REDOX

Oxidation & Reduction Chemistry

Electrons get transferred, compounds form, we follow closely as to what's exactly going on with these electrons.

<u>According to NY State Regents Chem Guidelines, this is what we have to learn</u>

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

2. Oxidation is the loss of electrons (<u>LEO</u> 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 <u>GER</u>).

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.

Let's look at these 10 objectives.

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 + double replacement, & combustion. Then acid-base neutralizations.

Finally in organic chem we learned about… addition and substitution, esterification, polymerization, fermentation and saponification.

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

REDOX is the "12+1th" reaction so far.

Redox reactions occur whenever there is a transfer of electrons.

Many of the reactions above are <u>also</u> Redox reactions. If you look closer at the balanced chemical equations we've seen in the past, and examine the oxidation numbers of the atoms & ions— if they change from one side of the yield arrow to the other it's redox!

2. Oxidation is the loss of electrons (LEO the Lion goes GER).

3. A half-reaction can be written to represent oxidation.

$$2Mg + O_2 \longrightarrow 2MgO$$

This is a common reaction for us, a synthesis that we even did in lab.

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

$$2Mg + O_2 \longrightarrow 2MgO$$

$$2Mg^{\circ} \longrightarrow 2Mg^{+2} + 2e^{-}$$

The magnesium atoms become +2 ions by losing 2 electrons each.

4. Reduction is the gain of electrons (LEO the Lion goes <u>GER</u>).

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

$$2Mg + O_2 \longrightarrow 2MgO$$

$$O_2 + 2e^{-} \longrightarrow 2O^{-2}$$

At the same time the magnesium atoms become ions,
the oxygen atoms become –2 anions by gaining one electron each.

By combining these two reactions, we have an oxidation reaction and a reduction reaction, that are perfectly balanced.

Mg loses two electrons and the oxygen picks them both up.

Redox has to be balanced. If you can control the flow of these electrons, they can do some work for you in between being oxidized and then reducing something else.

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. Objective 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 five different nitrogen and oxygen compounds). Oxidation numbers are listed on our periodic tables. Atoms always have oxidation numbers of ZERO. Ions have oxidation numbers equal to there 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. Poly atomic ions also have oxidation numbers (as ions it's the net ionic charge listed on table E) and as ions you should be able to determine the oxidation numbers of the parts of the whole polyatomic ion.

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

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

All group 1 atoms have a +1 oxidation state.

All group 2 atoms have a +2 oxidation state.

Transitional metals have one or more possible oxidation states
(hence the roman numerals in naming some transitional metal ionic compounds.

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

Noble gases have a “0” since they do not make any compounds (except Kr and Xe).

Let’s look at these molecules and formula units and figure out the oxidation numbers for each atom or ion inside.

compound or ion	net charge	oxidation numbers of the parts
NaCl	0	Na^{+1} Cl^{-1}
NaOH	0	Na^{+1} O^{-2} H^{+1}
H_2SO_4	0	H^{+1} H^{+1} S^{+6} O^{-2} O^{-2} O^{-2} O^{-2}
N_2O_5	0	N^{+5} N^{+5} O^{-2} O^{-2} O^{-2} O^{-2} O^{-2}
NH_3	0	N^{-3} H^{+1} H^{+1} H^{+1}
NH_4^{+1}	+1	N^{-3} H^{+1} H^{+1} H^{+1} H^{+1}
MnO_4^{-1}	-1	Mn^{+7} O^{-2} O^{-2} O^{-2} O^{-2}
PO_4^{-3}	-3	P^{+5} O^{-2} O^{-2} O^{-2} O^{-2}
HCO_3^{-1}	-1	H^{+1} C^{+4} O^{-2} O^{-2} O^{-2}
$Cr_2O_7^{-2}$	-2	Cr^{+6} Cr^{+6} O^{-2} O^{-2} O^{-2} O^{-2} O^{-2} O^{-2} O^{-2}

If you cannot make a particular polyatomic ion “work” as above, remember there are many more oxidation numbers listed outside your “selected” ones. Also keep in mind that this is your first chemistry course.

