

Electrochemistry:

Definition: the branch of chemistry concerning the interaction between chemical reactions and electricity.

The last unit was about the transfer of protons. This unit is about the transfer of electrons.

When the number of electrons in an atom changes:

the CHARGE changes

Therefore, in order to recognise reduction-oxidation reactions (redox reactions):

we look at the change in charge

Oxidation Number: "The charge an atom in a molecule would have if all the electrons in its bond belonged entirely to the more electronegative atoms" OR "A number assigned to an element to indicate its position on a scale of oxidation levels defined by an arbitrary set of rules"

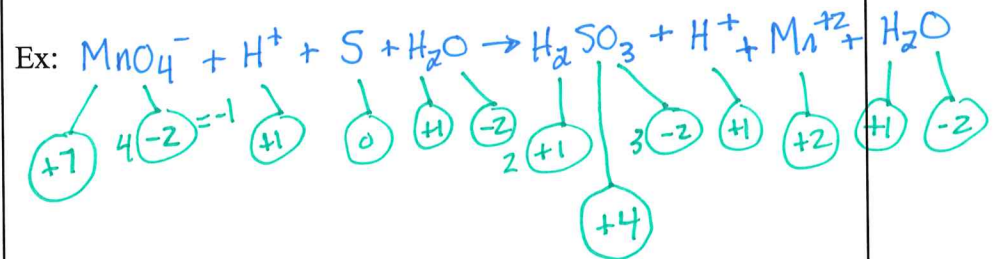
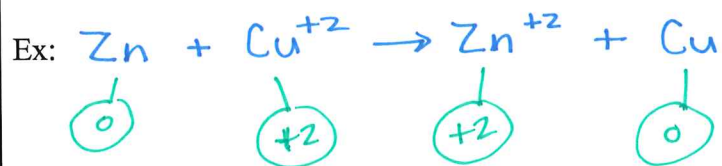
Determining the oxidation number:

The Rules:

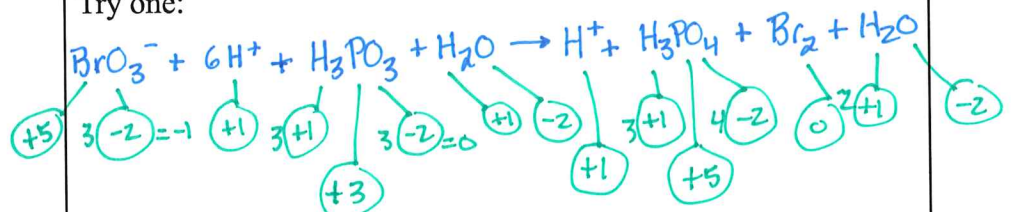
- 1) The oxidation number (O.N.) of an atom in elemental form is zero
- 2) The O.N. of a monoatomic ion is equal to the charge on the ion
- 3) The O.N. of oxygen is almost always -2 (exceptions: $O_2 = 0$; peroxides = -1) and the O.N. of hydrogen is almost always $+1$ (exceptions: $H_2 = 0$; attached to a metal = -1)
- 4) The O.N.s of atoms in a neutral

compound or molecule will add up to zero.

5) The O.N.s of atoms in a polyatomic ion will add to the charge on the ion.



Try one:



Read pg 193-194 and do #3

Oxidation Reaction:

* Used to be: a gain in the amount of oxygen

* Now is: a loss of electrons

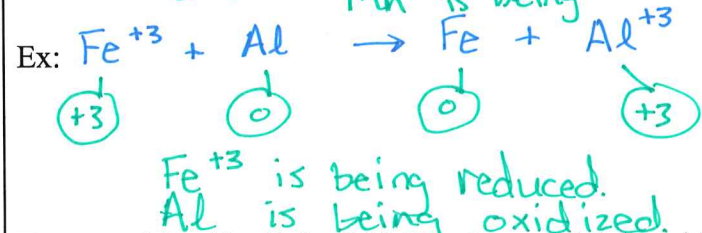
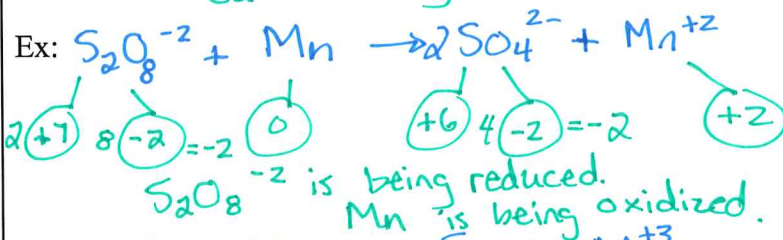
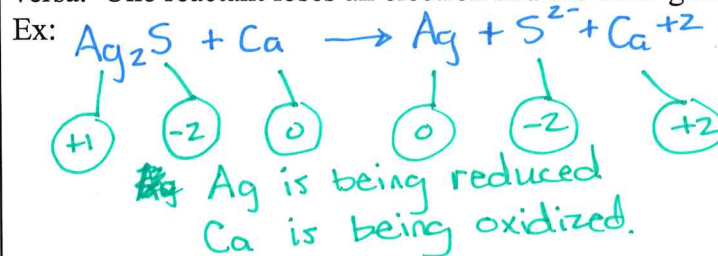
* Involves: an increase in O.N.

Reduction Reactions:

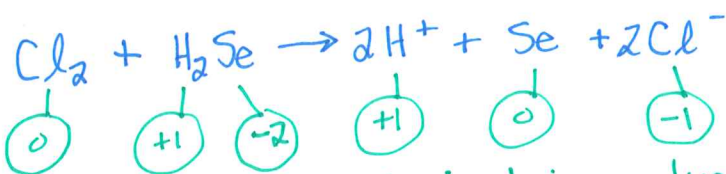
- * Used to be: a reduction in the amount of oxygen
- * Now is: a gain of electrons
- * Involves: a reduction in O.N.

LEO says GER loss of electrons oxidation
 gain of electrons reduction

* These two processes happen at the same time. In order for there to be a reduction, there must also be an oxidation and vice versa. One reactant loses an electron and the other gains it.



