\ e^-$$
$$Ag_2O(s) + H_2O(l) + 2\ e^- \rightarrow 2\ Ag(s) + 2\ OH^-(aq)$$
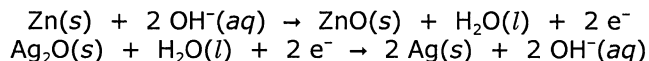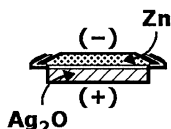
This cell gives 1.55 V, and very reliably so. The cost of silver typically limits its applications to small sizes and small devices, but large versions can be found in specialized applications.

Lithium primary batteries have become increasingly common and they are available in cylindrical or button versions. Lithium primary batteries use $Li(s)$ as the 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 batteries utilize a nonaqueous (and flammable) solvent. There are a considerable number of choices available for the cathode, and cells up to and exceeding 3 V are available. For example, $Li(s)$ batteries which use $MnO_2(s)$ as cathode are rated ~3 V and these are common in the button format. The half-reactions are the following.

$$Li(s) \rightarrow Li^+(soln) + e^-$$
$$MnO_2(s) + Li^+(soln) + e^- \rightarrow LiMnO_2(s)$$
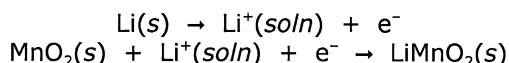
As another example, batteries with $FeS_2(s)$ as cathode are rated ~1.5 V and these are common in cylindrical format to compete in the traditional 1.5 V market. The anode half-reaction is the same as above, while the cathode can involve two different half-reactions.

$$FeS_2(s) + 2 Li^+(soln) + 2 e^- \rightarrow Li_2FeS_2(s)$$
$$Li_2FeS_2(s) + 2 Li^+(soln) + 2 e^- \rightarrow 2 Li_2S(s) + Fe(s)$$
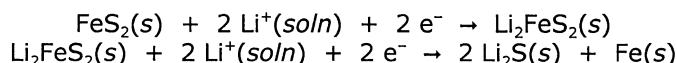
Notably, FeS_2 is not iron(IV) sulfide, although it may look like that from the formula. The anion is actually the disulfide ion, S_2^{2-}, so the compound is iron(II) disulfide.

The cylindrical lithium batteries are constructed differently from the zinc-carbon and alkaline cylindrical cells described above. Individual layers of anode/separator/cathode are sandwiched together, rolled up, and then placed into the can of the cylinder to give a "jellyroll" configuration, giving a better performance of the battery overall.

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 and/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 can occur slowly over time; that can lead to degradation of reactants or physical components. Nevertheless, many rechargeables can handle hundreds of charge/discharge cycles, and some can do over a thousand. 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 the generation of $H_2(g)$ and $O_2(g)$. 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 construction 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.

NiCd (or nicad) batteries were one of the first, reliable, rechargeable batteries to achieve widespread use in common, consumer devices. The labels NiCd and nicad relate to the use of Ni and Cd components which are used in the cells. The half-reactions are the following.
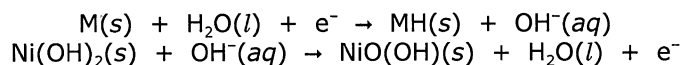
$$Cd(s) + 2 OH^-(aq) \rightarrow Cd(OH)_2(s) + 2 e^-$$
$$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$$
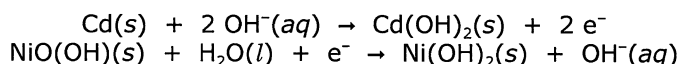
Despite some good performance and very widespread usage, the presence of Cd and $Cd(OH)_2$ in these cells was always a concern due to the toxicity of cadmium and its compounds; these cells constitute health and environmental hazards after use and disposal, although there are recycle programs available. While there are yet some specialized applications, consumer uses have dwindled, largely replaced by nickel metal hydride batteries, NMH (or NiMH). 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. The cathode half-reaction is the same as in the NiCd batteries, while the anode reaction is the following, where M is generic for the metal network.

$$MH(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^-$$
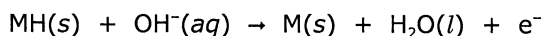
The actual identity of M can vary, and alloys (such as La and Ni) are typically used. The M:H ratio can also vary. Both the NiCd and the NMH cells are rated ~1.2 V. These 1.2 V batteries typically work in a device which is rated for 1.5 V, but that's because the usual 1.5 V zinc-carbon and alkaline batteries typically drop to 1.2 V and even lower during their useful lifetime. Nevertheless, some 1.5 V devices do not function properly with NiCd or NMH batteries.