One of our example reactions from earlier is this one. Let’s look at the oxidation numbers of all the species involved.

$$2Mg + O_2 \longrightarrow 2MgO$$

Mg atoms are Mg°

Oxygen molecules (a pair of atoms) are also O_2°

In MgO there is Mg^{+2} ion. The oxygen ion is O^{-2}

The sum of the oxidation numbers of each formula unit of MgO is

+2 plus −2 = zero (as expected and required)

In another rection, for example:

$$2K_{(S)} + CaCl_{2(AQ)} \longrightarrow 2KCl_{(AQ)} + Ca_{(S)}$$

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 already in solution must pick up these electrons, therefore the Ca^{+2} ions are reduced.

The redox half reactions would be:

$$2K° \longrightarrow 2K° + 2e^{-}$$

$$Ca^{+2} + 2e^{-} \longrightarrow Ca°$$

Some thing new…

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'll write the NET IONIC EQUATION

$$2K° + Ca^{+2} \longrightarrow 2K° + Ca°$$

It shows that potassium ions become potassium +1 ions, and the calcium +2 cations become atoms. It shows only the NET ion transfer inside the redox reaction.

Let's look at one more reaction now…

$$Cl_2 + 2HBr \longrightarrow 2HCl + Br_2$$

The oxidation (loss of electrons) half reaction is:

$$2Br^{-1} \longrightarrow Br_2° + 2e^-$$

The reduction (gain of electrons) half reaction is:

$$Cl_2° + 2e^- \longrightarrow 2Cl^{-1}$$

The net ionic equation is:

$$2Br^{-1} + Cl_2° \longrightarrow Br_2° + 2Cl^{-1}$$

The hydrogen ions, which do not change during this reaction
are merely specators to the redox.
They are called SPECTATOR IONS for this reason.

Single replacement reactions are also redox.

Things get one step 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 first. For example...

$Al_{(S)}$ + $CaCl_{2(AQ)}$ is a single replacement reaction

Since aluminum will oxidize here, forcing the calcium to become reduced, let's look at these half reactions, after we balance and complete this reaction..

Note: each Al loses $3e^-$ but each Ca only gains $2e^-$, we must balance FIRST.

$$2Al_{(S)} + 3CaCl_{2(AQ)} \longrightarrow 2AlCl_{3(AQ)} + 3Ca_{(S)}$$

Oxidation is loss of electrons,

$$2Al \longrightarrow 2Al^{+3} + 6e^-$$

Reduction is gain of electrons,

$$3Ca^{+2} + 6e^- \longrightarrow 3Ca°$$

Objective 8 & 9—electrochemical cells

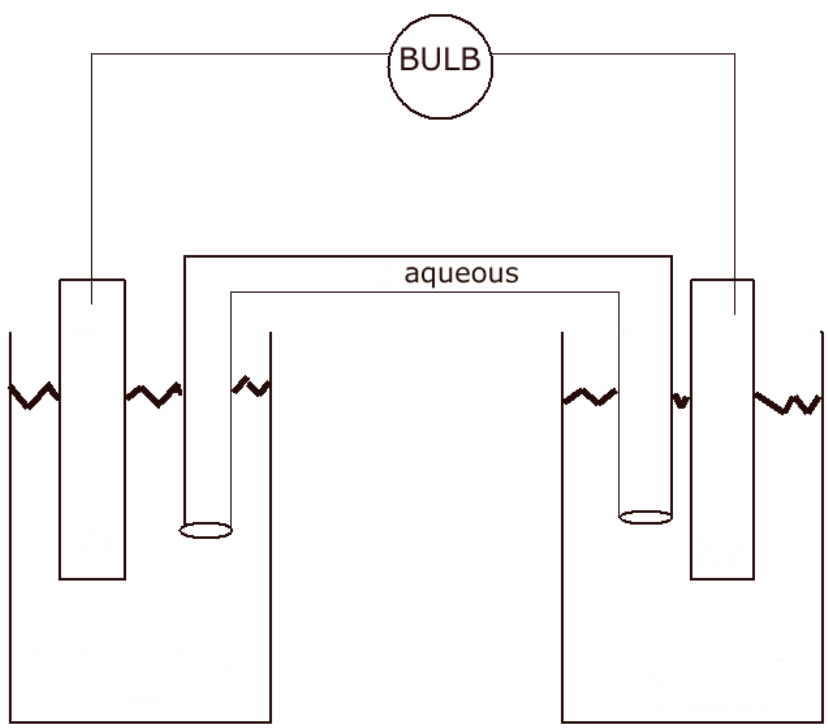
An electrochemical cell can either be voltaic or electrolytic. In an electrochemical cell, oxidation occurs at the anode and reduction at the cathode (Leo's a RED-CAT)

