

Chapter 62

ECHEM, Part 2

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It is now time to take a more circuitous path, at least for the electrons which are transferred during a redox process. We will also now bring electricity into the picture. As noted in the opener for Chapter 61, you can get electrical energy out of an exergonic redox reaction or you can supply electrical energy to do an endergonic redox reaction. Either way, we do this by transferring the electrons from the reductant to the oxidant via some wiring, and the amount of electrical energy will be a consequence of the free energy which is involved.

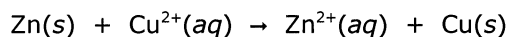
We will now consider a basic setup, some terminology and some concepts. As we go, our emphasis will be aqueous systems, although you can do echem in other solvents, too.

62.1 Cell anatomy

A cell is the physical setup, including reagents, which constitutes a functional electrochemical reaction. As such, the cell includes both half-reactions. In a typical application, the cell is connected by wires to some external device. For an exergonic process, the external device is something we wish to power, such as a motor or a light. For an endergonic process, the wires will go to a power source which will provide the cell with the energy needed for the reaction.

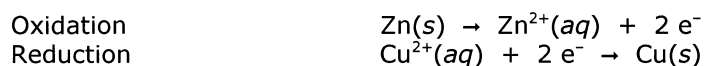
We begin our coverage using an exergonic process. In this application, the cell can serve as a battery. Historically, many common batteries have been called AA-cells, C-cells, etc., but there is a technical distinction between the terms cell and battery that you should be aware of. A cell comprises a single, whole reaction; it generates electrical energy. A battery is composed of one or more cells. The small commercial batteries which deliver 1.2 - 1.5 V, such as AA, C, or any of the various button batteries, tend to be single cells. A battery which can deliver over 3 V is likely composed of multiple cells arranged in series. (I said "likely". There are some cells which do go above 3 V.) For example, a common 3.6 V battery could be composed of three individual cells inside which are 1.2 V each. An automotive battery is typically composed of six cells, each ~2.1 V for a total of ~12.6 V. (That's why there are six caps on the top of the battery, although some caps may be connected to each other.) We're going to discuss various types of batteries in Chapter 64. For now, we are simply dealing with a single cell.

We begin with a reaction which was among the most common and earliest used for batteries, back in the 1800's.



Using values for ΔG_f° from Appendix A, you would be able to calculate $\Delta G^\circ = -212.55 \text{ kJ}$ and then $K = 1.81 \times 10^{37}$ at 25 °C. This is a largely exergonic process which will go completely to the right. Loosely speaking, the large negative ΔG° says that $\text{Cu}^{2+}(aq)$ can take electrons out of $\text{Zn}(s)$ or, alternatively, $\text{Zn}(s)$ can give electrons to $\text{Cu}^{2+}(aq)$. The ΔG° is the measure of the drive behind the give/take. If you were to conduct this reaction by simply placing a piece of $\text{Zn}(s)$ into a container of $\text{Cu}^{2+}(aq)$, then Cu^{2+} ions would collide with the solid zinc; electrons would exchange directly between the two; some Zn would dissolve as $\text{Zn}^{2+}(aq)$, and some $\text{Cu}(s)$ would form. The Cu metal may stick to the remaining Zn metal or it may fall off. Throughout the process, the piece of zinc is being oxidized and it is dissolving, while the Cu^{2+} ions are being reduced and forming copper metal. Free energy is being released, mostly as heat because we cannot tap into it as electrical energy by this setup. In order to obtain electrical energy and current, we must prevent the direct collision and direct electron transfer between the $\text{Zn}(s)$ and $\text{Cu}^{2+}(aq)$ reactants; we must instead require the electrons to go through an external circuit.

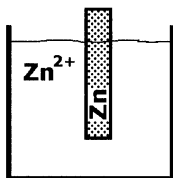
The half-reactions are the following.



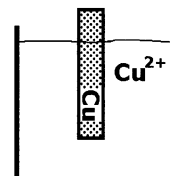
Now let's physically separate the two half-reactions by placing them in their own individual compartment. Each of these compartments is called a half-cell; there will be one half-reaction occurring in each half-cell. Thus, we will have an oxidation half-cell and a reduction half-cell. Together, the two half-cells make up the whole cell just as the two half-reactions make up the whole reaction. Some people confuse the terms cells and reactions, either as half or as whole. Just remember that the cell is the physical device which includes the reagents, while the reaction is simply the chemical change involved.

Let's start building the whole cell for the above reaction.

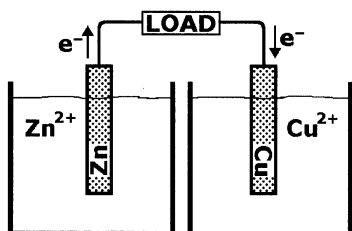
We'll begin with the oxidation half-cell; the half-reaction shows that $\text{Zn}(s)$ and $\text{Zn}^{2+}(aq)$ are involved. For now, we will deal with standard conditions as given by the ΔG° earlier, so $[\text{Zn}^{2+}] = 1 \text{ M}$ in the solution; the Zn^{2+} ions will be present in solution as some salt such as ZnSO_4 , $\text{Zn}(\text{NO}_3)_2$ or etc. Thus, anions are also present but they are spectators to the chemical reaction. A piece of $\text{Zn}(s)$ will serve as an electrode; an electrode is a component of a half-cell which makes physical contact with the reaction mixture and which conducts electricity into or out of the cell. Thus, an electrode must be an electrical conductor, which is commonly an elemental form of a metal, or graphite (since graphite is also a conductor, Section 38.4), or a related material. For our present half-cell, Zn metal will serve as the electrode. During the operation of this oxidation half-cell, the surface of the Zn metal electrode will be oxidized to Zn^{2+} ions and these dissolve into solution; the electrons from the oxidation will flow through the electrode to an external circuit. Over time, the mass of the Zn electrode will decrease while the concentration of Zn^{2+} in solution will increase.



