

Chapter 61

ECHEM, Part 1

© 2012 Mark E. Noble
noblereaction.org

We now embark on a series of five Chapters dealing with electrochemistry. Electrochemistry, which is commonly contracted to echem, deals with chemical reactions and processes which involve the flow of charge, whether that charge involve electrons or ions. Charge flow is the basis of electricity, and echem reactions can generate or they can use electricity directly. Fundamentally, electrochemistry involves oxidation-reduction. As discussed way back in Chapters 13 and 14, redox involves the transfer of electrons between chemical units, during which the oxidant takes electrons from the reductant. In those early Chapters, the reaction was considered to occur in one pot; kinetically, the reaction occurred by direct collision between the reactants or intermediates. Now, we will often physically separate the oxidant and the reductant into their own compartments. By separating them, they can no longer do a direct transfer of electrons. Instead, we provide an external wire to connect the compartments; this allows the electrons to flow out of the reductant compartment, through the wire, and into the oxidant compartment, and this completes the redox reaction. The flow of electrons through the external wire is an electric current, and that gets us into the electricity aspects. For an exergonic reaction, we can tap into the free energy of the reaction by using the external circuit for electrical energy. This approach is the basic principle behind every battery, and its application was forecast at the end of Chapter 14.

“ You also use redox in other applications of your everyday world; for example, every time you use a battery, you're using redox. Most batteries no longer involve aqueous solutions, although this is how they originally developed. Typical batteries nowadays (C, AA, AAA, buttons, etc.) use pastes instead of aqueous solutions. Nevertheless, there is one battery which is still very common and which still uses aqueous solutions: the standard lead-acid battery in cars and other vehicles. Regardless of type, all batteries use redox reactions. The trick is to design the reaction so that the oxidant has to work for the electrons. This is done by physically separating the oxidant and reductant within the battery cell. Under this setup, the oxidant must now pull the electrons through a circuit. We'll see more of how this happens starting in Chapter 61. Redox chemistry lights your light, plays your music, and starts your engine. These things are part of your world. A REALLY BIG part. ”

Batteries involve an exergonic reaction. On the other hand, for an endergonic reaction, we provide the necessary energy into the system in the form of electrical energy. There are various uses of this approach. Industry uses echem processes on a huge scale to produce numerous metals (e.g., Al) and other products (e.g., NaOH). More commonly for you, recharging a battery involves an endergonic electrochemical process.

Historically, they were doing electrochemistry and electricity in the 1800's long before they even understood what electrons were, and long before they knew how many electrons were in any single atom. Echem has evolved over many years since, but some electrical terms from early times remain a part of the vocabulary. For example, we will be doing volts (V) and coulombs (C) as we go. Keep in mind, however, that the fundamentals yet lie in the thermodynamics and everything still goes back to ΔG and J's. Even V's and C's connect to J's, as we shall see. Kinetics can also play an important role because electrochemistry can allow for different kinds of mechanisms. Furthermore, the kinetics of electrochemical processes can be fast or slow, and this also has important consequences. We will not be dealing so much with the kinetics, however, although some issues will be mentioned as we go. For the most part, we will be connecting to the free energy of the reaction.

Now that you're all charged up, let's get underway. The very first thing we must do is review and refresh redox in general, and bring in a new approach for balancing equations.

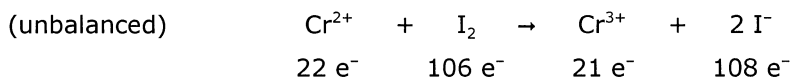
61.1 Some preliminaries

We spent quite a bit of time balancing redox equations in Chapter 14 and that was by using oxidation numbers. We will be changing that approach in our present pursuits. Regardless of approach, the bottom line remains getting the electron loss equal to the electron gain. Let's go back to Section 14.1:

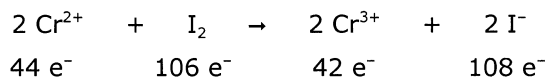
“ THE KEY TO BALANCING REDOX IS ELECTRON BALANCE AND THE KEY TO ELECTRON BALANCE IS TO GET THE NUMBER OF ELECTRONS LOST EQUAL TO THE NUMBER OF ELECTRONS GAINED.

