

## REDOX BASICS - Oxidation & Reduction Chemistry

According to NY State Regents Chem Guidelines, this is what we have to learn

1. An oxidation-reduction (redox) reaction involves the transfer of electrons ( $e^-$ )
2. Oxidation is the loss of electrons (LEO the Lion goes GER).
3. A half-reaction can be written to represent oxidation.
4. Reduction is the gain of electrons (LEO the Lion goes GER).
5. A half-reaction can be written to represent reduction.
6. In a redox reaction, the number of electrons lost = the number of electrons gained.
7. Oxidation numbers (states) can be assigned to atoms and ions. Changes in oxidation numbers indicate that oxidation and reduction have occurred.
8. An electrochemical cell can either be voltaic or electrolytic. In an electrochemical cell, oxidation occurs at the anode and reduction at the cathode (Leo's a RED-CAT)
9. A voltaic cell spontaneously converts chemical energy to electrical energy.
10. An electrolytic cell requires electrical energy to produce chemical change. This process is known as electrolysis.

1. An oxidation-reduction (redox) reaction involves the transfer of electrons

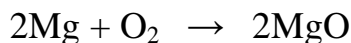
We've learned already of many kinds of reactions in chemistry; Synthesis, decomposition, single replacement, double replacement, & combustion. Then acid-base neutralization. Finally in organic chem we learned about addition and substitution, esterification, polymerization, fermentation & saponification.

That's 12 so far (and several more await in nuclear chem).

REDOX is the next reaction, but it's not really a separate one, many of the reactions above are ALSO redox reaction.

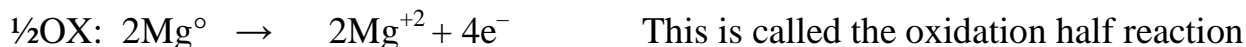
Redox reactions occur whenever there is a transfer of electrons, when atoms become cations or anions, or the reverse, when ions become atoms.

2. Oxidation is the loss of electrons (LEO the Lion goes GER).
3. A half-reaction can be written to represent oxidation.



This is a common reaction for us, a synthesis that we did in lab earlier in the year.

What's going on with the electrons here? Let's take a close look.



Both of the magnesium atoms become +2 ions by losing 2 electrons each. (that's 4 electrons total)

4. Reduction is the gain of electrons (LEO the Lion goes GER).

5. A half-reaction can be written to represent reduction.



At the same time the magnesium atoms become +2 cations, the oxygen atoms become -2 anions.

By combining these two reactions, we have an oxidation reaction and a reduction reaction, that are perfectly balanced. The number of electrons that are oxidized must also be reduced.

There are no left over electrons, or IOU electrons.

There's just one easy rule to follow:

Make sure that you balance your oxidation & reductions.

For every single electron that is oxidized off, it has to be picked up by some other atom or ion and be reduced. No left over electrons ever. Not even one.

7. Oxidation numbers (states) can be assigned to atoms and ions. Changes in oxidation numbers indicate that oxidation and reduction have occurred.

Oxidation numbers were used earlier in the year when we put together various molecular compounds (remember the 5 different nitrogen/oxygen compounds, and the 2 different carbon/oxygen compounds)?

Oxidation numbers are listed on our periodic tables. Atoms always have oxidation numbers of ZERO.

Ions have oxidation numbers equal to their ionic charge. Atoms in molecular compounds can have a variety of oxidation numbers provided that all the oxidation numbers in a molecule sum to zero.

Polyatomic ions also have oxidation numbers equal to their charges. Using table E you can determine the oxidation numbers (charges) for each part of these polyatomic ions.

Selected oxidation numbers: (you MUST open your periodic table now, or just stop reading).

Our key element at the top of the page is carbon. Top right corner of the box shows 3 selected oxidation numbers. They are  $-4$ ,  $+2$ , and  $+4$ . There are others, but in our class we'll only use these selected oxidation states on our periodic table.

