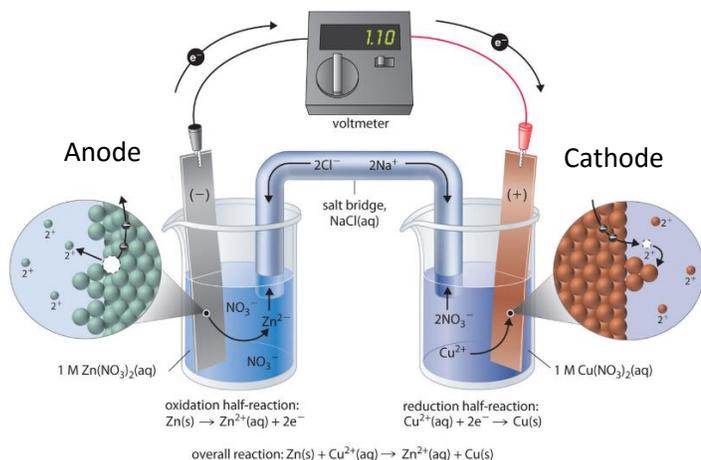


## AP Chemistry – Electrochemistry

### Galvanic/Voltaic Cells – Positive $E_{\text{cell}}$



Function of the parts:

1. Anode – oxidation occurs here (metal dissolves)
2. Cathode – reduction rxn occurs here (ppt.)
3. Electrode – metal used to transfer electrons
4. Inert electrode – non reactive electrode (Pt)
5. Salt bridge – uses ionic salt to balance out charge in each half cell, positive ion travels towards cathode and negative ion to anode
6. Standard conditions – 1M and 25°C

\*\* Metal ions precipitate at the Cathode

**RED CAT** – reduction occurs at the cathode

**FAT CAT** – electrons flow from anode to cathode

**Produces Current!** (think battery!)

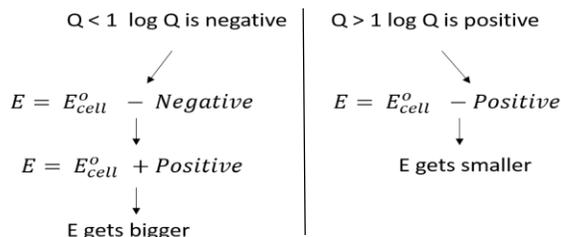
#### Balancing RedOx Reactions

1. Split overall rxn into  $\frac{1}{2}$  reactions (Ox and Red)
  - a. Ox rxn loses  $e^-$  ( $e^-$  is product)
  - b. Red rxn gains  $e^-$  ( $e^-$  is reactant)
2. Balance each half rxn
  - a. Balance elements NOT Hydrogen and Oxygen 1<sup>st</sup>
  - b. Then balance Oxygen by adding water and balance Hydrogen by adding  $H^+$
3. Electrons lost/gained must be equal
  - a. Might have to multiply half reactions
4. Add half reactions together (be sure to simplify)

#### Nernst and Non-Standard Cells

We use the Nernst equation as a predictive tool to determine how  $E^{\circ}_{\text{cell}}$  will be affected by nonstandard conditions

$$E = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

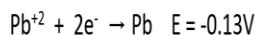


**Positive E is Thermo Favorable!**

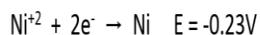
So reaction proceeds forward,  $-\Delta G$  and  $K > 1$

#### Using Reduction Potentials

The larger reduction value is reduced  
(the other will be oxidized and you have to flip reaction)



Larger, so will be reduced



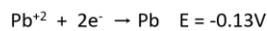
Smaller, so will be oxidized  
(need to flip rxn and sign of E)

Watch your negatives... A bigger negative number is actually a smaller value!!!!!!