Once you achieve electron balance, the rest of balancing will be much easier.

I will use our example from the end of the last Chapter to illustrate this point. Our first step was to place a coefficient of two on I^- which was wrong if you ended there.

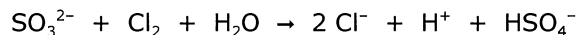


The reason that it was wrong was because the electrons did not balance. The reason the electrons did not balance was because the loss did not equal the gain. Notice in the reaction that the chromium loses one electron but the iodines gain two electrons total. That's no good. LOSS MUST EQUAL GAIN. If loss does not equal gain, then the electrons won't balance and the charges won't balance. Now consider the right answer.



The chromiums together lose a total of two electrons. The iodines together gain a total of two electrons. Loss equals gain. That's the key.

One last thing before jumping into balancing redox. I need to introduce a new term: couple. A couple of what? No, no, not that kind of couple. A redox couple. A redox couple is a redox reactant/product relationship. An oxidant and its product are one couple. A reductant and its product are another couple. Sometimes this is evident in the equation itself, especially after you've done a bunch of them, but sometimes it's not. You can identify each couple by oxnos: a redox couple is that reactant and that product which contain the atom(s) undergoing a change in oxnos. For example, in the equation above, $\text{Cr}^{2+}/\text{Cr}^{3+}$ is one redox couple; I_2/I^- is the other redox couple. Notice that each couple is comprised of one reactant and its product. Let me do another example, using the sulfite and chlorine reaction from the last Chapter.



For this reaction, $\text{SO}_3^{2-}/\text{HSO}_4^-$ is one couple and Cl_2/Cl^- is the other couple. ”

Here we are now in Chapter 61 and there's a lot in those quotes which you will again need as we proceed. In fact, if you're redox rusty, it would be useful for you to go back and review Chapter 13 also. There will be one substantial difference between then and now, however: we will now be balancing equations using the half-reaction method. That doesn't mean you can forget oxidation numbers, since those will remain very handy. But now we will need half-reactions.

So what is a half-reaction and why do we need them?

Again, a redox reaction involves both an oxidation part and a reduction part. Electrons are taken from the reducing agent (which is oxidized) by the oxidizing agent (which is reduced). A half-reaction is just one of these: it's the reaction for the oxidation part of the process or the reaction for the reduction part of the process. You cannot run a single half-reaction by itself; a half-reaction is still only half of an actual reaction. Both an oxidation and a reduction half-reaction must run concurrently, and the loss of electrons must still equal the gain of electrons. Nevertheless, separating an electrochemical reaction into its half-reactions is conceptually very useful: it's useful in balancing, as to be seen here, and it's useful in other ways as will be seen in the upcoming Chapters. Keep in mind that we can physically separate the two compartments, so a half-reaction is the reaction occurring in each compartment.

In the equation for a half-reaction, electrons will appear either on the right side of the equation or on the left side. Let's take a look at a few examples, using the Cr^{2+} reaction with I_2 above.

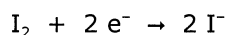
Cr^{2+} undergoes oxidation, which involves the loss of electrons.



This is the half-reaction for the $\text{Cr}^{2+}/\text{Cr}^{3+}$ couple. An electron is released in the process, and it appears on the right side of the equation. This will be true for every oxidation half-reaction:

IN THE EQUATION FOR EVERY OXIDATION HALF-REACTION,
THE ELECTRONS ARE ON THE RIGHT SIDE.

For the other half-reaction, I_2 undergoes reduction, the gain of electrons.



This is the half-reaction for the I_2/I^- couple. Electrons are used up in this process, and they appear on the left side of the equation. This will be true for every reduction half-reaction:

IN THE EQUATION FOR EVERY REDUCTION HALF-REACTION,
THE ELECTRONS ARE ON THE LEFT SIDE.

Notice that the individual half-reactions for both couples are atom-balanced and charge-balanced. The electrons are not counted toward the atom-balance, but they do count for the charge-balance.

