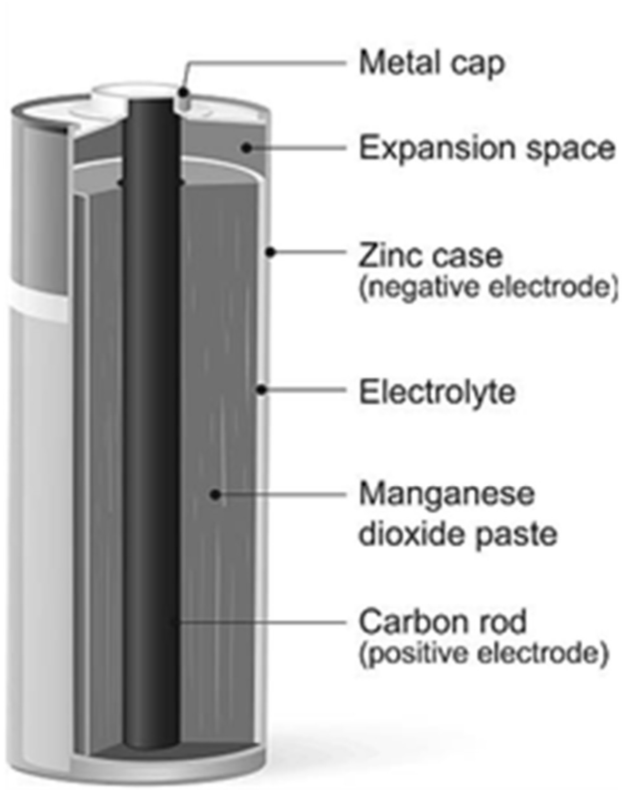
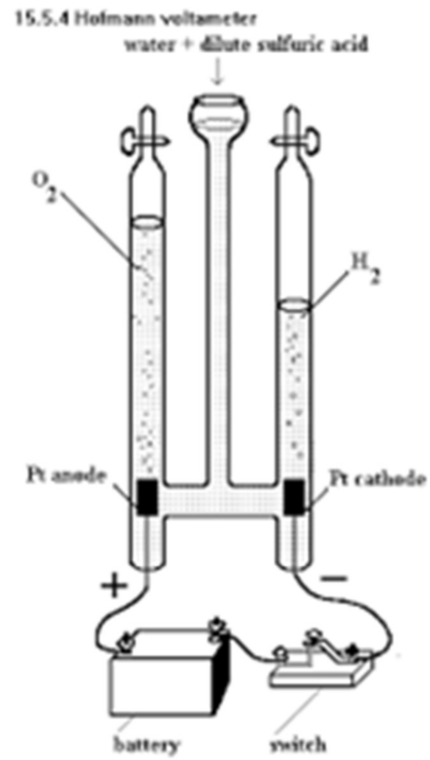
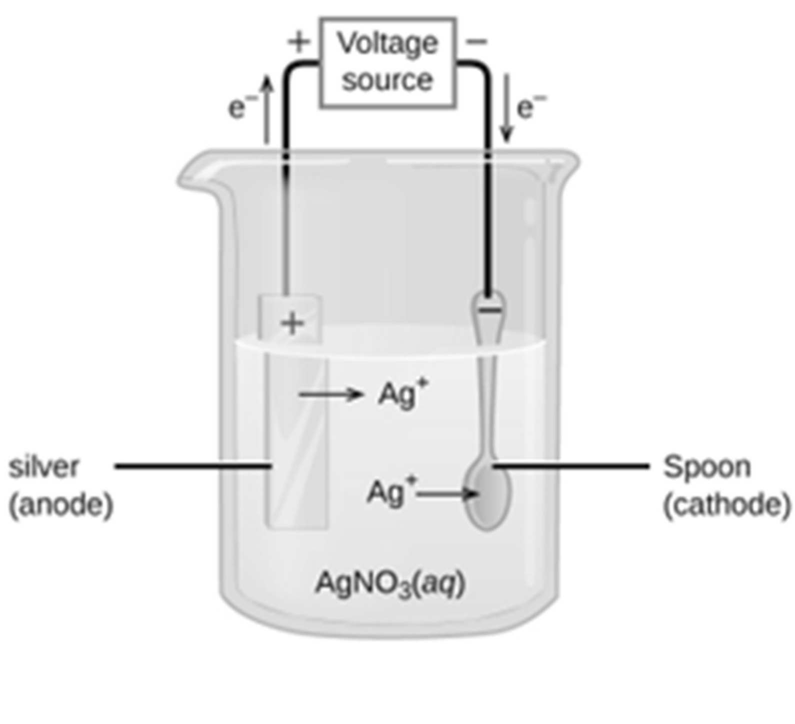
REDOX

Electrochemistry: Batteries, Electroplating, and Electrolysis







name

Redox Class Notes	
Redox is the chemistry of	
1	
2	
3	
4	The two ½ reactions of Redox are always paired and balanced.
5	In the old days…
6	Now scientists understand this as…
7	To remember this, we'll say LEO the lion goes GER!! LEO = GER =

8	word eq	
9	skeleton	
10	balanced	
11	with oxidation numbers	
12	What's happening here?	
13	Skip this one	Ha!
14		
15		
16		
17		
18		
19		

	$2Mg^0 + O_2^0 \rightarrow Mg^{+2} + O^{-2}$
20	In this synthesis/redox reaction, which species is oxidized?
21	In this synthesis/redox reaction, which species is reduced?
22	What's up with saying "species" in chemistry?
23	
24	
25	
26	

	The word equation is… silver nitrate solution + copper yields copper (I) nitrate + silver metal
27	Write the balanced chemical equation.
28	Write in the ion charges for all species.
29	So, what’s happening here?
30	Add the oxidation numbers to this balanced single replacement reaction $Li_{(S)} + NaCl_{(AQ)} \rightarrow LiCl_{(AQ)} + Na_{(S)}$
31	Write out the half reactions for this single replacement reaction
32	Write out the net ionic equation for this single replacement reaction

Add the oxidation numbers, or ionic charges to this single replacement reaction, it is already balanced	
33	$Mg + 2HCl \rightarrow MgCl_2 + H_2$
34	Write out the half reactions and the net ionic equation
35	Balance this equation with oxidation numbers (not ionic charges) carbon monoxide & oxygen make carbon dioxide
36	Write out the half reactions and the net equation

