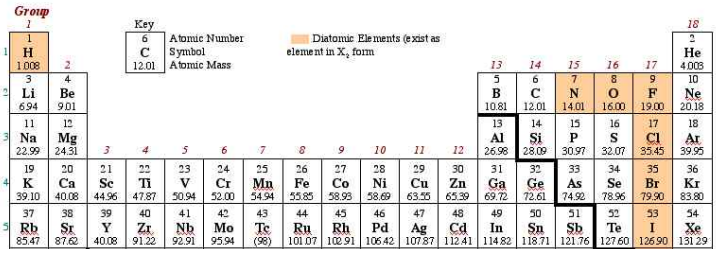
# Electrochemistry Notes:

- Electrochemistry is the study of the relationship of how chemical reactions contribute to electrical circuits. The reaction that takes place is called a redox reaction, which stand for reduced-oxidized reaction and involves the transfer of electrons from reactants to products.

- Before we can talk about how electrical circuits are involved in the study of electrochemistry we need to go over how to find the number of electrons that are involved in a particular reaction by assigning oxidation numbers.

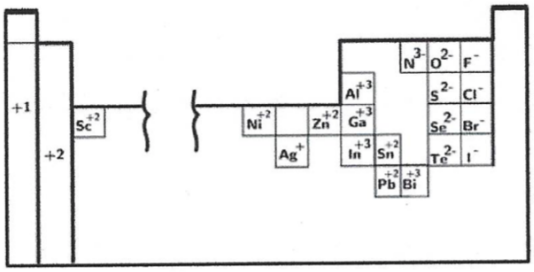
## Assigning Oxidation Numbers

- Elements in elemental form has an oxidation number equal to zero.
  - $N_2$ , $H_2$ , Na(s), $Cl_2$ , C(s)
  BEWARE: Diatomic elements include N, H, F, O, I, Cl, Br




Makes a 7 for the 7 diatomic elements (plus hydrogen)

- Monoatomic ion oxidation number is equal to the charge on the ion.
  - $Na^+ = +1$, $S^{-2} = -2$
  BEWARE: Remember that ions like $OH^-$ are polyatomic ions.
- Compounds with two elements:
  -$PCl_3$, Cl is the atom with greater electronegativity. $Cl^-$ has an oxidation number equal to the charge when this atom forms an ionic compound. The $Cl^-$ in NaCl has a -1 charge so the oxidation number is -1.




  -For $CO_2$ , O is the most electronegative atom. In the ionic compound, $Na_2O$, O has a -2 charge so the oxidation number is -2.
- O is usually -2, except in peroxides, $O_2^{2-}$, like $H_2O_2$, where is it -1.
- H is usually +1 with nonmetals, and -1 with metals.
- F is always -1
- Sum of oxidation numbers must be equal to the charge on the ion of molecule

*Example -1:*

What is the oxidation number for $MnO_4^-$?

-Oxygen is more electronegative than Mn, so from looking at the periodic table for O it is a -2. Therefore each Oxygen in $MnO_4^-$ will have a charge of -2.—

$MnO_4^-$

O O O O
-2 -2 -2 -2 = -8

BEWARE: Although the Oxygen's add up to -8, each Oxygen is still a -2.

—If all of the Oxygens add up to -8 and there is one Mn, then the Mn must be +7 to get an overall -1 charge.—

*Example -2:*

What is the oxidation number for $Cr_2O_7^{-2}$ ?

—In $Cr_2O_7^{-2}$ Oxygen is more electronegative and it has a -2 charge and there are seven of them, so it is -14. There are two Cr's, so each Cr would be +7, but the overall charge is -2 which makes each Cr a +6.—

$Cr_2O_7^{-2}$

Cr Cr
+6 +6 = +12

$Cr_2O_7^{-2}$

O O O O O O O
-2 -2 -2 -2 -2 -2 -2 = -14

Overall Charge

+12 + -14 = -2

BEWARE: For ionic species the charges reflect the actual charge on the ion. In molecules that use covalent bonding the oxidation numbers do not represent the actual charges on the atoms.

## Oxidation and Reduction

- In order to determine which way the transfer of electrons goes in a redox reaction we need to assign each atom in the reaction an oxidation number. If the oxidation number increases it means that atom lost electrons and is **oxidized**. If the oxidation

number decreases it means that atom gained electrons and is **reduced**. (GER and LEO). The **oxidized agent** is the reactant that assist in oxidation and by itself is oxidized. The r**educing agent** is the reactant that assist in reduction and by itself is oxidized.

- Anytime an oxidation process happens it requires a reduction process to happen. These two process must occur in pairs and cannot occur on their own.

- To determine how many electrons are involved in the atom that is being oxidized or reduced take the difference in the two oxidation numbers.