This ends the preliminaries. We will now proceed into balancing half-reactions and the whole reactions of which they are a part. This is a bit different from the oxnos method in Section 14.2; you can flip back there and compare the two approaches as we go. Some of the wording is the same here but some is different. We will also be changing the setup of the problem a bit: instead of being given all reagents to start, some reagents may be missing from the information given by the problem. This new setup corresponds to problems of Type 3 which were mentioned but not covered in Section 14.1.

61.2 Half-reaction method

There are two aspects to consider here: balancing a half-reaction by itself and balancing a whole reaction from two half-reactions. In order to do the latter, you must be able to do the former. As always, the critical step in balancing a whole redox reaction is to get the electron loss equal to the electron gain, and it doesn't matter whether it's done by oxidation numbers or half-reactions. On the other hand, when balancing a single half-reaction by itself, you are only working with loss or gain but not both, and those problems are easier. We will mostly work on balancing the whole equation.

There are six Steps.

- Step 1. Identify the redox atoms and set up a half-reaction for each couple.
Having been through Chapters 13 and 14, albeit some time ago, then you may have some feel for identifying at least some redox atoms readily. However, some cases will still not be so simple. The fallback method remains the use of oxidation numbers: whatever atoms are changing oxnos are the redox atoms. The methods used in Section 13.2 for assigning oxidation numbers will still work in most applications here, although the methods of Section 27.3 may be needed in some cases.
- Step 2. Atom-balance each half-reaction.
Do the redox atoms first, then the others. Also, see the Fine Print after Step 6 below.*
- Step 3. Charge-balance each half-reaction, using electrons as needed.
Since electrons are negative charges, you put them into the half-reaction on the side which has too many positives or not enough negatives.

NOTE: If the problem is just to balance one half-reaction by itself, then you're done after this Step. Continue with Step 4 for balancing a whole reaction from two half-reactions.

- Step 4. Set the number of electrons equal for the two half-reactions, using multipliers as needed.
This Step fulfills the absolutely necessary requirement to set loss equal to gain.
- Step 5. Add the two half-reactions together and cancel any items which appear on both sides.
- Step 6. Verify the result.
Things can get tricky doing these, so it's always useful at the end to verify atom-balance and charge-balance and to look for anything else unusual.

* Here's the Fine Print for Step 2. This is necessary because we are now changing the format of the problem a bit: not all reagents may be provided in the given information, so you may need to add one or two others. The reagents which can be absent from the given information are H_2O , H^+ or OH^- ; these are simply assumed to be available since we are dealing with aqueous systems, some of which may be acidic or basic. If you need to add one or two of these to the equation, then this will show up in Step 2 when you are not able to balance all H's and/or all O's. If this is the case, you will need to bring in H_2O , H^+ or OH^- , according to one of the following two scenarios.

Scenario A. The reaction or half-reaction is stated to be in acidic solution OR acid-base conditions are not specified.

For these, first check to see if atom-balance is straightforward using H^+ and/or H_2O . If not straightforward, then first balance O's by adding H_2O 's to whichever side needs them. Then, balance the H's by adding H^+ 's.

Scenario B. The reaction or half-reaction is stated to be in basic solution.

For these, first check to see if the balance is straightforward using OH^- and/or H_2O . If not straightforward, then these can get quite tedious. We will follow a common, indirect approach: first do the atom-balance by the method of Scenario A. Once that is done, then you may end up with H^+ on one side of the equation. That won't work for a final answer in basic solution, since H^+ would be neutralized. To correct for that, add one OH^- to both sides for every H^+ which is present. On the side which has both H^+ and OH^- , convert these to H_2O according to neutralization ($\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$). If you end up with H_2O 's on both sides, then cancel as needed.

This ends the six Steps and the Fine Print. Let's do some Examples to illustrate the process.

Example 1. We'll start with the first balancing Example from Chapter 14:

“ Balance the equation for the reaction of aluminum metal with tin(IV) ion, which produces aluminum ion and tin(II) ion.

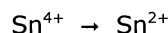
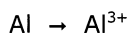
From those words, you can write



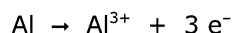
Notice that the atoms are balanced here, but the charges are not. A total of +4 is on the left but a total of +5 is on the right. That's no good. It's wrong. Let's fix this. ”

We fixed this by oxnos method in Chapter 14. Now we will fix this by half-reaction method.

