Chapter 14 Electrode Potentials
Problems 7, 8, 10, 12, 15, 17

Electrodes- Devices to measure chemical concentrations or activities by either measuring electrical potential (Voltage) or current.

1. Most familiar with pH electrodes - These are actually pretty complicated to won’t look at them for a chapter or two.
2. Electrode can be much simpler; a wire stuck in a solution. These are much easier to figure out so will start off with these in this chapter

Since are dealing with the interaction between chemistry and electricity, guess what kind of chemical reactions we will be working with? Redox So let’s start there.

14-1 Redox Chemistry and Electricity

To make an electrode work, we will have to make electrons run down a wire. How do you do that? Well with a generator you can make magnets push electrons down and wire, but how do you do it chemically? Put a reaction that generates electrons at one end of the wire, and a reaction that uses electrons at the other end of the wire.

Reaction that generates electrons:
A–B + e⁻ (Electron as product so generated an electron)

Reaction that uses electrons:
C+e⁻ → D (Electrons needed as a reactant, so electron using reaction.)

Which reaction is the reduction? Which the oxidation?

A–B + e⁻ electrons on right, oxidation
C+e⁻ → D electrons on left. Reduction

(OIL RIG - Oxidation involves loss, reduction involves gain)

Or, if these were charges compounds with properly balances charges

A⁺→A²⁺ + e⁻ oxidation; oxidation number ↑
C⁺ +e⁻ → C⁰ Reduction; oxidation number ↓

Now a bit of confusing nomenclature

Since A is being oxidized in its reaction, it is the substance being oxidized
Since B is being reduced in its reaction, it is the substance being reduced
Since the reduction reaction can’t occur without an oxidation, A is also called a reducing agent.
Similarly, since the oxidation can’t occur without the reduction reaction, B
is also called the oxidizing agent

Now that you have been reminded about redox reaction, now let’s look at the math
Will see various constants used here, because the physicists set up their units for measuring electricity before the chemists could get their licks in and define using in terms of Avogadro’s number so....

Force (potential?)
E the basic unit of electrical potential or force
(Properly EMF electromotive force).
E is measured in Volts
So all 1.5V batteries, big or small push electrons with the same 1.5V force through a wire

Work
In mechanical systems work = f \cdot d
In electrical systems work = E \cdot q
E, is potential (measured in V, defined above)
q charge measured in coulombs

What the heck is a coulomb?
Since the unit of work in the SI system is Joules, so make everything hang together
A coulomb of charge is defined as the amount of charge that must be moved over a potential of 1 V to give you 1 joule of work

1 J = 1 V \cdot 1 coulomb

Now let’s make this a little more chemical.
A single electron has a charge of 1.602x10^{-19}C
Since chemists deal with moles
A mole of electrons would have a charge of
1.602x10^{-19}C \times 6.022x10^{23} \text{ electrons/mole}
=9.649x10^4 \text{ C/mol electrons}

This is one of the constants I was telling you about

1 Faraday = charge/mole of electrons
=9.649x10^4 \text{ C/mol electrons}
=96,485 \text{ C/mol}
Using our def of electrical work

\[ \text{work} = qE \text{ (or } E \cdot q) \]

Let's measure charge \((q)\) in chemical terms

\[ Q = n \text{ moles of electrons} \times F \]

Work = \(nFE\)

In chemical systems

Energy measures I you have seen

- E Internal energy = sum of energies of all particles in a system
- H Enthalpy = \(E + PV\) Heat released or gained at constant \(p\) in a chemical reaction
- S randomness
- G Free Energy = \(H - T\Delta S\)

Saw as measure of spontaneity
- - if favorable reaction
- 0 if at equilibrium
- + is unfavorable

What probably didn’t get to was that is called Free energy, because it can be thought of as the energy (free & available to do work

And, since a negative \(\Delta G\) will give us positive work

Work = \(-\Delta G\)

Putting the two together

\(nFE = -\Delta G; \)

\(\Delta G = -nFE\) So here is tie between chemical work and electrical work.
14-2 Galvanic Cells

A **Galvanic cell** is one in which a spontaneous chemical reaction generates and electromotive force (emf). **As opposed to an electrolytic cell where the current forces unfavorable chemical reactions.** Example include car batteries, flashlight batteries etc.