All group 1 ions have a  $+1$  oxidation state (charge). All group 2 ions have a  $+2$  oxidation state (charge).

Transitional metals have one or more possible oxidation states (charges). That's why we need to use the roman numerals in naming some transitional metal ionic compounds.

Most of the nonmetals have many possible oxidation states, both positive or negative.

Almost all of the Noble Gases have a "0" since they do not make any compounds.

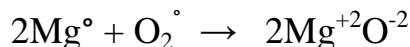
Let's look at these compounds and see how their oxidation numbers sum to zero (for compounds) or to a positive or negative charge (for the ions).

| compound or ion              | net charge | oxidation numbers of each of the parts                                                                                                            |
|------------------------------|------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| NaCl                         | 0          | $\text{Na}^{+1}$ $\text{Cl}^{-1}$                                                                                                                 |
| NaOH                         | 0          | $\text{Na}^{+1}$ $\text{O}^{-2}$ $\text{H}^{+1}$                                                                                                  |
| $\text{H}_2\text{SO}_4$      | 0          | $\text{H}^{+1}$ $\text{H}^{+1}$ $\text{S}^{+6}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$                                   |
| $\text{N}_2\text{O}_5$       | 0          | $\text{N}^{+5}$ $\text{N}^{+5}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$                                   |
| $\text{NH}_3$                | 0          | $\text{N}^{-3}$ $\text{H}^{+1}$ $\text{H}^{+1}$ $\text{H}^{+1}$                                                                                   |
| $\text{NH}_4^{+1}$           | +1         | $\text{N}^{-3}$ $\text{H}^{+1}$ $\text{H}^{+1}$ $\text{H}^{+1}$ $\text{H}^{+1}$                                                                   |
| $\text{MnO}_4^{-1}$          | -1         | $\text{Mn}^{+7}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$                                                                  |
| $\text{PO}_4^{-3}$           | -3         | $\text{P}^{+5}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$                                                                   |
| $\text{HCO}_3^{-1}$          | -1         | $\text{H}^{+1}$ $\text{C}^{+4}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$                                                                   |
| $\text{Cr}_2\text{O}_7^{-2}$ | -2         | $\text{Cr}^{+6}$ $\text{Cr}^{+6}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ $\text{O}^{-2}$ |

Sometimes you will meet a compound or ion that won't "work" with the selected oxidation numbers on our table. Remember, they are called "SELECTED" oxidation numbers, there are more of them. This is an intro class and sometimes "real" chem blurs into "regents" chemistry. If you can't make the numbers jive, ask your teacher.

Let's look at the oxidation numbers of all the species involved. Species is a biology word but the State Education department loves it. Here, magnesium comes in 2 "species", the atom and the +2 cation. Here, the oxygen is in two species as well, the atom and the oxide -2 anion.

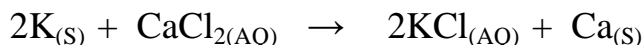
$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$  can be thought of this way too:



Mg atoms are  $\text{Mg}^\circ$     Oxygen molecules (a pair of atoms) are also  $\text{O}_2^\circ$   
 In MgO there is a  $\text{Mg}^{+2}$  cation, and the oxide anion  $\text{O}^{-2}$

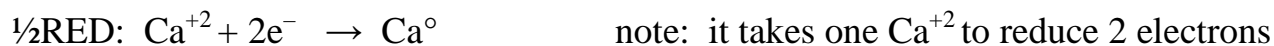
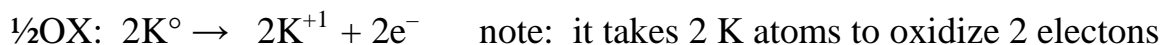
The sum of the oxidation numbers in the MgO is  $(+2) + (-2) = 0$  (as expected and required)

### A second example reaction:



This is a single replacement reaction, table J shows K higher than Ca, so the reaction goes forward as potassium has a higher activity and it will go into solution and bump out the calcium. To do this, the potassium must oxidize (or lose electrons). When this happens, the calcium ions in solution are forced to pick up these electrons, therefore the  $\text{Ca}^{+2}$  ions are reduced.