For the reduction half-cell, we will have a solution of $\text{Cu}^{2+}(aq)$ with $[\text{Cu}^{2+}] = 1 \text{ M}$ for standard conditions; the Cu^{2+} will be provided as some salt such as CuSO_4 , $\text{Cu}(\text{NO}_3)_2$ or etc. A piece of copper metal will serve as the electrode. During the operation of this half-cell, the $\text{Cu}^{2+}(aq)$ will be reduced at the surface of the Cu electrode, where it will form more $\text{Cu}(s)$; the electrons for the reduction will come from an external circuit into the electrode. Over time, the mass of the Cu electrode increases while the concentration of Cu^{2+} in solution decreases.



OK, so far we have two separate half-cells doing nothing. We must now provide a means for the electrons to transfer from one half-cell to the other. In order to accomplish that, we bring in a bit of wiring and we connect to it something which we wish to power such as a light or a motor or whatever.



Generically, the light or motor or whatever is called a load. The overall cell so far is shown at left. Note that electrons would flow out of the oxidation half-cell, through the wires and load, and into the reduction half-cell. ΔG° provides the drive for the electron flow and that energy lights the light or runs the motor or does whatever the load will do.

But not quite. If you set it up like this, nothing would happen. Nothing would happen because the circuit is not complete and that prohibits any current from flowing. You cannot simply pass a gazillion electrons from one compartment into any other compartment under these conditions because that would cause a gross imbalance in total charges and that cannot happen. That cannot happen because it requires a very large amount of energy to separate a huge number of charges. (Technically, it is possible to separate an extremely minute number of charges, but you won't get a measurable reaction out of that.) Each half-cell must stay charge-balanced and neutral of its own. If this cell were able to operate, then the zinc half-cell would lose negative electrons while producing more cations; this half-cell would end up with an increasing positive charge overall. The copper half-cell would gain negative electrons and use up cations; this half-cell would end up with an increasing negative charge. But that cannot happen. Each half-cell must balance its charges and remain chemically neutral. We need to provide a means to prevent an imbalance of total charge.

Notice that I said total charge. Although we commonly think of electric current as the flow of electrons, that is not a complete description. In everyday experience, we are constantly surrounded by electrical devices which use the flow of electrons. For example, a simple household lamp is powered by plugging it into a wall outlet where it gets $\sim 120 \text{ V}$. That provides some amount of electron flow through the light, depending on the wattage/resistance of the bulb. For another example, we use batteries which are labeled $(-)$ on one end and $(+)$ on the other; those signs are electrical polarities and not chemical charges. Electrical polarity tells us the direction of electron flow during operation: electrons flow out of the negative end and into the positive end. All of these simple, common applications involve the flow of electrons through a device. But there's more to electric current than just electron flow. Current is all about charge flow, and electrons are not the only things with a charge. Ions also have a charge, and if you can get ions going in a particular direction, then you have ion flow and that is also charge flow. Thus, directional ion flow is also current. In fact, this relates to how some aqueous solutions conduct electricity in the first place. Section 10.1:

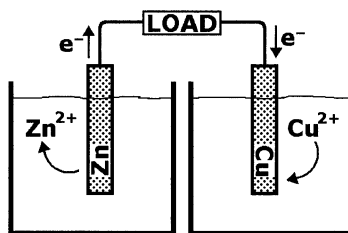
“ Historically, some of the early studies of ions involved electricity. This related to the fact that water solutions with ionic solutes can conduct electricity, whereas pure water does not

significantly conduct electricity. One term that arose from this historical connection is still in use: "electrolyte". Compounds which dissolved in water and allowed the solution to conduct electricity (e.g., table salt, NaCl) were called electrolytes. Compounds which dissolved in water and did not give rise to significant conductivity (e.g., table sugar, $C_{12}H_{22}O_{11}$) were called "nonelectrolytes". Many people equate electricity with some electrons flowing through a metal conductor but, in an ionic solution, it's the ions doing the electricity, not electrons. Electricity is really about charge flow, not just electron flow. Since ions have charges, too, then you can conduct electricity by letting ions move around: cations go one way and anions go the other way. That's electricity. That's how your nerves send electrical signals: it's how you breathe, it's how you eat, it's how your heart beats, it's how you move. Electricity by ion flow, not by electron flow. These things are part of you. Whether you know it or not. ”

Thus, the role of ions as a form of current was noted way back in Chapter 10. From Chapter 54, we now know that pure water by itself has very few ions: only 2.0×10^{-7} M are present and that's from autoionization. That is why pure water cannot conduct electricity well at all. But as soon as you dissolve an electrolyte into water, then the solution conducts electricity. A solution of 1 M NaCl (strong electrolyte) will conduct electricity very well. A solution of 1 M CH_3CO_2H (weak electrolyte) will conduct electricity but not as well. A solution of 1 M sucrose, $C_{12}H_{22}O_{11}$ (nonelectrolyte), will not conduct electricity well at all, similar to pure water. Electrons do not flow through these solutions; ions do. When electricity flows through an electrolyte solution, the cations flow in one direction and the anions flow in the opposite direction. That's current.

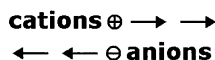
Now, let's return to our cell where we left it above. Again, if it were to operate as constructed so far, we would have a buildup of chemical charges in the separate half-cells.

The zinc half-cell would be losing negative electrons and gaining positive cations. The half-cell would be increasing in positive charge overall.

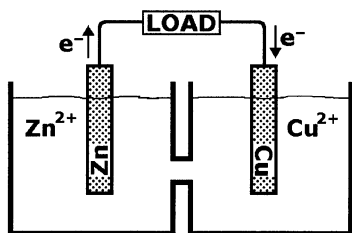


The copper half-cell would be gaining negative electrons and losing positive cations. The half-cell would be increasing in negative charge overall.

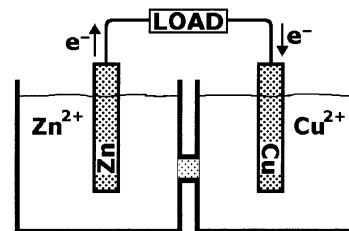
To offset the net change in charges, we now provide for ions to flow between the two half-cells. We can do this by allowing cations to flow from left to right, and/or by letting anions flow from right to left.