The diagram that we use for a galvanic cell is designed to clearly show things like which way electrons move, what material need to be where, where the + and - poles are, but doesn't look much at all like a flashlight battery.

The standard cell diagram looks something like this:

![Figure 1 Galvanic cell](image)

In this starting cell note the following features:
1. a voltmeter to measure the potential between the cells
2. 2 cells holding different solutions
3. electrodes attached to the wires, electrodes may be inert, like platinum, or may be part of the reaction itself, like the lead in a lead-acid battery.

You then build the cell by adding important features.
1. By convention **e flow from left to right.** If you get this right, everything else will follow.
2. if electrons flow from l to r, then the left electron pole must be negative (more negative electrons) and the right must be positive (electrons are attracted to +.)

(Left) + - (Right)

Left negative - Anode, oxidation (anion?); right positive reduction cathode (cation)

(Left) + , Anode - , cathode (Right)
3. If electrons flow from \( l \) to \( r \), then the reactions supplying the electrons must be on the left, reaction consuming the electrons on the right.

   a. If right electrode is consuming electrons, it is the reaction with electrons as a reactant, hence it is the cell in which reduction is occurring.
   
   b. By alternate logic or by elimination left electrode must be where oxidation occurs.

   \[(\text{Left}) +, \text{Anode, oxidation} \quad - , \text{cathode, reduction (Right)}\]

4. Finally have left out one important feature. By now you should know that for electricity to flow you need a closed circuit. Is this a closed circuit? NO. Need some way for ions to move from one cell to other so don’t get charge imbalance. Add a salt bridge between the cells.

Redox reactions, like most chemical reactions are reversible, so they can go forwards or backwards. Guess what the reverse of an oxidation reaction is a reduction, and vice versa.

So if any given redox half reaction can go either forwards or backwards, that is, be an oxidation or a reduction, how can you chose the right reaction for your two different cells?

To decide if a redox reaction will go in the oxidation direction or the reduction direction, chemist use a ‘Table of Standard Reduction Potential’ (have overhead, 1 page Appendix C end of text)

To create this table have written all reactions as reductions (Hence the name Reduction potential) Then linked all reaction with each other to see which were stronger (went in forward reduction direction) and which were weaker (got reversed so went in backward oxidation direction). The reaction that were the strongest reducers got the highest numbers weakest reduction reactions (strongest oxidizing reactions) got the lowest numbers. (More on where the exact number come from in 14-3)

So you use the Table of Standard Reduction Potential to select which reaction goes where. You do this by placing the reaction with the highest standard potential in the RIGHT hand cell so it will go as written, as a reduction. Naturally the reaction with the lowest reduction potential goes on the left, where is gets reversed and becomes an oxidation.

For our example \( 2H^+ + 2e^- \rightarrow H_2 \) has a reduction potential of 0.00 V, \( Pb^{2+} + 2e^- \rightarrow Pb \) has the reduction potential of -.126 V. The hydrogen \( \frac{1}{2} \) reaction has the higher potential, so it will be placed on the right, and the reaction will go in the forward direction (as a reduction) and will consume electrons. The Pb \( \frac{1}{2} \) reaction has the lower potential, so it will be on the left, and the reaction will go in the reverse direction (an oxidation) \( Pb \rightarrow Pb^{2+} + 2e^- \) In this direction the reaction will act as an
electron source.
The overall potential of the cell is given by

\[ E_{cell} = E_r - E_l = E_R - E_L \ ; \ 0.00 - (-0.126) = 0.126 \]

(Book uses \( E_r - E_l \), I personally prefer \( E_R - E_L \))

More on this in a minute.

There is a shorthand convention for writing galvanic cells, where you use a single line to show a change of phase (like between an electrode and to solvent, and a double line to show a salt bridge. For example Pb acid might be represented as:

\[
\begin{array}{c}
\text{Pb} \mid \text{Pb}^{2+} \text{(aq)} \ \| \ \text{H}^+ \text{(aq)} \mid \text{H}_2 \text{(g)} \mid \text{Pt}
\end{array}
\]

Note that on the left here, the metal of the electrode is part of the reaction. On the other hand, on the right, the Pt metal is just there to conduct electrons and does not take part in the reaction.