*Example-3:*

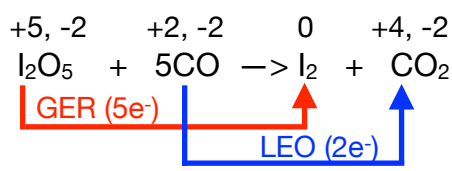
Given the following redox reaction determine what is being oxidized and reduced, then identify the oxidizing agent and the reducing agent.

$$I_2O_5 + 5CO \rightarrow I_2 + CO_2$$

—The first thing you want to do is assign oxidation numbers to each atom.—

$$\overset{+5,\ -2}{I_2O_5} + \overset{+2,\ -2}{5CO} \rightarrow \overset{0}{I_2} + \overset{+4,\ -2}{CO_2}$$

—The next thing you want to do is match up the atom from the reactant to the atom of the product.—




—Notice that the oxidation number of Oxygen does not change throughout this process. That is because it is neither reduced or oxidized in this reaction. I goes from +5 to 0 so it gains 5 electrons and is reduced. Carbon goes from +2 to +4 so it loses 2 electrons and is oxidized.—

## Balanced Number of Electrons

- When we balance redox reactions we need to take into account the electrons that are exchanged for the reduced and oxidized parts. Because the reduced part may have a different number of electrons than the oxidized part when we balance redox reactions we will write out each part separately called half reactions.

- When we assign oxidation numbers we assign them for a single atom, but a chemical reaction sometimes has more than one atom undergoing a reaction. So we need to multiply the change in oxidation number by the number of atoms of that atom.

- The oxidized half will produce electrons and the reduced half will require electrons.

*Example-4:*

Determine the balanced number of electrons in the following reaction:

$$I_2O_5 \quad + \quad 5CO \quad \text{—>} \; I_2 \quad + \quad CO_2$$

— To determine the number of balanced electrons we need to first write out the reduced and oxidized half reactions. We already did this in *Example-3*.—

$I_2O_5 \quad + \quad 5e^- \quad \text{—>} \quad I_2$ <— This GER, so the electrons are put on the reactant side.

$5CO \quad \text{—>} \; 2e^- \quad + \quad CO_2$ <— This LEO, so the electrons are put on the product side.

—For the reduced half ($I_2O_5$) there is a transfer of 5 electrons per atom of I. When we assigned oxidation numbers we did it per atom of Iodine. However, by looking at the reaction there are two atoms of Iodine in the reaction. Therefore, we would multiply 5 electrons by 2 to get 10 electrons for the reduced half reaction.—

each I gains $5e^-$ x 2 I atoms = $10e^-$
each C loses $2e^-$ x 5 C atoms = $10e^-$

$I_2O_5 \quad + \quad 10e^- \quad \text{—>} \quad I_2$

$5CO \quad \text{—>} \; 10e^- \quad + \quad CO_2$

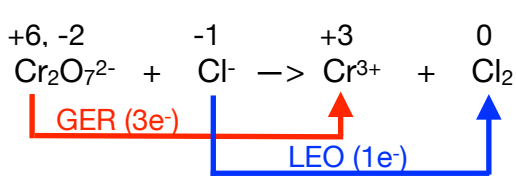
— The balanced number of electrons is 10 —

*Example-5:*

Determine the balanced number of electrons in the following reaction:

$$Cr_2O_7^{2-} \quad + \quad Cl^- \quad \text{—>} \; Cr^{3+} \quad + \quad Cl_2$$

—Just like before you need to assign oxidation numbers to all the atoms. —



—The next step is to write out each half reaction.—

$Cr_2O_7^{2-}$ + $3e^-$ —> $Cr^{3+}$

$Cl^-$ —> $1e^-$ + $Cl_2$

—Notice that we have 2 Cr's on the reactant side and 1 on the product side. We also have 7 O's on the reactant side and none on the product side. At this step do not worry about balancing the O's and H's (if there are any). At this step we need to balance everything that is not a hydrogen or an oxygen and count the number of atoms for the reduced and oxidized part—

$3e^-$ for each Cr x 2 Cr atoms = $6e^-$
$1e^-$ for each Cl x 2 C atoms = $2e^-$

$Cr_2O_7^{2-}$ + $6e^-$ —> $2Cr^{3+}$

$2Cl^-$ —> $2e^-$ + $Cl_2$

—When one mole of $Cr_2O_7^{2-}$ goes through a reduction process it requires 6 electrons. When 2 moles of $Cl^-$ goes through an oxidation process it will release 2 electrons.—

—Now we need to balance the number of electrons. If we multiply the oxidized half by 3 we can get 6 electrons for each half.—

3 ($2Cl^-$ —> $2e^-$ + $Cl_2$) ==> $6Cl^-$ —> $6e^-$ + $3Cl_2$

—Now we will just add the reactions back up to get one single reaction. When we add the reactions back up the electrons will cancel out because we have the same number of electrons on the reactant and product side.—

$Cr_2O_7^{2-}$ + $\cancel{6e^-}$ —> $2Cr^{3+}$

\+ $6Cl^-$ —> $\cancel{6e^-}$ + $3Cl_2$

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$Cr_2O_7^{2-}$ + $6Cl^-$ —> $2Cr^{3+}$ + $3Cl_2$

The balanced number of electrons is 6

## Balancing Redox Reaction in Acidic and Basic Soln

- Because redox reactions involve the transfer of electrons, they will occur in acidic (H) or basic (OH) solutions that also need to be balanced.