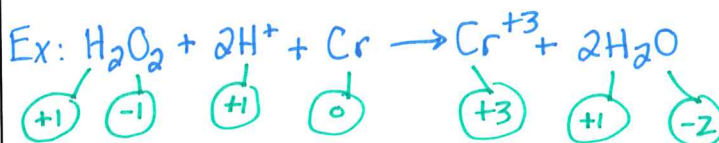
Try one: (identify all the O.N.'s and say which is oxidized and which is reduced)



Cl₂ is being reduced.
H₂Se is being oxidized

Remember that one is oxidized and when it oxidizes, it reduces the other? It is called the: **Reducing Agent**

Remember that one is reduced and when it reduces it oxidizes the other? It is called the: **Oxidizing Agent**



H₂O₂ is being reduced ∴ is the oxidizing agent
Cr is being oxidized ∴ is the reducing agent.

*For it to be a redox reaction, there must be a gain AND a loss

Assignment: Read pages 193-194 & 189-191 and do questions # 4, 5, & 1

Spontaneity of Red-ox Reactions:

When 2 reactants are mixed, the questions are:

- 1) will they react? and if so,
- 2) will the reaction not be spontaneous? or
- 3) will the reaction be spontaneous

Let's look at our last table

Standard Potential of Half Cells

Some points to consider:

- All reactions are written as reductions
- the ones that reduce strongly (a.k.a. strong oxidizing agents) are at the top left. THEY **Gain electrons easily**

- the ones that oxidize strongly (a.k.a. strong reducing agents) are at the bottom right. THEY *lose electrons easily*

Some tips:

- metals are usually at the bottom right
- halogens and oxygen containing things are at the top left
- CAREFUL: some things appear more than once and metals may have more than one charge.

- Reactions can go both ways. Reactions that are near the top of the table will tend to go forward, near the bottom will tend to go backward.

***** be really careful many are on both sides

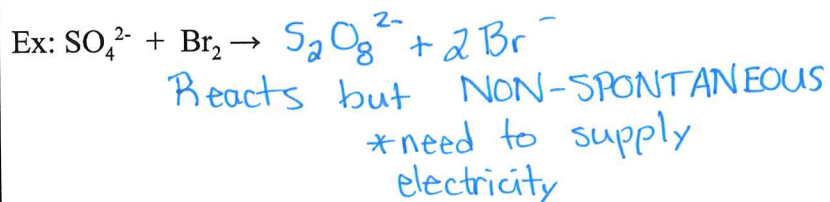
The Possibilities:

1/ Both reactants are on the same side:



2/ Reactants are on opposite sides:

- a) the reactant to be reduced (on the left) is lower in the table than the one to be oxidized (on the right)



b) The one to be reduced is higher than the one to be oxidized



\uparrow
needs 8H^+

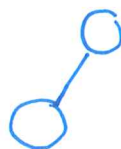
Reacts SPONTANEOUSLY

*can generate electricity

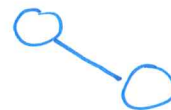
Summary:



no
reaction



not
spontaneous



spontaneous

One more thing:

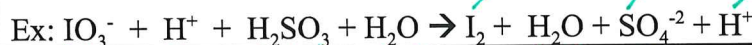
- some things require $\text{H}^+/\text{H}_2\text{O}$ (acidic conditions)
- some things require $\text{OH}^-/\text{H}_2\text{O}$ (basic conditions)

Read pages 195-199 and do questions #7, 8, 11, & 12

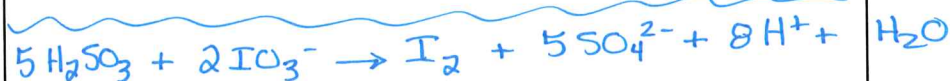
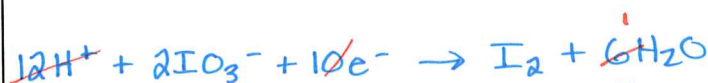
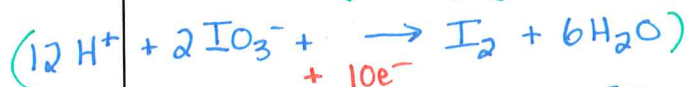
Balancing Half-Reactions:

Steps:

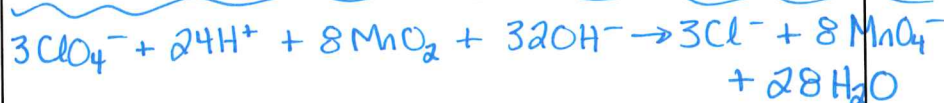
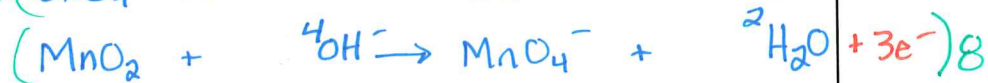
- 1/ Redox?
- 2/ Split into half reactions
- 3/ Balance the number of atoms
- 4/ balance the charge
- 5/ balance the number of electrons
- 6/ net reaction
- 7/ check



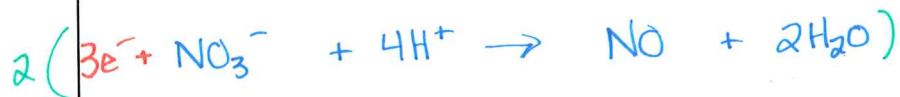
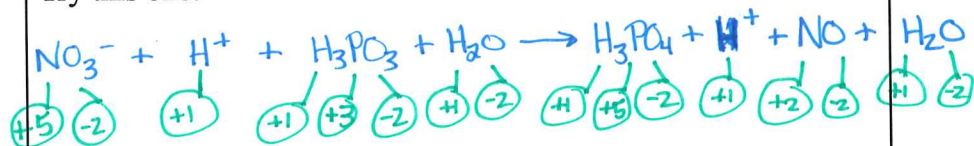
* the 2 things changing are $\text{IO}_3^- \rightleftharpoons \text{H}_2\text{SO}_3$



Ex: $\text{ClO}_4^- + \text{H}^+ + \text{MnO}_2 + \text{OH}^- \rightarrow \text{MnO}_4^- + \text{H}_2\text{O} + \text{Cl}^- + \text{H}_2\text{O}$



Try this one:



Another tip: We need to make sure that when we are doing the half reactions, we include all atoms involved with the atom that has changed.

Balancing in Acidic Conditions:

Steps:

1/ Redox?