4. At this point there is one thing missing a salt bridge that completes the circuit. (if wasn't there charge imbalance would create a back emf which would shut down current flow)

Let's try a couple of other examples and see how you do:

Make cells out of

\[
\begin{align*}
\text{Co}^{3+} + \text{e}^- & \rightarrow \text{Co}^{2+} \ E_\circ = 1.92 \ \text{V} \\
\text{Cu}^{2+} + \text{e}^- & \rightarrow \text{Cu}^{1+} \ E_\circ = 0.161 \ \text{V}
\end{align*}
\]

(Co right, Cu left, \( V = 1.92 - 0.161 = 1.759 \))

and

\[
\begin{align*}
\text{Ni}^{2+} + 2\text{e}^- & \rightarrow \text{Ni(s)} \ E_\circ = -0.236 \ \text{V} \\
\text{Cd}^{2+} + 2\text{e}^- & \rightarrow \text{Cd(s)} \ E_\circ = -0.402 \ \text{V}
\end{align*}
\]

(Ni right, Cd left, \( V = -0.236 - (-0.402) = 0.166 \))

14-3 Standard potentials

I just said the way to figure out which chemical to put where was by looking at their standard reduction potentials. What is a standard potential

A standard potential is the potential you measure when you measure a given \( \frac{1}{2} \) reaction against a “Standard” that everyone in the chemical world has agreed on.

This 'standard' cell uses the reaction

\[
\text{H}^+ \text{(aq, } A=1) + \text{e}^- = \frac{1}{2} \text{H}_2 \text{(g, } A=1)
\]

and is called the hydrogen electrode

It is constructed by having \( \text{H}^+ \) at 1 M activity in solution with \( \text{H}_2 \) gas being
bubbled at 1 atmosphere of pressure.

The chemical world has agreed to give this potential a value of 0, and to measure all other potential against it.

Note: Some confusion here about the standard state for gases
some sources give as 1 bar = 100,000 Pa
Some give as 1 atm = 101325 Pa =1.01325 bar
Only a 1% error so don’t sweat it

Appendix C lists lots and lots of half reactions measured against this cell.
Reagents with large positive potentials usually used as the reduction ½ reactions, and thus are considered to have good oxidizing power, while those with large negative numbers are usually the oxidation ½ reactions and are said to have good reducing power.

*Formal Potentials*

Appendix C also occasionally lists additional potentials for instance the
\[ \text{AgCl(s) + e}^- \rightarrow \text{Ag(d) + Cl}^- \]

\[ 0.222 \text{V} \]

\[ 0.197 \text{V} \text{ saturated KCl} \]

The standard potential for a reaction is always measured using standard state concentrations (1M). But sometimes it is more convenient two use some other concentrations, like \( \text{Cl}^- = \text{saturated KCl} \) in this case

When we have a potential measured at a non-standard state we call this a **formal potential**

Biochemical texts are the books that most often use formal potentials. Most biochemical reaction occur at nor near pH 7 so \( [\text{H}^+] = 1 \times 10^{-7} \) NOT 1M. As a result most biochemical reaction are based on formal potentials in which \( [\text{H}^+] = 1 \times 10^{-7} \)

14-4 The Nernst Equation

Chemical potentials are the key to understanding REDOX reaction. They can be related directly to the K or equilibrium values that tell us whether a reaction is favorable or unfavorable.

You have just been exposed to standard potential this is the potential of a reaction when all reactants are at 1M activity, relative to the standard potential. But what about reaction where the reactants are NOT at standard state activities, or when you have two different reactions, rather than one reaction and the standard hydrogen reaction What about then??

The key to determining chemical potentials in non-standard state is the NERNST equation.

For a half reaction
The Nernst Equation is:

\[ E = E^o - \frac{RT}{nF} \ln \frac{A^b_a}{A^a_b} \]
Let’s talk about this. The E° term is the potential if everything is in the standard state, the -RT/nF ln conc term is the term that takes care of things when you aren’t at the standard state. The RT/nF are just some constants that covert a potential measured by concentration to a potential measured in voltage.

R is the gas constant, 8.314510 J/Kmol
T is the temperature in Kelvin, which we will assume to be 298 (25°C)
n is the number of electrons I the half reaction
F is the Faraday Constant (14-1) 9.6485309x10^4C/mole
A are the activity coefficient

The ratio is the same Q ratio that we have used to determine the direction that a reaction will go, ie it looks much like an equilibrium constant, but, the activities are the current concentrations not have to be equilibrium values. Like equilibrium however, when you are dealing with solids or liquids with activities of 1, they are eliminated from the equation.