Redox Class #2 assigning oxidation numbers plus how **voltaic cells** work.		
	Reactants → Products	Reaction types
37	$Li_{(S)} + Zn(NO_3)_{2(AQ)} \rightarrow 2LiNO_{3(AQ)} + Zn_{(S)}$	
38	$CaCl_{2(AQ)} + 2NH_4OH_{(AQ)} \rightarrow Ca(OH)_{2(S)} + 2NH_4Cl_{(AQ)}$	

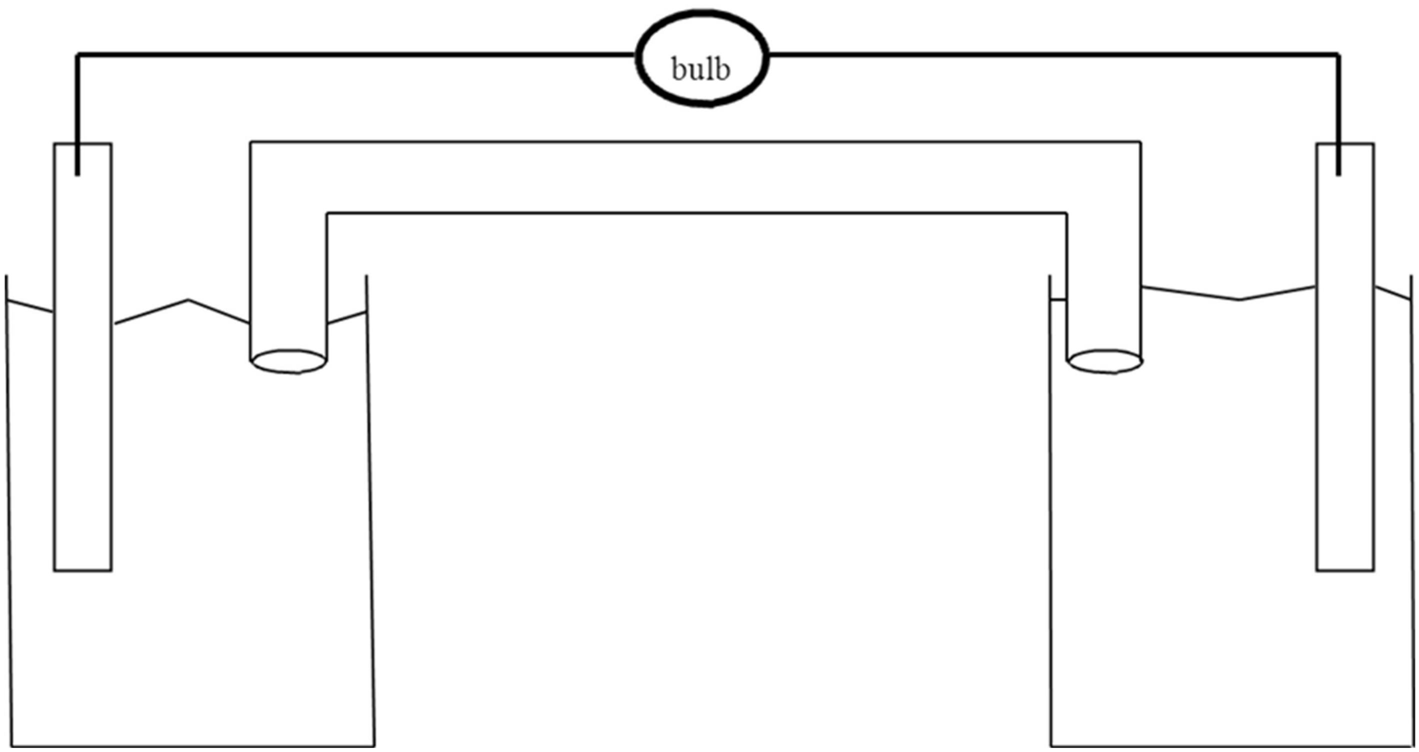
What are the individual oxidation numbers for all these species? (they sum to zero*)		
39	$Cr_2O_7^{-2}$	CO_2
40	$CaCl_2$	CO
41	N_2O_5	NO
42	H_2SO_4	NO_2
43	H_2O	NH_3

Copper (I) nitrate solution + potassium forms potassium nitrate solution + copper	
Write the balanced equation for the word equation above. Add the ion charges. (no phases)	
44	
45	Write the half reactions and the net ionic equation
46	What species was oxidized?
47	What species was reduced?
48	What is the spectator ion?

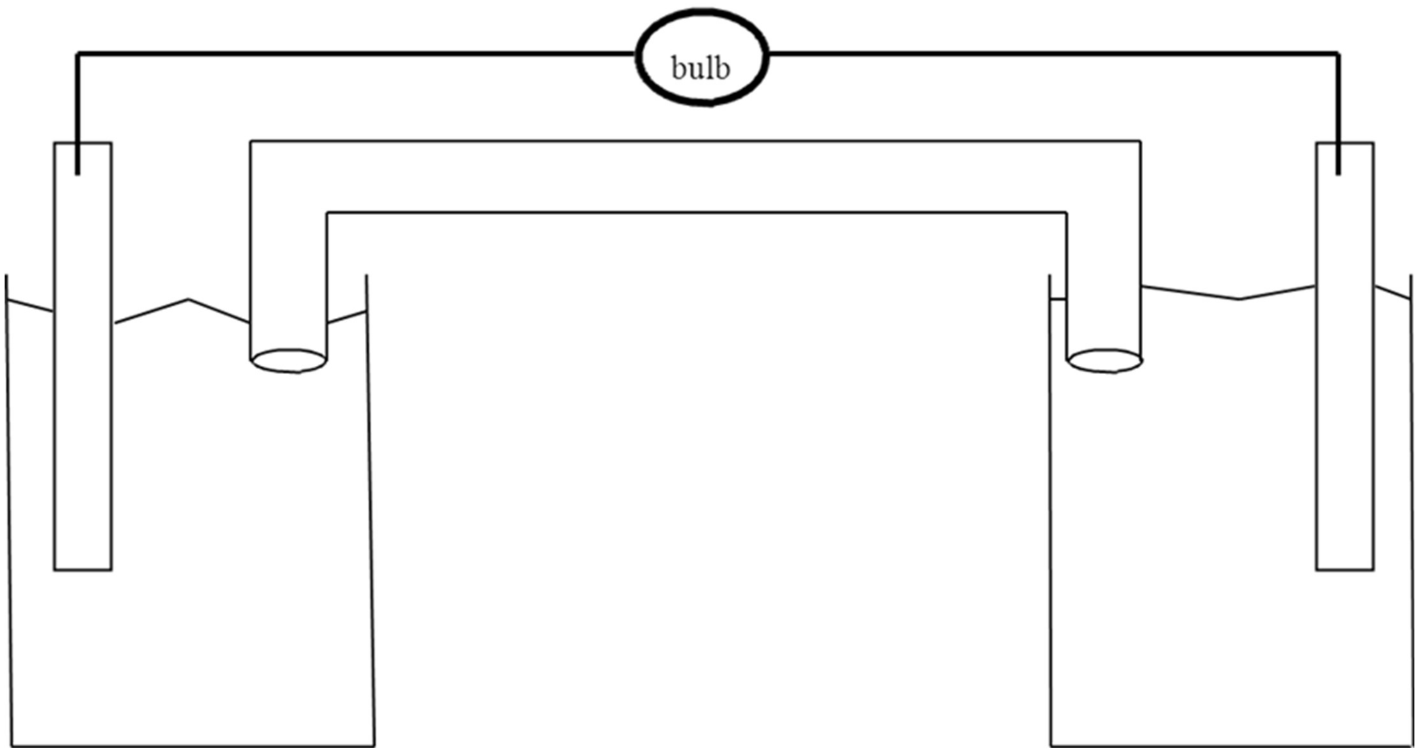
silver nitrate solution + copper forms copper (II) nitrate solution + silver	
Write the balanced equation for the word equation above. Add the ion charges. (no phases)	
49	
50	Write the half reactions and the net ionic equation
51	What species was oxidized?
52	What species was reduced?
53	What is the spectator ion?