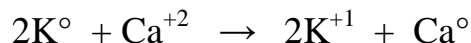
The redox half reactions would be:



Since each half reaction is perfectly balanced we can rewrite these pair of reactions together, omitting the electrons—since they balance out on each side of the arrow.

We can write what is called the NET IONIC EQUATION

(combining them together, after we cancel out the two electrons that are on opposite sides of the arrow).

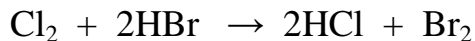


It shows both potassium atoms become  $\text{K}^{+1}$  cations, and the  $\text{Ca}^{+2}$  cation become a Ca atom. The net ionic equation shows only the NET ion transfer inside the redox reaction. It cancels out the electrons from each side of the arrow.

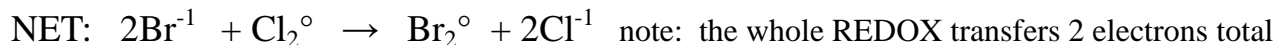
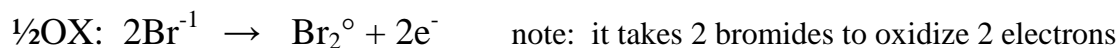
Please take a moment to "count" the charges on both sides, they even out perfectly.

This shows the "Conservation of Charge", which is like conservation of matter and conservation of energy. There must be conservation of charge (or you made a mistake).

Let's look at one more reaction now...



We can chemically write out both the oxidation and the reduction half reactions, and follow that with the NET IONIC EQUATION this way...

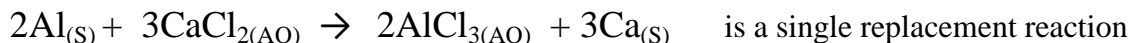


In this reaction, the  $\text{H}^{+1}$  ions from the HBr, which end up HCl, are called SPECTATOR IONS, because they just "watch" but don't do anything. They're required, but dull.

Single replacement reactions are also redox. Lots of reactions are redox too.

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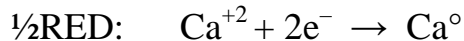
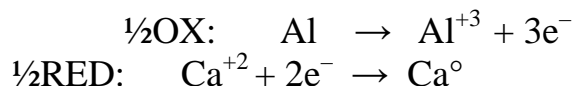
Things get a little bit more involved when the number of ions oxidized by one part does not match the number gained by the other. Then, balancing reactions comes into play. For example...



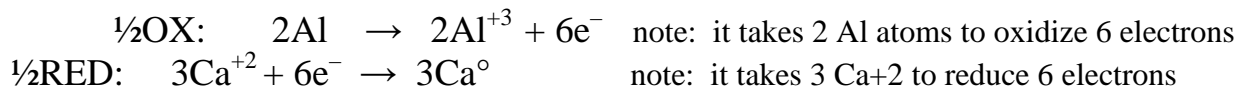
Since aluminum will oxidize here because Al is "higher" on table J compared to the Ca (that means the Al is more reactive than Ca) It forces the calcium to become reduced.

Note: each Al loses  $3\text{e}^{-}$  but each Ca only gains  $2\text{e}^{-}$ .

Oxidation is loss of electrons, Reduction is gain of electrons, so...



The electron transfer is NOT equal. Three electrons are oxidized, only two are used for reduction. This can't be. To "fix" this, we look for the lowest common factor (which is 6) and adjust the half reactions to match up the electrons being transferred.