- The first step in balancing a redox reaction is to find the balanced number of electrons and write out the complete equation. The next step is to balance the oxygens by adding $H_2O$ to the side that needs it. Because adding $H_2O$ to one side will add hydrogen atoms to one side, add hydrogen atoms to the other side if the solution is acidic. If the solution is basic add OH ions to each side that match the hydrogen ions. This will neutralize the acid and produce water. If water is on each side of the chemical equation use Hess's law to cancel out the excess water.

*Example-6:*

Balanced the following redox reaction in an acidic solution:

$$Cr_2O_7^{2-} + Cl^- \rightarrow Cr^{3+} + Cl_2$$

—To balance this redox reaction in an acidic solution you need to write out the overall reaction with the balanced number of electrons. We already did this in *Example-5*.

$$Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2$$

—Keep in mind the number of balanced electrons is 6, but they canceled out on each side of the chemical equation. The next step is to balance the number of Oxygens. There are 7 Oxygens on the reactant side and none on the product side. So we add 7 $H_2O$ to the product side.—

$$Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

—Now we need to balance the hydrogens. There are 14 Hydrogens on the product side so we will add 14 $H^+$ to the reactant side.—

$$14H^+ + Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

*Example-7:*

Balanced the following redox reaction in a basic solution:

$$Pb(OH)_4^{2-}\ (aq) + ClO^-\ (aq) \rightarrow PbO_2\ (s) + Cl^-\ (aq)$$

—The first step in balancing a redox reaction is to assign oxidation numbers and separate the two half reactions.—

$$\overset{+2}{Pb(OH)_4^{2-}} + \overset{+1}{ClO^-} \longrightarrow \overset{+4}{PbO_2} + \overset{-1}{Cl^-}$$

LEO ($2e^-$)

GER ($2e^-$)

—Pb goes from +2 to +4 so it lost 2 electrons and is oxidized. Cl goes from +1 to -1 to it gained 2 electrons and is reduced.

$ClO^- + 2e^- \longrightarrow Cl^-$ <— This GER, so the electrons are put on the reactant side.

$Pb(OH)_4^{2-} \longrightarrow 2e^- + PbO_2$ <— This LEO, so the electrons are put on the product side.

BEWARE: Other than the Oxygens this reaction is already balanced. Normally you would balance everything except for Oxygen and Hydrogen in the step.

—Now that the electrons are balanced on both sides of the reaction you add the two half reaction up.—

$$\begin{array}{lll} & ClO^- + \cancel{2e^-} \longrightarrow Cl^- & \\ + & Pb(OH)_4^{2-} \longrightarrow \cancel{2e^-} + PbO_2 & \\ \hline & Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- & \end{array}$$

—At this point everything is balanced except for the Oxygens and Hydrogens, so we will balance the Oxygens by adding water to the side that needs it. There are 5 Hydrogens on the reactant side and 2 on the product side, so we will add 3 $H_2O$ to the product side.—

$$Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- + 3H_2O$$

—Now we need to balance the hydrogens. There are 4 Hydrogens on the reactant side and 6 Hydrogens on the product side so we will add 2 $H^+$ on the reactant side.—

$$2H^+ + Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- + 3H_2O$$

—This would be the answer if the question ask us to balance the reaction in an acidic solution, but we are told this reaction occurs in a basic solution. Therefore, we need to neutralize the $H^+$ with the addition of $2OH^-$ to make water. However, we add $OH^-$ on one side of the reaction we need to add $OH^-$ to the other side.—

$$\boxed{2OH^- + 2H^+} + Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- + 3H_2O + 2OH^-$$

forms water

$$2H_2O + Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- + 3H_2O + 2OH^-$$

—For this last step we need to get rid of the excess water that is on both sides of the equation. We have 2 moles of water on the reactant side and 3 moles of water on the product side, so the 3 moles on the product side can eliminate 2 moles of water on the reactant side, which will give us 1 mole of water on the product side.—

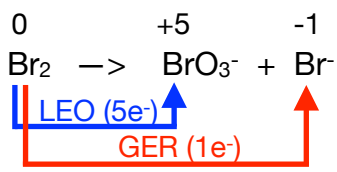
$$Pb(OH)_4^{2-} + ClO^- \longrightarrow PbO_2 + Cl^- + H_2O + 2OH^-$$

*Example-8*

Balance the following reaction in a basic solution:

$$Br_2 \longrightarrow BrO_3^- + Br^-$$

—The first thing we need to do is separate the two half reactions, balance the number of electrons, and balance all of the atoms (except oxygen and hydrogen).—




—In this reaction Br is both reduced and oxidized.—

$5(Br_2 + 2e^- \longrightarrow 2Br^-$ <— This GER, so the electrons are put on the reactant side.