54	
55	
56	

Our first Voltaic Cell

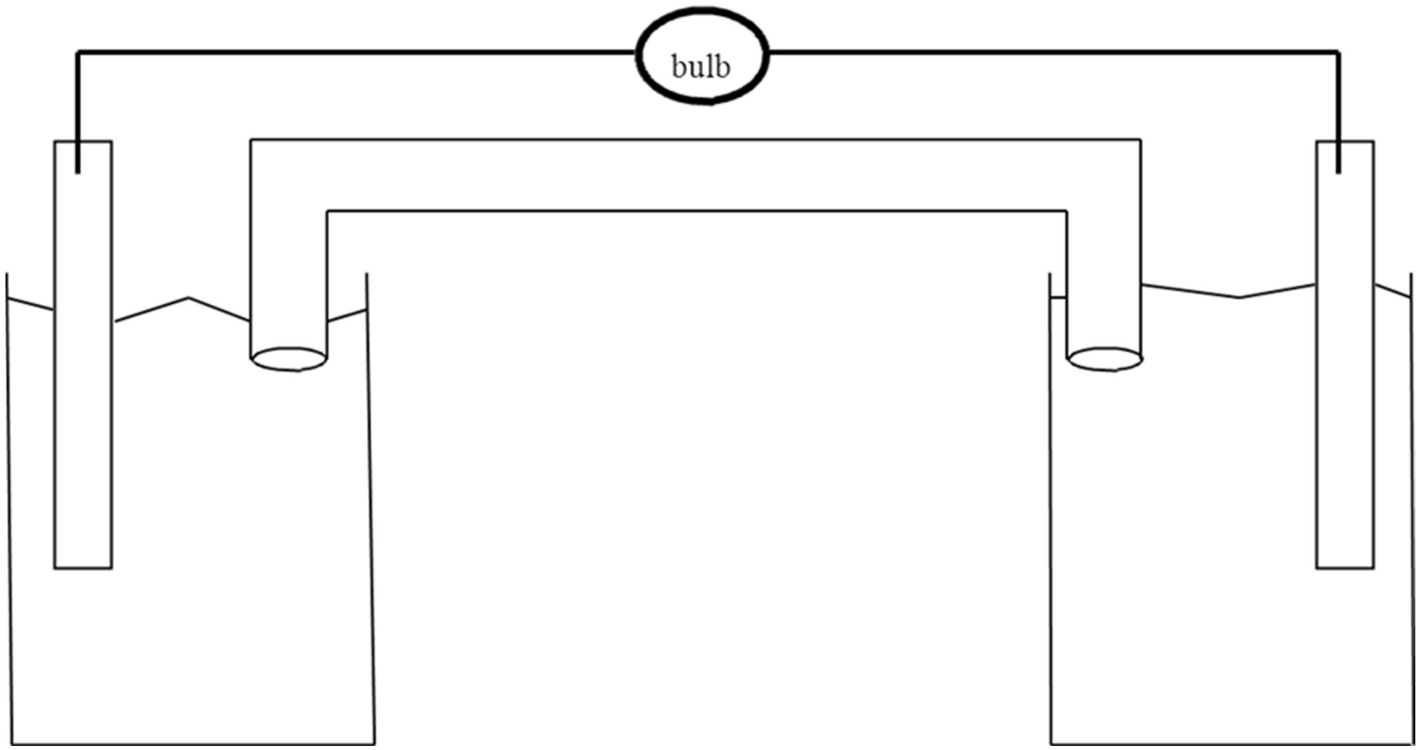


58. Mg-Pb BATTERY (label it as we go through how it works)



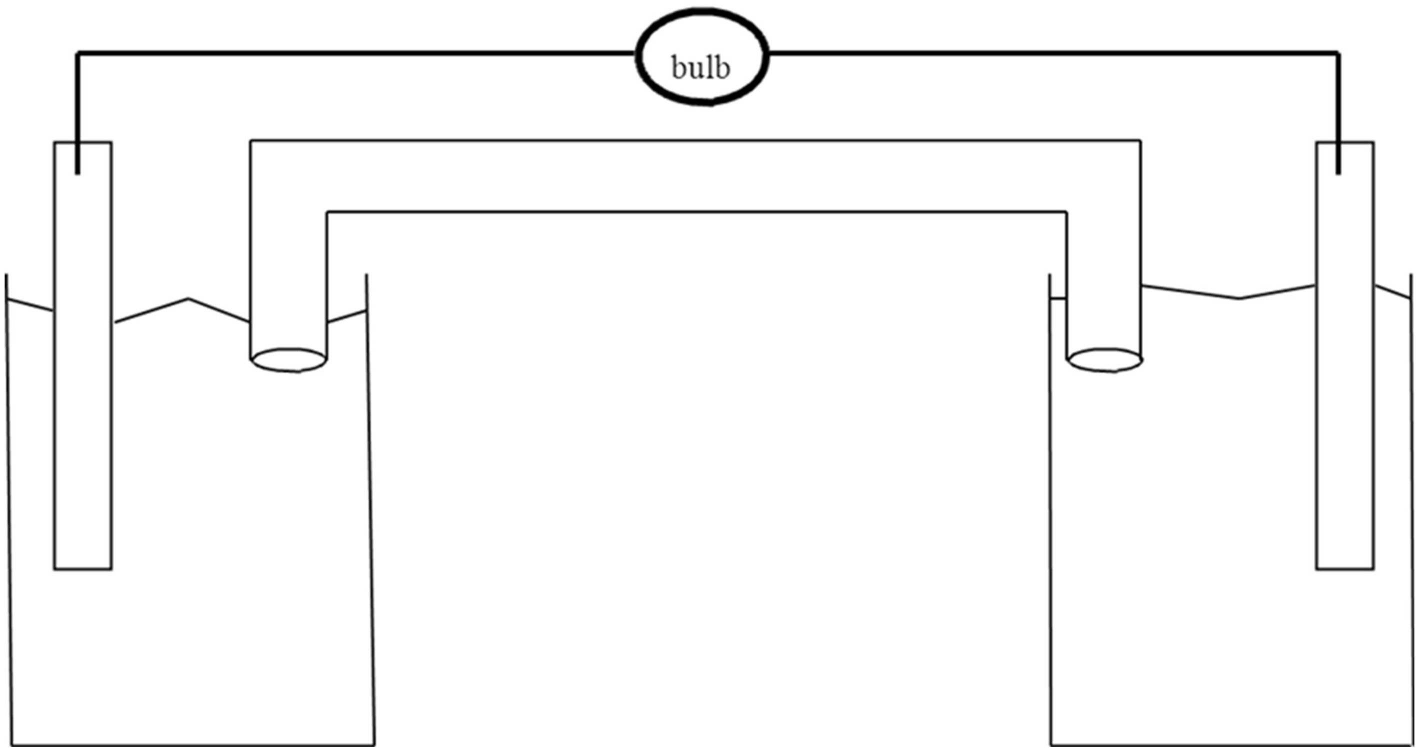
$^{1}/_{2}$ OX	
$^{1}/_{2}$ RED	
NET	
Why does this battery die?	