## Objective 8 & 9—Electrochemical Cells

An electrochemical cell can either be voltaic or electrolytic. In all electrochemical cells, oxidation occurs at the anode and reduction at the cathode (Leo's a RED-CAT)

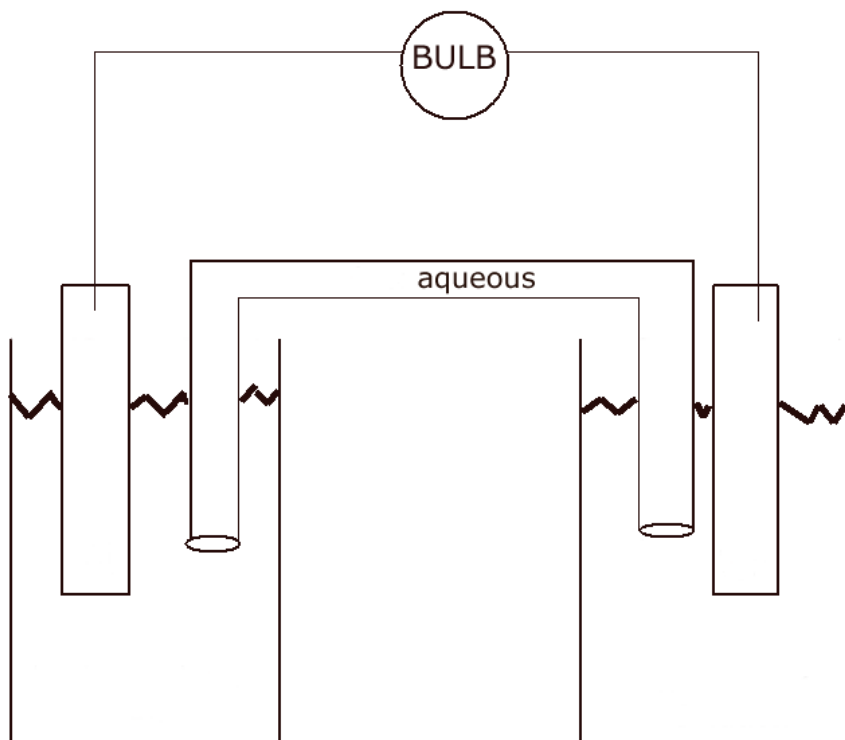
A voltaic cell is a battery, where chemistry SPONTANEOUSLY creates electricity. These run and run (unless a switch is put into the circuit).

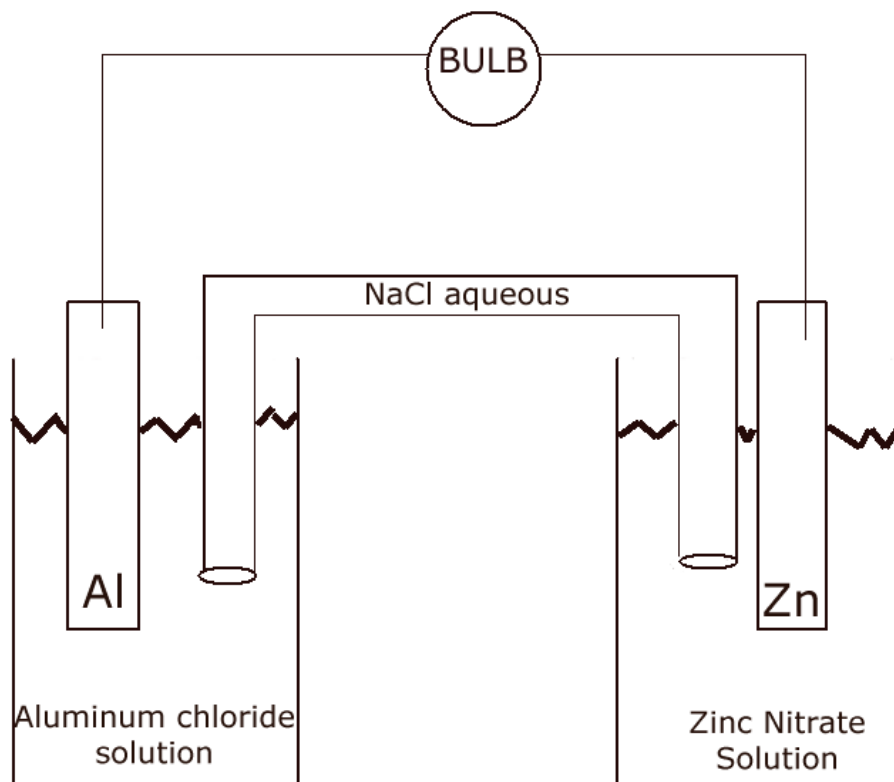
An electrolytic cell uses electricity to force a redox reaction that cannot happen spontaneously. These reactions are used to “electroplate” precious metals onto strong but inexpensive ones. An external battery is necessary to make this happen