$Br_2 \longrightarrow 10e^- + BrO_3^-$ <— This LEO, so the electrons are put on the product side.

BEWARE: This is a common mistake. The oxidation numbers what we assign are for a single atom of Br and there are two atoms of Br in the reaction, you need to multiple the number of electrons exchanged by two.

—The balanced number of electrons for this redox reaction is 10 electrons. Adding the two reactions back up gives the following.—

$$6Br_2 \longrightarrow 2BrO_3^- + 10Br^-$$

—There are 6 Oxygens on the product side and none on the reactant side. So we must add 6 moles of water to the reactant side. Then we need to add 12 Hydrogens to the product side.—

$$6H_2O + 6Br_2 \longrightarrow 2BrO_3^- + 10Br^- + 12H^+$$

—This would be the answer if the question ask for an acidic solution. Because this question ask for a basic solution we need to neutralize the acid we made by adding 12 moles of OH to each side of the reaction.—

$$12OH^- + 6H_2O + 6Br_2 \rightarrow 2BrO_3^- + 10Br^- + \boxed{12H^+ + 12OH^-}$$

forms water

$$12OH^- + 6H_2O + 6Br_2 \rightarrow 2BrO_3^- + 10Br^- + 12H_2O$$

—For the last step we need to eliminate some of the water because we have water on both sides of the reaction.—

$$12OH^- + 6Br_2 \rightarrow 2BrO_3^- + 10Br^- + 6H_2O$$

## Voltaic/Galvanic and Electrolytic Cells

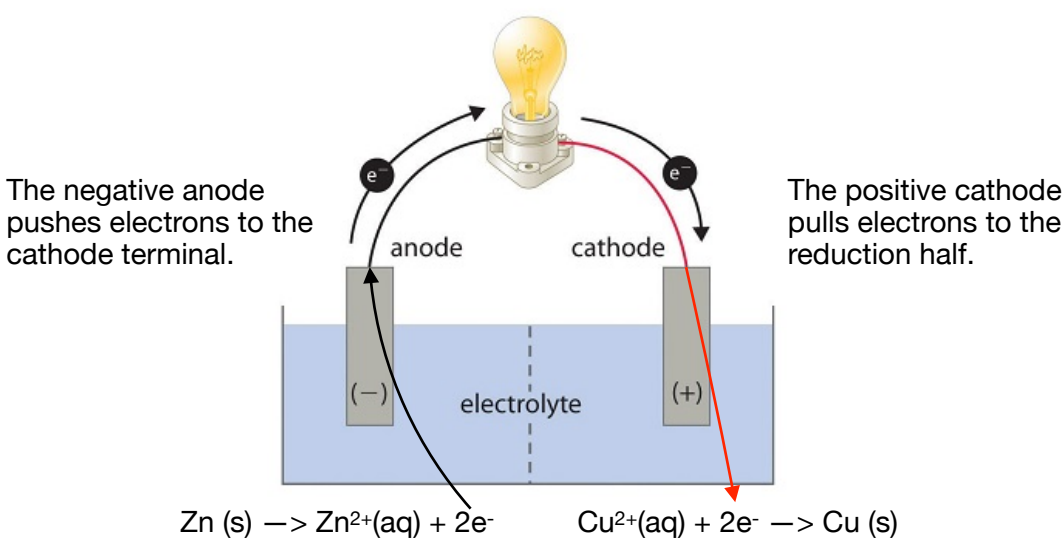
- The concept of part of a reaction producing electrons and another part of a reaction accepting electrons is useful at producing an electrical current. To do this we will separate each half reaction into two compartments and have a salt bridge made of electrolytes that will connect the two compartments together.

- Electrolytes include strong acid/bases and ionic compounds. Weak acids/bases make weak electrolytes. Molecular compound (chemicals with all nonmetals) are non electrolytes.