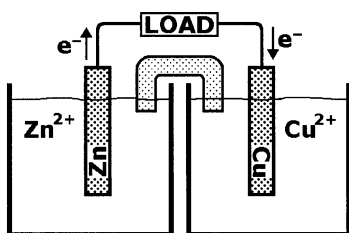


That will complete the circuit. (Although anions are not shown in the picture, they are still present from whatever compound was used to provide the Zn^{2+} and Cu^{2+} solutes.) The flow of ions will maintain the balance of charges in each of the half-cells. In order to allow the flow of ions, we must add a connection between the solutions of the two half-cells. Ions will flow through this connection. Electrons cannot flow through this connection; they must still go through the external circuit.



This type of connection can take various forms. The simplest is an open connection between the two half-cells, as shown at left. This does not work after a while, however, since the opening also allows the solutions to mix. The Cu^{2+} ions from the right half-cell will eventually find their way to the Zn electrode in the left half-cell and do a direct transfer of electrons again; we lose the external current. Another way is to incorporate a porous barrier, as illustrated at right. The porous barrier still allows ions to get through but it slows down the mixing of the solutions considerably. Another way is to use a "salt bridge". A salt bridge is an inverted U-tube filled evenly with a gel which contains a considerable amount of electrolytes. Think of this as salty gelatin. The gel is still mostly water but the water is partly immobilized within the gelatin. The salt does not need to include the ions in the half-cell reactions and different ions can serve

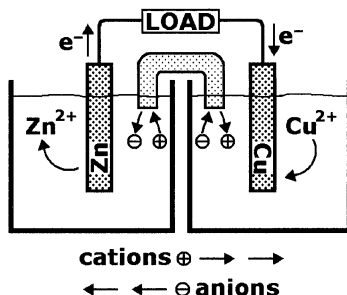




the purpose. For example, KCl is a common choice for a salt bridge. A cell with a salt bridge is shown at left. Ions can pass into and out of each end of the bridge, and charges can migrate between the two half-cells. Charges do not migrate through a salt bridge nearly as fast as through an open connection or a porous plug; this limits the amount of current which can flow. In a typical application with a salt bridge, the rate of ion charge passing through the bridge is modest, and the bridge is not gushing ions. This design is more applicable to applications which only need small currents.

By any of the above methods, the circuit is now complete. Remember that current is the flow of charge, whether the charge be electrons or ions. Let's look at all charges which are in motion in the cell. There's quite a bit going on.

As a result of the oxidation half-reaction, the zinc half-cell loses negative electrons and gains positive cations. To compensate for these charges, cations can flow into the salt bridge and/or anions can flow out of the salt bridge. The zinc half-cell stays balanced in total charges and neutral overall.



As a result of the reduction half-reaction, the copper half-cell gains negative electrons and loses positive cations. To compensate for these charges, anions can flow into the salt bridge and/or cations can flow out of the salt bridge. The copper half-cell stays balanced in total charges and neutral overall.

Although charges (electron or ion) are moving through the entire cycle of the system, each part of the system still has an equal number of plus and minus charges and each part of the system stays in balance of total chemical charge. Well, you might ask, if the total charges are balanced, then why are the charges flowing? That's ΔG° . Cu^{2+} still wants the electrons and Zn is still surrendering them. ΔG° says the reaction can happen and ΔG° provides the drive for the give/take of electrons. That drive provides the push/pull for moving the charges through the system. We can tap into that as electrical energy, and this allows us to operate the load device, whatever the device may be.

62.2 Terminals, terminology and notation

The above electrochemical cell provides electrical energy due to the exergonic reaction which occurs. A cell which provides electrical energy due to an exergonic reaction is called a galvanic cell. ΔG° (or ΔG if nonstandard) is negative; the joules of the process are available to do electrical work. The opposite type of cell is an electrolytic cell. For an electrolytic cell, we must send in the electrical energy to pay for the ΔG° (or ΔG) of an endergonic reaction. (A reaction done in this manner is called an electrolysis; the plural is electrolyses.) The joules for the reaction are delivered as electrical energy. For now, we will deal with the exergonic type, galvanic; we will come back to electrolytic applications in Chapters 64 and 65.

Let me return to the point about electrical polarity as previously mentioned for a battery. There is a necessary distinction to emphasize.

Electrons and anions carry negative charge while cations carry positive charge. Those are chemical charges. Electrical poles are assigned as negative or positive but that's not the same as a chemical charge. The (+) and (-) signs at the terminals on a battery tell us the direction of electron flow into and out of the battery while in use, but both ends of the battery are in charge-balance and are chemically neutral, just as are the individual half-cells above. For our cell above, electrons flow out of the Zn electrode into the external circuit; therefore, the zinc electrode is the electrical (-) side. Electrons return to the cell from the external circuit via the Cu electrode; the copper electrode is the electrical (+) side. You need to remember that electrical signs and chemical charges are not the same thing. Again, the electrical signs are simply the indicators of the direction of the electron flow, and that direction is determined by ΔG . Chemical charges stay balanced everywhere throughout. Be aware of the distinction between charges and electrical signs.

For our cell above, the Zn metal and the Cu metal are the electrodes. Electrodes are classified in two different ways. One way is anode vs. cathode; the other way is active vs. inert.

For the former classification, the anode is the electrode of oxidation and the cathode is the electrode of reduction. The Zn electrode is being oxidized, so it is the anode; the Cu electrode is where Cu^{2+} is being reduced, so it is the cathode. Sometimes these terms are applied to the half-cell itself; thus, we

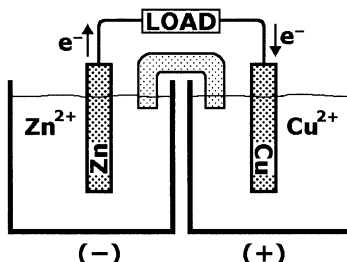
can say the zinc half-cell is the anode or the anode compartment while the copper half-cell is the cathode or the cathode compartment. For a galvanic cell, electrons leave the anode, so it is the electrical negative side; the cathode is the electrical positive side. Below is a summary of the terms.

OXIDATION HALF-REACTION

Zn is the anode.

This is the anode compartment.

Electrons leave this half-cell, so this is the electrical negative side.



