Redox Reactions and Electrochemistry

Redox Reactions

Oxidation-Reduction

- Reduction ALWAYS occurs with oxidation -- you can not have one without the other.
- One substance is oxidized and the other is reduced.

The table, below, summarizes some basic information about reduced and oxidized forms of matter:

Reduced Forms of Matter	Oxidized Forms of Matter
High energy	Low energy
Sugar Coal Gas	Carbon dioxide Water

- In a classic sense, redox reactions require some discussion about oxygen and hydrogen.

Oxygen

- Fossil fuels burn in the presence of oxygen.
- More than 90% of the energy in our society comes from fossil fuels.
- Oxygen causes iron to rust, copper to corrode and wood to rot.
- All of these processes are processes of OXIDATION.

Representative oxidation reactions are illustrated, below:

Process	Reaction	Comment
Rust formation	**$4Fe + 3O_2 \rightarrow 2Fe_2O_3$**	**The product is Iron (III) oxide or ferric oxide.**
Charcoal burning	**$C + O_2 \rightarrow CO_2\uparrow$**	**This is what happens on your charcoal grill.**
Burning sulfur	**$S + O_2 \rightarrow SO_2\uparrow$**	**This is one process that occurs in catalytic converters.**
Automobile engines at high temperatures	**$N_2 + O_2 \rightarrow 2NO$**	**Another wonderful thing that came from catalytic converters.**
Burning methane (natural gas)	**$CH_4 + 2O_2 \rightarrow CO_2\uparrow + 2H_2O$**	**Just like in the winter time when you run your gas furnace.**
Burning off hydrogen sulfide	**$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$**	
Oxidizing carbon disulfide	**$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$**	

- The combination of substances with oxygen is the classic definition of oxidation.
- When oxygen has combined with substances, they are said to have been OXIDIZED.

Three Definitions of Oxidation

- 1) A substance is oxidized when it GAINS oxygen atoms, e.g.:
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2\uparrow + 6H_2O$
- 2) A substance is oxidized when it LOSES hydrogen atoms, e.g.:
- Methanol (CH_3OH) → formaldehyde (CH_2O) + $H_2\uparrow$
- 3) A substance is oxidized when it LOSES electrons, e.g.:
- $Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl_-$ (equivalent to $MgCl_2$ -- Mg has to undergo electron loss, first)

Hydrogen

- Let's examine hydrogen, briefly. Nearly all compounds derived from living organisms contain hydrogen in fats, carbohydrates and proteins. Petroleum and natural gas are hydrocarbons that are derived from previously living organisms.
- Hydrogen is synthesized with ease in the lab (just like in the clock reaction you did at the beginning of this course):
- $Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$
- $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$

- Pt, Pd, and Ni "collect" condensed hydrogen on their surfaces. The absorbed hydrogen has a greatly increased activity (making it more reactive) and Pt, Pd and Ni (in the form of Rainey nickel -- his name was Rainey) are used as catalysts in hydrogenation reactions. Do you remember the orbital hybridization and molecular geometry of these three metals?
- Hydrogen reacts with oxygen, e.g.:
- $2H_2 + O_2 \rightarrow 2\ H_2O$ (requires a "spark" to catalyze this reaction)
- Hydrogen reacts with cupric oxide, e.g.,
- $CuO + H_2 \rightarrow Cu + H_2O$
- Hydrogen reacts with lead (II) oxide, e.g.:
- $PbO + H_2 \rightarrow Pb + H_2O$

Three Definitions of Reduction

- 1) A substance is reduced when it LOSES oxygen atoms, e.g.:
- $2\ KClO_3 + \text{heat} \rightarrow 2KCl + 3O_2\uparrow$
- 2) A substance is reduced when it GAINS hydrogen atoms, e.g.:
- $CO + 2H_2$ + Pt, Pd or Ni catalyst $\rightarrow CH_3OH$ (methanol)
- 3) A substance is reduced when it GAINS electrons, e.g.:
- $Cu^{2+} + 2e^- \rightarrow Cu$

Summary Thus Far

The table, below, summarizes oxidation and reduction definitions:

Oxidation	Substance/Particle Involved	Reduction
Gains	O_2	Loses
Loses	H_2	Gains
Loses	e^-	Gains

Redox Reactions -- More Terms

- When a redox reaction occurs, one substance is reduced and another oxidized.
  - The substance that is reduced is the OXIDIZING AGENT.
  - The substance that is oxidized is the REDUCING AGENT, e.g.:

$$CuO + H_2 \rightarrow Cu + H_2O$$

- The **CuO is the oxidizing agent** as the Cu in the CuO is reduced from the +2 state on the left side of the arrow to the elemental state on the right side of the arrow.
- The **H_2 is the reducing agent** as the H_2 goes from the elemental state on the left side of the arrow to a +1 state on the right side of the arrow.
- This reaction also demonstrates another way in which to remember reduction.
- Reduction of something occurs when its charge is further reduced.
- This means that if Cu is in a +2 state that it is reduced to Cu in a +1 state in the appropriate reaction.
- Likewise, Br in the elemental state (I'm using atomic -- not molecular Br_2) may be reduced to Br in the -1 state.
- As long as electrons may be GAINED, the substance will be reduced in its charge.

- The following three examples further illustrate the idea of oxidizing and reducing agents (NOTE: I've color coded them for you per the previous statement):

$$2C + O_2 \rightarrow 2CO$$

$$SnO + H_2 \rightarrow Sn + H_2O$$

$$Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$$

The table below summarizes examples of common oxidizing and reducing agents:

Common Oxidizing Agents	Common Reducing Agents
O_2 $Cr_2O_7^{2-}$* See below for example reaction H_2O_2 Halogens	C H_2 Silver halides# See below for example reaction
* $8H^+ + Cr_2O_7^{2-}$ (orange) + $3C_2H_5OH \rightarrow 2Cr^{3+}$ (green) + $3C_2H_4O + 7H_2O$	# $C_6H_4(OH)_2$ (hydroquinone -- "developer") + $2Ag^+ \rightarrow C_6H_4O_2 + 2Ag$ (dark part of the negative) + $2H^+$

Applications of Oxidizing Agents

Oxidizing Agent	Use/Comments
NaOCl -- sodium hypochlorite	Clorox -- used to be used in wound irrigation, not any more -- used to be used to treat bladder infections, not any more
$(C_6H_5COO)_2$ -- benzoyl peroxide	POWERFUL oxidizing agent; 5-10% ointments are used to treat acne; when used on regions that are exposed to sunlight, has been known to cause skin cancer, i.e., stay out of the sun OR cover up if you use this
$Ca(OCl)_2$ -- calcium hypochlorite	Bleach -- disinfect clothing, bedding
Cl_2 -- gaseous chlorine	Water purifier

NaOCl + $Ca(OCl)_2$	Bleach
H_2O_2 -- hydrogen peroxide $NaBO_2 \cdot H_2O_2$ -- sodium perborate Cl_2	All work through redox -- when hydrogen peroxide and cold water are used on fresh blood stains, the stain is removed -- gotta be careful, though, as the stain will return. If you really want to get the blood out, rinse it out of the fabric while it's still fresh and use normal saline -- won't lyse the cells so that they "stick" to the fabric like they do with H_2O_2.
$KMnO_4$ -- potassium permanganate	Removes most stains from white fabrics EXCEPT rayon. The purple MnO_4^- stain may be removed with oxalic acid ($H_2C_2O_4$): $5H_2C_2O_4 + 2MnO_4^-$ (purple) $+ 6H^+ \rightarrow 10\ CO_2 + 2Mn^{2+}$ (colorless) $+ 8H_2O$; oxalic acid also removes rust stains -- not by redox, though, by complex formation
$Na_2S_2O_3$ -- sodium thiosulfate	Removes iodine stains: I_2 (brown) $+ 2Na_2S_2O_3 \rightarrow 2NaI$ (colorless) $+ Na_2S_4O_6$

- Many stain removers are adsorbants:
  - corn starch for grease,
  - acetone for ballpoint pen and
  - detergents for mustard.

Oxidation Number/Oxidation State Defined

- We now have some introductory terms and ideas about redox reactions.
- The next step is to learn how to use this information with new skills so that we may balance redox reactions.
- Before we begin, though, understand that oxidation number and oxidation state mean the same thing.
- If you think this is confusing, read through the following list of definitions for oxidation state/number.

- Oxidation number is defined as the charge which an atom APPEARS to have when electrons are counted according to some rather arbitrary rules.

- Oxidation number represents the actual charge on a mono-atomic ion or a HYPOTHETICAL charge assigned by a set of conventions to an atom in a molecule or in a polyatomic ion.
- An oxidation number can be defined as the charge that an atom would have if both electrons in each bond were assigned to the more electronegative element.
- Oxidation number corresponds to the number of electrons gained or lost by the original atom. For an ion, the oxidation number is equal to the ionic charge.
- Oxidation number is a number that reflects the extent to which an element has been oxidized or reduced. Therefore, for elements, the oxidation number = 0; when oxidized, the oxidation number is more positive; when reduced, the oxidation number is more negative.
- Oxidation state designates the number of electrons that an atom loses, gains or otherwise uses in joining with other atoms in compounds.

- Oxidation state of an atom in a substance is either the actual charge, if the atom exists as a mono-atomic ion, or else a hypothetical charge assigned by simple rules.
- The oxidation number of a bonded atom is the charge it would have if the electrons in every bond were given to the more electronegative atom.
- Oxidation state is used to designate the positive or negative character of atoms. Oxidation numbers are due to a SHIFT (NOT a transfer) of valence electrons from the more electropositive atom to the more electronegative atom.
- Oxidation number is the charge an atom would possess IF the bonding were ionic.

- The oxidation number of a covalently bonded element is the charge the element would have if all the shared pairs of electrons in the Lewis structure for the species were transferred to the more electronegative atoms. The oxidation number of covalently bound elements are not real charges like the charges on ions. Hence, they may not be experimentally measured. Only for simple mono-atomic ions such as Ba^{2+}, Na^{+}, S^{2-} and for elements such as N_2, O_3, are oxidation numbers real numbers that are easily obtained in the lab. In binary ionic compounds, the bonding electrons are already on the more electronegative atom because ionic bonds result from electron transfer, therefore, the oxidation number of mono-atomic ions equals the ionic charge. This is the definition that I favor for this course.

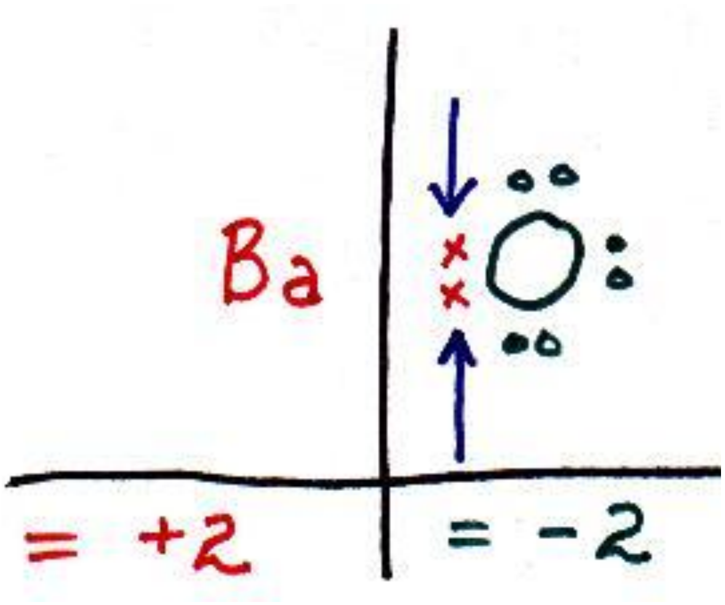
- Oxidation number is defined as the charge which an atom APPEARS to have when electrons are counted according to the following rules:
  1. electrons shared between 2 unlike atoms are counted with the more electronegative atom and
  2. electrons shared between 2 like atoms are divided between the sharing atoms.

E.g., determine the oxidation number of N_2:

- Three (3) electron pairs are shared by two (2) identical atoms, hence, by #2, above, half the electrons are counted with each atom.
- The nitrogen nucleus has a +7 charge (7 protons) and with 7 negative charges (7 electrons), the apparent charge is 0. Therefore, the oxidation number of N_2 is zero (0).

E.g., determine the oxidation numbers of Ba and O in BaO:

- **Oxygen is more electronegative and so, by #1, above, the shared electrons are counted with oxygen as shown right:**
- **The line shows the SHIFTING of electrons.**
- **Since oxygen has 6 protons and APPEARS to have 8 electrons, the oxidation state of oxygen is -2.**
- **Note the movement of the 2 electrons away from the Ba and towards the O (arrows pointing to).**
- **Ba APPEARS to have "lost" 2 electrons and its oxidation state is +2 since its nucleus now has an excess of 2 protons relative to the number of electrons left behind.**



- Note that 21 different authors have 21 different definitions -- it's no wonder that students find this topic mind boggling!

Oxidation Number Rules

1) All elements have an oxidation number of zero (0):

E.g.	H_2	O_2	N_2	Ca
Oxidation Number	0	0	0	0

2) Monoatomic ions' charges equal the oxidation number of that monoatomic ion:

E.g.	Na^+	K^+	Sr^{2+}	F^-
Ionic Charge	+1	+1	+2	-1
Oxidation Number	+1	+1	+2	-1

3) Cations from Groups I and II have oxidation numbers equal to +1 and +2, respectively:

E.g.	Na^+	Ba^{2+}	K^+	Mg^{2+}
Ionic Charge	+1	+2	+1	+2
Oxidation Number	+1	+2	+1	+2

4) With only a few exceptions,
the oxidation number of H is +1:

E.g.	H^+	H^-
Ionic Charge	+1	-1
Oxidation Number	+1	-1 (as the HYDRIDE ion)

5) The oxidation number of O is -2; exception: when it's in a peroxide, it's oxidation number is then -1:

E.g.	O^0	H_2O	H_2O_2 (hydrogen peroxide)	NaOH
Ionic Charge of O	0	-2	-1	-2
Oxidation Number of O	0	-2	-1	-2

6) The sum of all the oxidation numbers in a compound is equal to zero (0):

E.g.	$KMnO_4$	K^+	Mn^{+7}	O^{-2}
Oxidation Numbers	0	+1	+7	-2
TOTAL Oxidation Numbers	0	+1	+7	-8 (4 of them in the compound)
Sum of TOTAL Oxidation Numbers	0			

- Arithmetic example:

1(ox # of K^+) + 1(ox # of Mn^{+7}) + 4(ox # of O^{-2})

= (1*1) + (1*7) + (4*-2) = 0

7) The sum of all the oxidation numbers in an ion is equal to the charge on the ion:

E.g.	$Cr_2O_7^{-2}$	Cr^{+6}	O^{-2}
Oxidation Numbers	-2	+6	-2
TOTAL Oxidation Numbers	-2	+12 (2 of them in the ion)	-14 (7 of them in the ion
Sum of TOTAL Oxidation Numbers	-2		

- Arithmetic example:

$$2(\text{ox \# of } Cr^{+6}) + 7(\text{ox \# of } O^{-2})$$

$$= (2*6) + (7*-2) = -2$$

Typical Oxidation Numbers of Common Elements : Positive Ox #'s

Positive Oxidation Numbers							
Ox #	+1	+2	+3	+4	+5	+6	+7
Examples	H, Na, K, Cu, Ag, Hg, N, Cl, Br, I	Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, N, Sn, Pb	Al, Cr, Mn, Fe, Co, N, P, As, Sb, Bi, Cl, Br	C, N, Si, S, Mn, Sn, Pb	N, P, As, Sb, Bi, Cl, Br, I	S, Cr, Mn	Cl, I, Mn, Br

Typical Oxidation Numbers of Common Elements : Negative Ox #'s

Negative Oxidation Numbers				
Ox #	-1	-2	-3	-4
Examples	H, F, Cl, Br, I	O, S, Se	N, P	C, Si

Three Methods of Balancing Redox Reactions

Method 1	Method 2	Method 3
Oxidation Number Method	Oxidation Number Method for Aqueous Solutions	Half-Reactions for Aqueous Solutions Method

EXAMPLE 1

- For the second example for ALL three methods (after you get through the homework, I don't care which method you utilize as long as you can do it), we'll use the following UNBALANCED equation:
- $Cr_2O_7^{2-} + HNO_2 + H^+ \rightarrow Cr^{3+} + NO_3^- + H_2O$