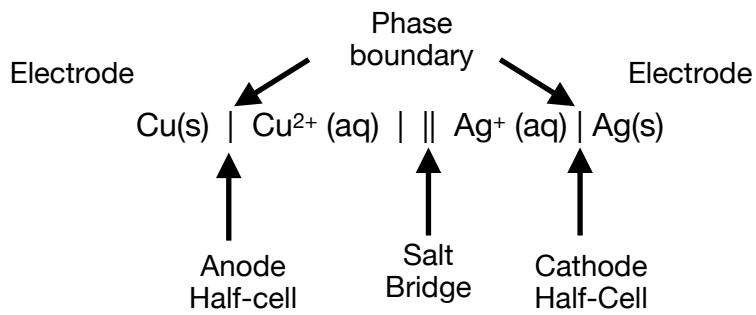
- Any electrical circuit needs to have a complete connection. This is the purpose of the salt bridge. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral

- A Voltaic also called a Galvanic cell is a type of redox reaction that are used in batteries to produce an electrical current. The oxidized half occurs at the anode terminal, which is negative, and reduction occurs at the cathode terminal, which is positive.

- Voltaic cells occur spontaneously as soon as the circuit is connected.The picture below shows an example of a voltaic cell.



- Because you don't want draw out a picture when you want to describe a voltaic cell there is a shorthand way to write out voltaic cells. The way you would write out a the previous voltaic cell is with the following notation:

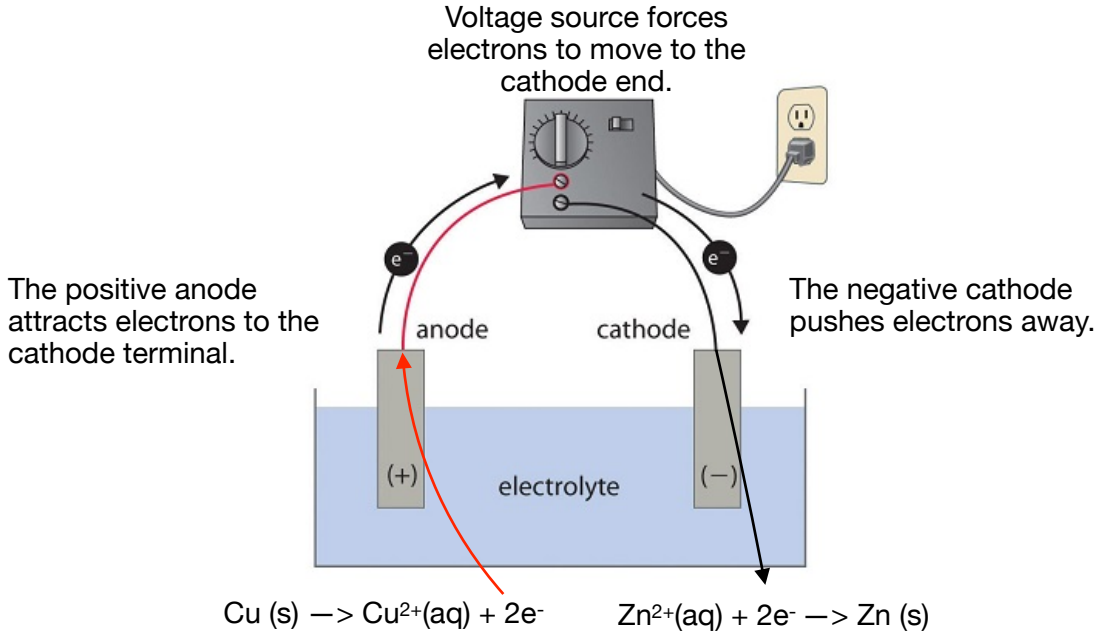



- The other type of cell is called an Electrolytic cell. Electrolytic cells do not occur spontaneously. We have to put energy into the system to make this reaction happen. The energy that we put into the system must be greater than the voltage generate by the redox reaction.

- Both Voltaic and Electrolytic cells have an anode end where oxidation takes place and a cathode end where reduction takes place. The difference between a voltaic and electrolytic cell is that an electrolytic cells requires a voltage source to get the reaction to occur because the reaction is non spontaneous.

- Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

- The picture below shows an example of an electrolytic cell.



# Redox Voltage

- For voltaic cells a voltage is produced and for electrolytic cells a minimum voltage source is required. To find the voltage that is produced or required you use a table with an equation shown below:

$$E^0 = \underset{\text{Red Half}}{\text{Red}} - \underset{\text{Red Half}}{\text{Oxi}}$$

- To determine the voltage (E) of a redox reaction you need to identify each half reaction as being reduced or oxidized then look at a table with with the reduction half.

**Standard Potentials at 25°C**

| Half Reaction | Potential |
|---|---|
| $F_2 + 2e^- \rightarrow 2F^-$ | +2.87 V |
| $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ | +2.07 V |
| $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ | +2.05 V |
| $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$ | +1.69 V |
| $Au^+ + e^- \rightarrow Au$ | +1.69 V |
| $Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ | +1.67 V |
| $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13 V |
| $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.14 V |
| $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.23 V |
| $V^{3+} + e^- \rightarrow V^{2+}$ | −0.26 V |
| $Co^{2+} + 2e^- \rightarrow Co$ | −0.28 V |
| $In^{3+} + 3e^- \rightarrow In$ | −0.34 V |
| $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | −0.36 V |

- The "o" above the E refers to 1 atm at 25C and all concentrations must be 1M.