REDUCTION HALF-REACTION

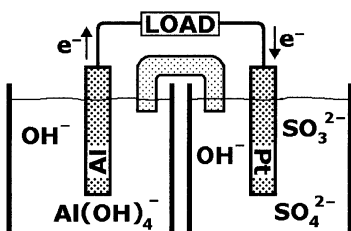
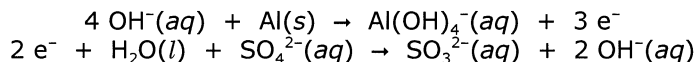
Cu is the cathode.

This is the cathode compartment.

Electrons enter this half-cell, so this is the electrical positive side.

Now let's consider the active vs. inert classification. An active electrode is one which is also a reagent in the half-reaction; in other words, an active electrode is chemically active in the reaction and it is shown in the half-reaction itself. In the above cell, both electrodes are involved in the chemical reaction, so both are active electrodes. For our coverage, active electrodes will be limited to an elemental form of a metal when that elemental form is part of the half-reaction. This also works for alloys of the metal. The metal elemental forms can be a solid piece of the metal or, in the case of $Hg(l)$, it will be some amount of liquid.

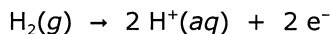
An inert electrode is not a part of the chemical reaction; it only serves to conduct the electrons into or out of a half-cell, and the half-reaction itself occurs between other components in the half-cell. Many metal elements cannot serve as an inert electrode for the simple, practical reason that they can react and interfere with a variety of redox reactions. One metal which is used as an inert electrode, however, is platinum, since Pt tends to be inactive in most (but not all) redox reactions. Other metals can serve in some specific applications, and C(*graphite*) is also used in various applications. Nevertheless, for simplicity of generalization, we will use Pt(s) in our examples here. For an example of a situation which requires an inert electrode, consider Example 3 of Chapter 61. The individual, balanced half-reactions are repeated below.



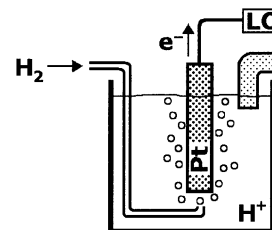
For the first half-reaction, we would use Al(s) as an active anode. For the second half-reaction, none of the reagents are metal elemental forms and the electron transfer is between $SO_4^{2-}(aq)$ and $SO_3^{2-}(aq)$; thus, no active electrode can be used. We would select Pt(s) to serve as an inert electrode. A picture of a whole cell for the whole reaction is shown at left, incorporating a Pt(s) cathode.

Although an inert electrode is chemically inactive, it is still the site for a transfer of electrons. For a reduction using an inert electrode, a reagent (or intermediate) would contact the electrode (cathode), picking up an electron or more, and that enables the reduction to occur. For an oxidation using an inert electrode, a reagent (or intermediate) would contact the electrode (anode), transferring an electron or more, thus enabling the oxidation to occur.

There are some variations to the setup of an inert electrode. For example, if a solid reagent (which is not a metal) is part of the half-reaction, then the solid can be coated onto the inert electrode to allow for physical contact. This is not required in all cases, however, and it is also common to simply have the solid elsewhere in the half-cell. As we have seen in Chapters 59 and 60, even "insoluble" solids will have some amount of solute dissolved. For gas reagents, the gas is bubbled into the solution directly over the inert electrode. For example, consider the following half-reaction.



A half-cell for this oxidation is shown at right. Since a gas phase is specified, then its pressure will need to be indicated; for standard conditions, the gas is provided at one atm. The bubbling stirs the solution and maintains saturation for the gas in the solution in the immediate vicinity of the electrode surface. There can even be some interaction between the gas compound and the solid electrode, but those details are beyond what we need here.



Let's summarize the roles of active and inert electrodes.

If an elemental form of a metal is a reagent in a half-reaction, then that metal will be the active electrode in that half-cell.

If there are no elemental forms of any metal in the half-reaction, then an inert electrode (Pt(s)) would be used in that half-cell.

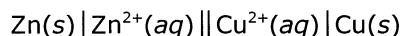
There is a corollary to note.

For any particular problem or example in our coverage here, if an electrode is not Pt(s), then it is an active electrode and it is a reagent in the balanced equation.

Know these.

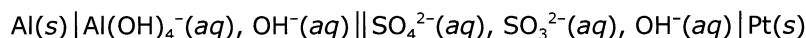
Let me make a point about the drawings so far. The drawings show a general layout of a cell in terms of physical design and in terms of chemical components. For each half-cell, you must include the chemical reactants and products which are present in the half-reaction, except for H₂O. You don't label H₂O in the picture because these are aqueous systems and the availability of water is assumed. Just be sure to include every other reagent, including H⁺ and OH⁻ in a drawing. Go back and examine each picture so far; you will see that all reagents from all half-reactions were included except H₂O.

Pictures are informative but they are not always drawn due to their tedious and bulky nature. Instead, a shorthand format is adopted for conveying the cell information; this shorthand format is called cell notation. To illustrate cell notation, we begin with our simplest reaction so far, the Zn + Cu²⁺ reaction. The cell notation for this is the following.



Here's how this notation works. A single vertical | separates different phases or a distinct change in composition. A double vertical || indicates a salt bridge; in essence, this tells us the separation between the half-cells. The far left and the far right entries are the electrodes. The aqueous solutions will be to the immediate left and right of the double vertical. There can also be other entries (as will be seen below). Notice that the anode half-cell is to the left of the double vertical and the cathode half-cell is to the right. This is a required sequence which you need to follow; by following this practice, we immediately know which half-cell is which and from this we know the direction for writing the equations (as will be seen below). On the other hand, for pictures of cells such as the prior drawings, there is no required left/right sequence for the anode and cathode; I did draw the pictures above to be consistent with our notation, but the anode and cathode half-cells in a drawing can be switched left to right. Be careful with this: if you are given a cell notation, then you know the anode is on the left but if you are given a drawing, then you don't know which is which just from the drawing (unless your instructor specifies it to be a certain way).

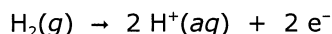
For another illustration, consider the cell notation for the Al + SO₄²⁻ reaction.