59. Rb-Cs BATTERY (label it as we go through how it works)



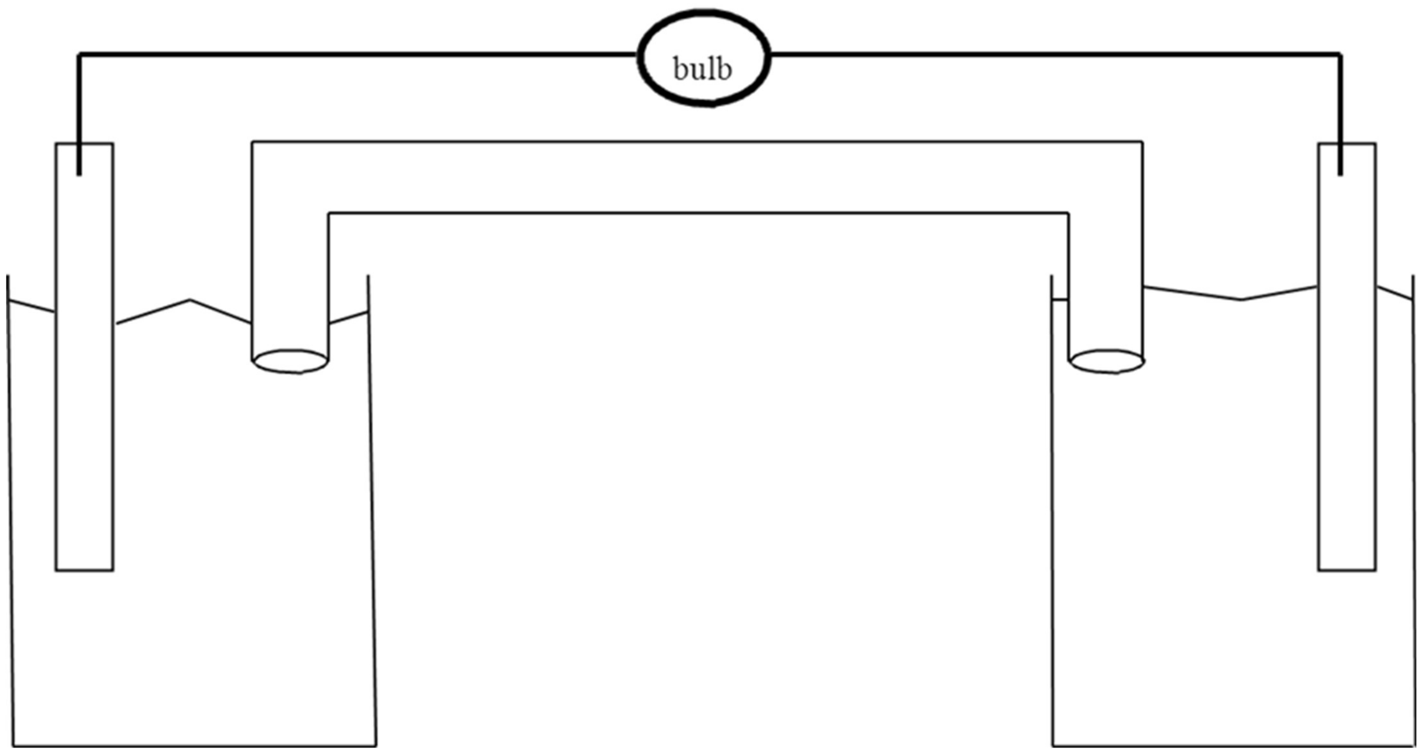
$^{1}/_{2}$ OX	
$^{1}/_{2}$ RED	
NET	
Why does this battery die?	

60. Ba-Sr BATTERY (label it as we go through how it works)



$^{1}/_{2}$ OX	
$^{1}/_{2}$ RED	
NET	
Why does this battery die?	