2/ Split into half reactions

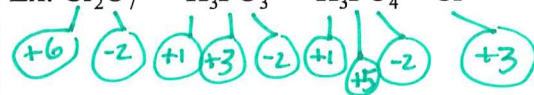
3/ Balance the number of atoms (add H₂O to side with less Ox)

4/ balance the charge

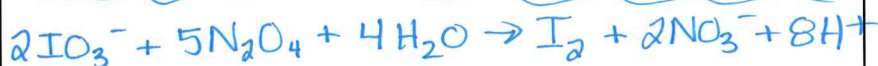
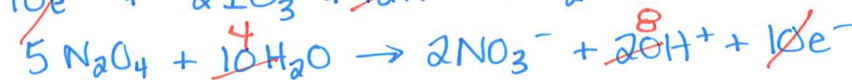
5/ balance the number of electrons

6/ net reaction

7/ check



Try one: $\text{IO}_3^- + \text{N}_2\text{O}_4 \rightarrow \text{I}_2 + \text{NO}_3^-$



Balancing in Basic Conditions:

Steps:

1/ Redox?

2/ Split into half reactions

3/ Balance the number of atoms (add OH^- to side with less O)

4/ balance the charge

5/ balance the number of electrons

6/ net reaction

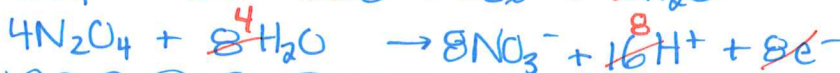
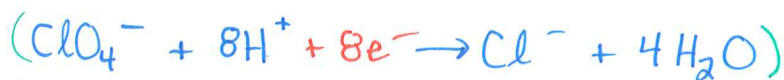
7/ check



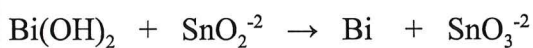
First Way:



Second Way: * the make believe way - pretend it's acidic



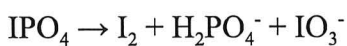
Try one:



- make sure you show each step for these ones.

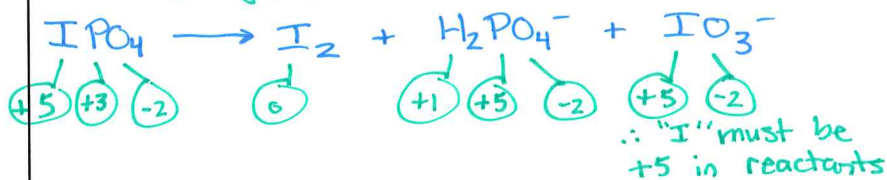
A Nasty: (on Feb 08's provincial)

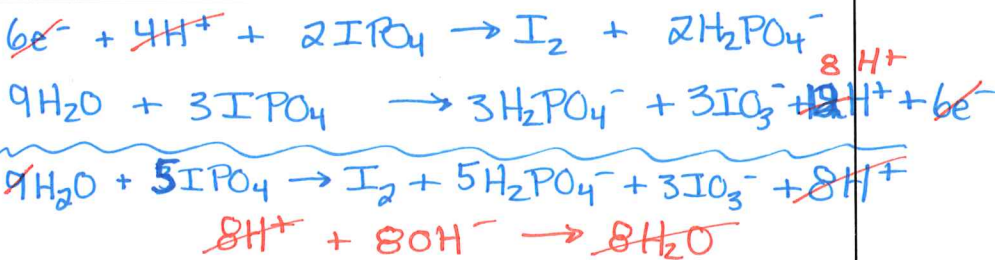
Balance in Basic Conditions:



(by the way, this is called a **disproportionation reaction** – when the reactant both reduces and oxidizes)

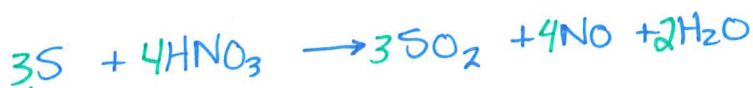
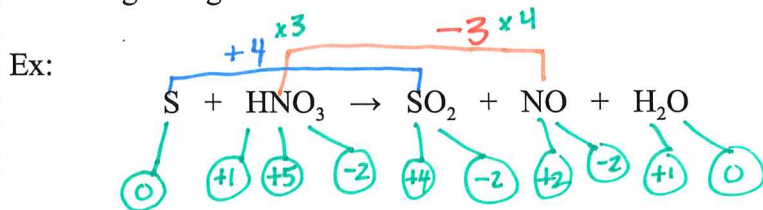
* you have to assume that "I" is only going to change once.



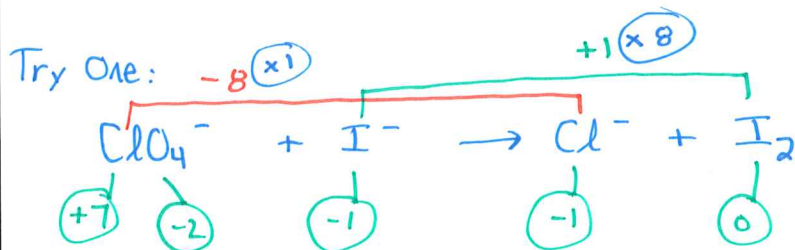


Assignment: Read pages 201-207 and do questions 24 a, f, k, n, u

Balancing Using The Whole O.N. Method:



Acidic
Conditions



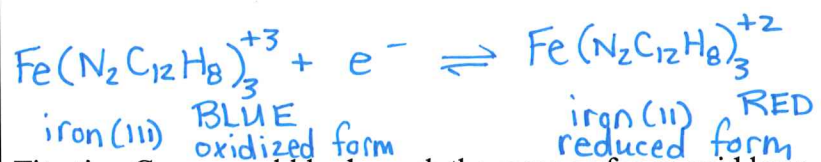
Read pages 208-209 and do questions #25 a, e, & m
Redox Titrations:

* the slow reaction of a reducing agent and an oxidizing agent.

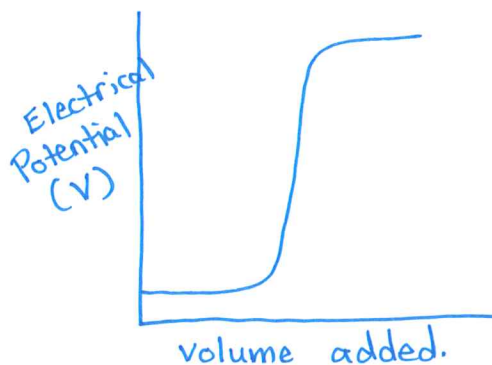
* Equivalence is viewed (endpoint) via an indicator OR as a huge change in voltage. A redox indicator changes colour when it goes from its oxidized to its reduced form.