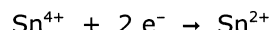
- Step 1. Identify the redox atoms and set up a half-reaction for each couple.
The redox atoms are aluminum and tin, and the couples are Al/Al^{3+} and $\text{Sn}^{4+}/\text{Sn}^{2+}$. Set up a half-reaction for each.



- Step 2. Atom-balance each half-reaction.
This one is easy: both are atom-balanced. There are no H's or O's to deal with, so we don't need the Fine Print for Scenario A or B.
- Step 3. Charge-balance each half-reaction, using electrons as needed.
We now add electrons to each half-reaction, according to the side which needs negative charges. For the aluminum half-reaction, the left side has zero charge and the charge on the right side is +3. The right side is too positive; it needs three negatives to balance the charges.

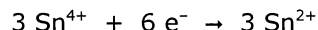


For the tin half-reaction, the charge on the left is +4 and the charge on the right is +2. The left side is too positive; it needs two negatives to balance the charges.



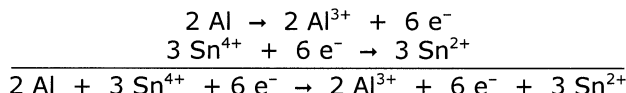
The half-reactions are now fully balanced by themselves. Notice that Al is losing three electrons, which means that it is undergoing oxidation; Sn^{4+} is gaining two electrons, which means that it is undergoing reduction.

- Step 4. Set the number of electrons equal for the two half-reactions, using multipliers as needed.
We have a loss of three electrons in one half-reaction and a gain of two electrons in the other half-reaction. We must get loss equal to gain. We can double the Al half-reaction and triple the Sn^{4+} half-reaction to get six electrons for both.

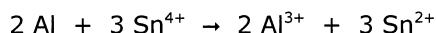


Loss now equals gain.

- Step 5. Add the two half-reactions together and cancel any items which appear on both sides.



The 6e^- cancel out to give the following.



- Step 6. Verify the result.

Two aluminums each side, three tins each side, +12 each side. Done.

Let me make two points.

In Step 3, remember that you add electrons to the more positive/less negative side of each equation. Also (and ALWAYS!), one half-reaction gets the electrons on the left and the other half-reaction gets the electrons on the right. If you're puzzled by what side the electrons might go on for one of the half-reactions, then check the other half-reaction. The electrons must go into opposite sides for the two.

In Step 4, you set the loss equal to the gain. If done correctly, all electrons will cancel out in Step 5. If the electrons do not cancel out in Step 5, then you screwed up. Find out where and fix it.

OK, here's a general summary of things to keep in mind so far.

OXIDATION HALF-REACTION	REDUCTION HALF-REACTION
Electrons are lost by a reactant.	Electrons are gained by a reactant.
Electrons are on the right side of the equation.	Electrons are on the left side of the equation.
The oxnos increases for the redox atom.	The oxnos decreases for the redox atom.
This occurs for the reducing agent.	This occurs for the oxidizing agent.

This Example was fairly easy. We continue with new Examples which will illustrate Scenarios A and B.

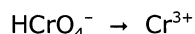
.....
Example 2. Derive the balanced equation for the reaction of iron(II) ion and hydrogen chromate ion in acidic solution. The redox products are iron(III) and chromium(III).

Set it up.



Those are the reagents given in the problem. The problem also specifies acidic conditions. Now start the Steps.

- Step 1. Identify the redox atoms and set up a half-reaction for each couple.
 The redox atoms are iron and chromium. (If you're not sure, check the oxnos.) The couples are $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{HCrO}_4^-/\text{Cr}^{3+}$. Set up a half-reaction for each.

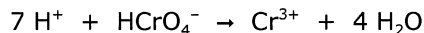


- Step 2. Atom-balance each half-reaction.

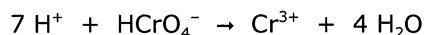
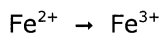
The $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-reaction is OK as is. The $\text{HCrO}_4^-/\text{Cr}^{3+}$ half-reaction is balanced for chromium but the oxygens and hydrogen cannot be balanced only by the reagents as shown. We must bring in one or two additional reagents. The given conditions are acidic, so we invoke Scenario A. According to Scenario A, we first check for a straightforward fix, but nothing seems obvious. We proceed to bring in some waters to balance the oxygens. We'll need four H_2O on the right.