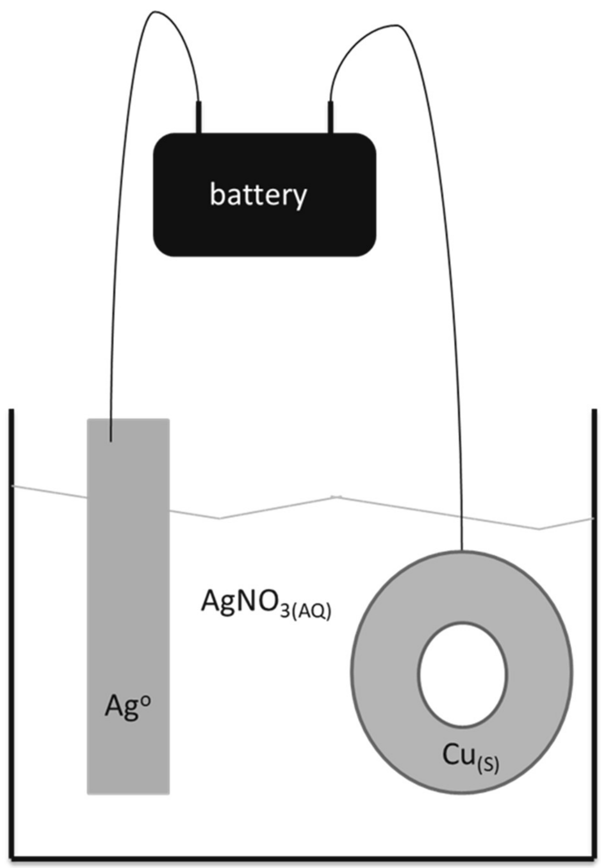
61. Ag-Mg BATTERY (label it as we go through how it works)



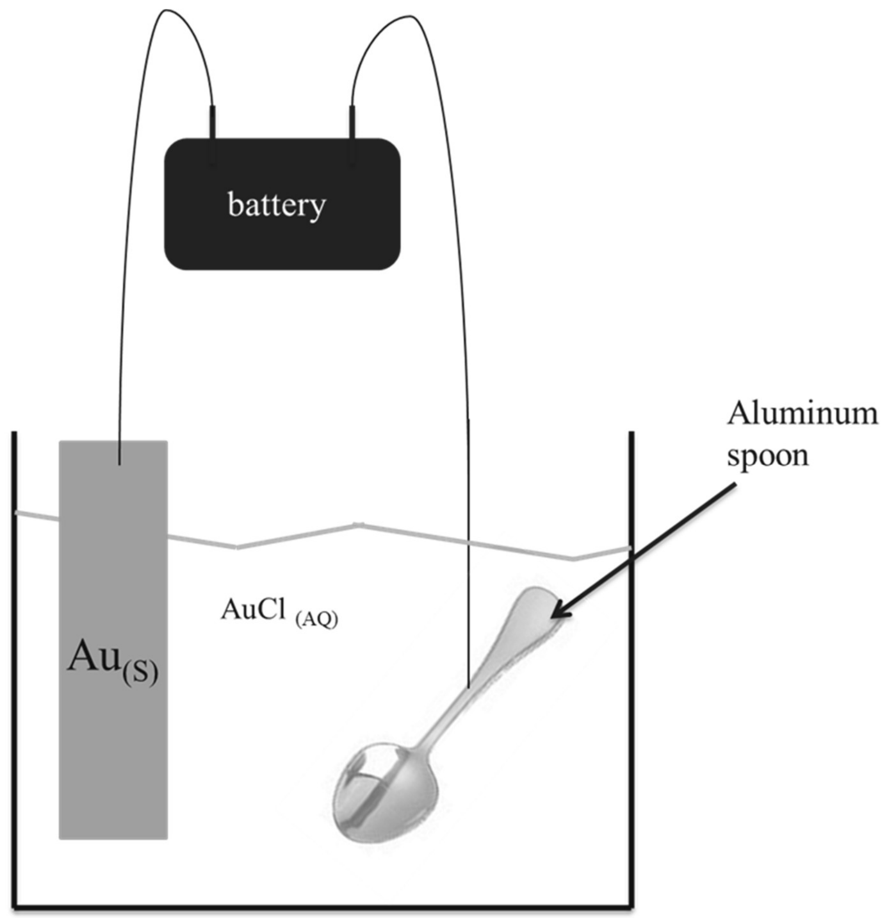
$^1/_2$ OX	
$^1/_2$ RED	
NET	
Why does this battery die?	

	Electrochemical cells combine chemistry with electricity
62	Voltaic cells…
	Electrolytic cells…
63	$Cu_{(S)} + 2AgNO_{3(AQ)} \rightarrow Cu(NO_3)_{2(AQ)} + 2Ag_{(S)}$ This reaction is…
64	$Cu_{(S)} + 2AgNO_{3(AQ)} \rightarrow Cu(NO_3)_{2(AQ)} + 2Ag_{(S)}$ We can stop this reaction…

65



½ Oxidation
½ Reduction
Net Ionic Equation

67	
68	Half reactions and net ionic equation
69	Electrolysis is Hydrolysis is
70	A Hoffmann Apparatus uses electricity to decompose water. The electricity…

71	The decomposition of water… Rewrite this with oxidation numbers in place. $$2H_2O_{(L)} \rightarrow 2H_{2(G)} + O_{2(G)}$$
72	Write the half reactions and net ionic equation for decomposition of water.. .
73	Which electrochemical cell spontaneously produces electricity from a chemical reaction?
74	Name the type of cell where electricity forces a redox reaction that would not be spontaneous.
75	What always happens at the anode?
76	What always happens at the cathode?
77	Is Leo ALWAYS a RED-CAT?

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 is known as electrolysis.

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

We've already learned 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 next. It's not really an independent reaction. Many of the reactions above are ALSO redox.

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

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

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

A half-reaction can be written to represent oxidation. A net ionic equation can be written to summarize the oxidation and reduction half reactions.

$2Mg + O_2 \rightarrow 2MgO$

This is a common reaction, you synthesized magnesium oxide in lab early in the year.
What's going on with the electrons here? Let's take a close look.

$2Mg + O_2 \rightarrow 2MgO$ — Looking only at the Mg now...
½ox: $2Mg^{\circ} \rightarrow 2Mg^{+2} + 4e^{-}$ — This is called the oxidation half reaction

Both magnesium atoms become +2 ions— they lose 2 electrons each. (that's 4 total electrons)

Reduction is the gain of electrons (LEO the Lion goes GER).
A half-reaction can be written to represent reduction.

$2Mg + O_2 \rightarrow 2MgO$ — Looking only at the oxygen now...
½red: $O_2^{\circ} + 4e^{-} \rightarrow 2O^{-2}$ — This is called the oxidation half reaction

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

By combining these two half reactions, we have an oxidation reaction and a reduction reaction. They are paired, and perfectly balanced. Two halves of the whole synthesis reaction. 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 must be picked up by some other atom or ion and be reduced.
No left over electrons ever. Not even one.

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 polyatomic ions.

Selected oxidation numbers

you MUST open your periodic table now or just stop reading.

The element at the top of the page is carbon. Carbon has 3 selected oxidation states, –4, +2, and +4.