Method 1: Oxidation Number Method

- Step Number One: Assign oxidation numbers.
- Do this just as I set up the rules for oxidation numbers, above, in the multiple tables.
- Keep track of your charges.

$$(Cr_2O_7)^{-2} = 2Cr + 7O$$

$$-2 = 2x + \underset{(7\cdot -2)}{-14}$$

$$\frac{-2+14}{2} = x = +6$$

$$HNO_2 = 1H + 1N + 2O$$

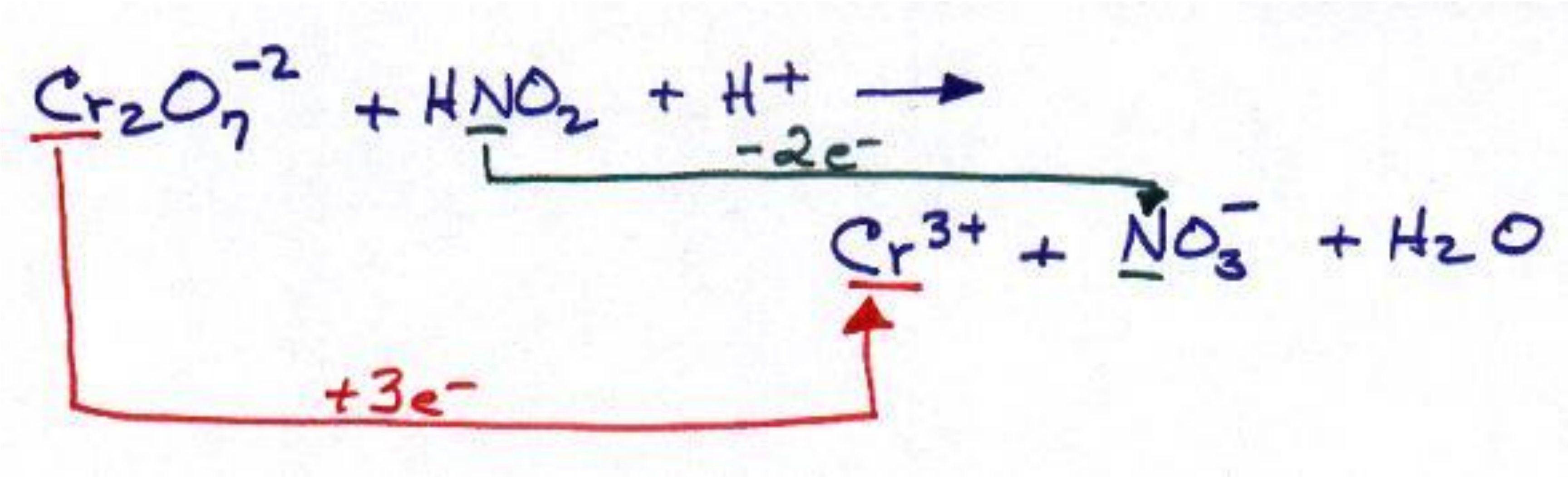
$$0 = (1\cdot 1) + x + (2\cdot -2)$$

$$0 = 1 + x + (-4)$$

$$0-1+4 = x = +3$$

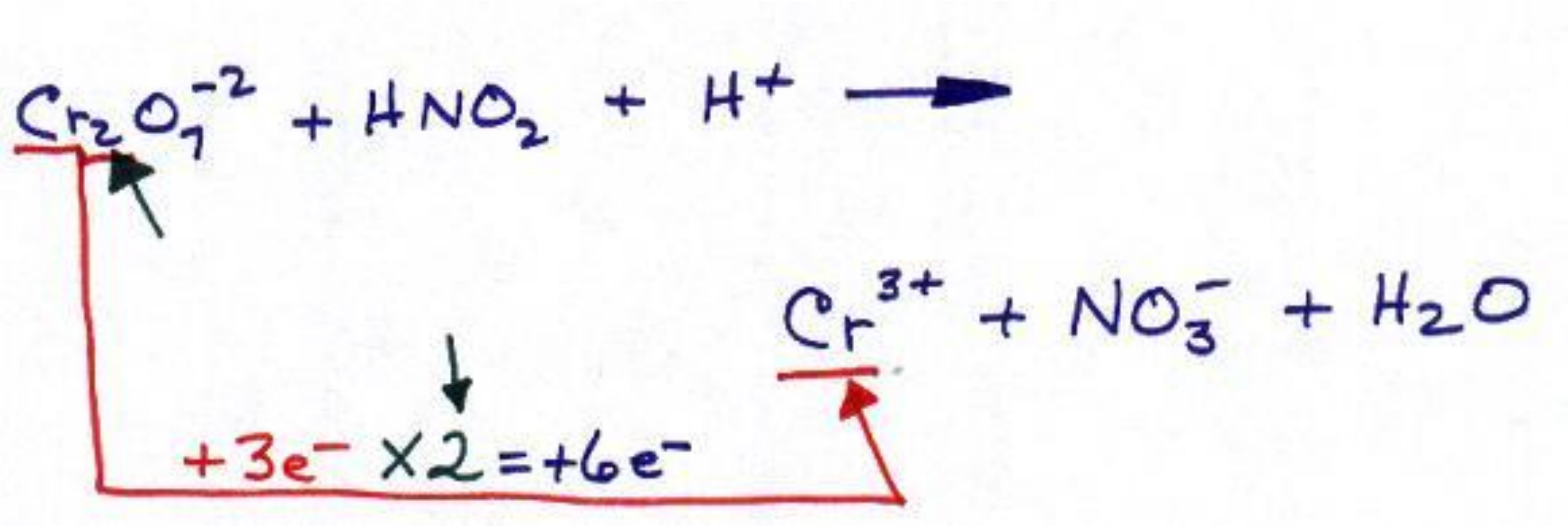
$$\overset{+6}{Cr_2}\overset{-2}{O_7}{}^{2-} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O_2} + H^+ \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O_3}{}^- + \overset{+1}{H_2}\overset{-2}{O}$$

- Step Number Two: You need to determine which reactant gains (oxidizing agent) or loses (reducing agent) electrons and identify how many electrons are lost per individual atom ONLY at this point.



$$\underline{Cr}_2O_7^{-2} + H\underline{N}O_2 + H^+ \longrightarrow \underline{Cr}^{3+} + \underline{N}O_3^- + H_2O$$

- Step Number three: Determine the gain or loss of electrons per formula unit -- this reaction is a great example: dichromate ion ($Cr_2O_7^{2-}$) has 2 Cr's.
- That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



$Cr_2O_7^{-2} + HNO_2 + H^+ \longrightarrow Cr^{3+} + NO_3^- + H_2O$

$+3e^- \times 2 = +6e^-$

- Step Number Four: Balance the left side of the reaction for gain and loss of electrons.

$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow$$

$$Cr^{3+} + NO_3^- + H_2O$$

- Step Number Five: Balance the redox pair, now, by balancing the right side of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow$$

$$2Cr^{3+} + 3NO_3^- + H_2O$$

- Step Number Six: Balance everything EXCEPT oxygen and hydrogen.
- Step Number Seven: Balance the oxygens.
- Step Number Eight: Balance the hydrogens.
- Step Number Nine: Write the balanced equation/reaction.

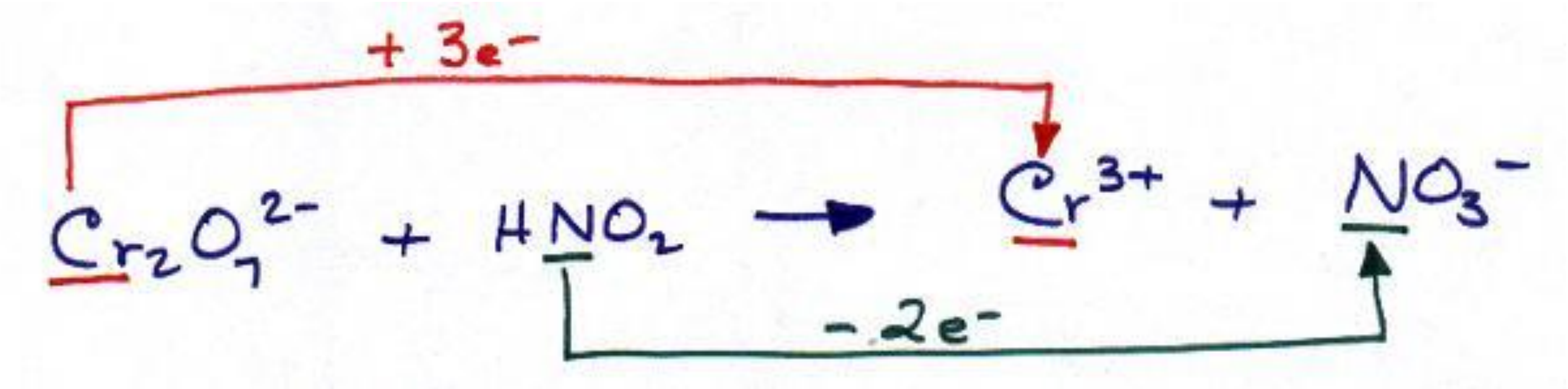
$$Cr_2O_7^{-2} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

Method 2: Oxidation Number Method for Aqueous Solutions

- We'll still use the same example reaction, above. This method requires a slightly different approach.
- Step Number One: write the net ionic reaction. This means to write the reaction that is going to occur between the redox pair ONLY.
- Step Number Two: Assign oxidation numbers just as we did in the first method.

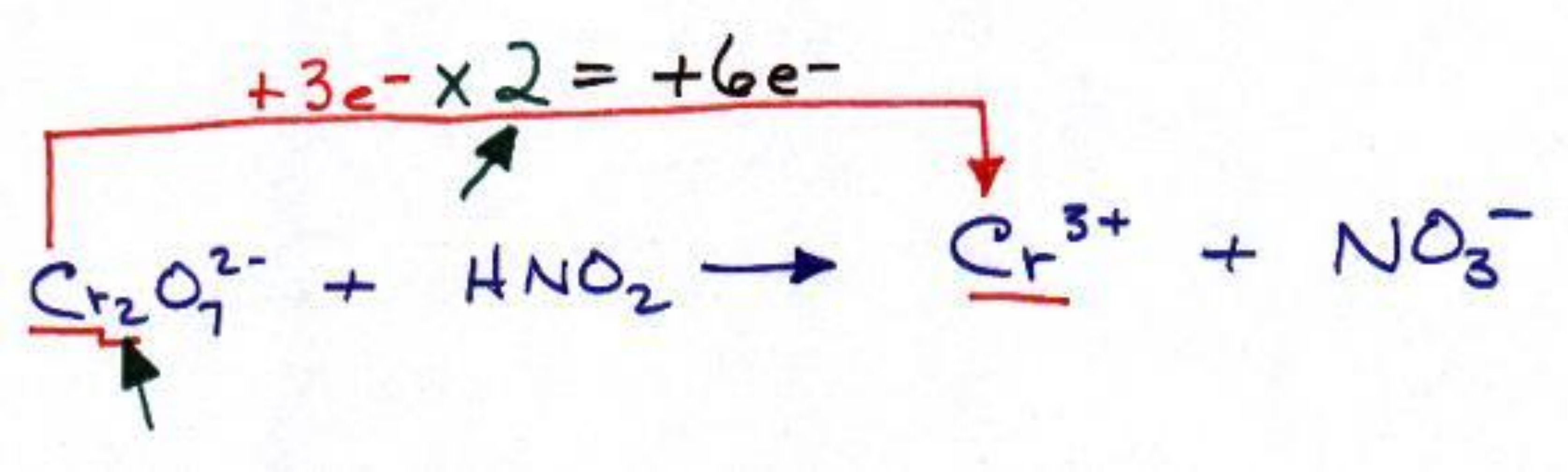
$$\overset{+6}{Cr_2}\overset{-2}{O}_7^{2-} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O}_2 \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O}_3^{-}$$

- Step Number Three: Determine which reactant gains and loses electrons.



$$\underline{Cr}_2O_7^{2-} + H\underline{N}O_2 \rightarrow \underline{Cr}^{3+} + \underline{N}O_3^-$$

- Step Number Four: determine the loss and gain of electrons per formula unit unit -- this reaction is a great example: dichromate ion (Cr_2O_{72-}) has 2 Cr's.
- That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



$+3e^- \times 2 = +6e^-$

$$Cr_2O_7^{2-} + HNO_2 \longrightarrow Cr^{3+} + NO_3^-$$

- Step Number Five: Balance the left side of the reaction based on electron gain/loss.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow Cr^{3+} + NO_3^-$$

- Step Number Six: balance the right side of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^-$$

- Step Number Seven: balance all but oxygen and hydrogen.
- Step Number Eight: Add up the charges on both sides of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^-$$

$$-2 + 0 = -2 \qquad +3 = +6 - 3$$

- Step Number Nine: balance the charges by adding H^+ for positive charges and OH^- for negative charges.

$$\begin{aligned} &\mathrm{Cr_2O_7^{2-}} + 3\,\mathrm{HNO_2} + 5\,\mathrm{H^+} \longrightarrow \\ &\qquad 2\,\mathrm{Cr^{3+}} + 3\,\mathrm{NO_3^-} \end{aligned}$$

- Step Number Ten: Balance the oxygens by putting water (H_2O) on the side opposite the hydroxide ions.
- Step Number Eleven: hydrogens ought to balance.
- Step Number Twelve: Write the balanced reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow$$

$$2Cr^{3+} + 3NO_3^- + 4H_2O$$

Method 3: Half-Reactions for Aqueous Solutions Method

- Step Number One: write out the unbalanced reaction.
- Step Number Two: find the half reactions for each of the redox pair. This is done by looking them up in the appendix of traditional chemistry texts (Redox Potentials) or in the CRC Handbook of Chemistry and Physics.
- They will be given to you during the exams if they are needed and if they actually exist in the literature -- there are times there are no accessible half reactions for use; when that occurs, these problems are usually fairly simple.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$

- Step Number Three: Balance all but the oxygen and hydrogen in each half reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3(HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e^-)$$

- Step Number Four: Balance oxygens with water added to the oxygen deficient side of the reaction.
- Step Number Five: Balance the hydrogens:
  - 1) in ACID with H^+;
  - 2) in BASE with 1 H_2O per needed hydrogen with an equal number of OH^- on the opposite side of the reaction.
- Step Number Six: Balance the charges with electrons on the side of each half reaction with the least negative charge.
- Step Number Seven: between the two half reactions, now balance electron gain and loss. In this step, it becomes necessary to turn one of the reactions around so that it will add to the other half-reaction, eventually. Note that two half reactions will make a whole reaction.
- Step Number Eight: Cancel out common elements, ions, and/or electrons between the 2 half reactions now balanced.

$$Cr_2O_7^{2-} + \overset{5}{\cancel{14}}H^+ + \cancel{6e^-} \rightarrow 2Cr^{3+} + \overset{4}{\cancel{7}}H_2O$$

$$3\,HNO_2 + \cancel{3H_2O} \rightarrow 3NO_3^- + \cancel{9H^+} + \cancel{6e^-}$$

- Step Number Nine: Add them up and write out the balanced reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow$$

$$2Cr^{3+} + 3NO_3^- + 4H_2O$$

- One key concept to keep in mind is that if you've balanced the same reaction by each method above, and you don't get the same answer each time, then there is an error in the balancing.
- Go back and find it -- it usually jumps right out at you.

EXAMPLE 2

Method 1: Oxidation Number Method

- For this example for ALL three methods (after you get through the homework, I don't care which method you utilize as long as you can do it), we'll use the following UNBALANCED equation:
- $MnO_4^- + S^{2-} + H_2O \rightarrow MnO_2\downarrow + S + OH^-$
- Note that the S on the right is in the elemental form and has an oxidation number of zero (0).