That takes care of O's but now we need to add some H^+ 's on the left to balance the hydrogens.



Now both half-reactions are atom-balanced.



- Step 3. Charge-balance each half-reaction, using electrons as needed.

The Fe^{2+} half-reaction is too positive by one on the right side; add one electron.



Since we added an electron on the right side of that equation, we must add them on the left for the HCrO_4^- equation. How many? The charges on the left side add to +6; the charges on the right side add to +3. The left side is too positive by three; you need three electrons on that side.



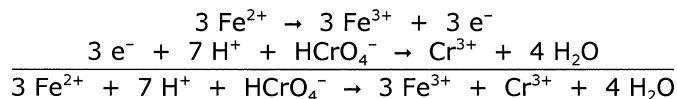
The half-reactions are now fully balanced by themselves. We can see that Fe^{2+} is being oxidized while HCrO_4^- is being reduced.

- Step 4. Set the number of electrons equal for the two half-reactions, using multipliers as needed. We have a loss of one electron versus a gain of three electrons. We need to get the numbers equal. Multiply the Fe^{2+} half-reaction by three.



Loss now equals gain.

- Step 5. Add the two half-reactions together and cancel any items which appear on both sides.



The 3e^- on each side will cancel out, so I didn't bother showing them in the sum this time.

- Step 6. Verify the result. Both sides show three irons, eight hydrogens, one chromium and four oxygens. Total charges on the left add to +12; total charges on the right add to +12. It's a done deal.

This Example 2 illustrated the use of Scenario A. Now we show one with Scenario B.

.....

Example 3. Derive the balanced equation for the reaction of aluminum and sulfate in basic solution. The products include sulfite and the complex $\text{Al}(\text{OH})_4^-$.

.....

Set it up.



That's all we have so far, along with the basic part. Start the Steps.

- Step 1. Identify the redox atoms and set up a half-reaction for each couple. The redox atoms are aluminum and sulfur. The couples are $\text{Al}/\text{Al}(\text{OH})_4^-$ and $\text{SO}_4^{2-}/\text{SO}_3^{2-}$. Set up a half-reaction for each.

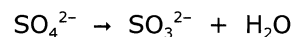


- Step 2. Atom-balance each half-reaction.

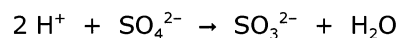
The $\text{Al}/\text{Al}(\text{OH})_4^-$ half-reaction has one aluminum on each side and the $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ half-reaction has one sulfur on each side, but neither half-reaction can be atom-balanced without bringing in some more reagents. The given conditions are basic, so that calls for Scenario B. The Al half-reaction actually has a somewhat straightforward fix: notice that the difference between the left and right sides is an equal number of O's and H's. For that, we can bring in hydroxides since they contain an equal number of O's and H's. We'll need four on the left.



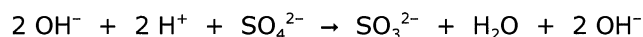
That takes care of atom-balance for that case. These "straightforward" fixes may not always be obvious, in which case you execute the full Scenario method. For the other half-reaction, a fix is not straightforward. We'll do this via the indirect approach by first invoking Scenario A. Scenario A says balance O's with H_2O 's; we need one H_2O on the right.



Now balance the H's.



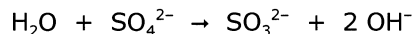
That is now atom-balanced, but we must convert this to the specified basic conditions. We bring in one OH^- for each H^+ ; to keep in balance, we must add equal numbers of OH^- to both sides. Since the left side has two H^+ , we bring in two OH^- for each side.



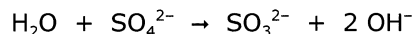
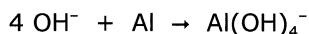
On the left, the two OH^- and the two H^+ constitute two H_2O



and that completes the neutralization aspect. This leaves us with some H_2O on both sides, which we must now fix.



We now have atom-balance for both half-reactions.