Ex: ferroin

= 5299 / 500 mL
0.1%



Titration Curve would look much the same as for an acid base reaction.



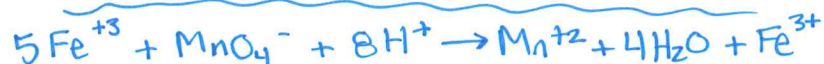
Picking an oxidizing agent:

* You want to pick one that can oxidize many things:



Ex: MnO_4^- titrating Fe^{2+}

① Reaction:



25.00 mL of unknown $[\text{Fe}^{2+}]$ is titrated to the endpoint with acidic KMnO_4 . The titration requires 17.52 mL of 0.1000 M KMnO_4 . What is the original $[\text{Fe}^{2+}]$?

$$0.1000 \frac{\text{mol MnO}_4^-}{\text{L}} \times 0.01752 \text{ L} = 0.001752 \text{ mol MnO}_4^-$$

$$0.001752 \text{ mol MnO}_4^- \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 8.76 \times 10^{-3} \text{ mol}$$

$$[\text{Fe}^{2+}] = \frac{8.76 \times 10^{-3} \text{ mol}}{0.02500 \text{ L}} = 0.3504 \text{ M}$$

* another reason to pick MnO_4^- : it acts as its own indicator



* when MnO_4^- hits the flask, it reacts and turns clear. When unknown is used up, MnO_4^- stays unreacted $\hat{=}$ purple.

Picking a Reducing agent:

Skip

* I^- is used a lot because it can be oxidized by many things and we can use it (indirectly) as an indicator.

Two Steps to this titration:

1/ I^- is oxidized to I_2 by another reactant

2/ I_2 is reduced back to I^- with a second reactant to get a colour change.

Skip

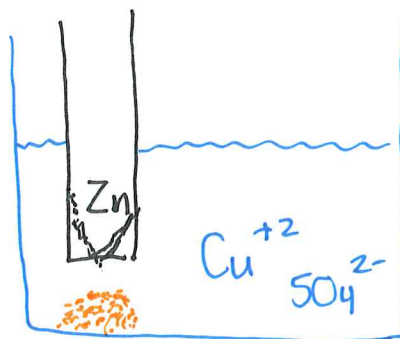
It's called a back titration and you really don't have to know anything about it. Just read that section in the text.

Read Pages 210-212

Electrochemical Cells:

* Redox reactions are capable of producing an electrical current.

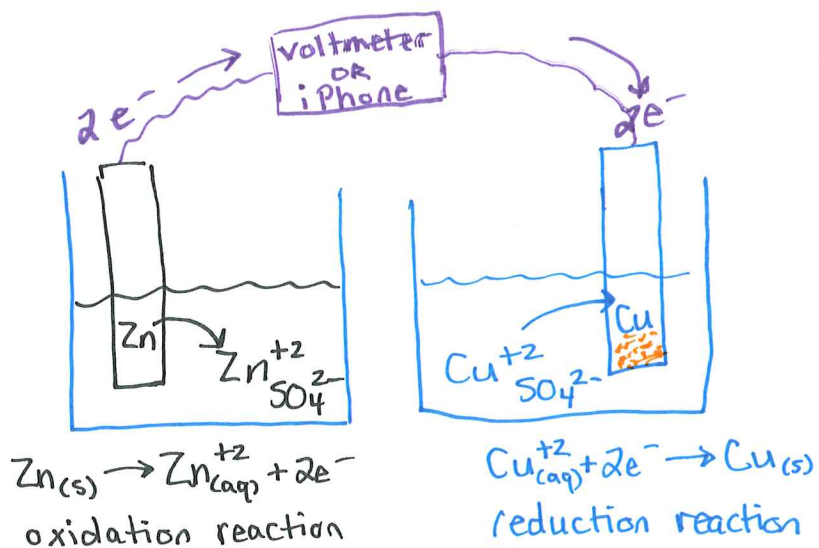
Ex: A piece of Zn is immersed in aqueous copper(II) sulphate



* After a while, the redox reaction will cause Zn to dissolve to form Zn^{2+} and copper solid forms. The solution will also lose its blue colour as all the Cu^{2+} is changed to Cu.

* Because it happens, we can assume the reaction is spontaneous.

Unfortunately, it does not work for us.



* when we separate the containers (now called half-cells), the electrons must travel through the wire to get to Cu^{2+} . We can then harness them to generate electricity.

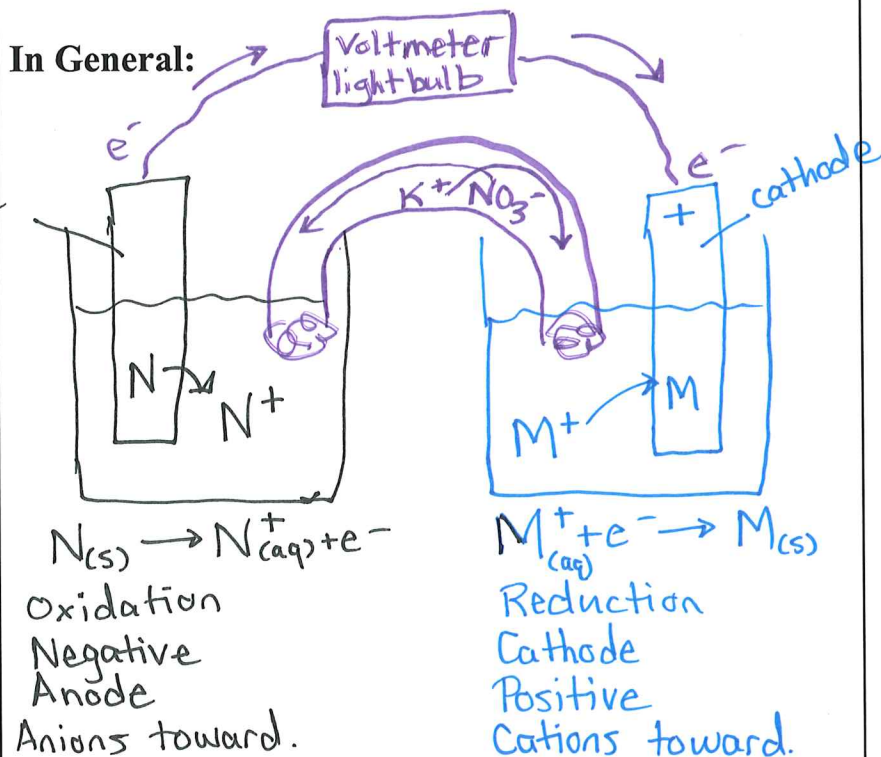
BUT: It turns out that the current goes for a few seconds, but then quits.