- If you are given the voltage for an oxidized half of a reaction and want to find the voltage of the reduced half you just flip the sign.

*Example-9*

Determine the voltage of the following redox reaction:

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

—To determine the voltage for this redox reaction we need to determine which half is reduced and which is oxidized by assigning oxidation numbers.—

$$\overset{0}{Zn}\ (s) + \overset{+2}{Cu^{2+}}\ (aq) \rightarrow \overset{+2}{Zn^{2+}}\ (aq) + \overset{0}{Cu}\ (s)$$

LEO ($2e^-$)

GER ($2e^-$)

—Now that we know which is reduced and which is oxidized we go to a table and use the equation $E^0_{cell} = E^0_{red}$ (RED) - $E^0_{red}$ (LEO)—

$Zn^{2+} + 2\ e^- \rightarrow Zn\ (s)$ $E^0 = -0.76V$ <— This one is oxidized

$Cu^{2+} \rightarrow 2e^- + Cu\ (s)$ $E^0 = +0.34$ <—This one is reduced

$E^0_{cell} = 0.34 - (-0.76) = 1.10V$

*Example-10*

Determine the voltage for the oxidized potential for the following reaction:

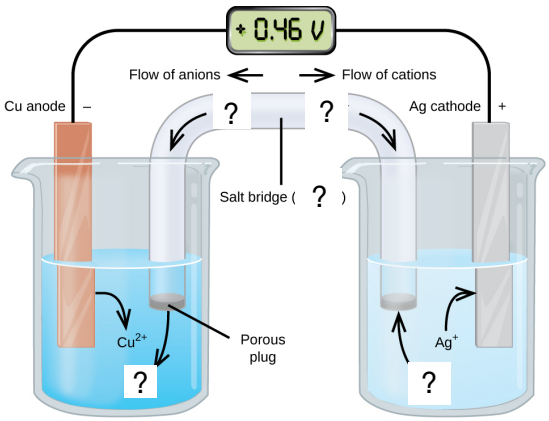
$$Au^{3+} + 3e^- \longrightarrow Au \qquad E = +1.4\ V$$

—If we are given the voltage of a reduced reaction and we want to find the oxidized potential we just switch the signs.—

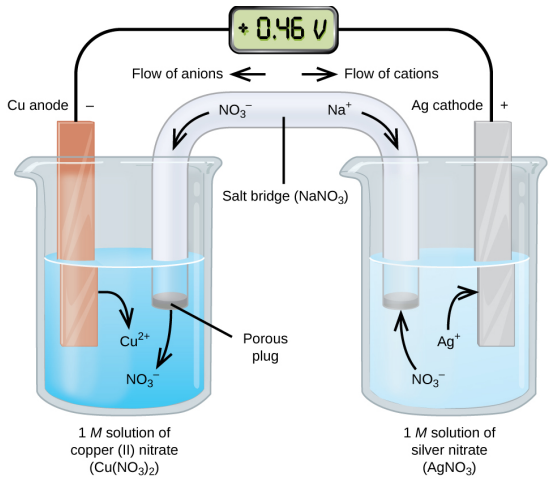
$$Au \longrightarrow Au^{3+} + 3e^- \qquad E = -1.4\ V$$

*Example-11*

Determine the flow of cations and anions in the salt bridge in the redox reaction.




—At the anode $Cu^{2+}$ are produced and anions (negative ions) will be attracted to the positive $Cu^{2+}$ ions made and cations (positive ions) will be attracted to the other end.—



*Example-12*

Use cell notation to describe the electrochemical cell from question 11.

—When you use cell notation the anode is written to the left, then the anode solution, then the salt bridge marked with a || then the cathode solution, and last the cathode.—

$$Cu(s) \mid Cu^{2+}(aq, 1M) \mid \mid Ag^{+}(aq, 1M) \mid Ag(s)$$

*Example-13*

For the following galvanic cell write out the cathode and anode half reactions.

$$Cr(s) \mid Cr^{3+}(aq) \mid \mid Ag^{+}(aq) \mid Ag(s)$$

—From looking at the cell notation the Cr(s) is oxidized and produces a $Cr^{3+}$ which means it produces 3 electrons to go from a 0 oxidation number to a +3 oxidation number.—

—The double line separates the the other part of the cell. The Ag(s) represents the Ag(s) that is produced and the $Ag^{+}$ represents the oxidized agent or what is reduced.—

$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$ <—Anode half-reaction

$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$ <— Cathode half-reaction

- There is a relationship between the voltage a redox reaction and the amount of Gibbs free energy. That relation is described with the following equation:

$$\Delta G^{0} = -nFE^{0}$$

- Notice that if the voltage of the redox reaction is positive, then the amount of gibbs free energy will be negative and if the the voltage of the redox reaction is negative, then the amount of gibbs free energy will be positive (the voltage and the amount of gibbs free energy will be opposite in sign).