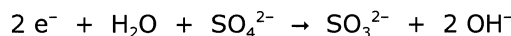


- Step 3. Charge-balance each half-reaction, using electrons as needed.

The Al half-reaction has four negatives on the left side and only one negative on the right. We need three more negatives on the right side.



Now, which side gets the electrons for the SO_4^{2-} half-reaction? How many? The charges on the left side add to -2 ; the charges on the right side add to -4 . You need two electrons on the left.

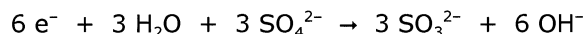
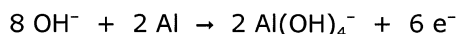


The half-reactions are now fully balanced by themselves.

Which reactant is oxidized? _____ Which reactant is reduced? _____

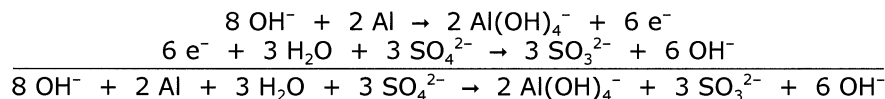
- Step 4. Set the number of electrons equal for the two half-reactions, using multipliers as needed.

We have a loss of three electrons and a gain of two electrons and we need to get them equal. We will double the three and triple the two.

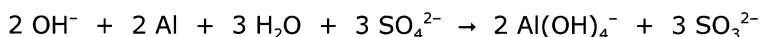


Loss now equals gain.

- Step 5. Add the two half-reactions together.



I already cancelled the electrons from both sides, but we're also left with OH^- on both sides. Cancel six on both sides.



- Step 6. Verify the result.

Go ahead and check it out.

We've now seen three Examples of balancing redox by half-reactions, and these have covered acidic and basic conditions. Now it's your turn.

.....
Example 4. Balance the equation for the oxidation of iodide by chlorate to form iodine and chloride.

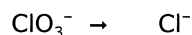
Start with a general setup equation:

Start the Steps.

- Step 1. Identify the redox atoms and set up a half-reaction for each couple.

- Step 2. Atom-balance each half-reaction.

One is easy and one is not. The former was given earlier in the Chapter. The latter will start out as shown below at right. (Clue: Scenario A for this one.) Go ahead and work them both out.



- Step 3. Charge-balance each half-reaction, using electrons as needed.
Write in the electrons above if you have room or just write it all out here again.

Which couple is involved in the oxidation half-reaction? _____

Which couple is involved in the reduction half-reaction? _____

- Step 4. Set the number of electrons equal for the two half-reactions, using multipliers as needed. Rewrite the equations below, one above the other, so you can sum them in the next Step. Be sure that loss and gain are equal.

- Step 5. Add the two half-reactions together and cancel any items which appear on both sides.
- Step 6. Verify the result.

You can also verify the final result by checking Example 3 in Section 14.2.

This ends the discussion for balancing redox equations by half-reaction methods.

Problems

- Consider the reaction of thiosulfate ion and hypobromous acid, HBrO , to form sulfate ion and bromide ion.
 - Identify the redox couples.
 - Derive the balanced equation for each half-reaction.
 - Derive the overall balanced equation.
 - What reactant is oxidized? What reactant is reduced?
- Consider the reaction of Cd metal with solid NiO(OH) in basic conditions to produce the solids Cd(OH)_2 and nickel(II) hydroxide.
 - Identify the redox couples.
 - Derive the balanced equation for each half-reaction.
 - Derive the overall balanced equation.
 - What reactant is oxidized? What reactant is reduced?
- Consider the reaction of dinitrogen oxide and cobalt(III) ion in acidic conditions to produce nitrous acid and cobalt(II) ion.
 - Derive the balanced equation for each half-reaction.
 - Derive the overall balanced equation.
 - What is the oxidizing agent? What is the reducing agent?
- Consider the following unbalanced equation for a reaction in basic conditions.

$$\text{PO}_4^{3-} + \text{Cr} \rightarrow \text{CrO}_2^- + \text{HPO}_3^{2-}$$
 - Derive the overall balanced equation.
 - What is the oxidizing agent? What is the reducing agent?