* the problem is that the SO_4^{2-} from the copper(II) sulphate becomes a problem. On one side Cu^{2+} is converted to Cu, leaving SO_4^{2-} and only negative charge. On the other side Zn is converted to Zn^{2+} and giving an overall positive charge. There is a charge imbalance.

* we need some way of getting rid of the charge imbalance or POLARIZATION.

We use: **A salt Bridge**

NOA — negative
 — oxidation
 — anode
 CPR — cathode
 — positive
 — reduction



Mass decreases

Mass increases

Electrodes are surfaces where electrons are transferred and occur in 2 types:

1/ Anode: oxidation occurs here; electrons flow away; negative; anions of salt bridge move towards; mass often decreases ($(s) \rightarrow (aq)$)

2/ Cathode: reduction occurs here; electrons flow toward; positive; cations of salt bridge move towards; mass often increases ($(aq) \rightarrow (s)$)

AN	ox	CARED	anode oxidation
			cathode reduction

The three requirements for an electrochemical cell:

1/ an external wire

2/ a spontaneous reaction

3/ a salt bridge

Read pages 215-217 and do questions # 34 & 35

Cell Potential:

* Just like a ball rolls downhill, electrons will flow from anode to cathode.

* The “force” that pushes electrons this way is called the electromotive force (emf) and it has to do with the electrical potential difference between the two electrode plates.

* The Cell Potential or Cell Voltage is the energy that is released when the electrons move from high potential energy plate to lower potential energy plate. It is this energy that we can use to do work.

* The Cell Potential will be different for each cell. It is easily measured and when it is measured at standard conditions (1 atm, 25°C, 1M ionic concentration), it is called the standard cell potential (E° cell)

* Remember that E° cell is the difference between the potentials of the two plates (anode vs. cathode). What could we say about E° cell if the anode has a high electrical potential and the cathode has a low electrical potential?

* If E° cell is big, the cell has a large capacity to do work for us.

* E° cell depends on:

- 1) temperature
- 2) pressure
- 3) ion concentration
- 4) identity of the electrodes

Finding E° cell:

$$E^{\circ}\text{cell} = E^{\circ}\text{oxidation} + E^{\circ}\text{reduction}$$

We can get these values from the last table in our data booklet. BUT, these are all written as reduction reactions, so we have to do a little bit of work to get an E° oxidation.



If we switch the arrow direction, we switch the sign. THEREFORE:

$$E_{OX}^\circ = - E_{RED}^\circ$$

Calculating an E° cell:



$$E_{CELL}^\circ = E_{RED}^\circ + E_{OX}^\circ$$

$$= 0.34V + 0.76V$$

$$= 1.10V$$

if we hook up this E.C. cell, it will generate 1.10V

One more note:

***** Stoichiometry DOES NOT AFFECT E°

Using the table:

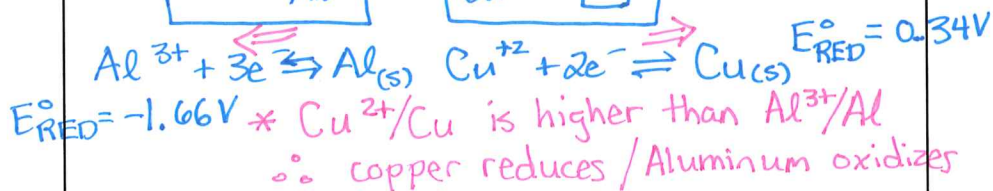
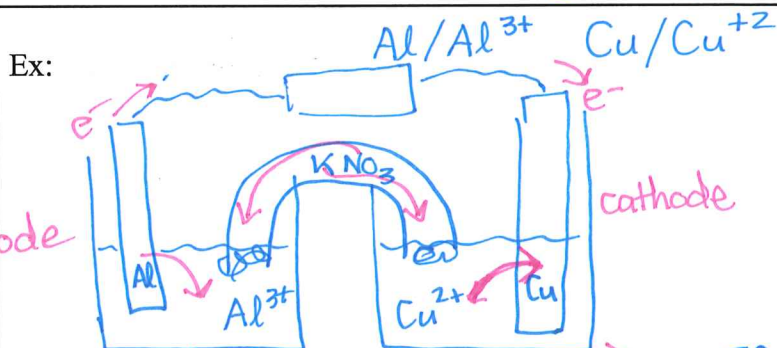
* The ones toward the top left reduce most strongly and the ones toward the bottom right oxidize more readily. However, there is another way we can do it.

* It turns out the ones with the more positive E°_{RED} reduce most strongly and, when we switch the sign, the ones with the more positive E°_{OX} oxidize most strongly.

* When we mix a reactant that has a strong need to reduce with another that has a strong need to oxidize, the reaction is SPONTANEOUS.

* AND when we go to calculate E°_{cell} with 2 somewhat large numbers, the E°_{cell} will be positive.

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{RED}} \quad E^\circ_{\text{cell}} = \begin{matrix} \oplus & \text{Spontaneous} \\ \ominus & \text{non-spontaneous} \end{matrix}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{RED}} + E^\circ_{\text{ox}} \quad E^\circ_{\text{cell}} = 2.00\text{V}$$

$$= 0.34\text{V} + 1.66\text{V}$$

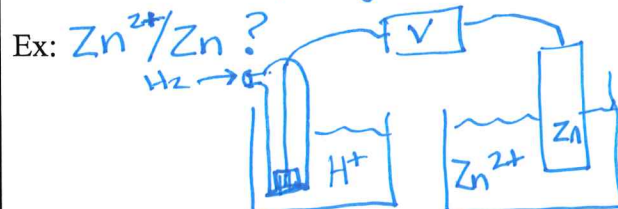
How did they come up with those E° values?