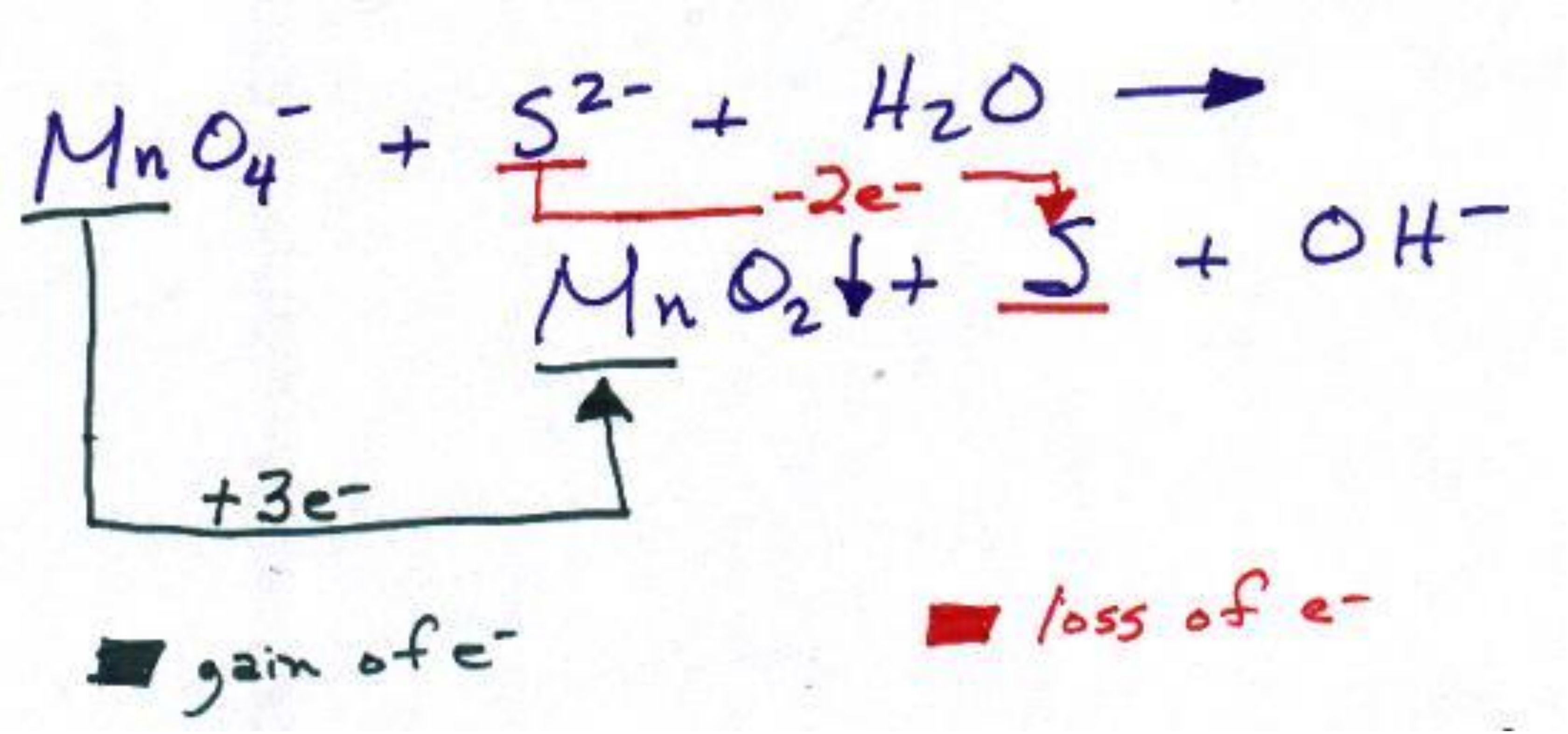
- Step Number One: Assign oxidation numbers. Do this just as I set up the rules for oxidation numbers, above, in the multiple tables. Keep track of your charges.

$$(MnO_4)^{-1} = 1\,Mn + 4\,O$$
$$-1 = x + \underbrace{4(-2)}_{-8}$$
$$-1 + 8 = +7$$

$$MnO_2 = 1\,Mn + 2\,O$$
$$0 = x + \underbrace{2(-2)}_{-4}$$
$$0 + 4 = +4$$

$$\overset{+7}{Mn}\overset{-2}{O}_4^{-} + S^{2-} + \overset{+1}{H}_2\overset{-2}{O} \longrightarrow \overset{+4}{Mn}\overset{-2}{O}_2\downarrow + \overset{0}{S} + \overset{-2}{O}\overset{+1}{H}^{-}$$

- Step Number Two: You need to determine which reactant gains (oxidizing agent) or loses (reducing agent) electrons and identify how many electrons are lost per individual atom ONLY at this point.



The sulfide loses 2 electrons and the manganese gains three.

- Step Number Three: Determine the gain or loss of electrons per formula unit -- this reaction is a bad example as there is only one formula unit for each -- the second set of examples will illustrate this idea.

- Step Number Four: Balance the left side of the reaction for gain and loss of electrons.
- This balancing is done by looking at the numbers of electrons gained and lost. They must be equal.
- Sometimes the easiest thing to do is to just multiply them together if there is no obvious lowest common multiple.

$$2MnO_4^- + 3S^{2-} + H_2O \longrightarrow MnO_2\downarrow + S + OH^-$$

- Step Number Five: Balance the redox pair, now, by balancing the right side of the reaction.

$$2MnO_4^- + 3S^{2-} + H_2O \longrightarrow 2MnO_2\downarrow + 3S + OH^-$$

Make sure you've got as many atoms on the right as you do on the left.

- Step Number Six: Balance everything EXCEPT oxygen and hydrogen.
- Step Number Seven: Balance the oxygens. See below.
- Step Number Eight: Balance the hydrogens. See below.
- Step Number Nine: Write the balanced equation/reaction.

$$2MnO_4^- + 3S^{2-} + 4H_2O \longrightarrow 2MnO_2\downarrow + 3S + 8OH^-$$

Method 2: Oxidation Number Method for Aqueous Solutions

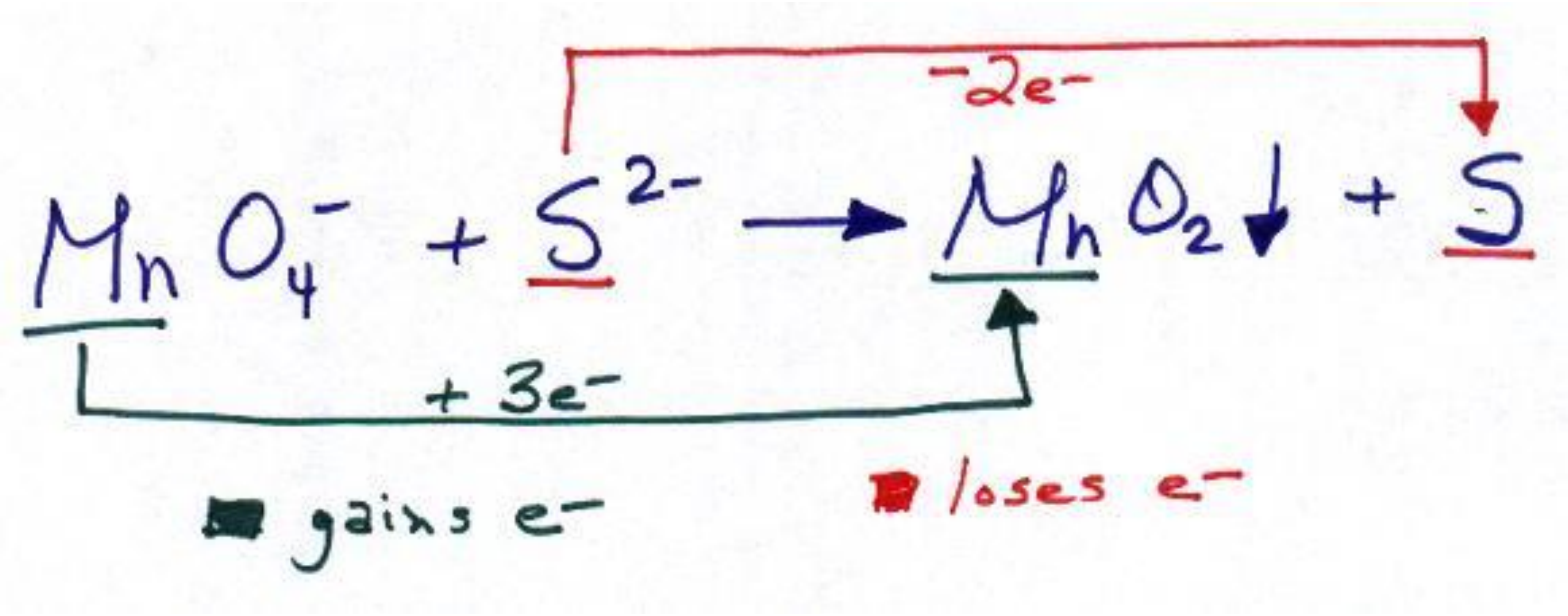
- We'll still use the same example reaction, above. This method requires a slightly different approach.
- Step Number One: write the net ionic reaction. This means to write the reaction that is going to occur between the redox pair ONLY.

$$MnO_4^- + S^{2-} \longrightarrow MnO_2\downarrow + S$$

- Step Number Two: Assign oxidation numbers just as we did in the first method.

$$\overset{+7}{Mn}\overset{-2}{O}_4^- + S^{\overset{\swarrow}{2-}} \longrightarrow \overset{+4}{Mn}\overset{-2}{O}_2\downarrow + S^{\overset{\swarrow}{0}}$$

- Step Number Three: Determine which reactant gains and loses electrons.



$$MnO_4^- + S^{2-} \longrightarrow MnO_2\downarrow + S$$

🟩 gains e^-

🟥 loses e^-

- Step Number Four: determine the loss and gain of electrons per formula unit (again, this is not a good example and will be dealt with in the second example).
- Step Number Five: Balance the left side of the reaction based on electron gain/loss.

$$2MnO_4^- + 3S^{2-} \longrightarrow MnO_2\downarrow + S$$

- Step Number Six: balance the right side of the reaction.

$$2MnO_4^- + 3S^{2-} \longrightarrow 2MnO_2\downarrow + 3S$$

- Step Number Seven: balance all but oxygen and hydrogen.
- Step Number Eight: Add up the charges on both sides of the reaction.

$$2MnO_4^- + 3S^{2-} \longrightarrow 2MnO_2\downarrow + 3S$$

$$\underset{\substack{\swarrow\\(2\cdot -1)}}{-2} + \underset{\substack{\downarrow\\(3\cdot -2)}}{-6} = -8 \qquad 0 = \underset{\substack{\swarrow\\(2\cdot 0)}}{0} + \underset{\substack{\downarrow\\(3\cdot 0)}}{0}$$

- Step Number Nine: balance the charges by adding H^+ for positive charges and OH^- for negative charges.

$$2MnO_4^- + 3S^{2-} \rightarrow 2MnO_2\downarrow + 3S + 8\,OH^-$$

Note that I used OH- to balance the negative charges on the right.

- Step Number Ten: Balance the oxygens by putting water (H_2O) on the side opposite the hydroxide ions.

$$2MnO_4^- + 3S^{2-} + 4H_2O \longrightarrow$$

$$2MnO_2\downarrow + 3S + 8OH^-$$

- Step Number Eleven: hydrogens ought to balance.
- Step Number Twelve: Write the balanced reaction, just as above.

$$2MnO_4^- + 3S^{2-} + 4H_2O \longrightarrow 2MnO_2\downarrow + 3S + 8OH^-$$

Method 3: Half-Reactions for Aqueous Solutions Method

- Step Number One: write out the unbalanced reaction.
- Step Number Two: find the half reactions for each of the redox pair.
- This done by looking them up in the appendix of traditional chemistry texts (Redox Potentials) or in the CRC Handbook of Chemistry and Physics.
- They will be given to you during the exams if they are needed and if they actually exist in the literature -- there are times there are no accessible half reactions for use; when that occurs, these problems are usually fairly simple.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2\downarrow + 4OH^-$$

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

Note that for each reactant there is a half reaction – eventually, we'll add 'em up to make a whole reaction.

- Step Number Three: Balance all but the oxygen and hydrogen in each half reaction.
- Step Number Four: Balance oxygens with water added to the oxygen deficient side of the reaction.
- Step Number Five: Balance the hydrogens:
  - 1) in ACID with H^+;
  - 2) in BASE with 1 H_2O per needed hydrogen with an equal number of OH_- on the opposite side of the reaction.
- Step Number Six: Balance the charges with electrons on the side of each half reaction with the least negative charge.

$$2(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2\downarrow + 4OH^-)$$

$$3(S^{2-} \rightarrow S^0 + 2e^-)$$

- Note that we multiply the top half reaction by the number of electrons from the bottom reaction and vice versa.
- While this works in most cases, remember that once the reaction is balanced, you must use the lowest possible coefficients, i.e., if the coefficients are divisible by the same number across the reaction, the final reaction must by divided by that number to yield numbers that are no longer divisible, yet consist of a whole number.

- Step Number Seven: between the two half reactions, now balance electron gain and loss. In this step, it becomes necessary to turn one of the reactions around so that it will add to the other half-reaction, eventually. Note that two half reactions will make a whole reaction.
- Step Number Eight: Cancel out common elements, ions, and/or electrons between the 2 half reactions now balanced.

$$2MnO_4^- + 4H_2O + \cancel{6e^-} \rightarrow 2MnO_2\downarrow + 8\ OH^-$$

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

- Step Number Nine: Add them up and write out the balanced reaction.

$$2MnO_4^- + 3S^{2-} + 4H_2O \rightarrow 2MnO_2\downarrow + 3S + 8OH^-$$

Problem Set 23

Table of Half Reactions

IMPORTANT: When necessary, turn the reactions around to fit your needs – do NOT, however, change the contents of the half-reactions

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$

$Zn^{2+} + 2e^- \rightarrow Zn$

$Cu^{2+} + 2e^- \rightarrow Cu$

$2IO_3^- + 12H^+ + 10\ e^- \rightarrow I_2 + 6H_2O$

$NO_3^- + 4H^+ + 3\ e^- \rightarrow NO + 2H_2O$

$ClO_3^- + 6H^+ + 6\ e^- \rightarrow Cl^- + 3H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6\ e^- \rightarrow 2Cr^{3+} + 7H_2O$

$NO_3^- + 3H^+ + 2\ e^- \rightarrow HNO_2 + H_2O$

$PbO + H_2O + 2\ e^- \rightarrow Pb + 2OH^-$

1.Balance the following reactions by each of the first two methods of balancing redox reactions:

A) $Zn + NO_3^- \rightarrow Zn^{2+} + N_2\uparrow$

B) $NO_3^- + I_2 \rightarrow IO_3^- + NO_2\uparrow$

C) $Cu + NO_3^- \rightarrow Cu^{2+} + NO_2\uparrow$

D) $H_2O_2 + MnO_4^- \rightarrow Mn^{2+} + O_2\uparrow$

E) $CuS + NO_3^- \rightarrow Cu^{2+} + S + NO\uparrow$

F) $NO_3^- + Zn \rightarrow NH_3\uparrow + Zn(OH)_4^{2-}$

G) $ClO_3^- + I_2 \rightarrow IO_3^- + Cl^-$

H) $Cr_2O_7^{2-} + HNO_2 \rightarrow Cr^{3+} + NO_3^-$

I) $H_2SO_4 + HBr \rightarrow SO_2\uparrow + Br_2\uparrow$

J) $C + HNO_3 \rightarrow NO_2\uparrow + CO_2\uparrow$

2. Balance the following reactions from #1, above, by the third method: D, G and H.

3. Balance the following reactions by whichever methods you so desire:

A) $NO_3^- + Pb \rightarrow NO + PbO$

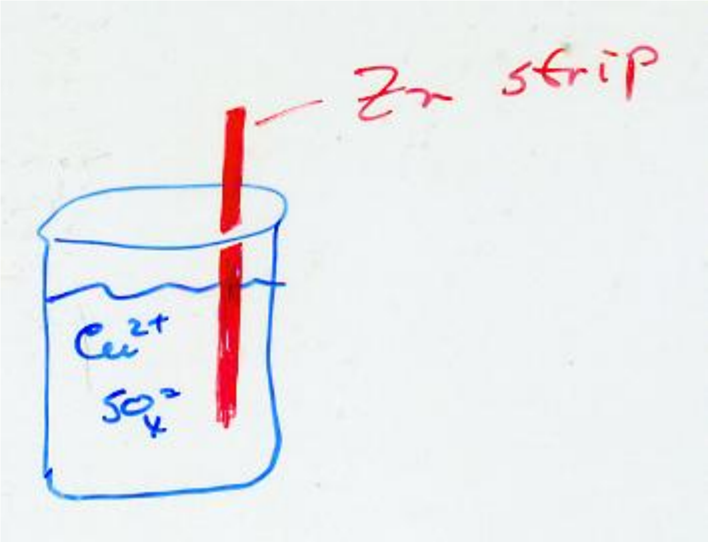
B) $Cl^- + Zn^{2+} \rightarrow ClO_3^- + Zn$

Batteries

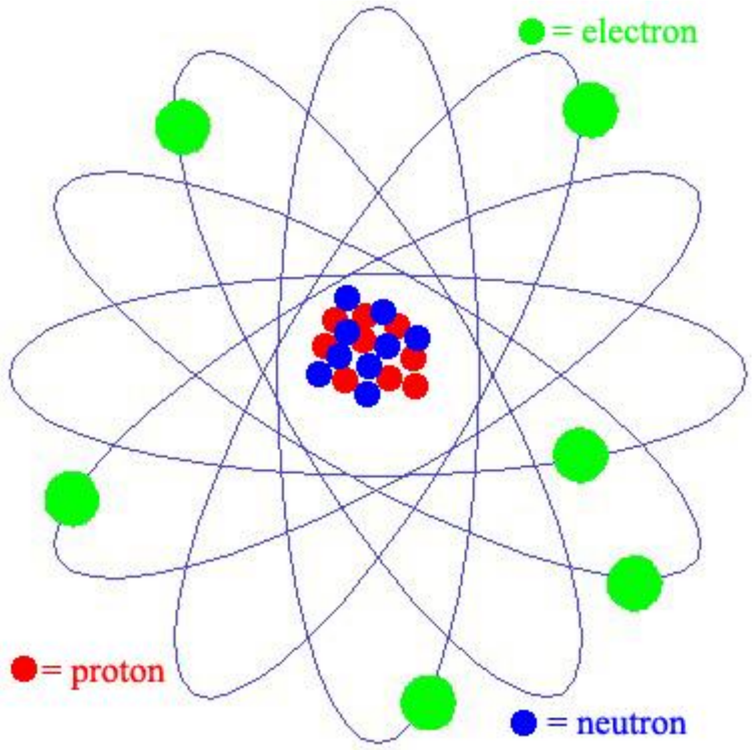
- Classic redox reactions
- Chemical changes can produce electricity
- Reaction below:

$$\text{Zn:} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu:}$$

- The flow of electrons = the electric current



Electricity and The Atomic Nature of "Things"



- Electrostatics = study of fixed or stationary, electric charges.
- Static electricity is the most common form we encounter.
- Electric charges = ±
- Smallest units = electrons (-) and protons (+)
- Have equal magnitude with opposite signs

Electrons

- May travel from atom to atom
  - Protons don’t
- Discussions of electricity, then, with negative charges

- An object is electrified if it has excess or missing electrons

- How lose or gain electrons?
- Touch
- Sock feet on carpet
- Using a magnet to induce an electrical current.