This is a generic diagram for a battery, or voltaic cell. There are 2 beakers, with a metal bar in each, connected to each other by a wire. Wires carry electricity.

There is an upside down “U” tube, that contains a salt solution, connecting the two beakers.

In each beaker is an aqueous solution. Batteries that you are used to are modifications of this set up, cool technological advances in package design so that you don't have to fit two beakers into your cell phone or calculator. This is how scientists created the first batteries, the science part, not the packaging part. You're so lucky, feel it now.





This is called an aluminum/zinc voltaic cell (battery).

Each metal bar must be in a solution which has that metal as an ion. Aluminum metal is in  $\text{AlCl}_{3(\text{AQ})}$

The Zinc is in a  $\text{Zn}(\text{NO}_3)_{2(\text{AQ})}$

There is a  $\text{NaCl}_{(\text{AQ})}$  aqueous solution in the salt bridge.

The metal bars are connected by wire, through a bulb, which lights up if electricity flows through it.

Both Al and Zn would *like to* oxidize into ions, by losing electrons. Only one will, Table J decides.

It's aluminum that will oxidize, not zinc, you know this because the Al is "higher" than Zn on table J.

When  $\text{Al} \rightarrow \text{Al}^{+3}$  cations, the ions go into solution, the electrons flow up through the wire to the zinc bar.

Zinc wants to oxidize but it cannot with aluminum, so it is forced to be the reduction side of this redox.

The  $\text{Zn}^{+2}$  ions in solution are attracted to all the electrons on the zinc bar, so they jump onto the bar, gaining 2 electrons each, and are reduced into zinc atoms.

The addition of  $\text{Al}^{+3}$  cations to the left solution creates a + charge in the solution.

The removal of  $\text{Zn}^{+2}$  ions from the other solution makes a - charge in that solution.

This is a **BIG PROBLEM**, big enough to stop the electricity flow immediately.