- If ΔG is negative the reaction will be spontaneous and is referring to a voltaic cell. If the ΔG is positive then the reaction will be non spontaneous and is referring to an electrolytic cell. A dead battery would be an example of a voltaic cell at equilibrium.

- The n in the equation represents the number of balanced moles of electrons from the redox reaction. The F in the equation represents faradays constant, which is 96,485 C per mole of electron.

*Example-14*

Given the two reduction half reaction determine the balanced reaction for a voltaic cell.

| | | |
|---|---|---|
| $Co^{2+}$ (*aq*) + 2e$^-$ → Co(*s*) | $Co^{2+} + 2e^- \rightarrow Co$ | −0.28 |
| $Cr^{3+}$(*aq*) + 3e$^-$ → Cr(*s*) | $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.744 |

—We are told that this reaction is from a voltaic cell and a voltaic cell occurs spontaneously, which means the voltage for the reaction must be positive.—

—If $Cr^{3+}$ is reduced and $Co^{2+}$ is oxidized then the voltage of the cell would be -0.744 - -0.28 = -0.464. Because this results in a negative number $Cr^{3+}$ can not be reduced. A negative voltage means a positive change in gibbs free energy and a voltaic cell must have a negative change in gibbs free energy.

—If $Co^{2+}$ is reduced and $Cr^{3+}$ is oxidized then the voltage of the cell would be -0.28 - -0.744 = 0.464. This means that the overall reaction is as follows:

$Co^{2+}$ (*aq*) + 2e$^-$ → Co(*s*)
Cr(*s*) → $Cr^{3+}$(*aq*) + 3e$^-$

—Now we to balance the number of electrons. We have 2 electrons for the reduced half and 3 electrons for the oxidized half. Therefore we will multiply the reduced half by 3 and the oxidized half by 2 to get an overall number of electrons of 6.—

3 [ $Co^{2+}$ (*aq*) + 2e$^-$ → Co(*s*) ]
2 [ Cr(*s*) → $Cr^{3+}$(*aq*) + 3e$^-$ ]

3$Co^{2+}$ (*aq*) + 6e$^-$ → 3Co(*s*)
2Cr(*s*) → 2$Cr^{3+}$(*aq*) + 6e$^-$

—Now we will just add the reactions back up and cancel out the electrons to get the overall reaction.—

$$3\ Co^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Co(s) + 2\ Cr^{3+}(aq)$$

- Standard reduction potential tables can be used to determine which reactant will be the strongest oxidizing agent and which will be the strongest reducing agent. If we arrange the half reactions in order of decreasing potentials the strongest oxidizing agent will be at the top left and the strongest reducing agent will be at the bottom right as shown below:

**Standard Potentials at 25°C**

| Half Reaction | Potential |
|---|---|
| $F_2 + 2e^- \rightarrow 2F^-$ | +2.87 V |
| $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ | +2.07 V |
| $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ | +2.05 V |
| $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$ | +1.69 V |
| $Au^+ + e^- \rightarrow Au$ | +1.69 V |
| $Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ | +1.67 V |

Strongest Oxidizing Agent

High To Low

Strongest Reducing Agent

BEWARE: When trying to compare oxidizing/reducing agents make sure the voltage potentials go from high to low.

- So far we only went over the voltage a reaction gives off at standard conditions where the concentrations are 1M. You know from the reaction quotient (Q) that as a process approaches equilibrium the amount of gibbs free energy will change and the equation delta $G^0 = -nFE^0$ must also change. The equation delta $G^0 = -nFE^0$ tells us the voltage and as it relates to gibbs free energy for only a moment in time. If we don't have concentrations of 1M we can use the following equation:

$$\text{delta } G = -nFE$$

- Notice that this equation does not have the $^0$ above the G and E. That is because both delta G and E occur at the same temperature, pressure, and concentration.

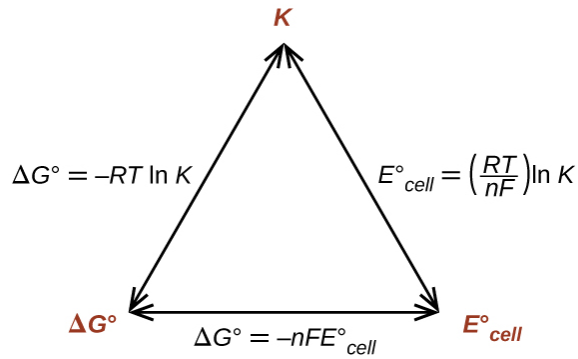
- The Nernst Equation relates voltage, temperature, and concentration and is shown below:

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q$$

- From thermodynamic we know the relationship between delta G, delta G at standard conditions, and Q with the following equation:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

- When a system is at equilibrium Q = K and delta G = 0. Therefore, we can get the following sets of equations.