Four Laws of Electrostatics

1) Law of Electrical Charges
2) Law of Electrification
3) Law of Electric Charge Distribution
4) Law of Electric Charge Concentration

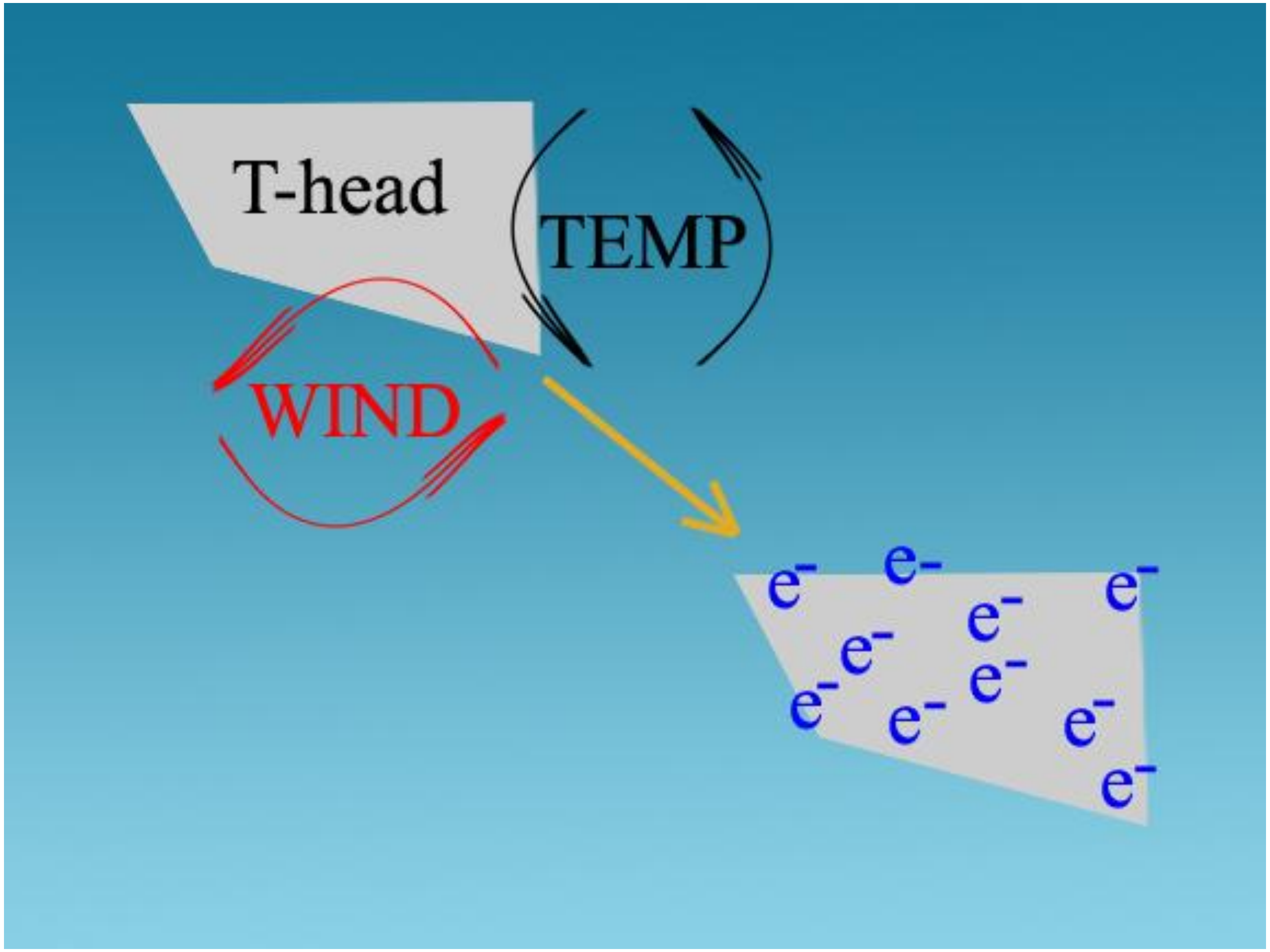
Law of Electrical Charges -- #1

- Unlike charges attract
- Like charges repel
- The force of attraction or repulsion is the electrostatic force

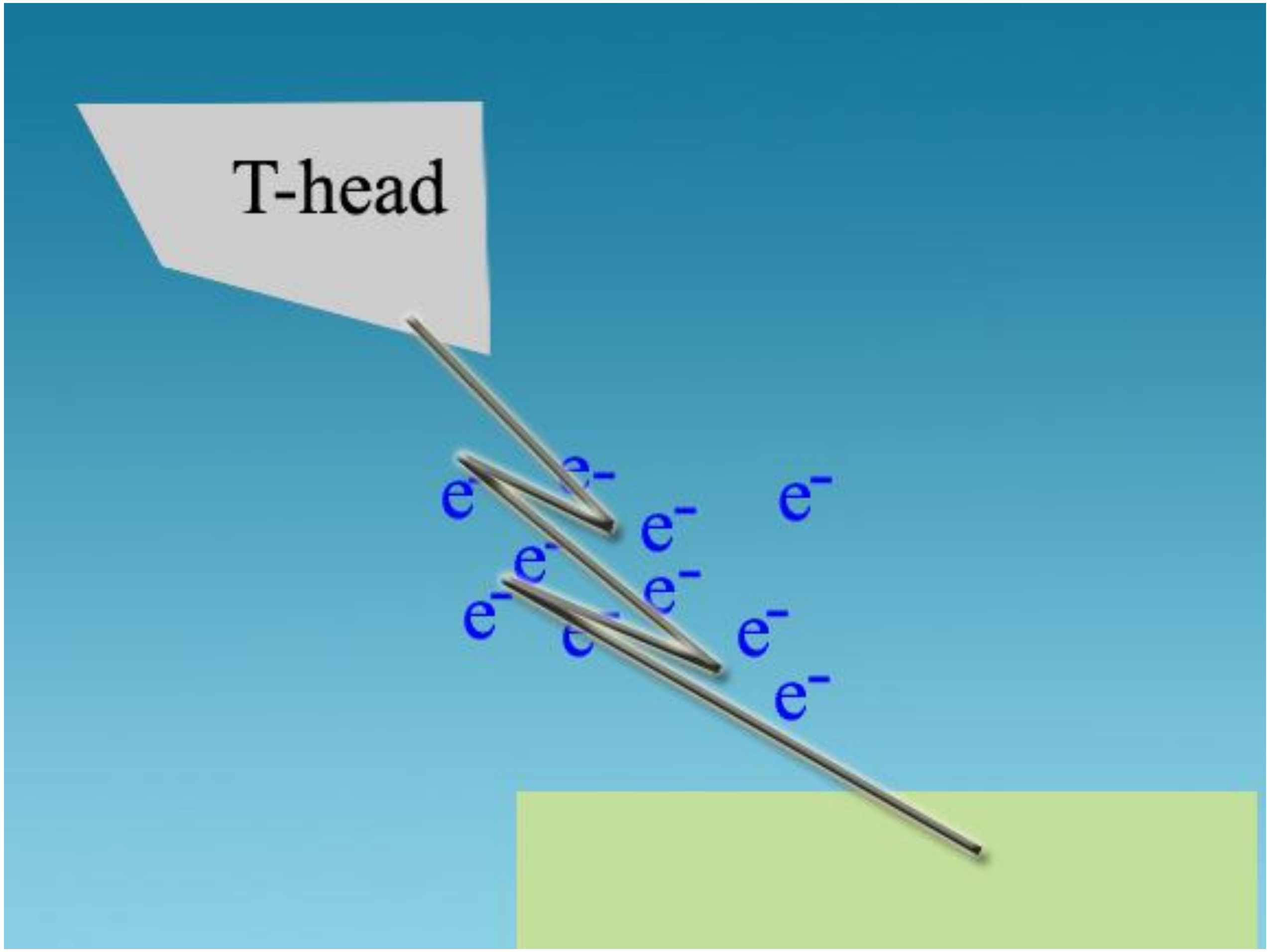
Law of Electrification -- #2

- Electrification occurs because of the movement of negative electric charges.
- When a negatively charged object is in contact with an electrically neutral object, charges are transferred to the neutral object.
- If the transfer is sufficiently violent, makes a spark – of interest is the strap in “booties” for OR – was to reduce sparking by grounding person so patient wouldn’t blow up on the table

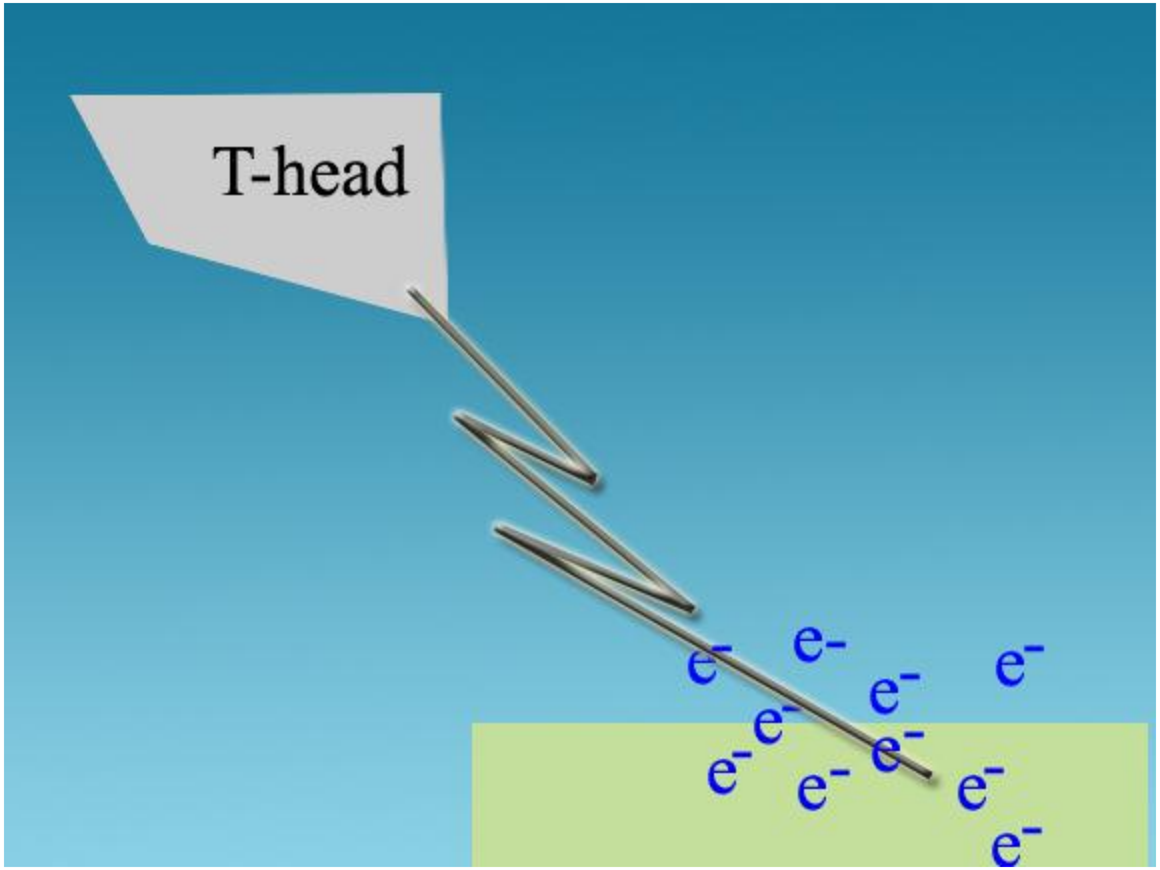
Thundercloud Example



Thunderhead #2



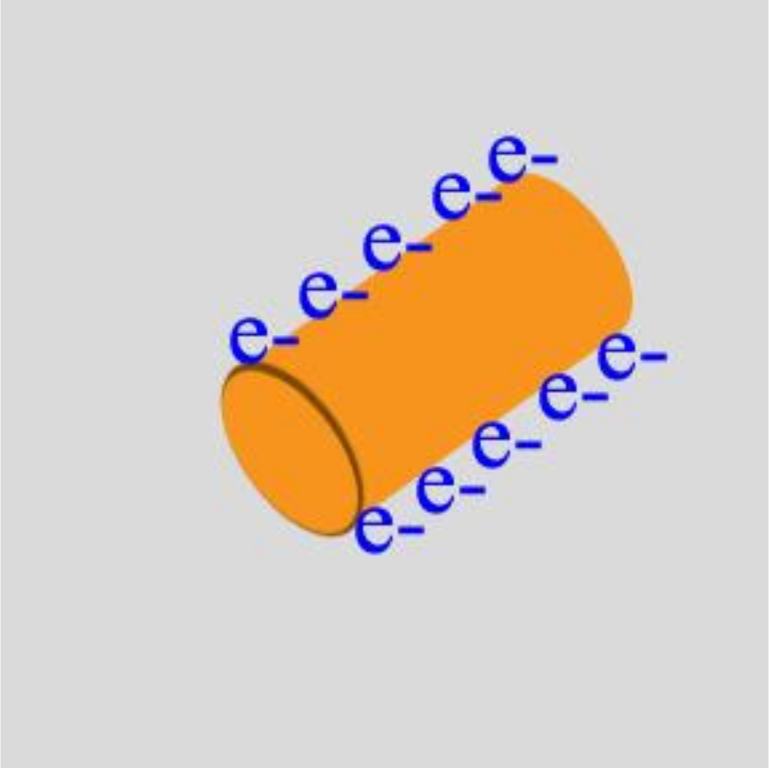
Thunderhead #3



- Electron movement = lightning
- CAN occur between clouds
- USUALLY between clouds and earth