The construction of the NiCd and NMH batteries follow the jellyroll design, as do the lithium ion batteries (below).

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 battery. Let me make a technical point here with some terminology. When you recharge a battery, you are reversing the reaction of the cell(s); this reverses the roles of the anode and cathode. For example, when you reverse the half-reactions of an NMH cell, you get

$$M(s) \ + \ H_2O(l) \ + \ e^- \ \rightarrow \ MH(s) \ + \ OH^-(aq)$$
$$Ni(OH)_2(s) \ + \ OH^-(aq) \ \rightarrow \ NiO(OH)(s) \ + \ H_2O(l) \ + \ e^-$$

and now the metal hydride 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 their galvanic use (discharge).

Lithium ion batteries have been the stellar performers in the secondary battery market in recent years over an ever-increasing range of applications. Let me note that there is an important distinction between a lithium battery and a lithium <u>ion</u> battery; the latter does not have elemental $Li(s)$. Although elemental $Li(s)$ is used in primary batteries (above), there are technical problems with reducing Li^+ back to Li metal during recharge in a secondary battery, and these systems are much more prone to catastrophic failure including fire. These problems have limited the widespread use of $Li(s)$ in secondary batteries, although research to alleviate this problem is ongoing. Lithium ion batteries use Li^+ but those ions themselves do not undergo oxidation or reduction; they are instead a vital part of the ion flow within the cell. Various combinations of anode and cathode materials are again available covering a range of voltages. I'll highlight one combination here.

Typically, the 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). In the background chemistry, it had long been known that this 2D sheet structure permitted things to get in between the layers, and that could include metal atoms. When graphite reacts with an elemental alkali metal, the alkali metal reduces the graphite and the resulting alkali 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 from the alkali metal which are now delocalized within each sheet of carbon atoms. You can actually do this reaction to a varying extent, meaning there can be varying numbers of electrons per sheet. For reaction with Li, the maximum number of electrons per sheet comes out to one electron for every six atoms of C in the sheet; we can represent this by C_6^-. The neutral product of this process is then denoted LiC_6, although this is simply an empirical formula and it does not imply a true chemical unit.

These LiC_6 materials are yet very strong reducing agents, although not as strong as Li metal itself. Nevertheless, these still allow for high voltage devices and they are still nonaqueous (and flammable). A key feature is that LiC_6 is far more reliable in a rechargeable cell than is elemental $Li(s)$. During use, the anode reaction is the following.

$$LiC_6 \ \rightarrow \ Li^+ \ + \ 6 \ C(graphite) \ + \ e^-$$

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 common cathode material for some time was composed of Li_yCoO_2, with $y < 1$ depending on the state of charge/discharge. This is another network solid which is composed of layers, although differently from graphite layers. Cobalt and oxygen ions make up the layers and each layer is now 2 - 3 atoms thick; Li^+ ions reside 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 and for simplicity, we can look at this material as a mix of $LiCoO_2$ and CoO_2, and the CoO_2 is reduced to produce more $LiCoO_2$.

$$CoO_2 \ + \ e^- \ + \ Li^+ \ \rightarrow \ LiCoO_2$$
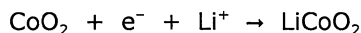
The Li^+ ions are taken up by the solid during the reduction. These cells are rated for ~3.6 V. Due to the high cost of cobalt, more recent versions have been developed using mixtures of metal oxides involving various combinations of Ni, Mn and Al, with or without Co.

Overall, during operation of the whole cell, Li^+ ions are released at the anode (from LiC_6) 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 electronics to help prevent a catastrophic failure.