*Example-15*

What is the standard free energy change and equilibrium constant for the following reaction at 25C?

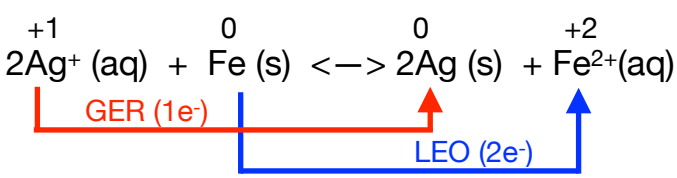
$2Ag^{+}$ (aq) + Fe (s) <—> 2Ag (s) + $Fe^{2+}$(aq)

| | |
|---|---|
| $Ag^{+} + e^{-} \rightarrow Ag$ | +0.80 V |
| $Fe^{2+} + 2e^{-} \rightarrow Fe$ | –0.44 V |

—If we want to know the equilibrium constant (K) and we have a reaction we just need to find the $E^0$ of the cell. We do this by assigning oxidation numbers then using $E^0$ = Red - Oxi—

—The equation that relates $E^0$ of the cell to the equilibrium constant (K) is shown below—

$$E^{\circ}_{cell} = \left(\frac{RT}{nF}\right)\ln K$$




—Because Ag is reduced and Fe is oxidized we do 0.8 - -0.44 to get 1.24 V for the E of the cell at standard conditions. Now we need to find K.—

$$1.24 = \frac{8.314 * 298}{2 * 96{,}485} \ln K$$

—The 2 in the equation above comes from the balanced number of electrons. Solving this equation gives K = 1.3 e 42.—

—Now to solve for delta G. Use the equation delta G = -nFE—
delta G = - 2 * 96,485 * 1.24 = 239,282.8 J or 240 kJ.—

## Current through a Cell

- Now we are going to focus on the current that is the result of electrons traveling through a wire that connects to two half reactions.

- The flow of electrons can be thought of as water coming out of a garden hose. The rate of the water that comes out of the hose is analogous to the electrical current measured in amps (An amp has units of a C/s or coulomb per second). The force that the water comes out as is analogous to the EMF of the voltage.

- You can use the following equations that relates charge, current, and time.

Charge = Current * Time

Moles of electrons = Charge * ( 1 / F )

*Example-16*

How many amperes of electricity are needed to electrolyze $Ti^{2+}$ to Ti if 1.23 moles of Ti is produced in 4.6 seconds?

—The first thing we will do is figure out how many moles of electrons we have by writing out the reaction.—

$Ti^{2+} + 2e^{-}$ —> Ti

—To figure out how many moles of electrons we have we will multiply the number of moles of Ti we have by 2 because from the reaction 1 mole will require 2 electrons.—

( 2 electrons per mol of Ti ) * ( 1.23 moles of Ti) = 2.46 electrons per mol of Ti.

—If we know the moles of electrons we can multiply by faradays constant to get the charge—

Moles of electrons = Charge * ( 1 / F )

2.46 * 96,485 = 237,353.1 C

—The last step is to divide by the time to get the current.—

Charge = Current * Time

237,353.1 / 4.6 = 51,598.5 amps

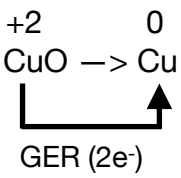
*Example-17*

Copper metal (63.546 g/mol) is purified by electrolysis. How much copper metal (in grams) could be produced from copper(II) oxide by applying a current of 10.0 amps at the appropriate negative potential for 12.0 hours?

—To figure out how many grams of copper metal is purified by electrolysis we need to write out the reaction.

CuO —> Cu

—The next thing we need to do it add in the electrons that are part of the reaction. We do this by assigning oxidation numbers.—




$CuO + 2e^- \rightarrow Cu$

—Notice that we only have a reduced half for this reaction and we do not have the oxidized half. We do not need the oxidized half of this reaction to solve this problem. By looking at the reduced half we can determine that for every 1 mole of Cu produced it will require 2 moles of electrons.—

—If we know the current and time (in seconds - which we will have to convert from 12 hours to seconds) we can find the charge.—

$$I = q / t$$

$$10 * 43200 = 432000 \text{ Coulombs}$$

—Now that we know the charge we need to find convert to moles of Cu then to grams of Cu. However, we first need to convert from the charge in coulombs to moles of electrons using Faraday's constant.—

$$\frac{432000 \text{ C}}{1} \times \frac{1 \text{ mole } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mole } e^-} \times \frac{63.546 \text{ g}}{1 \text{ mol Cu}} = 142.2 \text{ g}$$