A cell is an electrochemistry setup that allows for redox reactions to occur. Voltaic cells spontaneously transfer electrons (as long as they can flow), chemistry produces electricity. Batteries are voltaic cells.

In class we've seen the set up for a battery/voltaic cell. This happens SPONTANEOUSLY, without the addition of energy.

When we add in the metals, the solutions, and the salt bridge, then it becomes a battery.

Next is an aluminum/zinc voltaic cell.

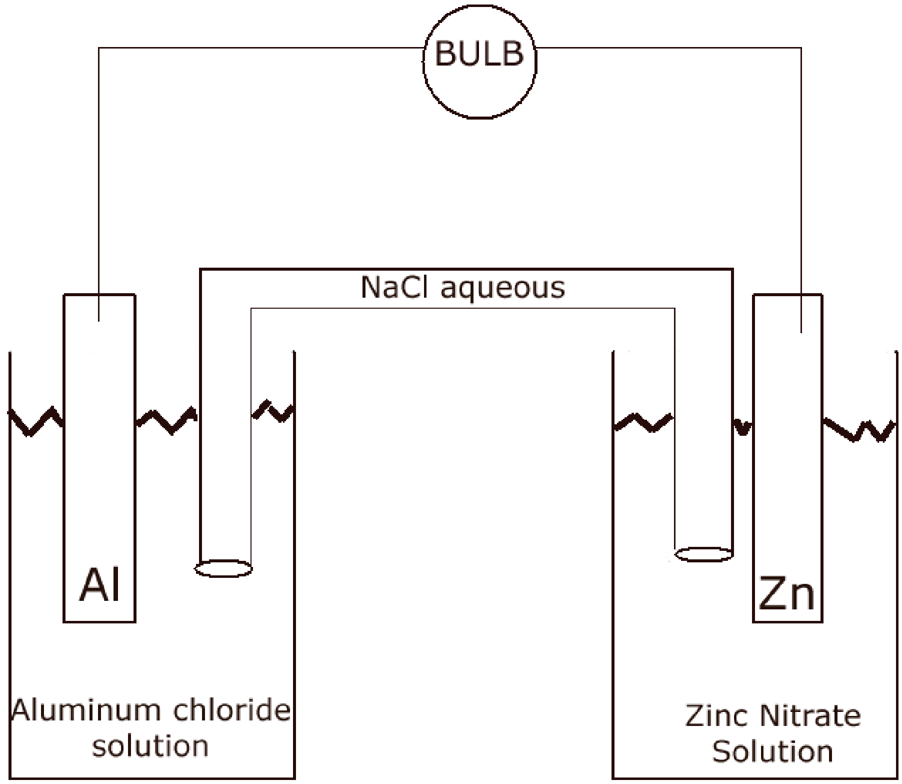


Each metal must be in a solution which has itself as an ion. Aluminum metal is in the aluminum chloride solution.

Zinc is in a zinc nitrate solution.

There is a NaCl aqueous solution in the salt bridge.

The metals are connected by wire, through a bulb.



Both Al and Zn would like to oxidize into ions, losing electrons. Only one can, table J decides for us.

It's aluminum that will oxidize, not zinc.