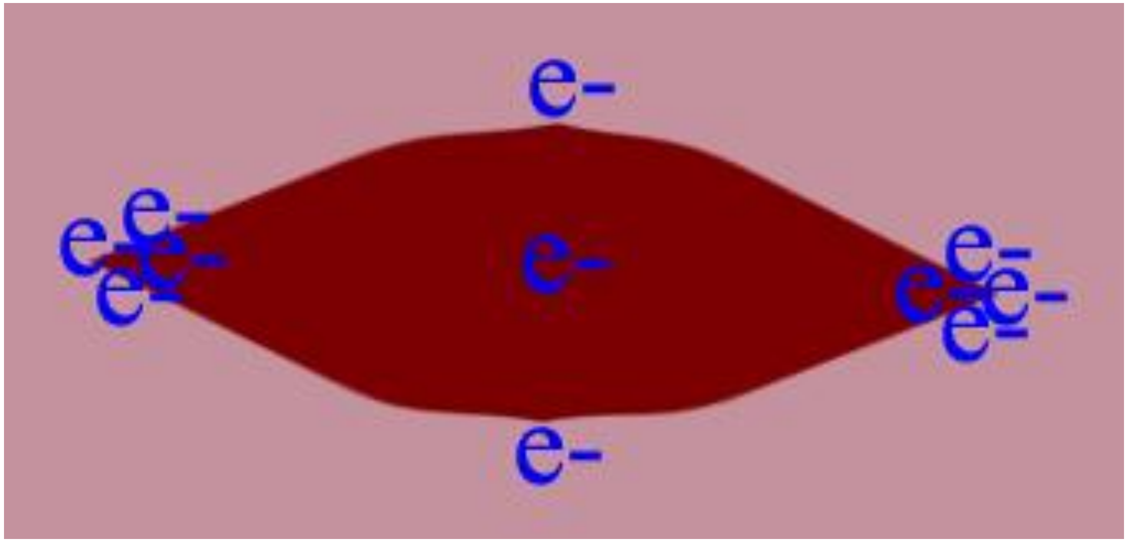
Law of Electric Charge Distribution -- #3

- A diffuse non-conductor object (cloud) has charges distributed throughout the object.
- A conductor (Cu wire) has excess electrons over its outer surface:



Law of Electric Charge Concentration -- #4

- Electric charges are concentrated along the sharpest curvature of a surface:



Remember

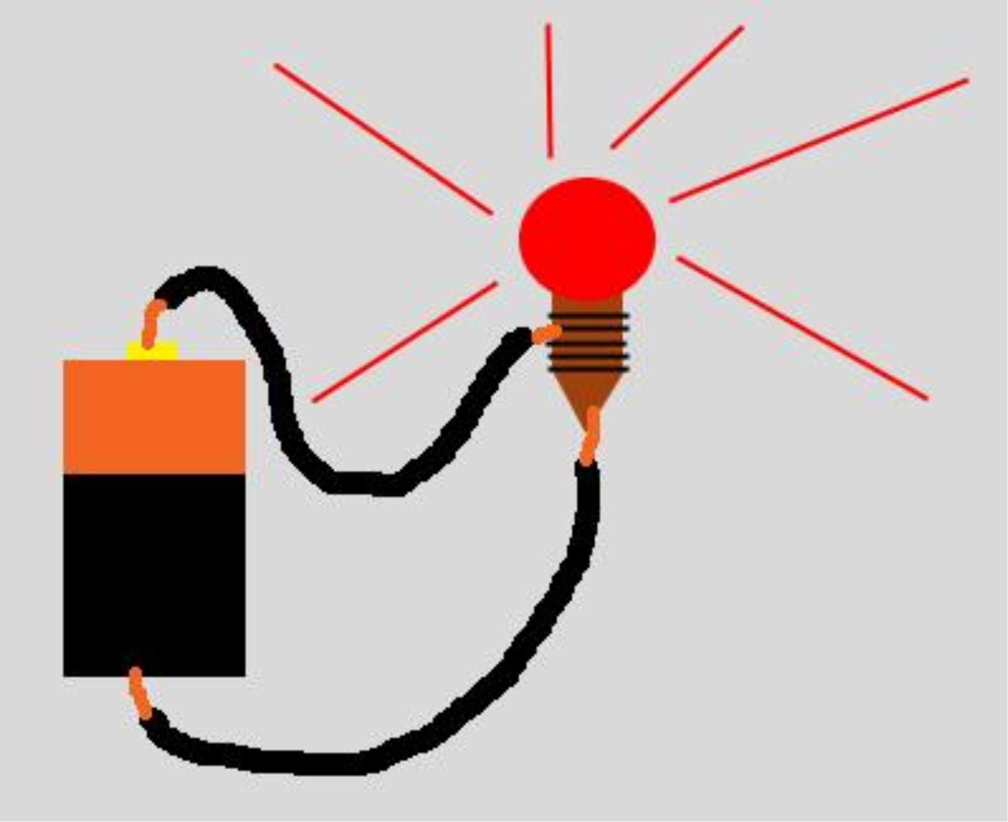
- Static electricity is about electricity “staying put” – it CAN move, though: cloud-to-cloud or cloud-to-ground.

Electrodynamics

- We recognize electrodynamic phenomena as electricity.
- The flow of electrons along a wire is the electric current.
- Any material through which electrons easily flow is called a conductor.

Electric Circuits

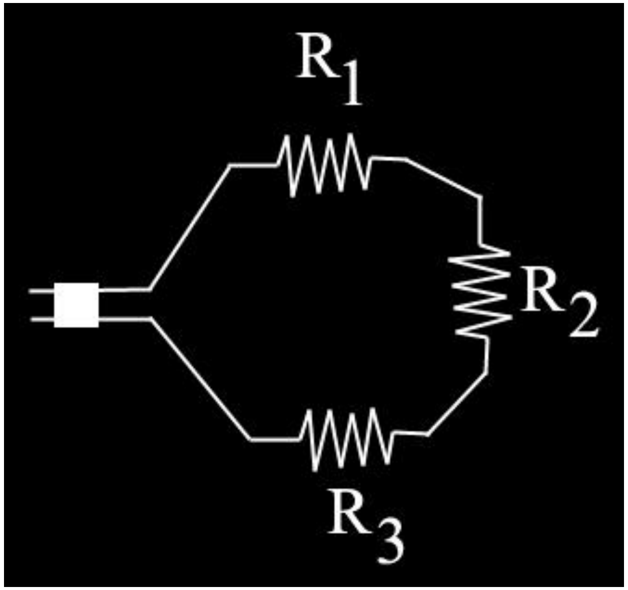
- Electrons flow along the outer wire surface.
- The wire can be modified to resist the flow in certain regions.
- When resistance (Ω) is controlled and conductor is in a closed path, you've got an electric circuit.

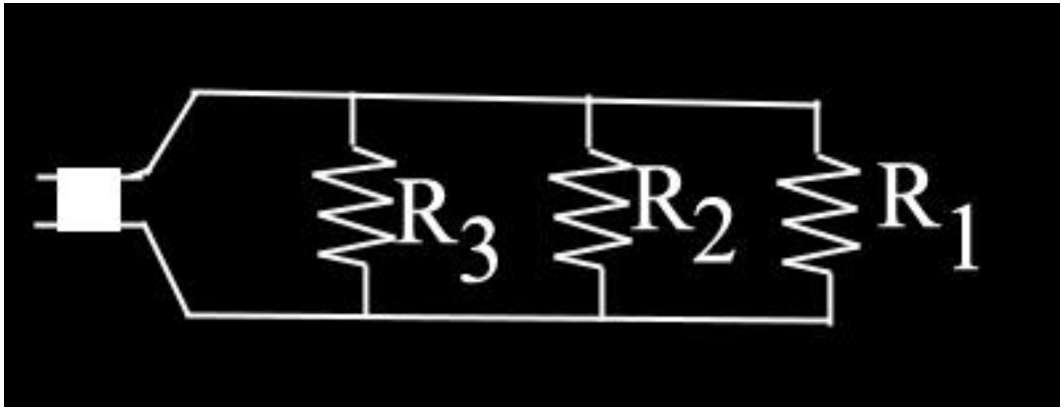


- Current is measured in amperes (amps; I in equations)
- The electrical potential is measured in volts (V)
- Resistance is measured in ohms (Ω; R in equations)

- Ohm’s Law
  - $V = I R$

Electrical Circuits





- Series (left) – set up like X-mas lights: one goes out, they all go out – Greatest Ω, least electron flow
- Parallel (right) – one goes out, the rest stay on – Least Ω, greatest electron flow (conductance)

Electric Power

- $P = I V = I^2 R$
- 1 kW = 1000 Watts
- 1kWh = 1000 watts used in one hour

Piezo Electric Effect

- Piezoelectricity = pressure electricity.

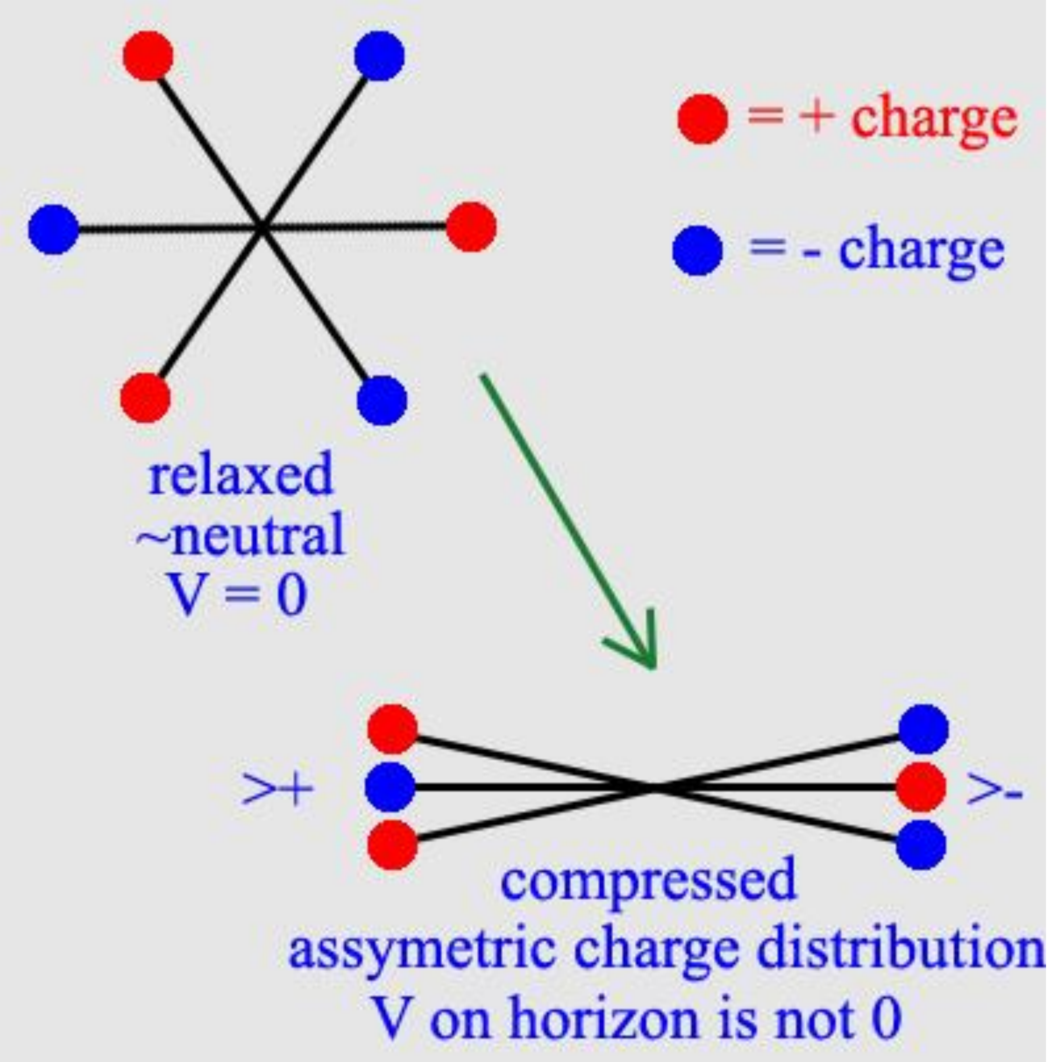
- We know it from BBQ grills with the propane “starter”.

- 1st discovered in quartz and tourmaline
- Found in tendon, dentin, aorta, trachea, elastin and BONE!

Piezo Electric Effect

- The effect is the ability of a mineral or crystal to acquire opposing electrical charges on opposing surfaces when bending, stretching or compression is applied to the crystal.
- Is caused by displacing ionic charges within a crystal structure – the magnitude of the charge is usually proportional to the amount of stress applied.

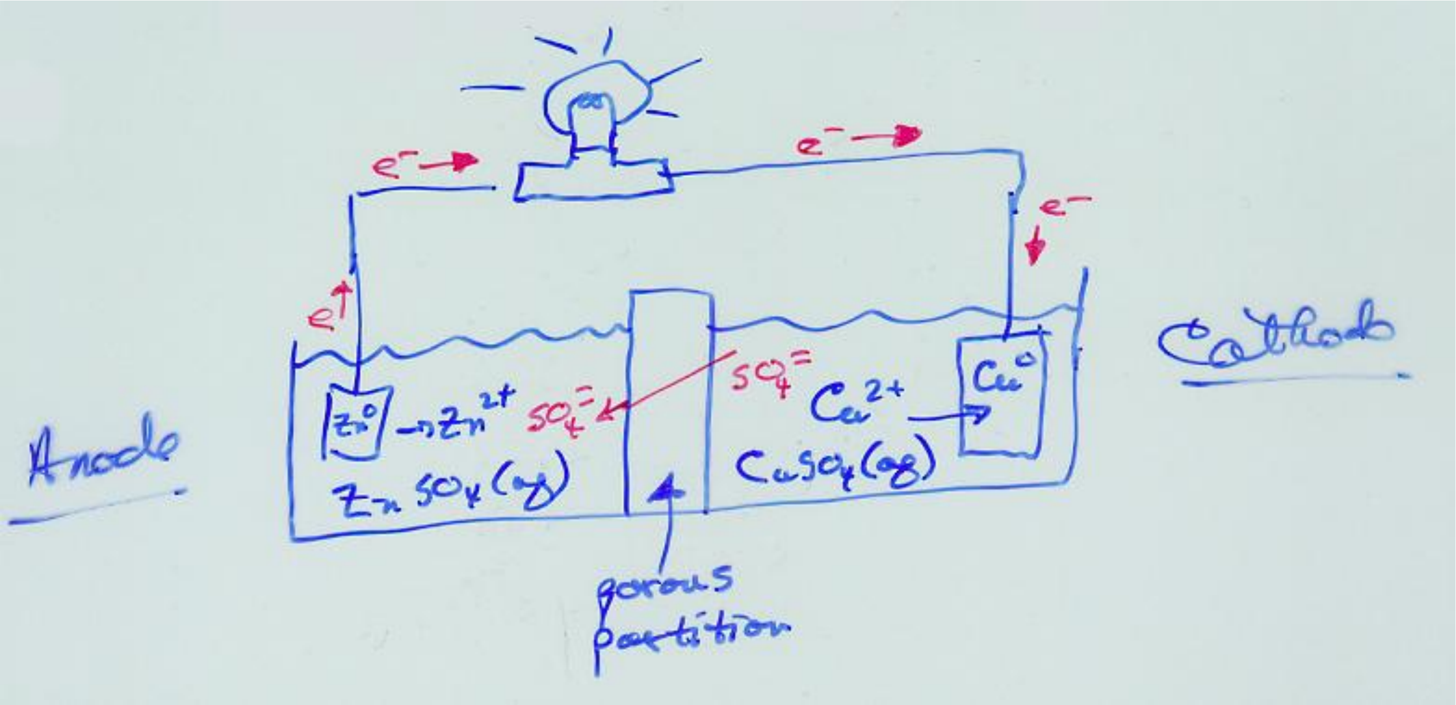
Piezo – How It Works



Piezo -- Bone

- This stress effect causes osteoblasts to secrete osteoid (CHON that permits Ca salt ppt’ation on/in it) to make/remodel new bone.