If we always work at 25°C, most of these constants, plus a constant for convert from ln to log can be lumped together to get the equation:

\[
E = E^\circ - \frac{0.05916}{n} V \log \frac{A_B^B}{A_A^A}
\]

Let's try this out on our introductory cell made with H⁺ and Pb.

Suppose [H⁺] is .05M, H₂(g) is going to be very low, so let’s call it .1 atm. I have no idea what [Pb⁺²] would be so let’s call it .5M . The potential for

\[2H^+ + 2e^- \rightarrow H_2\]

is 0 V

the potential for

\[Pb^{+2} + 2e^- \rightarrow Pb\]

is -.126

\[
\begin{align*}
E_R or E_+ &= E^\circ - \frac{0.059}{2} \log \frac{[H_2]}{[H^+]^2} = 0.00 - \frac{0.059}{2} \log \frac{1}{.05^2} \\
&= -.047 \\
E_L or E_- &= E^\circ - \frac{0.059}{2} \log \frac{Pb(s)}{Pb^{+2}} = -.126 - \frac{0.059}{2} \log 1 \\
&= -.117 \\
E_{cell} &= E_+ - E_- = E_R - E_L = -.047 - (-.117) \\
&= +.070
\end{align*}
\]
And we now have the potential for a cell under non-standard state conditions.

There is one place where I got lucky in this example, the n of the two half reaction was the same, what happens when they are different??

Using an example form the book
if we have
\[ \text{Ag}^{+} + e^{-} = \text{Ag} \quad E = 0.799 - 0.059/1 \log 1/[\text{Ag}^{+}] \]

and
\[ \text{Cd}^{2+} + 2e^{-} = \text{Cd} \quad E = -0.402 - 0.059/2 \log 1/[\text{Cd}^{2+}]^2 \]

How do we handle this??
If we are going to use this in a balanced reaction then the number of electrons must be equal in both half reactions. Thus to get this to balance we need to multiply the Silver reaction by 2
\[ 2\text{Ag}^{+} + 2e^{-} = 2\text{Ag} \]

What does this do to the NERNST equation for this reaction? It
**The \( E^o \) remains the same but n and the powers in the concentration change**

\[ \text{ie } E = 0.799 - 0.059/2 \log 1/[\text{Ag}^{+}]^2 \]

Our overall procedure then is:
1. Write reduction half reaction for both half cells and find \( E^o \) in appendix H. Multiply coefficient in half reaction as necessary to get an equal number of electrons (but Don’t multiply \( E^o \))
2. Write Nernst equation for the Right electrode (more positive \( E \)) (\( E_R \))
3. Write Nernst equation for the Left electrode (most negative \( E \)) (\( E_L \))
4. Find net cell potential =\( E_R - E_L \) or \( E_L - E_R \)
5. To write the balanced reaction use the half reaction of the \( E_+(E_R) \) electrode in the **Forward** direction and the \( E_-(E_L) \) reaction in the **Reverse** direction

Sometimes you can find different sets of reaction that can be combined to give you the reaction you want. It doesn’t matter which set you use, you should get the same answer.
14-5 E° and the Equilibrium constant

The reason you can get electricity from galvanic cells is that they are not at equilibrium. If you wanted to get a cell to equilibrium all you need to do is to run the battery until it dies. At that point it is in equilibrium because it the concentration will not change with time.

(And if it is a car battery you are in for a tow or a jump)

Let’s think about this with our example battery a bit.

\[
\begin{align*}
E_R &= 0.00 -0.059/2 \log[H_2]/[H^+] = E, \\
E_i &= -0.126 -0.059/2 \log[Pb(s)]/[Pb^{2+}] = E, \\
E &= E_{cell} - E_{self} = 0.00 -0.059/2 \log[H_2]/[H^+] - (-0.126 -0.059/2 \log[Pb(s)]/[Pb^{2+}]) \\
E &= E^o_{cell} - E^o_{self} = -0.059 \log[H_2][Pb^{2+}]/[H^+]^2 [Pb(s)]
\end{align*}
\]

Remember we said earlier that the log concentration part of this expression looks like an equilibrium constant, but the concentration did not have to be equilibrium concentrations

Well if our Cell potential is zero, then the concentration cannot change, and we must be at equilibrium.