Lithium ion secondary batteries are a huge deal for the future electrification of human society. One of the biggest applications in the eyes of the general public is electric vehicles, whose future (including cost) is highly dependent on the battery. Each battery type carries a host of properties, and there are pros and cons along the way in design and selection of the chemistry and engineering involved. Of course, the battery must deliver sufficient electrons at sufficient volts and amps, but it must also be suitably long lived, efficient to recharge, lightweight, affordable, safe, and environmentally benign from cradle-to-recycle. NMH batteries powered hybrid and electric vehicles for years, but newer models are switching to lithium ion batteries. One area of concern in lithium and lithium ion batteries has been the flammable solvent used for the electrolyte, but solid (dry) electrolytes are being developed wherein the Li^+ ions now pass through channels in a solid instead of migrating through a solvent. Another area of concern is that lithium is not a very available element on Earth; that drives up costs, but that is where recycling would come in. On the other hand, electric vehicles stand to reduce CO_2 emissions somewhat, but the electricity for recharging still comes predominantly from the combustion of fossil fuels. As such, these are definitely not zero emission devices although the marketeers will tell you otherwise. Overall, the challenges and the benefits are immense.

For our final example here of secondary batteries, we turn from the promise of the present and future to the workhorse of the past: the lead-acid battery used in automobiles, other vehicles, and a great many other applications historically. These were the first rechargeable batteries to become commonly available. There are various versions of the lead-acid battery depending on its purpose; there are even different versions which are intended for the same purpose. Let's look at some basics for a typical car battery.

A typical, 12 V, 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 in the range of 30-50% w/w, depending on the specific design of the battery; since it is a reactant, its concentration decreases while discharging. The actual potential of each cell is rated ~2.1 V. Both electrodes are usually a lead alloy, made in such a way as to have a highly porous structure. The cathode is additionally coated with PbO_2. 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. A simple version is shown at right.
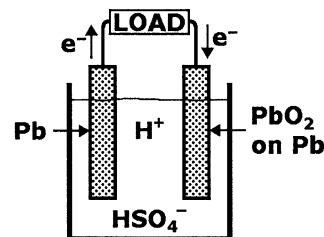
All redox components are insoluble solids and they all adhere to the electrodes themselves. The adhesion is a HUGE advantage, since it keeps the redox materials in contact with the electrodes and readily available for reaction. (The adhesion is not perfect, however, and some material can slough off the electrode over time, impacting battery life.) Importantly, 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, although a spacer is commonly used to keep the electrodes from touching. Now, the cathode and the anode are very close together, with only an acid solution containing a high concentration of ions between them; this 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 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 battery could be providing 200, 400, 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. 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. 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. More recent versions are more effectively sealed to prevent leaks.

Serious drawbacks also lie 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 for the lead which are actually very efficient, with estimates of up to $\sim$100% (in the U.S.). Processing of the lead, however, is often done globally without regard to human and environmental safety. 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 have used these, this is not a good, long term solution on the big scale. Stationary applications of the lead-acid battery, such as in backup power systems, grid energy storage, etc., are less impacted by the weight issue.

The survey of batteries here illustrates only a small portion of the diversity of types and chemistries available. While batteries have been powering all sorts of things for over 150 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 cell; the fuel cell continues running until 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 continuously coming in and exhaust products continuously going out. Fuel cells use a combustion reaction to generate electricity. Fundamentally, combustions of fuels 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 without a flame; 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 5 - 6 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 $H_2(g)$ at high pressures, although O_2 is readily available from air. Nevertheless, the uses of fuel cells extend into other markets such as backup power sources and service in remote locations, where fuel cells are often preferred over battery systems. Additional uses include vehicles, but hydrogen portability and availability are issues. Ironically and unfortunately, the largest sources of H_2 globally are 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.
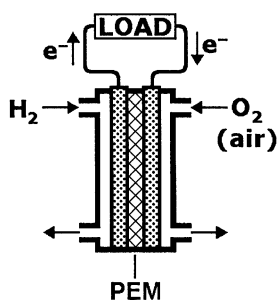

Let's consider a H_2/O_2 fuel cell more closely. There are actually several different designs for different sets of conditions. The description provided here is for a proton-exchange membrane fuel cell, PEMFC. A basic diagram is shown at left. The overall reaction is simple combustion

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$
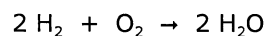
whose anode half-reaction is

$$H_2 \rightarrow 2\,H^+ + 2\,e^-$$
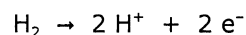
and whose cathode half-reaction is the following.