* If there was an electrode for which we did not know the E° value for, there is a way that we could get it.

* We could hook it up to another electrode that we know the E° value for, run the cell and get the E°_{cell} value.

The Formula: $E^\circ_{\text{cell}} = E^\circ_{\text{known}} + E^\circ_{\text{unknown}}$

* The electrode E° that we use to compare all others is:
 the hydrogen half cell. $E^\circ_{\text{RED}} = 0.00\text{V}$



when this cell gets hooked up, the voltmeter reads 0.76V and shows electrons flowing TOWARDS the H^+/H_2 half cell.
 $E_{ox}^{\circ} = 0.76V \therefore E_{RED}^{\circ} = -0.76V$

Assignment: Read pages 218-228 and do questions #36 a, d, & g and #38 & 47

A few other points about E° :

1/ Equilibrium: Like any other equilibrium reaction, the forward reaction rate will decrease and the reverse reaction will increase and eventually they will become the same. What this means, is that E°_{red} will decrease and E°_{ox} will start to increase. Pretty soon, the difference between them will become minimal and E°_{cell} will approach zero

2/ Surface area of the electrodes: Will have no influence on the E° value for the electrode. However, it will affect the rate of the reaction and the length of its life.

3/ Cells not at standard conditions: Use Le Chatelier's Principle to determine what the stress will do to the reduction reaction.

Electrochemical Applications (Spontaneous):

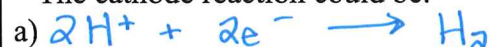
1/ Corrosion:

- * metals spontaneously go to oxides.
- * many metals form an oxide "skin" to prevent further oxidation (corrosion).
- * oxidation means that the metal DISSOLVES.

Ex: $Metal_{(s)} \rightarrow Metal^+_{(aq)} + e^-$
goes from (s) to (aq) \therefore dissolves

* During corrosion, the metal acts as an anode (oxidizes)

* The cathode reaction could be:

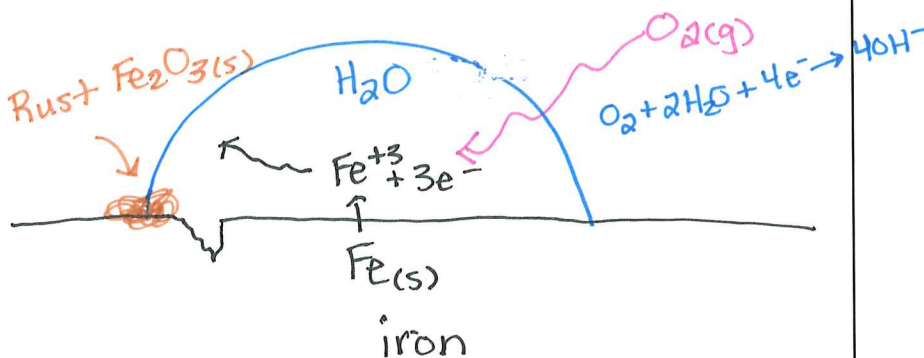




* Also need a salt. WHY? SALT Bridge

* Corrosion will occur in cracks in the metal oxide "skin"

Now let us draw:



* the electrons migrate through the metal to the surface where oxidation can occur (where O_2 can be reduced).

* Oxidation happens where the surface of the metal meets water and oxygen.

Protection from Corrosion:

a) inhibit the anodic process

b) inhibit cathodic process

c) do both.

a) Anodic Inhibition:

- paint the metal surface
 - allow an oxide "skin" to form on the metal surface
- } don't allow O_2 in

b) Cathodic Protection: (force the metal to become the cathode)

- sacrificial anode

* Ex: Aluminum \rightarrow easily oxidized
 \therefore it oxidizes before the metal does.

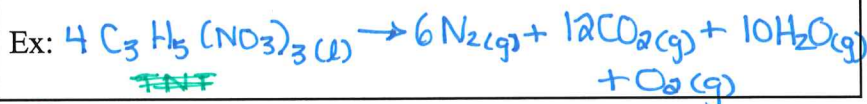
- ships attach platinum coated titanium to the hull & it is attached to a battery. Forces Pt to become the anode & ship's hull to be cathode.

2/ Bleaching:

- * used to eliminate unwanted colour from fabrics, etc.
- * colour is caused by the movement of electrons through energy levels.
- * OCl^- in bleach, in its need to reduce, rips the electrons away from the coloured dyes
- * Cl_2 and H_2O_2 do the same thing
- * H_2O_2 kills bacteria by oxidizing the cell wall.

3/ Fuels and explosives:

- * Fuels release energy when they are oxidized

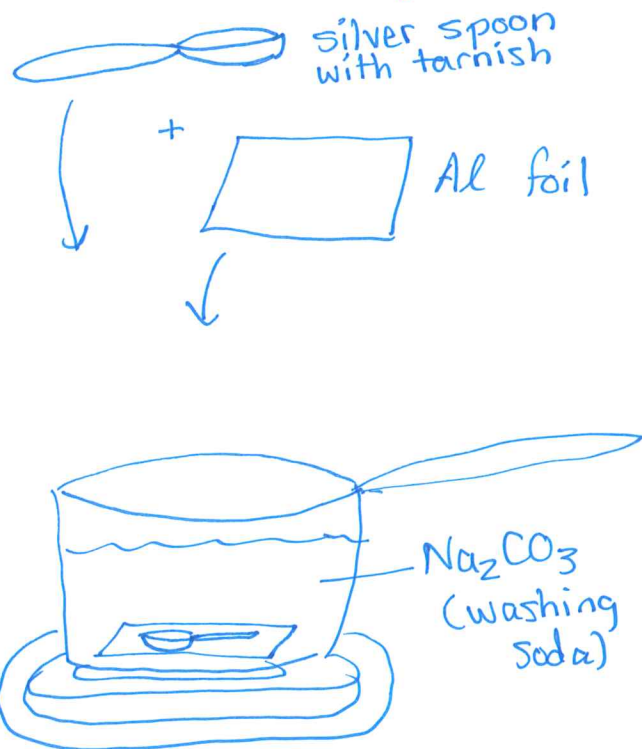


nitroglycerin

* explosives often contain both oxidizing and reducing agents (TNT)
* the rapid formation and expansion of gases cause the shockwave.