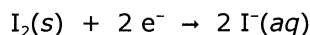
Anode is on the left, cathode is on the right. Notice that all reagents are shown except for H₂O; again, H₂O is not shown in pictures of cells and it is not listed in cell notation. For each aqueous solution, all reactant and product solutes must be listed although they can be listed in any sequence. Thus, the solutes for the cathode compartment can be listed as SO₄²⁻(aq), SO₃²⁻(aq), OH⁻(aq) or as SO₃²⁻(aq), OH⁻(aq), SO₄²⁻(aq), or in another sequence, and the order does not matter.

It is important to be able to write and to read cell notation. Here are four Examples, along with further variations. We start with an example with different phases to show how those are handled.

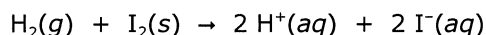
Example 1. Use the H₂ oxidation from above



and combine it with the reduction of I₂(s)



to get the overall reaction

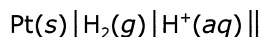


where the product is simply the strong acid HI(aq). Write the cell notation for this process.

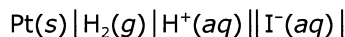
There are no metal elemental forms involved, so both half-cells will need an inert electrode. Let's start the cell notation on the left, first with the anode itself.



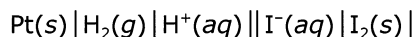
Two phases are present for the reagents of this half-cell: $\text{H}_2(g)$ and $\text{H}^+(aq)$. We put them into the notation, separated by a single vertical. The aqueous solution rides along the double vertical.



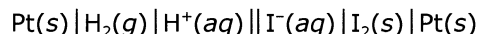
Proceeding to the cathode half-cell, we add its aqueous phase,



followed by a separate phase of $\text{I}_2(s)$.



This is followed by the electrode. Although both I_2 and the electrode are solids, they are chemically distinct solids, so they are treated as separate components.

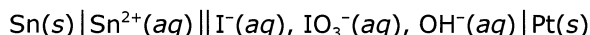


That's the cell notation for that cell.

Hopefully you can see already that cell notation is a convenient way to present the necessary information for a given redox operation. So far, we've written notations from a cell picture and from balanced equations, but you can go in the opposite direction with this also.

.....

Example 2. Consider the following cell notation.



Derive the balanced equations for the half-reactions and for the whole cell reaction.

.....

OK, this will follow the balancing act done in Chapter 61 but you have to extract the necessary information from the cell notation in order to get started. Here's what this cell notation tells you immediately.

The anode is to the left of $||$, and that's for the oxidation half-reaction. To the right of $||$ is the cathode and the reduction half-reaction.

$\text{Sn}(s)$ is a metal elemental form, so this is an active electrode; it will be in the equation for the anode half-reaction.

$\text{Pt}(s)$ is an inert electrode; it will not be in the balanced equation for the cathode half-reaction.

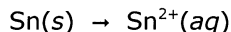
OH^- is shown in the cathode compartment, so that means basic conditions are present. It also means that OH^- will be somewhere in the balanced equation for that half-reaction. For the anode side, neither H^+ nor OH^- are shown, so those will not be present in the equation for that half-reaction.

Notice from the last point that cell notation tells us what reagents are or are not present, EXCEPT for water. Since H_2O is not shown in cell notation, you may need to add H_2O to a half-reaction.

Now go to balance.

Anode

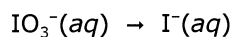
The redox couple is Sn/Sn^{2+} and we have to set this up for oxidation. Oxidation requires that the tin metal is losing electrons to form Sn^{2+} .



Go ahead and balance this half-reaction.

Cathode

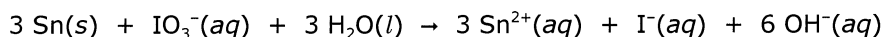
The redox couple is I^-/IO_3^- and we have to set this up for reduction. By the way, oxidation numbers remain very handy here. I^- has iodine with oxnos -1 while IO_3^- has iodine with oxnos $+5$. For reduction, we need to set this up as a decrease in oxnos.



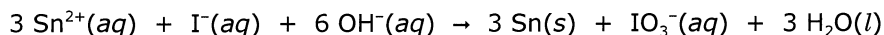
Balance this half-reaction. Don't forget: basic conditions were indicated by the cell notation.

Set your loss equal to gain and add the two half-reactions.

Here's the final result. Be sure you can get this.



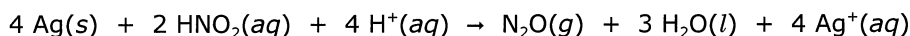
Notice how we derived this simply from the cell notation, and how the left/right requirement for anode/cathode leads to the intended direction of the reaction. If you failed to follow that convention, then you would end up with



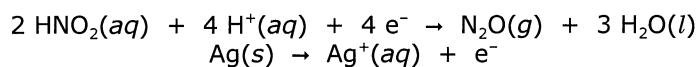
and that is wrong. You need to heed the left/right anode/cathode requirement for cell notation.

Next Example.

Example 3. Consider the following overall, balanced equation



which derives from the following half-reactions.



Write the cell notation for the overall reaction.

Be mindful that, in order to do cell notation, you must consider the separate half-reactions. A whole reaction does not necessarily tell you which reagents are in which half-cell, but you need to know this for the cell notation. This information will be found in the equations for the separate half-reactions. OK, let's get started. Which half-reaction from above is for the anode? What will be the electrode for this compartment?

|

What solutes are present in the anode solution? List these to the left of the double vertical.

| ||

Are there any other different phases in the anode compartment? If so, add them in, along with another |. Then, turn to the cathode. Enter the aqueous solutes after the double vertical.

| || |

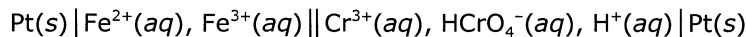
Are there any other different phases in the cathode compartment? If so, add them in, along with another |. At the far right, enter the electrode.

Done? Here are a few clues. One electrode is inert, one is active. One solution has one solute, the other solution has two solutes. One compartment has a gas phase present and you do need to add another single vertical, |.

One more Example for now.

.....

Example 4. Consider the following cell notation.



Derive the balanced equations for each half-reaction and for the whole reaction.