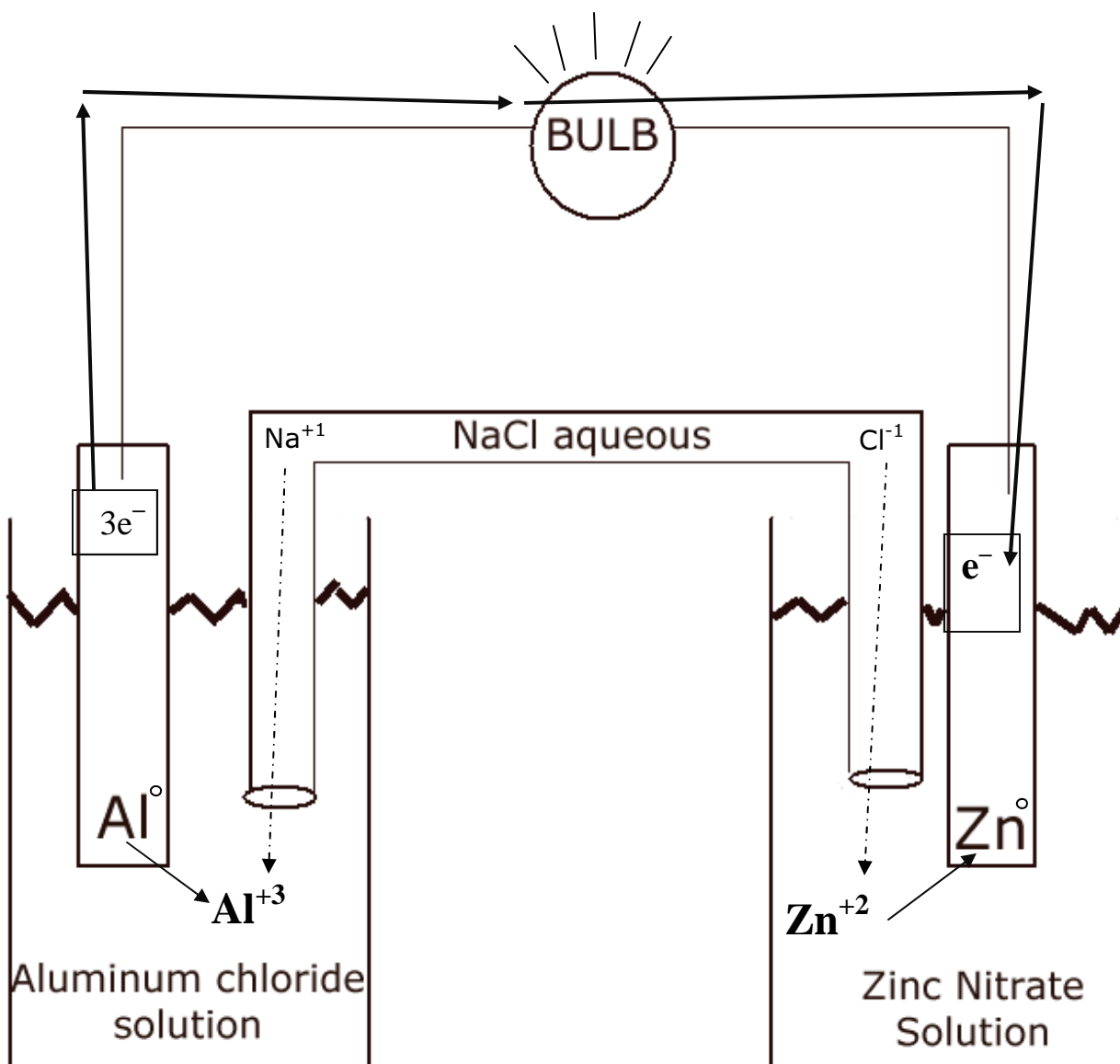
That's why we have an aqueous salt bridge. In this one are  $\text{Na}^{+1}$  and  $\text{Cl}^{-1}$  ions.

As the solution at left gains cations, it becomes POSITIVELY charged, so chloride anions flow into it through the “U” tube. Those chlorides offset the positive charge, keeping that beaker neutral.

As the solution at right gets more NEGATIVELY charged because it’s LOSING cations onto the zinc metal bar, the sodium cations flow to it, offsetting that charge, keeping this beaker neutral.

It’s this salt bridge ion flow that keeps the beakers neutral, and allows the electrons to flow. It lets the REDOX to continue.

Look below and make sure you see all of this. Note the light bulb is lit because electricity (electrons) flow from the aluminum bar to the zinc bar. We have separated the two half reactions and can “use” the moving electrons to do work. Some fancy packaging and we have our own aluminum/zinc battery.





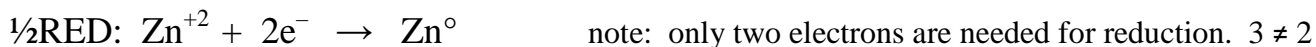
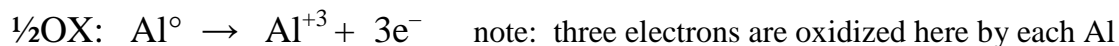
Each metal bar is an electrode. The names are cathode and anode. The way to keep them straight is to remember Leo the Lion. He's a RED CAT. That should remind you that reduction happens on the cathode. Oxidation happens on the anode.