4/ Batteries: read the text book and fill in the spaces beside each battery with a letter.

5/ Silver Tarnish: the brown stuff that is silver tarnish is $\text{Ag}_2\text{S}(s)$



$\text{Al}(s) \rightarrow \text{Al}^{3+} + 3e^-$ oxidation
 $\text{Ag}_2\text{S}(s) + 2e^- \rightarrow 2\text{Ag}(s) + \text{S}^{2-}_{(aq)}$ reduction
silver tarnish gets turned back into solid silver; Al gets dissolved; smells like rotten eggs

Assignment: Read pages 228-236

Electrolysis:

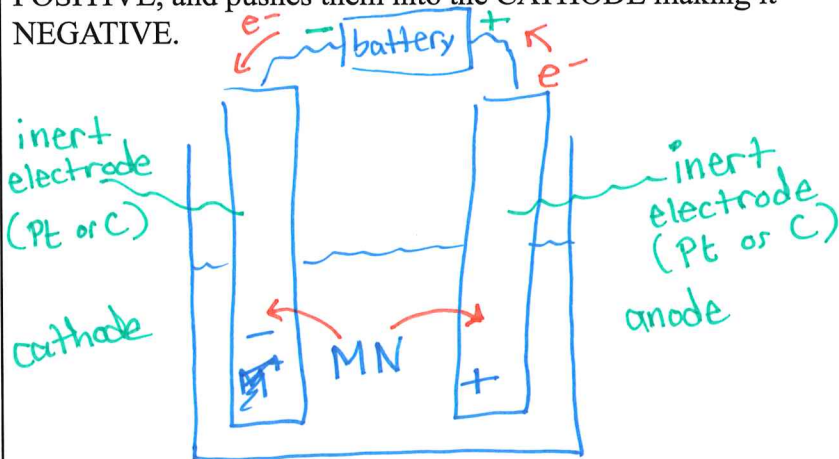
* It is like an electrochemical cell but, THE ELECTRODES PRODUCE A NON-SPONTANEOUS REACTION

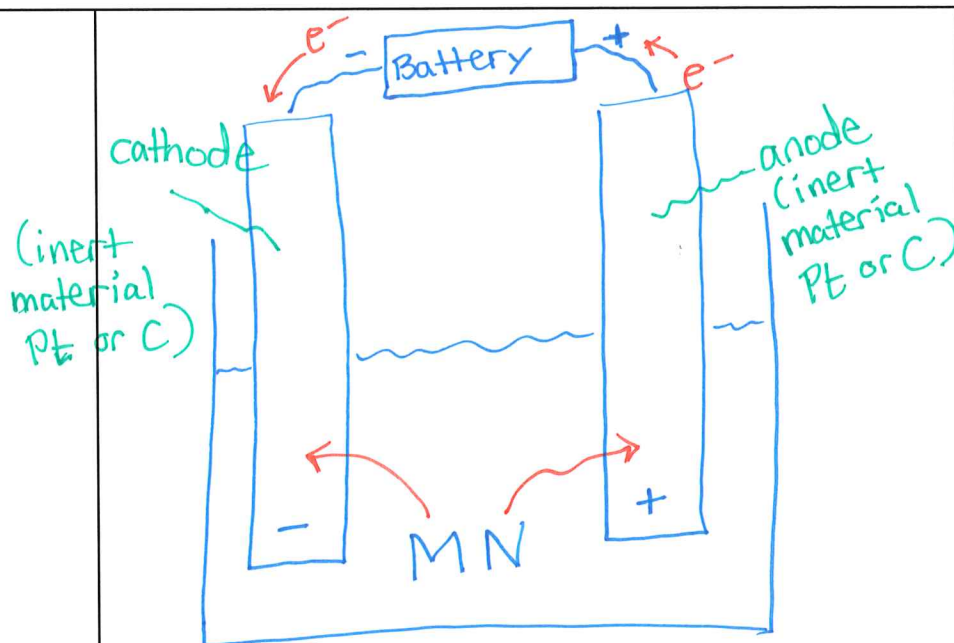
* this means that when we measure E°_{cell} , it will be negative and we will have to SUPPLY at least that much energy to make the cell work.

* Reactions of this type are called electrolysis and take place in electrolytic cells.

* It consists of a battery, which acts as an electron pump (pulls electrons from the anode and pushes them into the cathode), an external wire, and 2 electrodes that are immersed in a melted or aqueous salt solution. A salt bridge is not necessary.

* The battery sucks electrons out of the ANODE making it POSITIVE, and pushes them into the CATHODE making it NEGATIVE.





* once the battery is connected, e^- are sucked out of the inert anode making it \oplus and pushed into the cathode making it \ominus .

* since the anode is \oplus the anion of the salt is pulled toward. and it is oxidized.



* since the cathode is now \ominus the cation of the salt is pulled towards the cathode where it is reduced.



* the result is elements being made from a salt.

E.C. cell

anode → oxidation

cathode → reduction

anode ⊖

cathode ⊕

voltmeter or iPhone

e⁻ anode to cathode

* separate half cells

SPONTANEOUS

cations to cathode

anions to anode

E.L. cell

anode → oxidation

cathode → reduction

anode ⊕

cathode ⊖

Battery or power source

e⁻ anode to cathode

one container

NON-SPONTANEOUS

cations to cathode

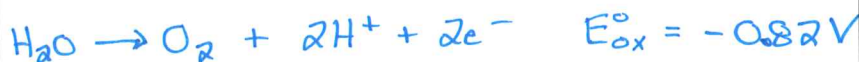
anions to anode

* In many electrolytic cells, the electrodes are INERT. They only serve as a source of electrons and do not appear in the overall reaction of interest. Examples of inert electrodes are:

Platinum or Carbon

Electrolysis in Aqueous Solutions:

* when the salt is in an aqueous solution (when the question says anything about molarity OR if it doesn't say molten), water becomes a possible player.

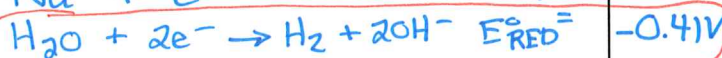


* In an aqueous solution water OR the ions may react and which one does is a function of where the reactions are in the table. The highest one will reduce (look for your reactant on the left side) and the lowest one will oxidize (look for your reactant on the right side).