.....

Note that both electrodes are inert. Although there are metal cations present in the solutions, there are no elemental form of those metals, so you have to use inert electrodes. Go ahead and work everything out here.

Clue: This may look familiar. It's Example 2 in Chapter 61. Try doing it here before you look back.

Now it's time to get the juice flowing.

62.3 Current topics

Now we start into more of the energy and electricity aspects. A few electricity terms which we shall need are volts, amps and coulombs. Volt is probably the most common of these three but let me begin with coulomb.

A coulomb, C, is a specific amount of charges.

$$C = 6.242 \times 10^{18} \text{ charges}$$

The charges could be negative charges or they could be positive charges. They could represent electron charges or they could represent ion charges. It doesn't matter. Here are examples.

A coulomb could be 6.242×10^{18} electrons carrying 6.242×10^{18} negative charges.

A coulomb could be 6.242×10^{18} Cl^- anions carrying 6.242×10^{18} negative charges.

A coulomb could be 3.121×10^{18} Zn^{2+} cations totaling 6.242×10^{18} positive charges.

The number 6.242×10^{18} may seem like a strange number, and you would think that they would base it on a mole of things, but the connection to moles came later in the history. We'll get to that in a moment.

Current is the rate of charge flow. As such, it is the number of charges flowing per time or the number of coulombs per time. Amperage is the measure for flow

$$\text{amperage} = \frac{\text{charges}}{\text{time}}$$

and the standard unit is an ampere or amp, A, which is a flow rate of one coulomb per second.

$$A = \frac{C}{s}$$

Another way to view this connection is that rate (A) multiplied by a time (s) gives the amount of charges (C) which have flowed.

$$C = A \times s$$

Thus, if you are operating a typical 100-W household lamp at 120 V and which draws 0.83 A, then a total of 50. C flow through the lamp in 60. s

$$60. \text{ s} \times 0.83 \text{ A} = 60. \text{ s} \times \frac{0.83 \text{ C}}{\text{s}} = 50. \text{ C}$$

and this corresponds to

$$60. \text{ s} \times 0.83 \text{ A} = 60. \text{ s} \times \frac{0.83 \text{ C}}{\text{s}} \times \frac{6.242 \times 10^{18} \text{ electrons}}{\text{C}} = 3.1 \times 10^{20} \text{ electrons}$$

which converts to moles of electrons by way of Avogadro.

$$60. \text{ s} \times \frac{0.83 \text{ C}}{\text{s}} \times \frac{6.242 \times 10^{18} \text{ electrons}}{\text{C}} \times \frac{\text{mol}}{6.022 \times 10^{23} \text{ electrons}} = 5.2 \times 10^{-4} \text{ mol}$$

We won't really get quantitative with amps until we get into echem stoichiometry in Chapter 65, so these kinds of calculations will wait until then.

A volt, V, is a unit of electric potential or cell potential, historically called electromotive force (emf). Such potential is designated E . You can think of E as the push behind the package or the pull on the package: a greater voltage corresponds to a stronger push or pull, while the package corresponds to an individual charge. Thus, in order to run an electrical device, the battery will push/pull charges through the device and that does work such as to light the light or run the motor. For a given device, if you use a stronger push/pull, then more charges go through faster, which means a higher current. The work involved is related to the electrical energy which is involved, and a very important relationship is the following.

$$\text{energy} = \text{number of charges} \times \text{potential}$$

We have been using joules for energy since Chapter 18. A joule has an important connection to the units here: one J equals the product of C and V.

$$\text{J} = \text{C} \times \text{V}$$

Now we bring in an extremely important connection to free energy

$$\Delta G = -nFE$$

which now incorporates moles of charge as n . Specifically, n is the number of moles of electrons which are transferred (lost or gained) for a given reaction. The connection between moles of charge and coulombs is provided by F , which is called the Faraday constant.

$$F = 96,485 \frac{\text{C}}{\text{mol}}$$

The numerical value of 96,485 may seem strange, but it combines Avogadro's number into coulomb.

$$\begin{aligned} \text{mol of charge} &= 6.022 \times 10^{23} \text{ charges} \\ \text{C} &= 6.242 \times 10^{18} \text{ charges} \end{aligned}$$

Dividing 6.022×10^{23} by 6.242×10^{18} gives 96,480 which becomes 96,485 when more sigfigs are used. While many electrical applications commonly use coulombs, many chemistry applications use moles, and F provides the connection. Returning to ΔG ,

$$\Delta G = -nFE$$

notice that the nF part will give coulombs. Now, look at all the units which are involved

$$\begin{array}{rcl} \Delta G & = & -nF \times E \\ \text{(J)} & & \text{(C)} \times \text{(V)} \end{array}$$

and those relate to the conversion above.

$$\text{J} = \text{C} \times \text{V}$$

There is one very important point to be aware of, and that involves the negative sign in the ΔG equation. The product nF is always a positive number; E can be positive or negative but it will always be the opposite sign relative to ΔG . Thus, a negative ΔG gives a positive E and vice versa.

Exergonic, allowed:	negative ΔG , positive E
Endergonic, forbidden:	positive ΔG , negative E

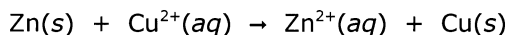
Remember the opposite signs between ΔG and E . And don't forget the meaning of exergonic and endergonic. An exergonic process can happen by itself under the given conditions. An endergonic cannot happen by itself under the given conditions, but we can pay into the process to make it happen.

Now that we have the thermodynamic connection, we can bring in the usual business about standard conditions.

$$\Delta G^\circ = -nFE^\circ$$

E° is called the standard potential.

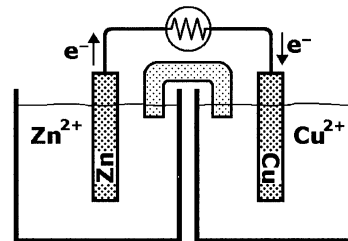
If we return to our Zn + Cu²⁺ cell



and replace the load with a sensitive meter to measure the voltage, then we would determine the standard potential to be 1.10 V. From the potential of 1.10 V, we can find ΔG° .