A Simple Battery



- Reaction:

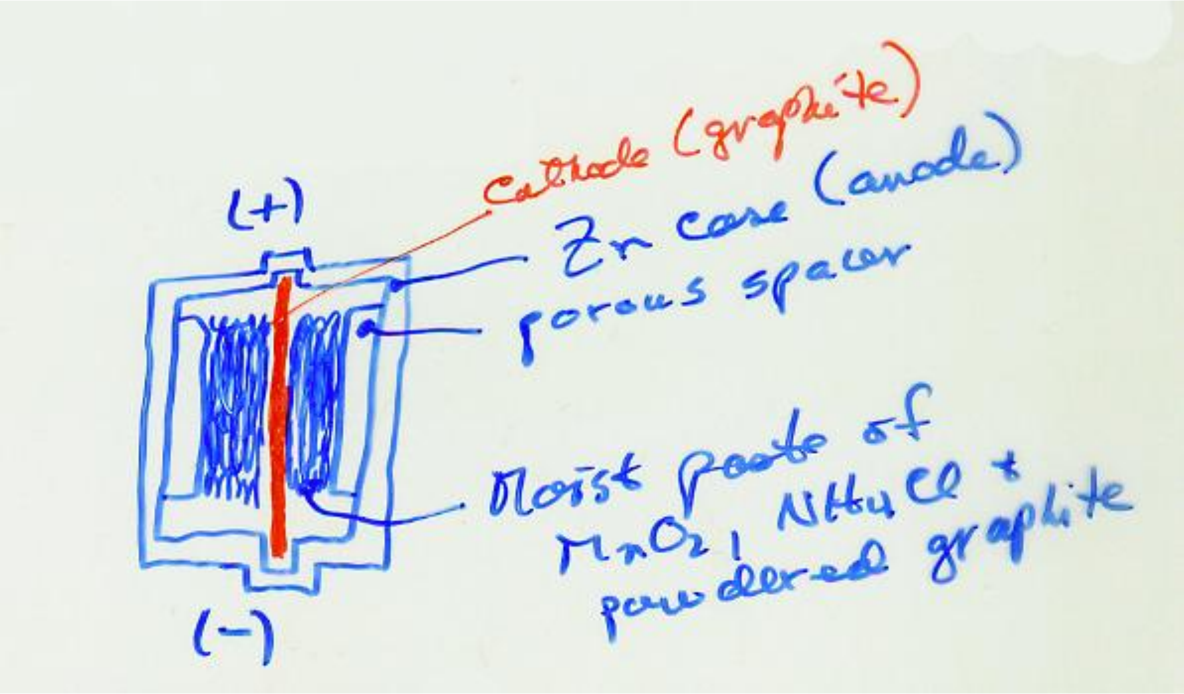
$$Zn: + Cu^{2+} \rightarrow Zn^{2+} + Cu:$$

- Zn electrode “disappears”
- Cu electrode “plates out”

Car Battery

- 6 cells wired together in series.
- On discharge:
- $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$
- On recharge:
- $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

Dry Cells



Reaction:

$$Zn + 2MnO_2 + 2H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$$

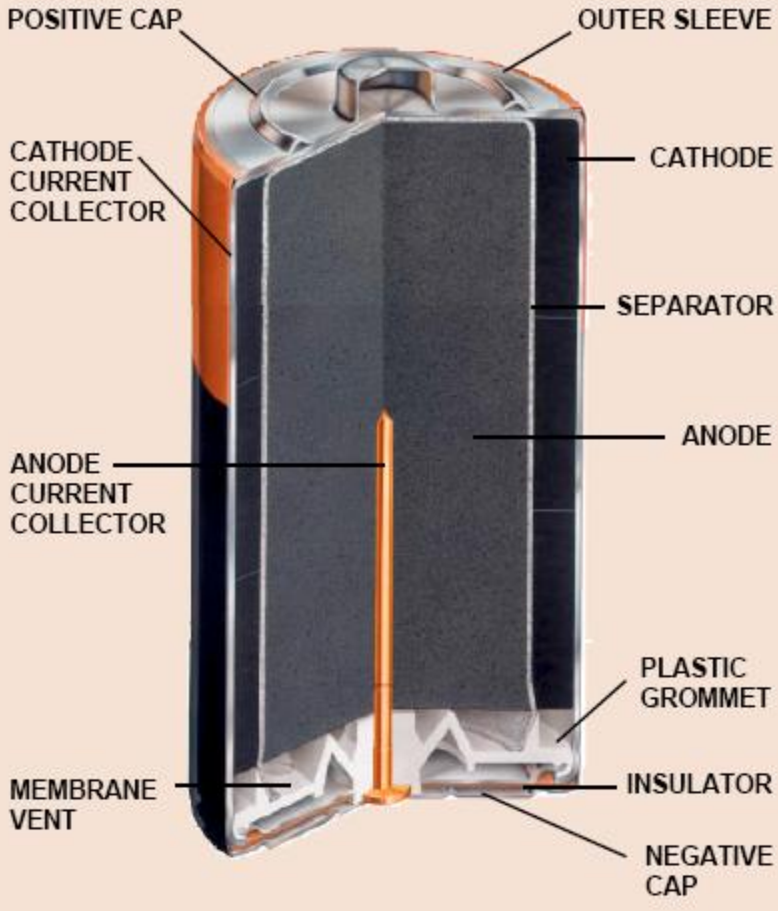
http://www.duracell.com/procell/pdf/ATB-full.pdf -- used with permission from Duracell

Anode = Zinc (Zn)

Cathode = manganese dioxide (MnO_2)

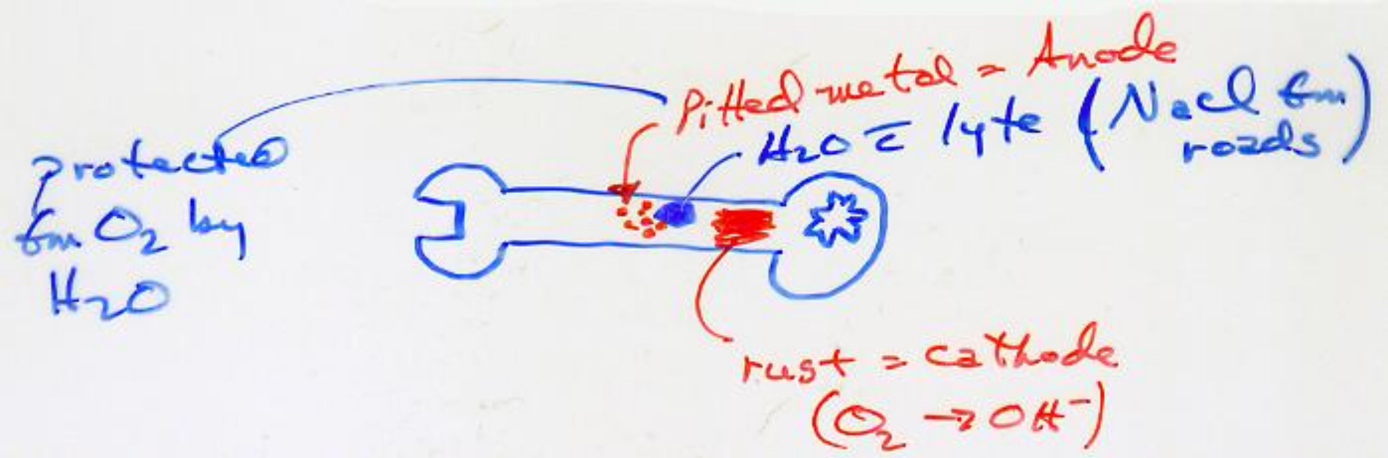
Electrolyte = potassium hydroxide (KOH)

Figure 1



DURACELL® cylindrical alkaline cell.

Corrosion: Another Battery

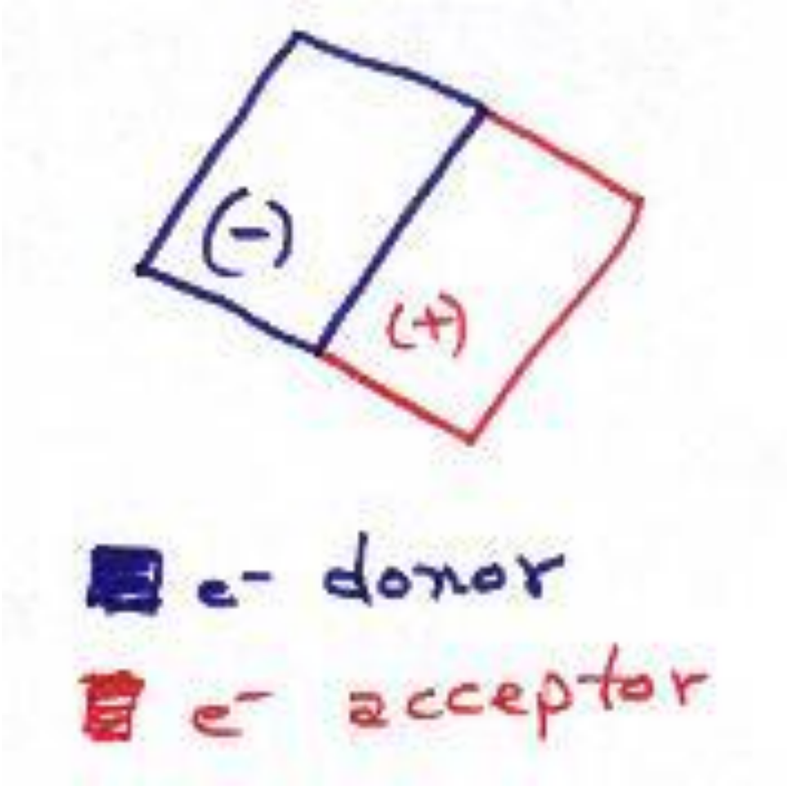


- At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$
- At Cathode: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
- $Fe(OH)_2 + O_2 \rightarrow Fe(OH)_3$
- $Fe(OH)_3$ + oxidizing agent $\rightarrow Fe_2O_3$
- The “pitting” makes the wrench more chemically reactive.

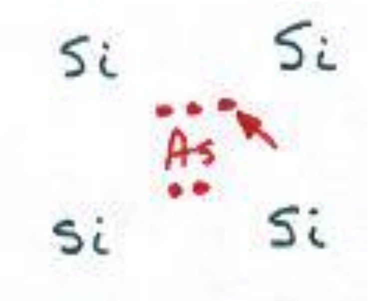
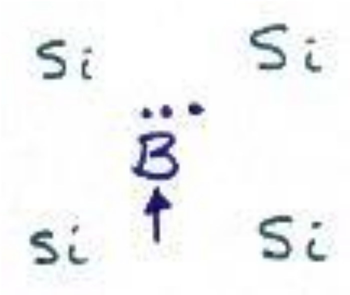
Solar Batteries

- Since I developed this part of the lecture, solar power has gone through numerous changes.
- I have given up trying to keep up with these changes, as they tend to be very rapid, i.e., by the time I get it updated, it's already changed, again.
- Hence, this is a very generic, low-key description to give you the idea behind solar batteries.

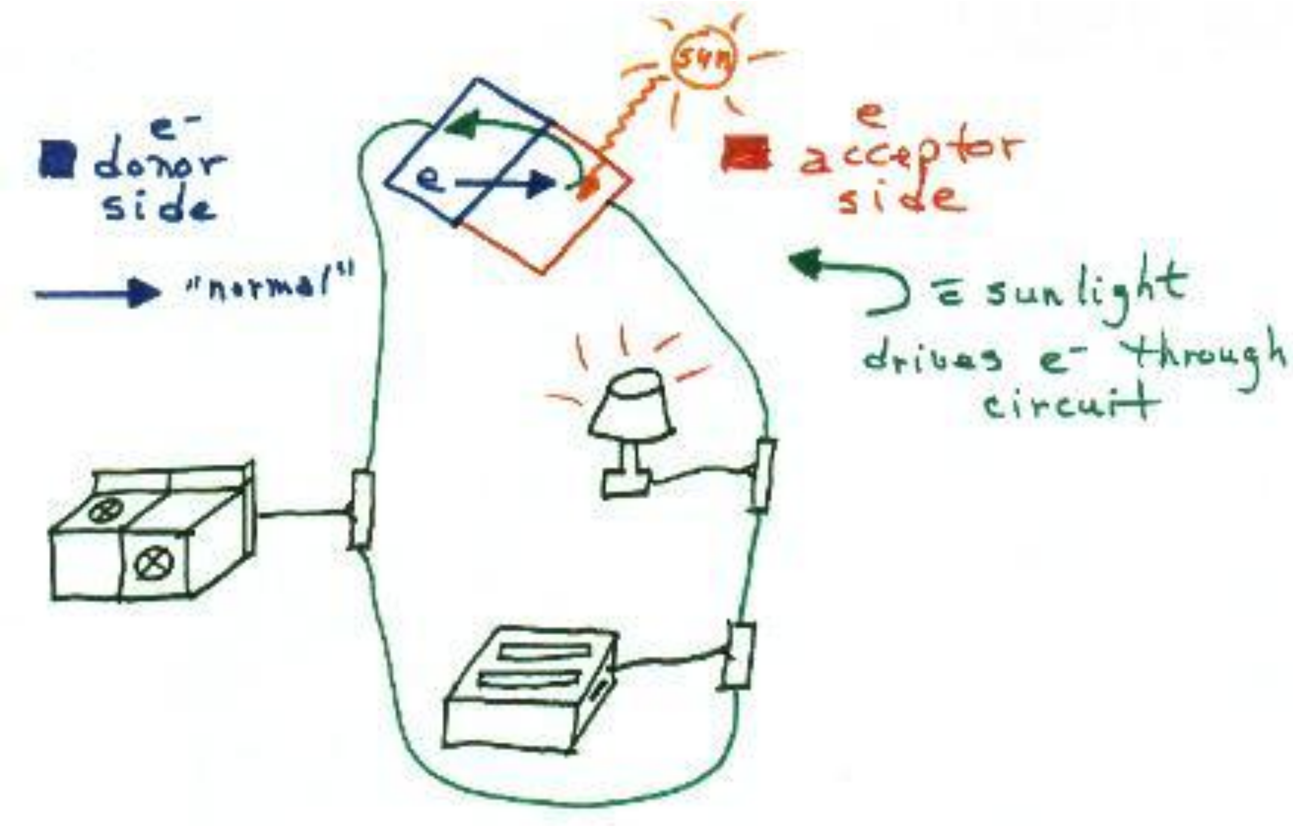
- In general, a solar battery is made up of two "wafers" of material: an electron donor wafer and an electron acceptor wafer.



The table, below, summarizes the characteristics of the donor and acceptor wafers:

Donor	Acceptor
Has 1 extra electron in its repeating structure, therefore, its partially negative.	**Has 1 less electron in its repeating structure, therefore, its partially positive.**
Si is the base and is "doped" with As to give the 5th electron (the extra electron pointed out, below).	**Si is the base and is "doped" with B to give three electrons (lacks the 4th electron pointed out, below; makes an electron "hole" in the repeating sequence).**
 **Rough illustration**	 **Rough illustration**

- By itself, electrons flow from the electron donor plate to the electron acceptor plate. Sunlight, though, reverses the "natural process" and electrons are driven through the circuit via the donor layer to the acceptor layer. This closes the circuit and runs electric appliances and toys (TV, stereos, ad nauseum).

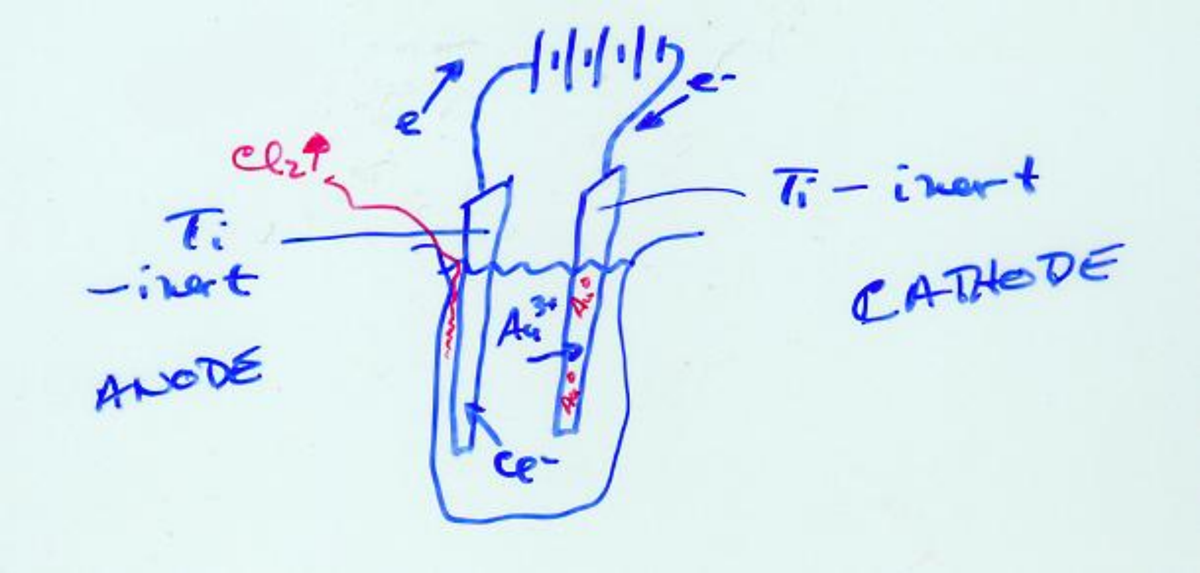


- At the time I put this together, solar cells were only about 10% efficient in energy conversion.
- What that meant was that to operate one 100W bulb would require a series of solar cells 1m by 1m.
- At that time, 5000 acres of solar cells would produce the energy equivalent to one nuclear power plant.
- To give you some perspective on this, one section of land is 640 acres and is one mile by one mile.
- This means that it would take (at old efficiency rates) a piece of ground that is 8 sections or 8 square miles in area (equivalent to a strip of land 4 miles long and 2 miles wide).