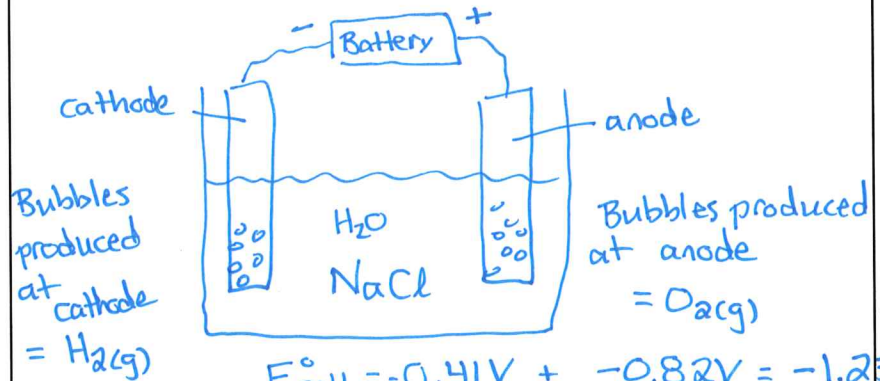
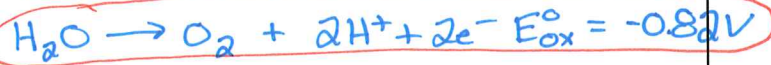
Ex: Electrolysis of 1M NaCl



Possible reductions:

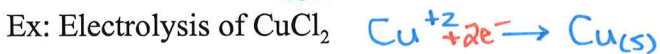


Possible Oxidations:



$$E_{\text{cell}}^\circ = -0.41\text{V} + -0.82\text{V} = -1.23\text{V}$$

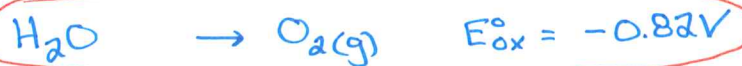
Ex: Electrolysis of CuCl_2



Reductions Possible:



Oxidations possible:



$$E_{\text{cell}}^\circ = 0.34\text{V} + -0.82\text{V}$$

$$= -0.48\text{V}$$

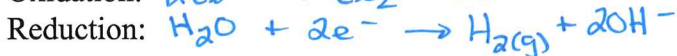
BUT WAIT! THERE'S MORE!!

The Overpotential Effect:

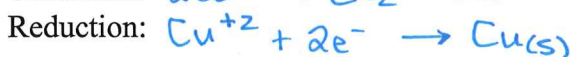
The half-reactions of H_2O involve mechanisms that may not allow for them to react at the E° values given in the table. The E°_{red} may be lower and the E°_{ox} may be higher (see arrows in table)

THEREFORE:

In example 1:



In example 2:



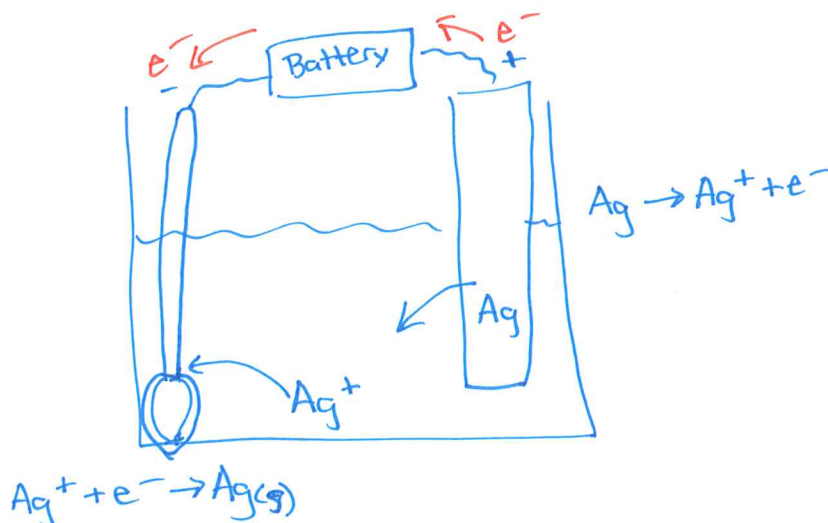
** From now on, we will pretend they will react where the arrows point DUE TO THE OVERPOTENTIAL EFFECT (yes, you have to say that)

Applications of Electrolysis:

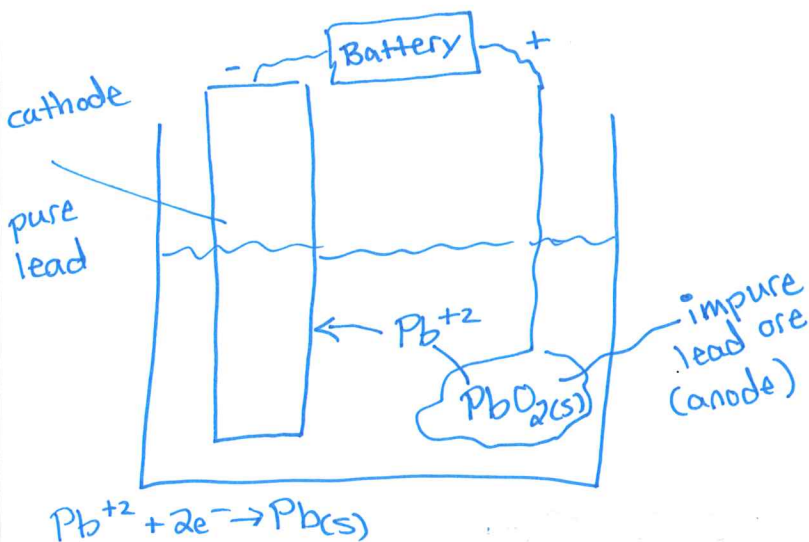
1/ Electroplating:

- * object to be plated needs to be the cathode
- * solution contains ions of the coating metal
- * anode is a bar of the coating metal OR an inert electrode (Pt/C)
- * voltage must be controlled so that water does not react

Ex: plating with silver:



2/ Electrorefining: Read text and make notes (what is the anode, cathode, solution, for example) Example: refining Lead ore



**Assignment: Read pages 237 –end and do questions
60, 65, 66, 69, 74, 75, 77, & 80**