If Al oxidizes into Al^{+3} cations, the ions jump into solution, the electrons flow up through the wire to the zinc bar.

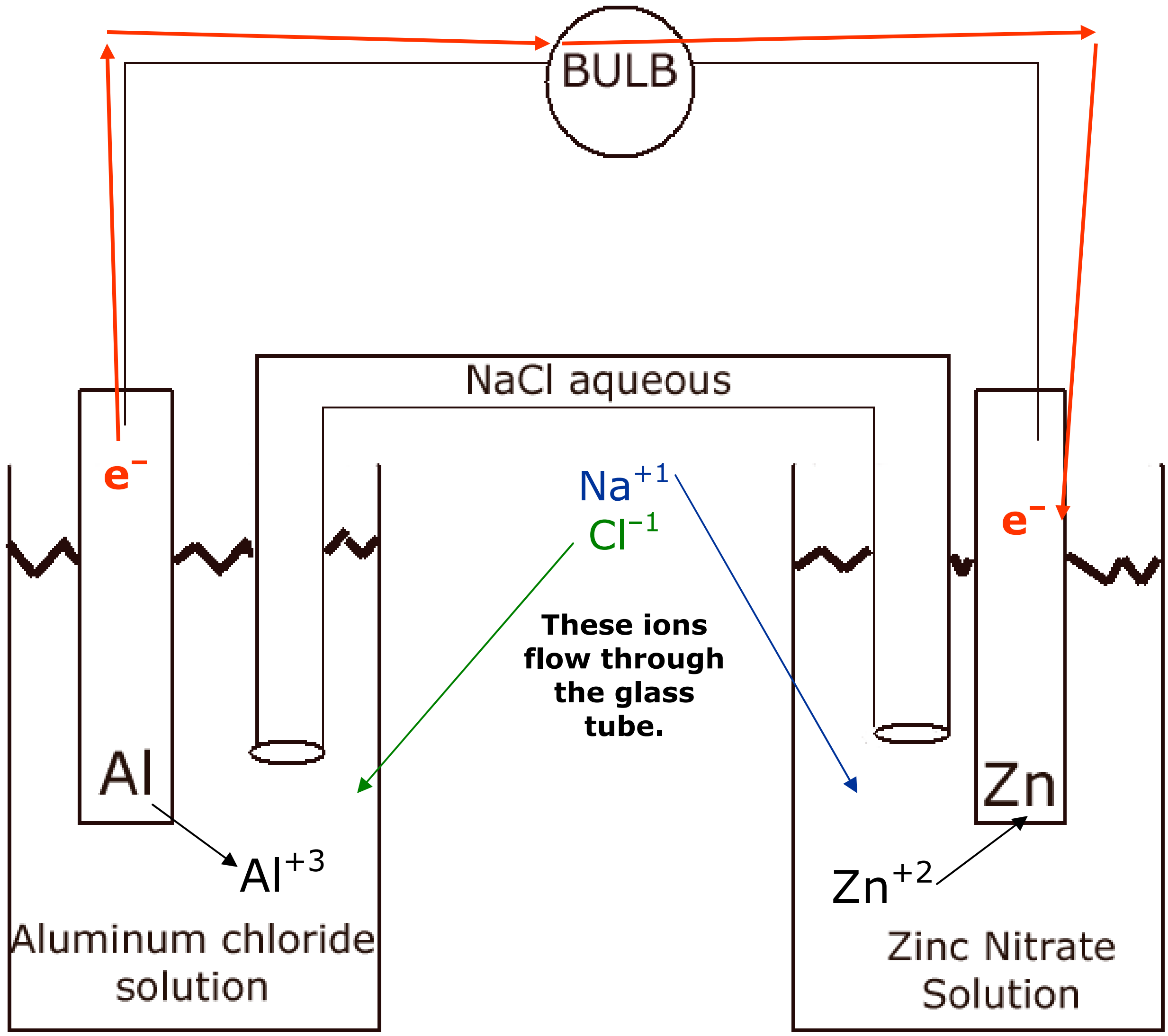
Zinc wants to oxidize but it cannot do so if aluminum does, so it is forced to be the reduction side of this redox.