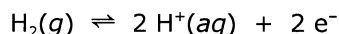
$$\begin{aligned} \Delta G^\circ &= -nFE^\circ = -2 \text{ mol} \times 96,485 \text{ C/mol} \times 1.10 \text{ V} \\ &= -212,000 \text{ C} \cdot \text{V} = -212,000 \text{ J} = -212 \text{ kJ} \end{aligned}$$

(Technical aside. In order to measure a true potential based on ΔG° , you cannot have a significant amount of current flowing. A simple reality with galvanic cells is that the voltage decreases as current increases, so we have to remove the load and use a suitable, sensitive meter for which there is no significant current. This is shown in the picture as simply a resistance squiggle. The potential measured in this way is called an open circuit potential and this represents the true thermodynamic potential as calculated by $\Delta G = -nFE$. This is just an aside for now; I'll come back to some of these aspects in Sections 64.3 and 65.1.)

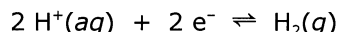


From the present calculation we have $\Delta G^\circ = -212 \text{ kJ}$ using E° ; this compares very well to $\Delta G^\circ = -212.55 \text{ kJ}$, as calculated in the beginning of this Chapter using values for ΔG_f° . Notice in the above calculation that $n = 2 \text{ mol}$, since that is the number of electrons transferred for the equation as written. **THIS IS AN IMPORTANT POINT.** The reaction as written involves one mole of Zn and one mole of Cu²⁺ but these transfer two moles of electrons; n is always for the moles of electrons. The value of n is also an exact number so it does not affect a round-off; the answer has three sigfigs due to the 1.10 V. By the way, like ΔG° itself, the value of n depends on the coefficients for the reaction as written. If you multiply an equation, you multiply ΔG° and you multiply n ; this point will be important later.

As we have seen since Chapter 18, standard thermodynamic parameters have been measured for a large number of compounds, a small fraction of which are in Appendix A. Likewise, standard cell potentials have also been measured. Instead of tabling the potentials for a very large number of specific cell reactions, however, the tables contain the potentials for half-cell reactions. Appendix C gives some half-cell potentials, and we will be doing much with those starting in the next Chapter. The reason for having tables of half-cell potentials is that you can construct a whole cell potential for a huge number of reactions just by combining the appropriate half-cell potentials. There is one catch to this approach: you cannot directly measure the actual value of any individual half-cell potential. Every time you experimentally measure a potential, it's always one half-cell against another. We can measure the voltage of one whole cell, but we cannot measure the voltage for any one, single half-cell by itself. To get around this, one half-cell is defined as a reference half-cell and its value is set to zero; all other half-cell potentials are relative to that. The reference half-reaction is the following, which we've used in a prior example.



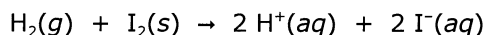
This reaction can be applied in either direction, either as an oxidation or, in reverse, as a reduction.



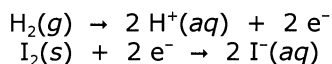
The two directions are also implied within the double half-arrow notation shown in the equations. Either way, this is the equation for what is called the hydrogen electrode; at standard conditions, this is specifically called the standard hydrogen electrode, abbreviated SHE. Recall that $\text{H}_2(g)$ is the standard reference elemental form for hydrogen and that $\text{H}^+(aq)$ is the standard reference ion for all ions. As such, each of these has a ΔG_f° which is set to zero.



Given the zeros, then ΔG° for the half-reaction is also zero. (We don't consider the electrons for the ΔG° and, besides, the electrons drop out when we add half-reactions together anyway.) Since $\Delta G^\circ = -nFE^\circ$, then this means E° for this half-reaction is also zero. Thus, everything about this reaction is a zero but that is how we set it up. This is the reference half-reaction; every other half-reaction potential is relative to this. For example, earlier we considered the production of HI(aq) from the elements.



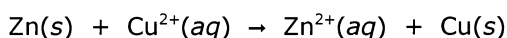
With a properly constructed cell, you could measure the actual standard potential for this reaction to be 0.54 V. That's for the whole cell overall. Here are the half-reactions.



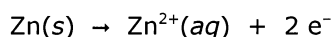
The reduction of $\text{I}_2(s)$ relative to the oxidation of $\text{H}_2(g)$ involves an overall potential of 0.54 V. Since we assign a standard half-cell potential of zero to the oxidation of $\text{H}_2(g)$, then this means a value of 0.54 V is assigned to the reduction of $\text{I}_2(s)$. Again, half-cell potentials are assigned values relative to a reference (SHE). When you combine an oxidation half-cell potential and a reduction half-cell potential for a whole cell, then the referencing drops out and you get the actual, measured voltage for the whole cell.

Let me expand for a moment on the derivation of free energies and potentials for whole cells from the corresponding values for half-cells. For clarity, I will subscript the half-cell values, such as $\Delta G_{1/2}^\circ$ and $E_{1/2}^\circ$; the parenthetical terms (oxid) or (redn) may also be added for oxidation or reduction.

We return to the $\text{Zn} + \text{Cu}^{2+}$ reaction



and we start with the oxidation part.



As for any reaction, we can find ΔG° using ΔG_f° values from Appendix A. For this half-reaction, this gives us $\Delta G_{1/2}^\circ(\text{oxid})$.

$$\Delta G_{1/2}^\circ(\text{oxid}) = -147.06 \text{ kJ} - 0 \text{ kJ} = -147.06 \text{ kJ}$$

As with potentials, the free energies of half-reactions are also relative to SHE, so this number of kJ's is relative to $\Delta G_{1/2}^\circ = \text{zero}$ for SHE. Using this $\Delta G_{1/2}^\circ$, we can find $E_{1/2}^\circ$ for this half-reaction.

$$E_{1/2}^\circ(\text{oxid}) = -\frac{\Delta G_{1/2}^\circ(\text{oxid})}{nF} = -\frac{-147,060 \text{ J}}{(2 \text{ mol})(96,485 \text{ C/mol})} = 0.76209 \text{ V}$$

That's the standard half-cell potential for the oxidation of $\text{Zn}(s)$ to $\text{Zn}^{2+}(aq)$, compared to SHE. Now, let's do the same procedure for the Cu^{2+} reduction half-reaction.