Electrolysis

- ≡ the use of electrical energy to drive an otherwise unfavored reaction to completion
- This is done in an electrolytic cell.

Electrolytic Cell



Reactions

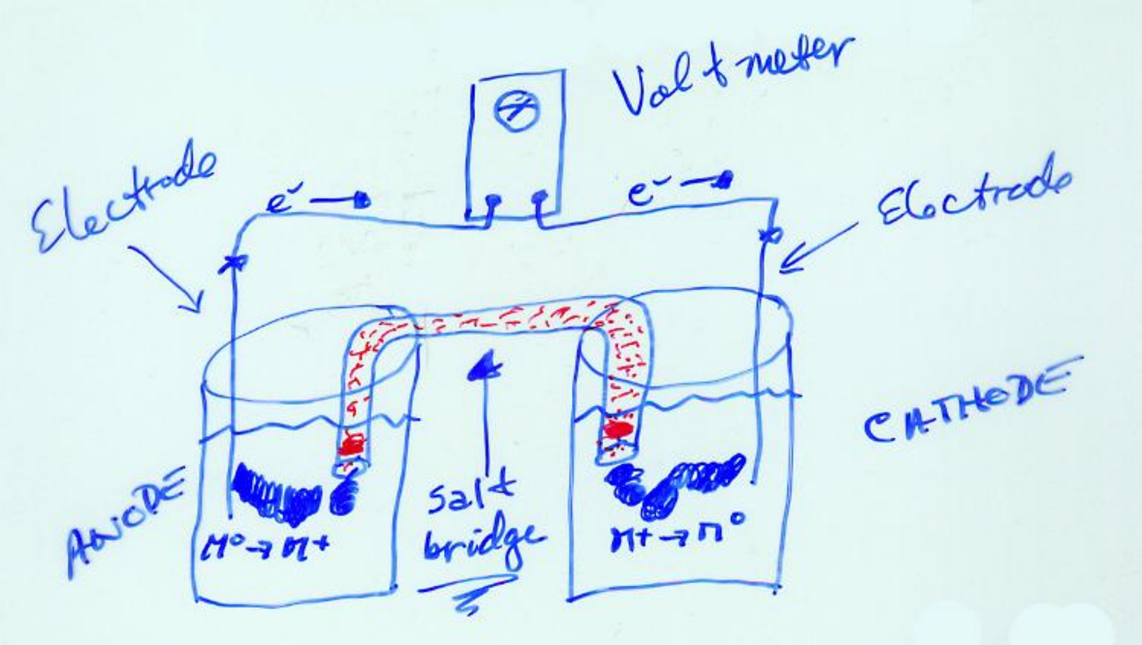
Anode: 2 $Cl^- \rightarrow Cl_2\uparrow + 2e^-$

Cathode: $Au^{3+} + 3e^- \rightarrow Au^0$

Au “plates out” on the inert electrode

Electrochemistry:

A Mathematical Introduction



- **The electrode that loses electrons = ANODE**
  - **OXIDATION occurs here**
- **The electrode that gains electrons = CATHODE**
  - **REDUCTION occurs here**

Elementary Electrochemistry

- Given the following 2 chemical reactions:
- $Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.763$ VOLTS
- $Cr^{3+} + 3e^- \rightarrow Cr$ $E^0 = -0.74$ VOLTS

- Which reaction represents the cathode?
- Which reaction represents the anode?
- How do we figure this out?

Formula

- $E^0_{cell} = E^0_{cathode} – E^0_{anode}$
- In order for the reaction to be spontaneous AND for the battery to work, E^0_{cell} MUST BE POSITIVE.
- That means that the difference between the cathode and anode potentials has to be positive.

$$-0.74-(-0.763)=0.023VOLTS$$

$$-0.763-(-0.74)=-0.023VOLTS$$

$$Which\ is\ correct?$$

$$Top\ result!!!!$$

- Note that the -0.74 VOLTS goes with the chromium and is first: CATHODE -- REDUCTION
- Note that the -0.763 VOLTS goes with the Zinc and is second: ANODE – OXIDATION
- When you combine them for the balanced reaction sum, write them as reduction and oxidation reactions, first, then balance, add and cancel just as you learned in CHEM 121 in redox reactions

Balanced equation

$$3\left[Zn \rightarrow Zn^{2+} + 2e^{-}\right] \quad OXIDATION - ANODE$$

$$2\left[Cr^{3+} + 3e^{-} \rightarrow Cr\right] \quad REDUCTION - CATHODE$$

$$2Cr^{3+} + 3Zn \rightarrow 3Zn^{2+} + 2Cr \quad COMBINED - REDOX$$

Another Example

- $Pb^{2+} + 2e^{-} \rightarrow Pb$ E^{0} = -0.126 VOLTS
- $Cu^{2+} + 2e^{-} \rightarrow Cu$ E^{0} = 0.337 VOLTS
- What’s the Cathode?
- What’s the Anode?
- Write the balanced equation for this battery.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$\therefore$$

$$E^0_{cell} = 0.337 - (-0.126) = 0.463 VOLTS$$

$$Cathode = Cu$$

$$Anode = Pb$$

$$Balanced\ \mathrm{Re}\,action:$$

$$\left(Pb \rightarrow Pb^{2+} + 2e^{-}\right) \quad OXIDATION - ANODE$$

$$\left(Cu^{2+} + 2e^{-} \rightarrow Cu\right) \quad REDUCTION - CATHODE$$

$$Pb + Cu^{2+} \rightarrow Cu + Pb^{2+} \quad TOTAL - REDOX$$

Another Example

- $Mg^{2+} + 2e^- \rightarrow Mg$ $E^0 = -2.37$ VOLTS
- $Co^{2+} + 2e^- \rightarrow Co$ $E^0 = 0.277$ VOLTS

- What’s the Cathode?
- What’s the Anode?
- Write the final balanced equation for this battery.

$$E_{cell}^{0} = -0.277 - (-2.37) = 2.093 VOLTS$$

$$Anode = Mg - Oxidized$$

$$Cathode = Co - \mathrm{Re}\,duced$$

$$Balanced\ \ \mathrm{Re}\,action : Co^{2+} + Mg \rightarrow Co + Mg^{2+}\ \ - Combined\ - \mathrm{Re}\,dox$$

- The fundamental equation
- $E^0_{cell} = E^0_{cathode} + E^0_{anode}$
- Works WELL at conditions given in Standard Reduction Potential Tables in reference texts
- What about with changing some of the conditions, specifically, the concentrations of the ionic species?
- Have to derive the Nernst Equation for that.

- Electrochemical cells produce as given Quantity (Q) of electricity per a specific number of moles of electrons (n) times a constant ($\mathfrak{I}$)
- $Q = n \mathfrak{I}$
- $\mathfrak{I}$ = Faraday = the charge carried by 1 mol of electrons

$$\Im = charge\ of\ electrons * \#\ electrons/mol$$

$$charge\ of\ electron = 1.6*10^{-19}\ Coulombs$$

$$\#\ electrons/mol = 6.023*10^{23}$$

$$\therefore$$

$$\Im = (1.6*10^{-19}\ Coulombs)(6.023*10^{23}\ electrons/mol)$$

$$\Im = 96{,}472\ C/mol \approx 96{,}500\ C/mol$$

- The current can be/is used for work and equals
- -n $\mathfrak{I}$ E, where E = E_{cell}
- This work is called Gibb’s Free Energy: ΔG
- If ΔG is negative, reaction is spontaneous
- If ΔG is positive, no reaction
- Formula is, then: $\Delta G = -n \mathfrak{I} E$

- Since E and G come from tables of standard conditions, $\Delta G = -n \mathfrak{I} E$ is re-written as

- $\Delta G^0 = -n \mathfrak{I} E^0$

- These standard conditions are as follow:
  - [ions] = 1 M
  - P_{gas} = 1 atm
  - T = 25°C **(CAUTION! From CHEM 121, remember that T at STP is 0°C – watch this so you don't get caught!)**

- Let’s define Q in more detail
- For the reaction:

$$\mathrm{eE} + \mathrm{fF} \rightarrow gG + hH$$

$$Q = \frac{\left(a\right)_G^g \left(a\right)_H^h}{\left(a\right)_E^e \left(a\right)_F^f}$$

$$which \ \ is \ \ for \ \ our \ \ purposes$$

$$Q = \frac{\left(G\right)^g \left(H\right)^h}{\left(E\right)^e \left(F\right)^f} = K_d$$

- Recall that ΔG^0 is found in tables for STANDARD Reactions
- Experimentally, we determine the actual laboratory Free energy, ΔG
- ΔG, ΔG^0 and Q are related as follows

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$OR$$

$$\Delta G = \Delta G^0 + RT \ln K_d$$

$$OR$$

$$-n\Im E = -n\Im E^0 + RT \ln K_d$$

- Divide both sides by –n $\Im$

$$E = E^0 - \frac{RT}{n\Im} \ln K_d$$

Nernst Equation

- E = observed EMF
- E^0 = Standard State EMF
- @ equilibrium, E = 0, and

$$E^0 = \frac{RT}{n\Im}\ln K_d = \frac{-\Delta G^0}{n\Im}$$

- Lab conditions are room temperature, so the entity RT/ ℑ can be determined where
- R = 8.314 J/K-mol
- T = 298 K (25°C)
- ℑ = 96,500C/mol, so:

$$\frac{RT}{\Im} = \frac{(8.314)(298)}{96{,}500} = 0.026\frac{J}{C} = 0.026\,VOLTS$$

$$\frac{1J}{1C} = 1\,VOLT$$

Remember

$$E^0 = \frac{RT}{n\Im} \ln K_d$$

$$\ln = 2.303 \log$$

$$hence,$$

$$E^0 = \frac{0.026V}{n} (2.303) \log K_d$$

$$\wedge E^0 = \frac{0.0591}{n} \log K_d$$

$$Nernst\ Equation = E = E^0 - \frac{0.0591}{n} \log K_d$$

Example

- For the following battery:
- $Cd^{2+} + Mn \rightarrow Cd + Mn^{2+}$

- With the following half reactions:
- $Cd^{2+} + 2e^{-} \rightarrow Cd$ $E^{0} = -0.403$ V
- $Mn^{2+} + 2e^{-} \rightarrow Mn$ $E^{0} = -1.180$ V
- And $[Cd^{2+}] = 0.15$ M and $[Mn^{2+}] = 0.35$ M
- Calculate the E_{cell} and determine the cathode and the anode of the cell.

$$E_{cell} = E^0{}_{cathode} - E^0{}_{anode}$$

$$E_{cell} = -0.403 - (-1.180) = +0.777V$$

$$Alternative\,Method$$

$$Cd^{2+} + 2e^- \rightarrow Cd \qquad E^0 = -0.403V$$

$$Mn \rightarrow Mn^{2+} + 2e^- \qquad E^0 = 1.180V$$

$$Add\,'em\,up! \quad +0.777V$$

$$and$$

$$Cd^{2+} + Mn \rightarrow Mn^{2+} + Cd$$

$$At\ STD\ Conditions$$

- Cd = Cathode
- Mn = Anode
- NOTE: solids and elements have activities of 1, so that the K_d is:

$$K_d = \frac{[Mn^{2+}][Cd]}{[Mn][Cd^{2+}]} \rightarrow \frac{[Mn^{2+}]}{[Cd^{2+}]} = \frac{[ion\ oxidized\ \ at\ anode]}{[ion\ reduced\ \ at\ cathode]}$$

$$and$$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[Mn^{2+}]}{[Cd^{2+}]} = E^0 - \frac{0.0591}{2}\log\frac{[Mn^{2+}]}{[Cd^{2+}]}$$

$$E = E^0 - 0.0296\ \log\frac{[Mn^{2+}]}{[Cd^{2+}]} = 0.777 + 0.0296\log\frac{[Cd^{2+}]}{[Mn^{2+}]} = 0.777 + 0.0296\ \log\frac{0.15}{0.35}$$