There are others, but in our class, we'll only use these selected oxidations states listed in our periodic table.

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

The transitional metals have one or more possible oxidation states (charges). That's why we need to use the roman numerals in naming most of 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 usually 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 for each species
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}

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.

$$2Mg + O_2 \rightarrow 2MgO$$

can be thought of this way too

$$2Mg^{\circ} + O_2^{\circ} \rightarrow 2Mg^{+2}O^{-2}$$

Mg atoms are Mg° Oxygen molecules (a pair of atoms) are also O_2°
In MgO there is a Mg^{+2} cation, and the oxide anion O^{-2}
The sum of the oxidation numbers in the MgO is (+2) + (–2) = 0 (as expected and required)

A second example reaction (single replacement & redox too)

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

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 in solution are forced to pick up these electrons, therefore the Ca^{+2} ions are reduced.
The redox half reactions would be:

½OX: $2K^{\circ} \rightarrow 2K^{+1} + 2e^{-}$ note: it takes 2 K atoms to oxidize 2 electrons
½RED: $Ca^{+2} + 2e^{-} \rightarrow Ca^{\circ}$ note: it takes one Ca^{+2} to reduce 2 electrons

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 the half reactions together, cancelling out the electrons on BOTH sides of the arrow)

NET IONIC EQUATION: $2K^{\circ} + Ca^{+2} \rightarrow 2K^{+1} + Ca^{\circ}$

This shows both potassium atoms become $2K^{+1}$ cations, and the Ca^{+2} cation become a Ca° neutral 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, the charges even out perfectly.
The net ionic equation shows "Conservation of Charge" which is like conservation of matter & conservation of energy. There must be conservation of charge (or you made a mistake).

Let's look at one more reaction now…

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

$$Cl_2^{\circ} + 2H^{+1}Br^{-1} \rightarrow 2H^{+1}Cl^{-1} + Br_2^{\circ}$$

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

½OX:	$2Br^{-1} \rightarrow Br_2^{\circ} + 2e^-$	it takes 2 bromides to oxidize 2 electrons
½RED:	$Cl_2^{\circ} + 2e^- \rightarrow 2Cl^{-1}$	it takes 2 chlorine atoms to reduce 2 electrons
NET:	$2Br^{-1} + Cl_2^{\circ} \rightarrow Br_2^{\circ} + 2Cl^{-1}$	the whole REDOX transfers 2 electrons total

In this reaction, the H^{+1} ions from the HBr, which end up HCl, are called SPECATOR IONS, because they don't change their charge, they seem to just "watch". They're required, but nonparticipants in the half reactions. . Single replacement reactions are also redox. Lots of chemical reactions are redox too.

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…

$2Al_{(S)} + 3CaCl_{2(AQ)} \rightarrow 2AlCl_{3(AQ)} + 3Ca_{(S)}$ is a single replacement reaction

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 $3e^-$ but each Ca only gains $2e^-$.
Oxidation is loss of electrons, Reduction is gain of electrons, so…

½OX:	$Al^{\circ} \rightarrow Al^{+3} + 3e^-$
½RED:	$Ca^{+2} + 2e^- \rightarrow Ca^{\circ}$

The electron transfer is NOT equal. Three electrons are oxidized, only two are used for reduction. This will not work this way, it needs to be fixed. To "fix" this, we look for the lowest common factor between the 3 and the 2, which is 6, and adjust the half reactions to match up the electrons being transferred.

½OX:	$2Al^{\circ} \rightarrow 2Al^{+3} + 6e^-$	it takes 2 Al° atoms to oxidize 6 electrons
½RED:	$3Ca^{+2} + 6e^- \rightarrow 3Ca^{\circ}$	it takes 3 Ca^{+2} to reduce 6 electrons

NET: $2Al^{\circ} + 3Ca^{+2} \rightarrow 2Al^{+3} + 3Ca^{\circ}$

In this net ionic equation, 6 electrons get oxidized and 6 get reduced as well

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)

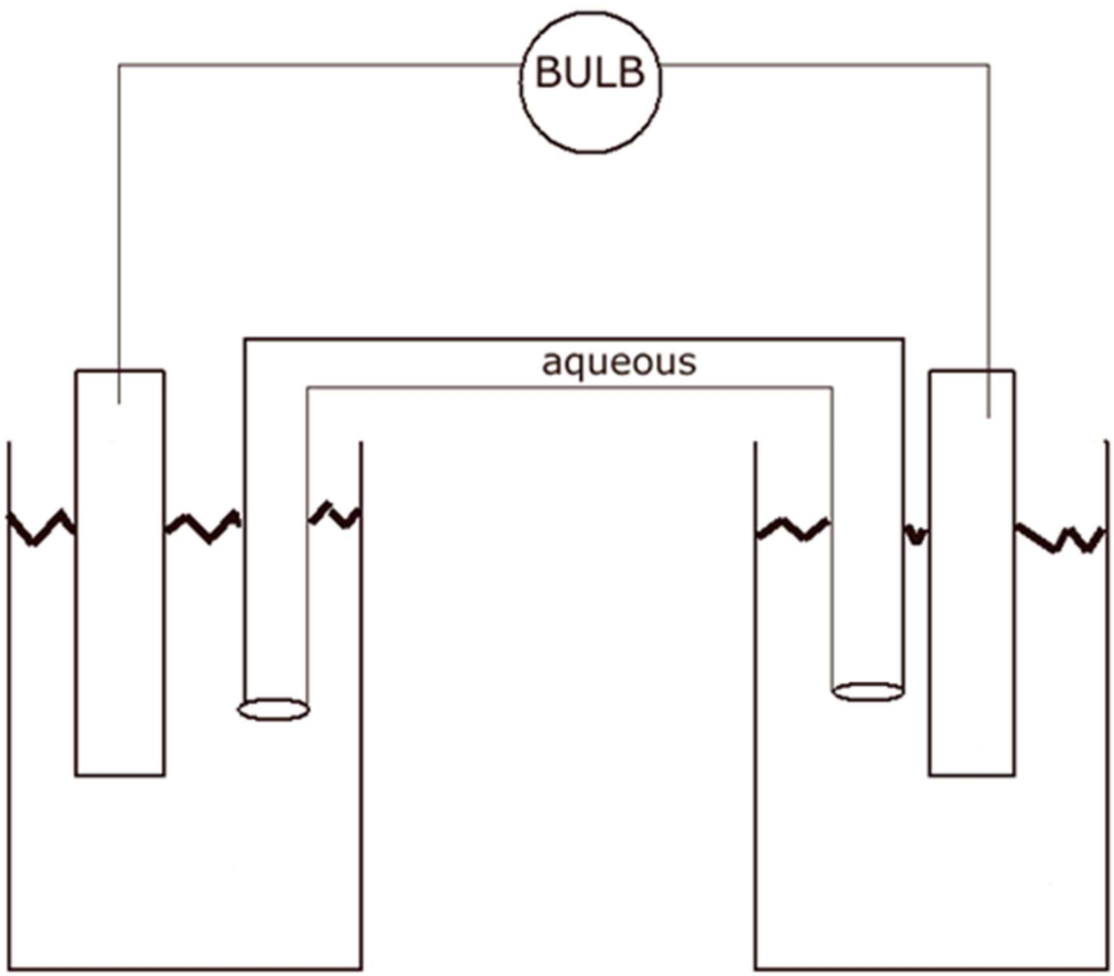
A voltaic cell is a battery, where chemistry SPONTANEOUSLY creates electricity. These run and run (unless a switch is put into the circuit).