So, aluminum is the anode, because the zinc is the cathode.

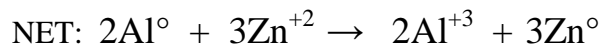
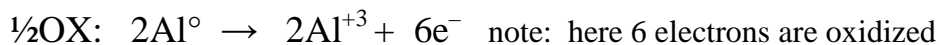
3 reasons that ALL batteries die...

1. Run out of anode. Sooner or later the aluminum atoms will all give up their electrons and jump into solution, and there will be no atoms left, the bar will be dissolved.
2. Run out of salt bridge ions. Sooner or later all of the salt ions will all move to opposite beakers to keep the beakers neutral (offset the electrical potential). When that occurs, the solutions immediately become charged, stopping the flow of electricity.
3. Run out of cathode side cations. (NOT run out of cathode, that NEVER happens). If enough electrons arrive on the zinc bar, all the zinc cations in the solution will have become zinc atoms. At that point no more reduction can occur. The cathode gets bigger as the battery runs. Battery recyclers recycle the cathodes. Cathodes ARE NOT used up, they get bigger. Anodes get used up (see #1 above).

Let's quickly look at the REDOX of this battery. The two half reactions and the Net Ionic Equation.



Let's balance using the LOWEST COMMON FACTOR (which is 6)



LOOK HARD: see that the charge is balanced in this net ionic equation, and that the six electrons oxidized are cancelled out by the six electrons that are being reduced. The electrons are omitted in the net ionic equation.

Charge must be conserved (the number of electrons are oxidized must be perfectly balanced by the number of electrons being reduced. If it ever doesn't work, you are mixing up the charges of the ions being used. Check your details.

# Electrolytic cells

In these cells, we use electricity to force redox, and we can use this to electroplate valuable metals onto less valuable metals. This makes our cheap filler be covered with precious metals, rings look great even though they might be inexpensive copper just coated with silver (for example).

These are NON-SPONTANEOUS reactions, but they are still redox. Below is an example diagram where we will “plate” silver onto a copper ring. Copper is cheap and strong but turns your finger green. Coating it in silver makes it look silver, makes you look richer, and keeps the green in the garden! Plus, copper insides are much stronger than a pure silver ring.

The electrons provided by the battery are pushed onto the copper ring. The silver ions in solution are attracted and get reduced to silver atoms, which plate on the copper. The longer this “runs” the thicker the silver coating gets.

To complete the circuit (and oxidize electrons to balance the reduction) the silver atoms in the silver bar oxidize, the silver cations replace the cations in solution, the electrons they oxidize run up the wire to the other side of the battery (replacing the electrons oxidized to provide the electricity in the first place that gets pushed onto the ring).

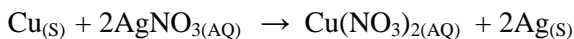
The  $\frac{1}{2}$ OX:  $\text{Ag}^{\circ} \rightarrow \text{Ag}^{+1} + 1\text{e}^{-}$   
this happens ON the silver bar

The  $\frac{1}{2}$ RED:  $\text{Ag}^{+1} + 1\text{e}^{-} \rightarrow \text{Ag}^{\circ}$   
this happens ON the ring

Electroplating is a billion dollar a year business.  
It is possible due to chemistry.

This is not a spontaneous redox, it requires energy,  
and that energy makes chemistry happen.

This is what happens when Copper is put into a  
silver nitrate solution:



This is single replacement, and if you LET THIS  
HAPPEN, the silver precipitates spontaneously.

An electrolytic cell IS NOT SPONTANEOUS.  
You have to be smart, and you have to USE  
electricity to force a chemical reaction that you  
want to happen.

In a voltaic cell (a battery) the redox *is* spontaneous.

Redox is the name of a thrash metal band from  
Barcelona, Spain. There are apparently no fun  
photos or jokes to tell about redox.

Thanks for reading.