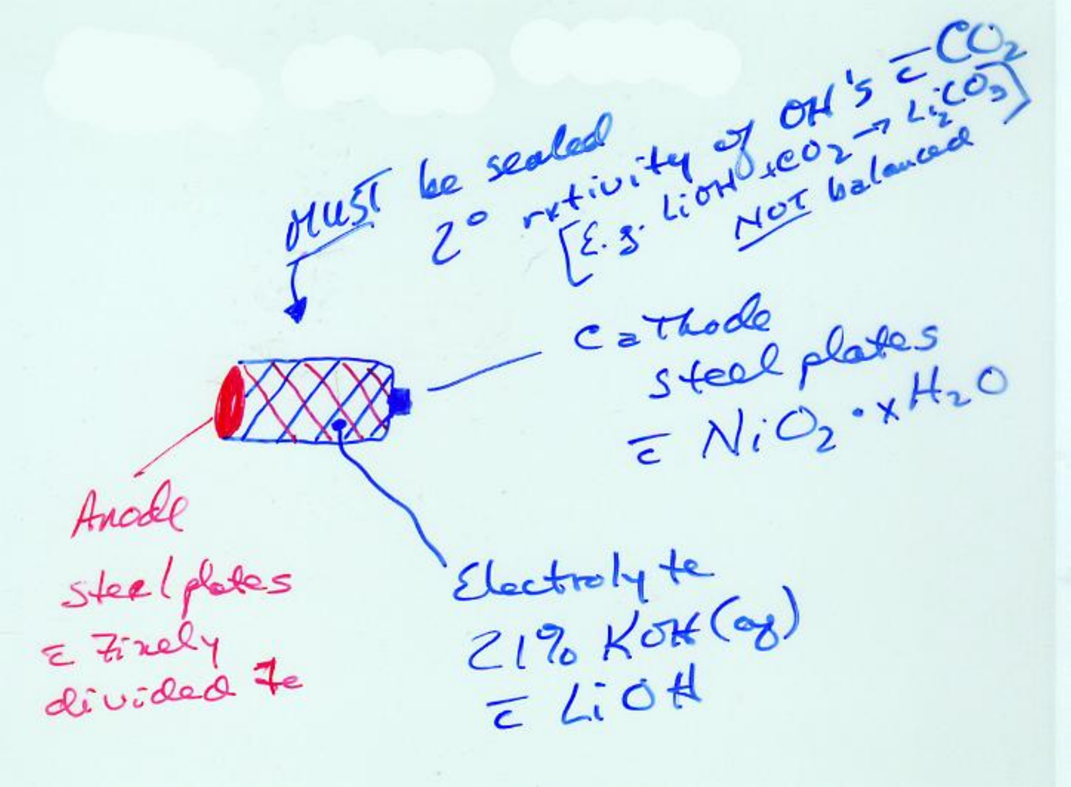
$$E = 0.777 - 0.0109 = 0.766V$$

Key Points

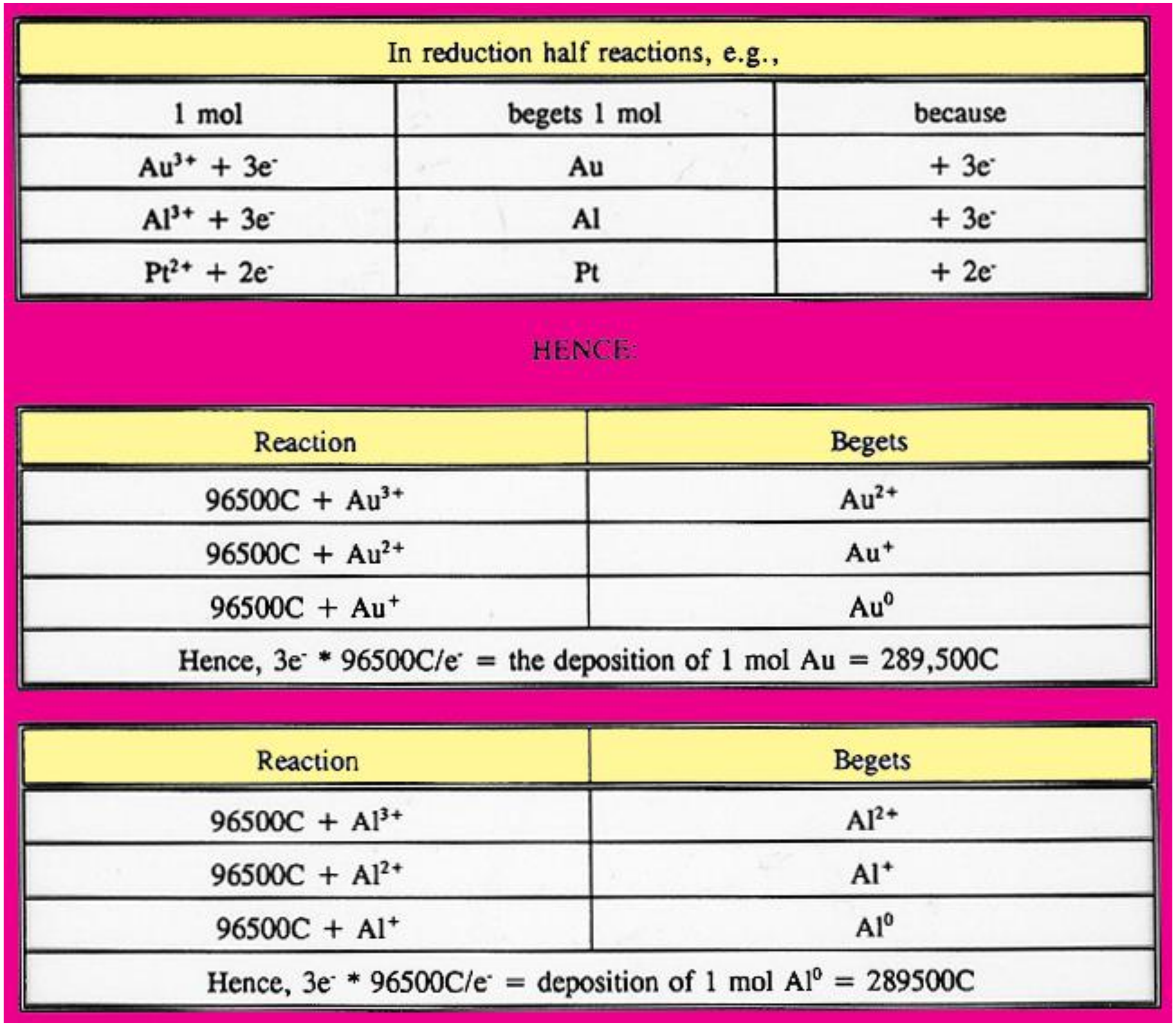
- E was observed in the lab
- 0.777 volts was from standard table calculation
- Ion ratio was from the K_d
- The sign was changed from “minus” to “plus” be flipping the log ratio
- The Nernst Equation works for (not inclusive):
  - Daniell cells: galvanic/voltaic – redox type reactions for EMF
  - Electrolytic cells with modifications
  - Ion selective electrodes
  - pH electrodes

Special Kind of Voltaic Cell

- Edison Storage Battery
- Reaction:
- Fe + $NiO_2 + 2H_2O \Leftrightarrow Fe(OH)_2 + Ni(OH)_2$
  - Forward reaction when DISchargin g
  - Backward reaction when REcharging
- Precursor to the NiCad batteries



Electrochemical Book-Keeping



In reduction half reactions, e.g.,

1 mol	begets 1 mol	because
$Au^{3+} + 3e^-$	Au	$+ 3e^-$
$Al^{3+} + 3e^-$	Al	$+ 3e^-$
$Pt^{2+} + 2e^-$	Pt	$+ 2e^-$

HENCE:

Reaction	Begets
$96500C + Au^{3+}$	Au^{2+}
$96500C + Au^{2+}$	Au^{+}
$96500C + Au^{+}$	Au^{0}
Hence, $3e^-$ * $96500C/e^-$ = the deposition of 1 mol Au = 289,500C	

Reaction	Begets
$96500C + Al^{3+}$	Al^{2+}
$96500C + Al^{2+}$	Al^{+}
$96500C + Al^{+}$	Al^{0}
Hence, $3e^-$ * $96500C/e^-$ = deposition of 1 mol Al^0 = 289500C	

Application

- How many g of Al will be deposited/precipitated when 96500 C are passed through an $AlCl_3$ solution?

$$96{,}500\,C * \frac{1\ mol\ e^-}{96{,}500\ C} * \frac{27\ g\ Al}{1\ mol\ Al} * \frac{1 mol\ Al}{3\ mol\ e^-} = 9\ g\ Al$$

Application

- How many g of Ni will be deposited/precipitated when 15,000 C are passed through a $NiCl_2$ solution?

$$15{,}000\,C * \frac{1\ mol\ e^-}{96500\ C} * \frac{1\ mol\ Ni}{2\ mol\ e^-} * \frac{58.7\ g\ Ni}{1\ mol\ Ni} = 4.56\ g\ Ni$$

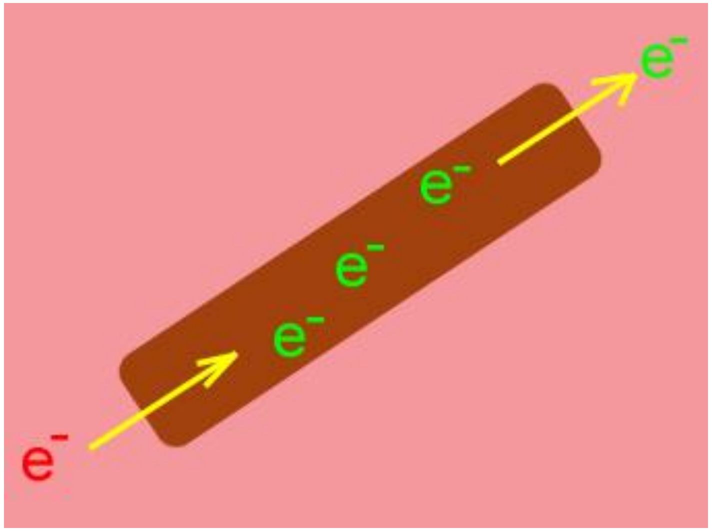
Application

- How many g Cr will be deposited/precipitated when 15,000 C are passed through a $K_2Cr_2O_7$ solution?

$$15{,}000\ C * \frac{1\ mol\ e^-}{96{,}500\, C} * \frac{1\ mol\ Cr}{6\ mol\ e^-} * \frac{52\, g\, Cr}{1\, mol\ Cr} = 1.35\, g\, Cr$$

Electric Current

- Electric current in a wire = the flow of the charge in amps
- It’s the rate at which a charge moves through the wire
- 1 amp = 1 C/sec
- I = current = Q/t = Coulombs/seconds
- I = charge in amps
- Q = charge in Coulombs
- And t = time in seconds



Application

- A watch battery supplies a constant current of 10 μA to a watch circuit. How many coulombs pass through this circuit in 24 hours?

$$Q = I * t = (10 * 10^{-6}\ Amps) * (86400\,\mathrm{sec}onds) = 0.864\,Coulombs$$

Application

- An AA battery supplies a constant current of 25 mA to a clock circuit. How many coulombs pass through this circuit in six hours?

$$Q = I * t = (0.025\,Amps) * (21{,}600\,\mathrm{sec}onds) = 540\,Coulombs$$

Application

- A Li battery in a computer provides a continuous current of 25 nA to the back up circuit. How many coulombs are passed through this circuit in seven days?

$$Q = I * t = (25 * 10^{-9}\ Amps) * (604{,}800\ \sec onds) = 0.01512\ Coulombs$$

Electroplating

- We can use the previous information in electroplating.
- How many days will it take for a 15 mA current to electroplate 160 g of Ag?
- Half reaction: $Ag^+ + 1e^- \rightarrow Ag^0$

$$160\,g\ Ag * \frac{1\,mol\ Ag}{107.9\,G\ Ag} * \frac{1\,mol\,e^-}{1\,mol\ Ag} * \frac{96{,}500\,C}{1\,mol\,e^-} * \frac{1\sec}{0.015\,C} * \frac{1\min ute}{60\sec onds} * \frac{1\,hr}{60\min utes} * \frac{1\,d}{24\,hours} = 110.41\,days$$

Application

- How many days will it take to electroplate 15 g Pt with a 75 Amp current?

$$15\,g\,Pt * \frac{1mol\,Pt}{195\,g\,Pt} * \frac{2\,mol\,e^-}{1mol\,Pt} * \frac{96500\,C}{1mol\,e^-} * \frac{1\sec}{75C} * \frac{1\min}{60\sec s} * \frac{1hr}{60\min s} * \frac{1day}{24hrs} = 0.00229\,days$$

$$Or\;\; about\;\; 3.3\;\min utes$$

Application

- How many minutes will it take to electroplate 60 g Ti with a 15 Amp current?

$$Half\ \mathrm{Re}action : Ti^{4+} + 4e^{-} \rightarrow Ti$$

$$60\ g\,Ti * \frac{1\,mol\,Ti}{47.9\,g\,Ti} * \frac{4\,mol\,e^{-}}{1\,mol\,Ti} * \frac{96{,}500\,C}{1\,mol\,e^{-}} * \frac{1\sec}{15\,C} * \frac{1\min}{60\sec} = 537.2\min utes$$

$$OR\ about\ 0.37\ days$$

Application

- How many g of Pb will be deposited from a Pb^{2+} solution by 0.25 Amp for 3 hours?

$$3\,hours * \frac{60\min}{1\,hr} * \frac{60\sec}{1\min} * \frac{0.25\,C}{1\sec} * \frac{1\,mol\,e^-}{96{,}500\,C} * \frac{1\,mol\,Pb}{2\,mol\,e^-} * \frac{207.2\,g\,Pb}{1\,mol\,Pb} = 2.899\,g\,Pb\,deposited$$

Application

- 1.1 Amps run through CuSo4 plates out 1.30 g Cu in 60 minutes. If the Cu in solution is represented by **<u>Cu^{n+}</u>**, use this data to show that n = 2.

$$\frac{1.1C}{\sec}*(3600\sec s)*\frac{1 mol\, e^{-}}{96{,}500\, C}*\frac{1 mol\, Cu}{n\, e^{-}}*\frac{63.5\, g\, Cu}{1 mol\, Cu}=1.3\, g\, Cu$$

$$n\, e^{-}=3960\, C*\frac{1 mol\, e^{-}}{96{,}500\, C}*\frac{1 mol\, Cu}{1.3\, g\, Cu}*\frac{63.5\, g\, Cu}{1 mol\, Cu}=2\, e^{-}$$

$$Hence, Cu^{n+}=Cu^{2+}$$

Application

- 50 mA are run through a Ni solution for 12 hours. 0.656 g of Ni were electroplated. Determine the oxidation state of Ni.

$$\frac{0.05\,C}{\sec} * 43{,}200\sec s * \frac{1 mol\, e^{-}}{96{,}500\,C} * \frac{1 mol\ Ni}{0.656\,g} * \frac{58.7\,g\ Ni}{1 mol\ Ni} = 2.00\,e^{-}$$

$$Hence, Ni^{n+} = Ni^{2+}$$

Electrical Work

- $W_E = Q * E$
- W_E = electrical work in Joules or calories
- Q = current in coulombs
- E = voltage of the battery in volts OR in Joules/Coulomb

Application

- Determine the maximum electric work in Joules that can be done by a 6-V VW battery supplying a current of 15 Amps for 45 seconds.

$$Q = \frac{15C}{\sec} * 45\sec = 675C$$

$$E = \frac{6J}{C}$$

$$W_E = 675C * \frac{6J}{C} = 4050J$$

$$4050J * \frac{1 calorie}{4.184J} = 968\ calories \approx 1\ Food\ \ Calorie$$

Application

- Determine the maximum electric work in Joules that can be done by a 1.5-V D-cell supplying a current of 5 mA for 6 hours.

$$W_E = I * t * E = \frac{0.005\,C}{\sec} * 21{,}600\,\sec * \frac{1.5\,J}{C} = 162\,J$$

Application

- Determine the maximum electrical work in Joules that can be done by a 9-V battery supplying a current of 5 μA for 10 minutes

$$W_E = I * t * E = \frac{0.000005\,C}{\text{sec}} * 600\,\text{sec} * \frac{9\,J}{C} = 0.027\,J$$

Further Applications

1. A Li camera battery is rated at 6V. If the camera draws 1 mA over 2 hours, calculate the following:
   - A. Coulombs that run through the circuit
   - B. Mass of Li in micrograms that forms
   - C. Maximum electrical work in Joules

A. Coulombs that run through the circuit

$$Q = I * t = (0.001\,Amps) * (7200\sec) = 7.2\,Coulombs$$

B. Mass of Li in micrograms that forms

$$(7.2\,Coulombs) * \frac{1\,mol\,e^{-}}{96{,}500\,C} * \frac{1\,mol\,Li}{1\,mol\,e^{-}} * \frac{6.9\,g\,Li}{1\,mol\,Li} * \frac{1{,}000{,}000\,\mu g}{g} = 514.82\,\mu g$$

C. Maximum electrical work in Joules

$$W_E = (7.2\,C) * \frac{6\,J}{C} = 43.2\ Joules$$

Further Application

- The “original” flashlight battery operated by the following reactions:

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$$

- If this “D cell” has a voltage output of 1.5 V and a current of 0.01 amps was pulled for 10 minutes, calculate the following:

A. mg Zn consumed
B. The number of mmol NH_3 formed
C. Determine the power output

A. mg Zn consumed

$$\frac{0.01C}{\sec} * 600\sec * \frac{1mol\,e^{-}}{96{,}500\,C} * \frac{1mol\,Zn^{2+}}{2\,mol\,e^{-}} * \frac{65.4\,g\,Zn}{1mol\,Zn} * \frac{1000\,mg}{1\,g} = 2.03\,mg\,Zn\,consumed$$

B. The number of mmol NH_3 formed

$$2.03\,mg\,Zn * \frac{1\,mmol\,Zn^{2+}}{65.4\,mg\,Zn} * \frac{2\,mmol\,NH_3}{1\,mmol\,Zn^{2+}} = 0.062\,mmol\,NH_3$$

C. Determine the power output

$$P = IV = (0.01A)*(1.5V) = 0.015 Watts$$

$$Power\ \ is\ \ measured\ \ in\ WATTS$$

Electroplating Application

- A bronze sphere with a diameter 15 cm is to be plated with Ag. The thickness of the Ag is to be 0.005 cm. The density of Ag is 10.5 g/cm^3.
  A. How many grams of Ag are needed for this?
  B. What is the minimum current required to electroplate the sphere with this much Ag in 2 hours?
  C. Assuming 85% efficiency for electroplating the Ag, how much current is REALLY needed to do this job?

A. How many grams of Ag are needed for this?

$1.\ Deter\min e\ bronze\ sphere\ volume:$

$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi * (7.5)^3 = 1767\,cm^3 = V_{bronzesphere}$$

$2.\ Deter\min e\ sphere\ volume\ WITH\ Ag\ on\ it:$

$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi * (7.5 + 0.0025)^3 = 1769\,cm^3$$

$3.\ Deter\min e\ volume\ of\ Ag\ used:$

$$1769 - 1767 = 2\,cm^3$$

$4.\ Deter\min e\ grams\ Ag\ required:$

$$2\,cm^3 * \frac{10.5\,g}{cm^3} = 21\,g\ Ag\ needed$$

B. What is the minimum current required to electroplate the sphere with this much Ag in 2 hours?

$$Ag^{+} + 1e^{-} \rightarrow Ag \ \textit{is the half reaction}$$

$$21\,g\ Ag * \frac{1\,mol\ Ag}{107.9\,g\ Ag} * \frac{1\,mol\ e^{-}}{1\,mol\ Ag} * \frac{96500\,C}{1\,mol\ e^{-}} = 18781.3\,C$$

$$Since\ Q = I * t,$$

$$\frac{Q}{t} = I = \frac{18781.3\,C}{7200\,\mathrm{sec}}\ \ 2.61\,Amps$$

C. Assuming 85% efficiency for electroplating the Ag, how much current is REALLY needed to do this job?

$$\frac{100}{85} * 2.61\,Amps = 3.07\ Amps$$