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.



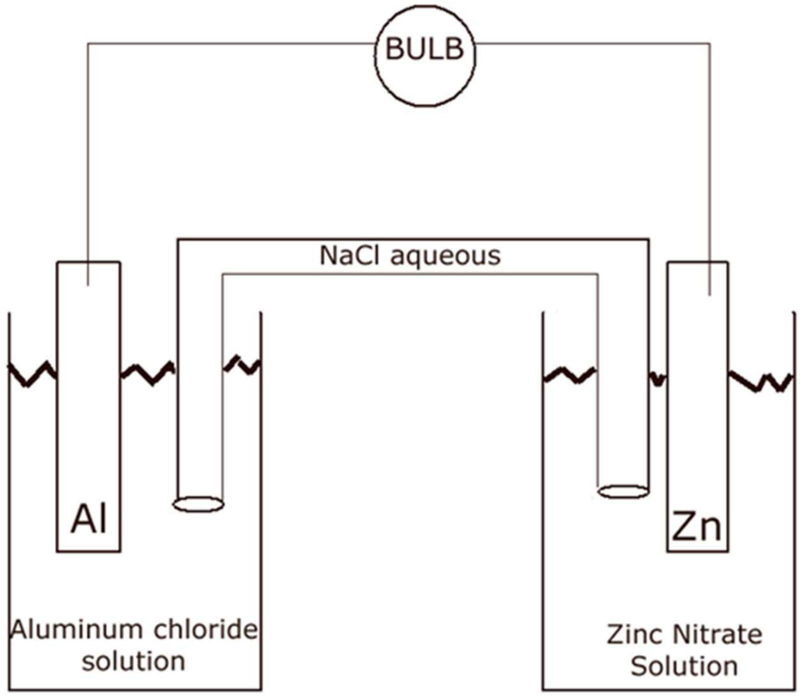
This is called an aluminum-zinc voltaic cell (or battery).

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

The Zinc is in a $Zn(NO_3)_{2(AQ)}$
There is a $NaCl_{(AQ)}$ 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 cations, 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 $Al^\circ \rightarrow Al^{+3}$ 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 Zn^{+2} ions in the 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 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 BIG PROBLEM, big enough to stop the electricity flow immediately.

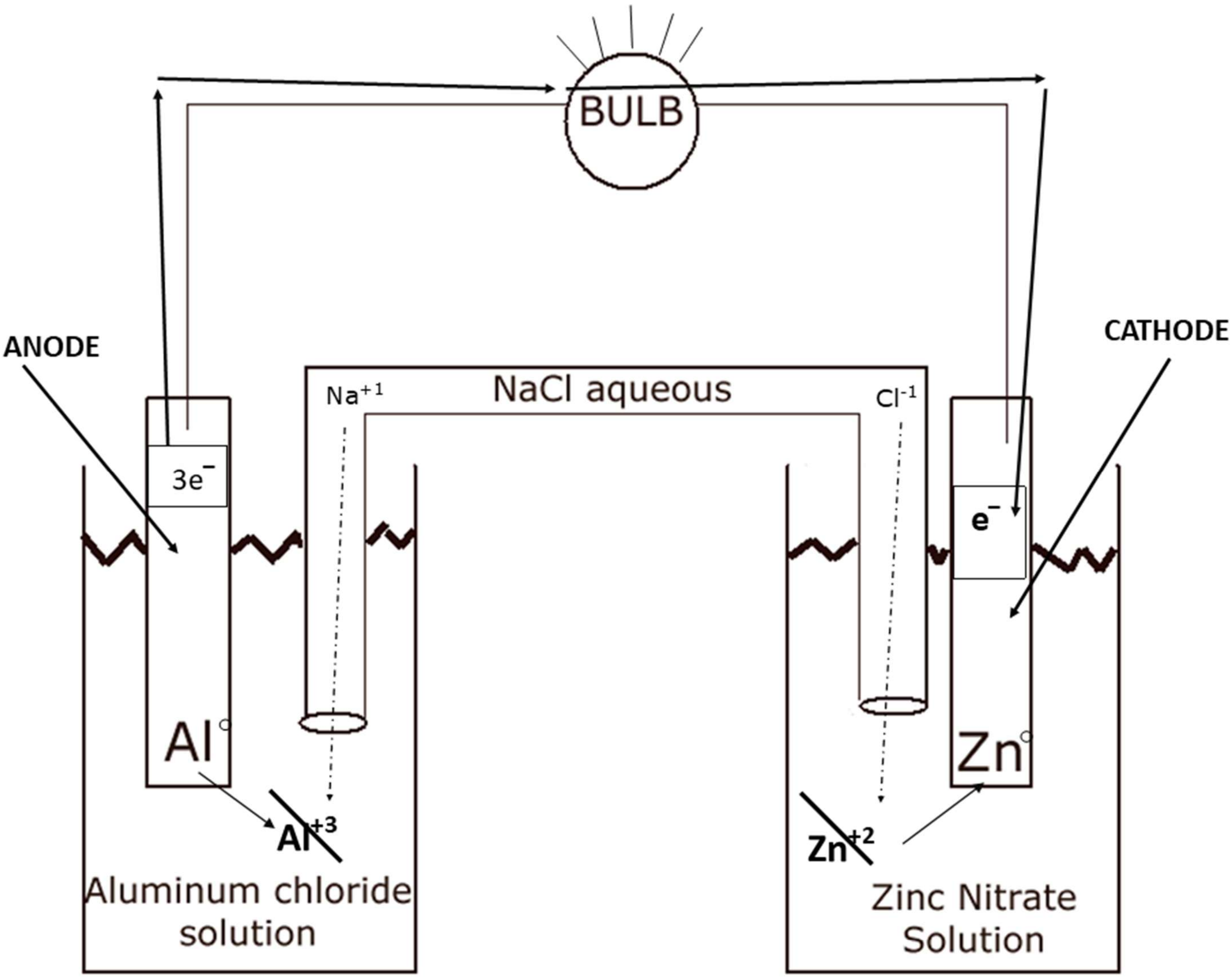
That's why we have an aqueous salt bridge. In this one are Na^{+1} and Cl^{-1} ions.