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$
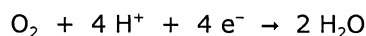
The gases enter from separate sides and come into contact with their separate electrodes; excess gases are vented. The anode includes a layer of Pt on carbon, serving as a catalyst. The catalyst breaks the H–H bond, the electrons are shuttled into the external wiring, and the protons migrate into and through

the proton-exchange membrane (PEM, also known as a polymer electrolyte membrane). Upon reaching the cathode, another Pt/C layer catalyzes the reduction of O_2 with H^+ (from the PEM) and electrons returning from the load. The H_2O product of the reaction can be present as liquid or gas, but excess H_2O exits as gas on the O_2 side. A single cell can generate 0.6 - 0.7 V depending on load; multiple cells are stacked to provide a desired voltage.

While it was noted upstairs that lithium ion secondary batteries are a big part of the picture, those are not the only stars in the sky. Serving moderate-to-large applications, fuel cells have been part of the picture for years, and stand to contribute further in the future. Extending into other applications still has some hurdles, however. Other methods of H_2 production which do not involve the release of massive amounts of CO_2 must be ultimately developed.

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. Chemistry is at the heart of these systems, even down to the materials used in the design of the cells. Again, these are high tech devices and improvements continue to be intensely explored. For many, their future will overshadow their past and present.

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. Recharging a secondary battery constitutes a galvanic process.

    d. When an automotive battery turns an engine, the energy is provided by the oxidation of lead and reduction of lead(IV) oxide.

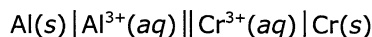   e. Fuel cells generate electricity via combustion.

2. Consider a galvanic cell using the following reaction.

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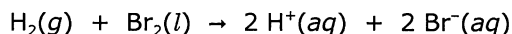
    The cell is operated at the following conditions.

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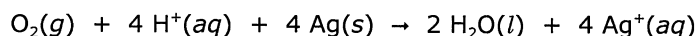
    a. What is $E°$ (in V)?

    b. What is the value of n (in mol)?

    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 $\qquad$ $[Cr^{3+}] = 0.00306$ M

    a. What is $E°$ (in V)?

    b. What is the value of n (in mol)?

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

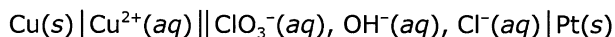4. Consider the following balanced equation.

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

    The cell is operated at the following conditions.

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

$$Cl_2(g) + 2\,I^-(aq) \rightleftharpoons 2\,Cl^-(aq) + I_2(s)$$
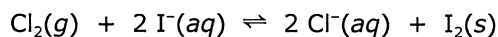
For each of the following changes, does E of the cell increase, decrease or stay the same?

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.
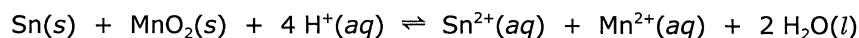
$$Sn(s) + MnO_2(s) + 4\,H^+(aq) \rightleftharpoons Sn^{2+}(aq) + Mn^{2+}(aq) + 2\,H_2O(l)$$

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.

$$Pb(s) + PbO_2(s) + 2\,H^+(aq) + 2\,HSO_4^-(aq) \rightleftharpoons 2\,PbSO_4(s) + 2\,H_2O(l)$$
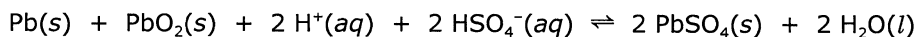
The actual (nonstandard) conditions involve a high concentration of sulfuric acid, and each cell is rated ~2.1 V. Using free energies of formation, calculate the standard value for $\Delta G°$ (in kJ) and then for $E°$ (in V).