Thus if

\[
\begin{align*}
E &= 0 = E^o_{cell} - E^o_{self} = -0.059 \log[H_2][Pb^{2+}]/[H^+]^2 [Pb(s)] \\
-E^o_{cell} + E^o_{self} &= -0.059 \log[H_2][Pb^{2+}]/[H^+]^2 [Pb(s)] \\
E^o_{cell} - E^o_{self} &= 0.059 \log[H_2][Pb^{2+}]/[H^+]^2 [Pb(s)]
\end{align*}
\]

And, if we remember that our net reaction is:

\[
2H^+ + Pb(s) = Pb^{2+} + H_2(g)
\]

Then we can see that

\[
E^o = 0.059/n \log K
\]

AND

\[
K = 10^{E^o/0.059}
\]

So for our reaction we have

\[
\begin{align*}
E^o &= 00 -(-0.127) =0.127 \\
K &= 10^{2(-0.127)/0.059} \\
&= 2.02 \times 10^{+4}
\end{align*}
\]

So now we can relate E° to K, and don’t forget the expression

\[
\Delta G = -nFE
\]

That we had at the beginning of the chapter.

\[
\Delta G = -2(96,485)C/mol \times 0.127 V (1V=J/C) = -24.5 \text{kJ/mol}
\]

So now you have three different ways to measure the potential of a chemical reaction
14-6 Electrodes
When you build a cell to measure a potential of a chemical reaction, each pole of the cell contains an electrode that transfers electrons from the solution to the wire or vice versa.

There are two main types of electrodes.
- Indicator electrodes - electrodes that respond to an analyte concentration (next chapter)
- Reference electrodes - electrodes that maintain a fixed potential.

An indicator electrode may be as simple as a piece of Pt wire that is inert, so it doesn’t take part in a reaction, but simply provides a path for the electrons to flow. Many times an indicator electrode may be made of a metal that takes part in the $\frac{1}{2}$ reaction, so indicator electrodes can be simple or more complicated.

We have already talked about 1 kind of reference electrode, the S.H.E. or standard Hydrogen Electrode. This is a great reference electrode, because you know its potential is 0, so there is no built in potential that you have to compensate for. It does have 1 disadvantage. It goes BOOM.

Since chemist’s don’t want to blow up the lab every time they do an experiment, there are two widely used alternative electrode that are much safer to use

Silver-Silver Chloride electrode (Figure 14-9)
- The structure of this electrode is shown in the figure.
- The potential of this electrode is base on the $\frac{1}{2}$ reaction:
  \[
  \text{AgCl(s)} + e^- = \text{Ag(s)} + \text{Cl}^-
  \]
  And it has potentials of +.222 V if you use 1M KCL, or .197 V is you use saturated KCL. Since both Ag and AgCl are solids the only thing that will vary to voltaage of this cell is Cl, hence the two different potentials. The saturated KCL is more reproducible in the lab, because you just add KCl to the electrode until you see crystals, and you don’t need to get the concentrations exactly 1M.

The silver-Silver Chloride is slightly expensive to make, so there is a less expensive alternative
The Calomel Electrode (Figure 14-10)

The potential for this electrode is governed by the equation

\[ \frac{1}{2} \text{Hg}_2\text{Cl}_2(s) + e^- \rightarrow \text{Hg}(l) + \text{Cl}^- \]

again all but Cl are solids to we get 2 potentials

+.268 if KCl=1M, +.241 if KCl is saturated

Given a potential measured against any one of these three common reference electrodes, you need to be able to convert the potential to figure out how it would measure against one of the other electrodes.

Lets' start easy. Say you measured a new potential gains an SHE electrode and found it has a +.2V potential, what would you expect for a potential if you measured it against a Saturated Calomel Electrode?

Problems like this are best determined using a diagram like figure 14-11 from the text. Your measured potential is +.2 relative to 0, and the SCE is at +.241 from 0, so using this electrode you would measure a +.041 (+.241-.2) potential.

Now let's try something more daring

You measure a potential of +.1 relative to a SCE electrode, What would this measure relative to a Ag/AgCl electrode?

+.241 + .1 = .341
+.341-.197 = .144