As the solution at left 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 (the aluminum is the anode, the zinc is the cathode. Electricity ALWAYS flows from anode to cathode). 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.



This is the final drawing, FULLY labeled, showing the movement of electrons, flow of ions, the neutralization of the solutions, the functioning 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.

½OX: $Al^\circ \rightarrow Al^{+3} + 3e^-$ note: three electrons are oxidized here by each Al

½RED: $Zn^{+2} + 2e^- \rightarrow Zn^\circ$ note: only two electrons are needed for reduction. $3 \neq 2$

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

½OX: $2Al^\circ \rightarrow 2Al^{+3} + 6e^-$ note: here 6 electrons are oxidized

½RED: $3Zn^{+2} + 6e^- \rightarrow 3Zn^\circ$ note: here, 6 electrons are reduced

NET: $2Al^\circ + 3Zn^{+2} \rightarrow 2Al^{+3} + 3Zn^\circ$

LOOK HARD: see that the charge is balanced in this net ionic equation, and that the 6 electrons oxidized are cancelled out by the 6 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 is not balanced, then 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).

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

$$Cu_{(S)} + 2AgNO_{3(AQ)} \rightarrow Cu(NO_3)_{2(AQ)} + 2Ag_{(S)}$$

This is single replacement, and if you LET THIS HAPPEN, the silver precipitates spontaneously. To make the silver plate ONTO the copper, making the strong but inexpensive copper ring LOOK like a silver ring, to become a copper ring coated in real silver metal, that takes energy.

Electrolytic cells use electricity and force NON-SPONTANEOUS redox reactions. 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 from forming! The copper inside of the ring is much stronger than a pure silver ring.

The electrons provided by the battery are pushed onto the copper ring. Instead of the reaction above happening, the silver ELECTROPLATES on top of the copper ring, making the outside SILVER coated. The ring looks like silver, tastes like silver, and is silver, but ONLY ON THE OUTSIDE. The silver plates on top of the copper.

The silver cations in the solution are attracted to these negative electrons on the ring and get reduced to silver atoms, which plates onto the copper. The longer this “runs” the thicker the silver atom 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.

See the diagram and the oxidation/reduction half reactions on the next page, and the WEIRD net ionic equation. It seems like nothing happens, but if you know where the atoms and ions are, they are changing places and it makes good sense.

Electroplating in the US is a big business, over $18,000,000,000 (!) in 2023, and it is expected to expand to $28 billion US dollars by the year 2033 [according to the MARKET.us website. The business seems to be mostly in automotive, space and electronics, where noncorrosive metals protect the more reactive metals on the inside of the plating, and for making things look nicer.

½OX: $Ag^\circ \rightarrow Ag^{+1} + 1e^-$
this happens ON the silver bar

½RED: $Ag^{+1} + 1e^- \rightarrow Ag^\circ$
this happens ON the ring

Net: $Ag^\circ + Ag^{+1} \rightarrow Ag^{+1} + Ag^\circ$

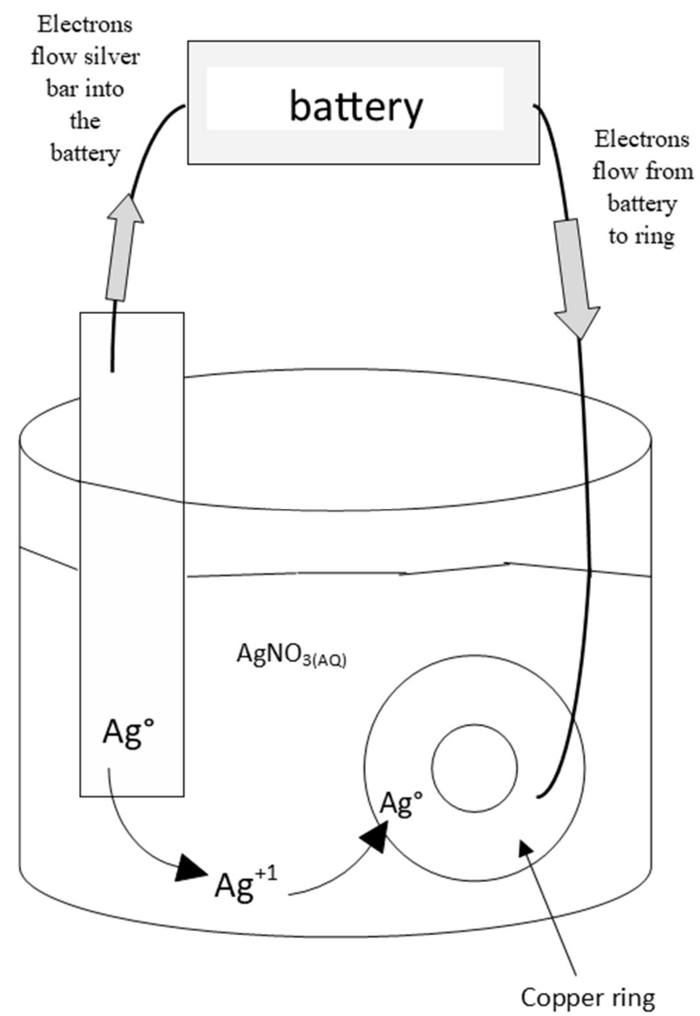
The silver atoms become cations, the silver cations become atoms, and the atoms on the bar transfer and coat onto the copper ring, because the battery won't let the SR reaction happen. The energy makes this NONSPONTANEOUS redox occur.

Energy makes the chemistry happen.

An electrolytic cell
IS NOT SPONTANEOUS.
It needs ELECTRICITY from a battery to make the redox chemistry.

The electricity forces a NONSPONTANEOUS chemical reaction that you want to happen, a reaction that won't happen on its own.

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



The silver bar is the ANODE, it provides the electrons that move toward the battery. The copper ring is the CATHODE, the reduction happens on the ring.

☺