The Zn^{+2} ions in solution are attracted to all the electrons on the zinc bar, so they jump onto the bar, picking up electrons, and get reduced into zinc atoms.

The addition of Al^{+3} cations to the left solution creates a + charge in the solution. The removal of Zn^{+2} ions from the other solution makes a – charge in that solution. This is a PROBLEM, big enough to stop the electricity flow immediately.

That's why we have an aqueous salt bridge. In this one are Na^{+1} and Cl^{-1} ions. As the solution at left becomes more + charged, the chloride anions flow into it, which offsets that electric potential. As the solution at right gets more negatively charged, the sodium cations flow to it, offsetting that tendency. It's this ion flow that allows the electrons to keep transferring, or allows this REDOX to continue.

Look at that next diagram and make sure you see all of this.



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 reminds 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 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 none left.
2. Run out of salt bridge ions, sooner or later the ions will all move to opposite sides due to the change in electrical potential due to electron transfer.
3. Run out of cathode side cations. If enough electrons arrive on the zinc bar, all the zinc cations will become zinc atoms. At that point no more reduction can occur.

Let's quickly look at the REDOX of this battery.

Oxidation is $Al^{\circ} \longrightarrow Al^{+3} + 3e^{-}$

Reduction is $Zn^{+2} + 2e^{-} \longrightarrow Zn^{\circ}$

Here it seems that the number of electrons is not balanced, that's because the half reactions set up is not balanced. The actual balanced half reactions are

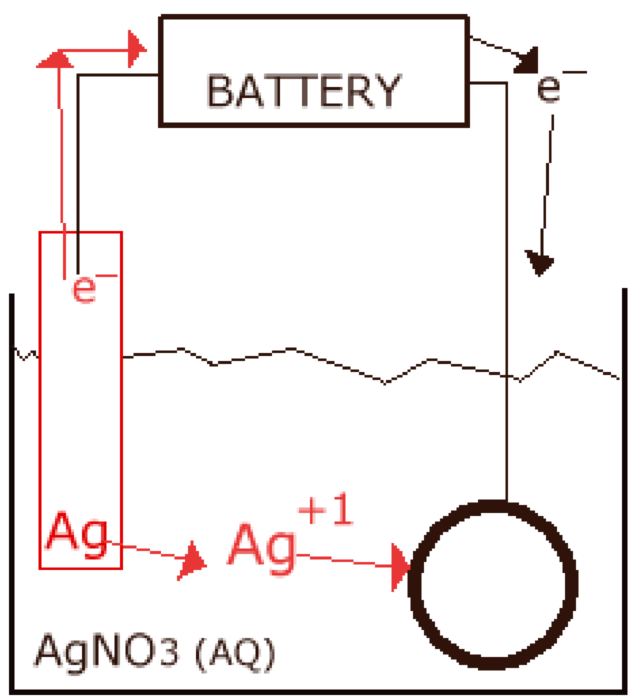
Oxidation is $2Al^{\circ} \longrightarrow 2Al^{+3} + 6e^{-}$

Reduction is $3Zn^{+2} + 6e^{-} \longrightarrow 3Zn^{\circ}$

That's the complete redox reaction. Always make sure your electrons balance, and if they don't balance your half reactions properly (like you'd balance your chemical equations).

The last objectives 8 & 10—electrochemical cells also called Electrolytic cells.

In these cells, we use electricity to force redox, and we can use this to electoplate 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).



The electrons provided by the battery jump onto the copper ring. The silver ions in solution are attracted and get reduced to silver atoms, which plate the copper.

To complete the circuit silver atoms in the bar oxidize and run up the wire to the other side of the battery.

The oxidation half reaction is $Ag° \longrightarrow Ag^{+1} + 1e^{-}$

The reduction half reaction is $Ag^{+1} + 1e^{-} \longrightarrow Ag°$

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.

In a voltaic cell (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.