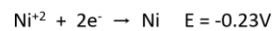
#### Calculating Overall $E_{\text{cell}}$

Determine Ox/Red reactions based on reduction potentials  
(don't forget to reverse and change sign of oxidation reaction)

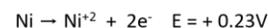
Then just ADD them together



Larger, so will be reduction



Oxidation, so becomes



$$\text{Overall } E_{\text{cell}} = -0.13V + 0.23V$$

$$E_{\text{cell}} = 0.10$$



#### Concentration Cells

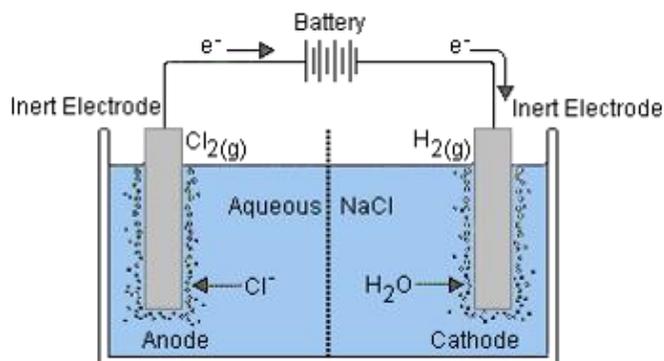
Rather than having two different species a concentration cell uses the same species at different concentrations

\*\* electrons will ALWAYS travel towards more concentrated Solution... So concentrated solution will be cathode (FAT CAT)  
(metals precipitate at cathode which will cause metal ion concentration to decrease)

$$\Delta G = -nFE^{\circ} \quad E = \frac{0.0592}{n} \log Q$$

$$1 \text{ mole } e^- = 1 \text{ Faraday} = 96,485 \text{ C}$$

### Electrolytic Cells – E<sub>cell</sub> Negative



- Notice it is a SINGLE container with 2 electrodes
- Current MUST be added to get this to function!
- There is no salt bridge

(trick alert: in questions.... If they say a current is added they are telling you the cell is electrolytic)

The only differences are the E<sub>cell</sub> will be negative (not thermo favorable) and the anode will be positive

**RED CAT** – reduction occurs at the cathode

**FAT CAT** – electrons flow from anode to cathode

Also notice a battery is hooked up here and not a volt meter... this is because current has to be added!!!!

### Predicting Products of Electrolysis

#### Molten Ionic Compounds (melted)

- ◆ Positive Ion ALWAYS get Reduced at cathode
  - ◆ Negative ion ALWAYS get Oxidized at anode
- (because it is not likely for a positive ion to lose more electrons and at the same time a negative ion to gain)

For example: Molten NaCl

Na<sup>+</sup> will be reduced at cathode ( Na<sup>+</sup> + e<sup>-</sup> → Na )

Cl<sup>-</sup> will be oxidized at anode ( 2Cl<sup>-</sup> → 2e<sup>-</sup> + Cl<sub>2</sub> )

#### Aqueous Ionic Compounds

- ◆ Still keep in mind that positive ions reduced at cathode and negative ions oxidized at anode BUT.....
- Now we have to determine if the element is more/less likely to react than water at each electrode

Oxidation of water: 2H<sub>2</sub>O → O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup> (E = -1.23V)

Reduction of water: 2H<sub>2</sub>O + 2e<sup>-</sup> → 2H<sub>2</sub> + 2OH<sup>-</sup> (E = -0.83V)

◆ The negative ion will be oxidized if its potential (after being switched to oxidation) is BIGGER than the oxidation potential of water

◆ The positive ion will be reduced if its potential is BIGGER than the reduction potential of water

#### Popular Electrolytic Calculation #1

How many grams of metal can be plated out if time (needs to be in seconds) and amount of electrical current (amps) are given?

#### Popular Electrolytic Calculation #2

How long will it take to plate out a given mass of metal if current (amps) is given?

### Flow of information for Electrolytic Calculations

Grams of Metal ↔ Moles of Metal ↔ Moles of e<sup>-</sup> ↔ Coulombs ↔ # of Coulombs = It

Trick alert: sometimes they ask for the molar mass of the metal (grams divided by moles)

#### Converting from moles of metal to moles of electrons

Multiply by mole ratio (mole ratio based on ½ reaction)

$$0.3 \text{ mole Ni} \times \frac{2 \text{ mole } e^-}{1 \text{ mole Ni}} = 0.6 \text{ mole } e^-$$

#### Converting from moles of electrons to Coulombs

It's stoich again (I used the equality 1 mole e<sup>-</sup> = 96,485 C)

$$0.3 \text{ mole } e^- \times \frac{96,485 \text{ C}}{1 \text{ mole } e^-} = 28,946 \text{ C}$$