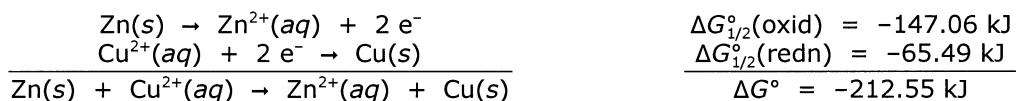
Using ΔG_f° values from Appendix A, we find $\Delta G_{1/2}^\circ(\text{redn})$

$$\Delta G_{1/2}^\circ(\text{redn}) = 0 \text{ kJ} - 65.49 \text{ kJ} = -65.49 \text{ kJ}$$

from which we find $E_{1/2}^\circ(\text{redn})$.

$$E_{1/2}^\circ(\text{redn}) = -\frac{\Delta G_{1/2}^\circ(\text{redn})}{nF} = -\frac{-65,490 \text{ J}}{(2 \text{ mol})(96,485 \text{ C/mol})} = 0.3394 \text{ V}$$

That's the standard half-cell potential for the reduction of $\text{Cu}^{2+}(aq)$ to $\text{Cu}(s)$, compared to SHE. Now we can derive values for the whole cell in the usual manner for adding equations together.



Since we are always able to add ΔG° 's and since $\Delta G^\circ = -nFE^\circ$, then we can also add $-nFE^\circ$ terms.

$\Delta G_{1/2}^\circ(\text{oxid}) = -147.06 \text{ kJ}$	$= -nFE_{1/2}^\circ(\text{oxid}) = -(2 \text{ mol}) F (0.76209 \text{ V})$
$\Delta G_{1/2}^\circ(\text{redn}) = -65.49 \text{ kJ}$	$= -nFE_{1/2}^\circ(\text{redn}) = -(2 \text{ mol}) F (0.3394 \text{ V})$
$\Delta G^\circ = -212.55 \text{ kJ}$	$= -nFE^\circ = -(2 \text{ mol}) F (1.1015 \text{ V})$

This gives $\Delta G^\circ = -212.55 \text{ kJ}$ and $E^\circ = 1.1015 \text{ V}$ for the whole cell. These final sums now represent the free energy and the potential for the oxidation of $\text{Zn}(s)$ relative to the reduction of $\text{Cu}^{2+}(aq)$. Since that is the reaction for the whole cell, then these values for ΔG° and E° are now the actual values for that reaction.

Notice in the far right column of addition that n is given by the (2 mol) term for each half-reaction and for the overall reaction. For the final addition of the $-nFE^\circ$ terms, the $-nF$ parts are a common factor which allows us to simply add the $E_{1/2}^\circ$'s directly. As long as n 's are the same for both half-reactions and

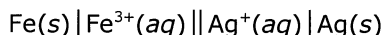
for the total reaction, then you can add $E^\circ_{1/2}$'s. Fortunately, this will always be true when deriving a whole reaction from two half-reactions; in this application, the n 's represent the number of electrons lost and gained and the numbers must be equal for balancing. The additivity of E° 's in this kind of application is an important result which we will utilize heavily.

Note the underlines. There are other applications in which the n 's can differ, and in those cases you cannot add E° 's directly. We will see such an application in Chapter 63.

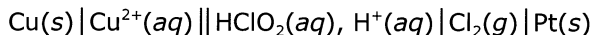
Problems

- True or false.
 - Ion flow allows for current through an aqueous solution.
 - In a cell, electrons pass through the salt bridge from one half-cell to the other half-cell.
 - In a galvanic cell, the cathode is the electrical (+) side.
 - An active electrode serves as a reactant or a product in a half-cell reaction.
 - The anode is the electrode of oxidation.
 - The Standard Hydrogen Electrode operates at one atm $H_2(g)$ and pH 7.00.

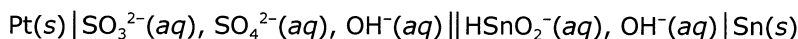
- Consider the following cell notation.



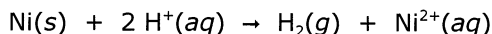
- Identify the redox couples.
 - Derive the balanced equation for each half-reaction. Which is the anode half-reaction and which is the cathode half-reaction? What reactant is oxidized? What reactant is reduced?
 - Derive the overall balanced equation.
- Consider the following cell notation.



- Derive the balanced equation for each half-reaction. Which is the anode half-reaction and which is the cathode half-reaction? What reactant is oxidized? What reactant is reduced?
 - Derive the overall balanced equation.
- Consider the following cell notation.

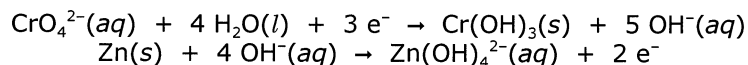


- Derive the balanced equation for each half-reaction. Which is the anode half-reaction and which is the cathode half-reaction? What reactant is oxidized? What reactant is reduced?
 - Derive the overall balanced equation.
- Consider the following balanced equation.



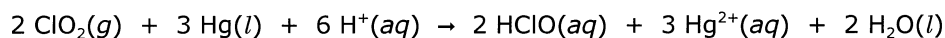
Write the cell notation.

- Consider a cell composed of the following two half-reactions.

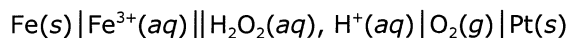


- Write the overall equation for the whole cell.
- Write the cell notation.

7. Consider the following balanced redox equation.

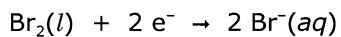


- Write the balanced equation for each half-reaction. Which is the anode half-reaction and which is the cathode half-reaction?
 - Write the cell notation for the overall reaction.
8. Consider the following cell.



For each statement below, is the statement true or false?

- One electrode is an active electrode, the other is inert.
 - As the reaction continues, more Fe^{3+} forms more Fe.
 - O_2 is oxidized.
 - Electrons leave the cell through the Pt electrode.
9. For the following half-reaction,



find $\Delta G_{1/2}^\circ$ (in kJ) from free energies of formation. Use that $\Delta G_{1/2}^\circ$ to find $E_{1/2}^\circ$ (in V).