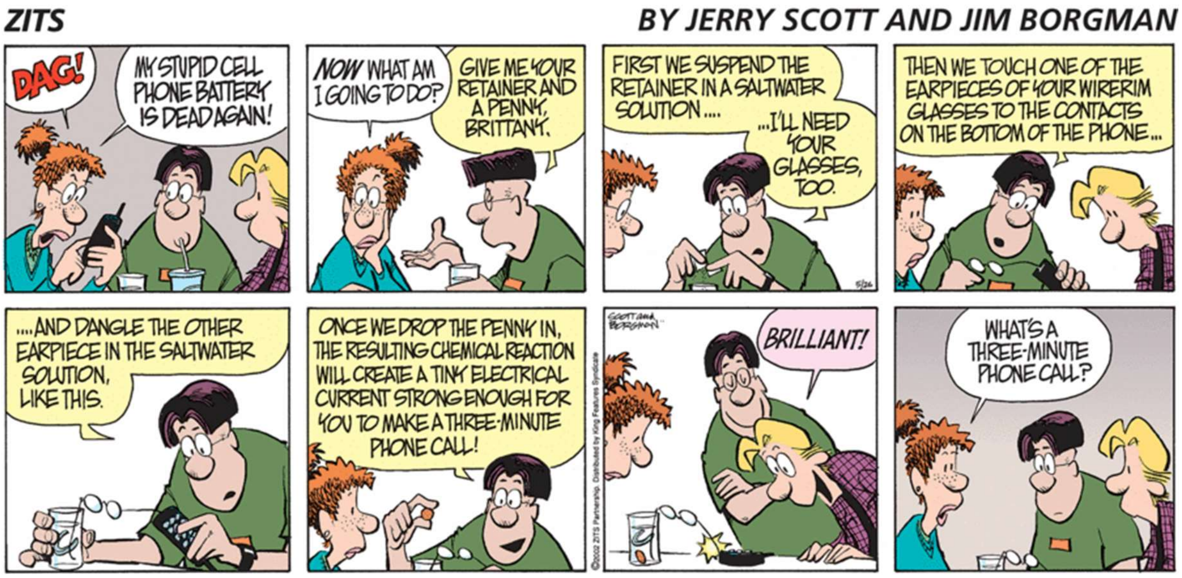
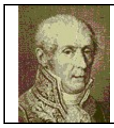


http://zitscomics.com/comics/may-26-2002/

Chemistry by Chang and Goldsby ~~19.01 Redox Reactions (covered in last unit)~~ 19.02 Galvanic Electrochemical Cells 19.03 Standard Reduction Potentials 19.04 Thermodynamic Favorability of Redox Reactions 19.05 The Effect of Concentration of Cell Emf ~~19.06 Batteries~~ ~~19.07 Corrosion~~ 19.08 Electrolysis in Electrolytic cells	I have posted a condensed version of Chang's 10th edition Chapter 19 on the classroom webpage that you can use with this outline.

	**Chapter 19 Electrochemistry** brought to you by Alessandro Volta	 Volta's battery, 1779

Normally redox reactions occur with the two substances are mixed together. The drop in potential energy is released in the electron transfer results in kinetic energy in the form of heat and light. However, redox reactions can occur if the reactants are physically separated if a conductive wire allows the redox electrons to move from one reactant to the other. The redox reaction will produce an electric current whose potential can be harnessed to do work. This is the fundamental reaction for all batteries.

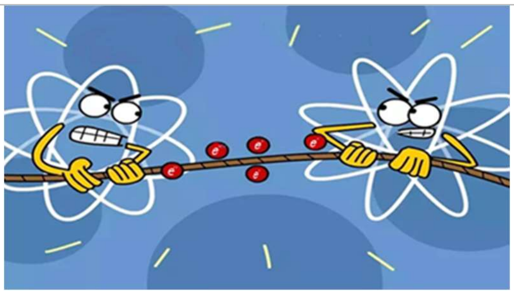
19.1 Redox Reactions

Covered in previous outline

19.2 Galvanic Electrochemical Cells Are Thermodynamically Favored Reactions

A galvanic electrochemical cell is an apparatus for generating an electric current using a thermodynamically favored oxidation-reduction reaction.

The galvanic cells consist of two separated cells called half-cells. Each container has a set of chemicals that can reduce and oxidize. The two half-cells are connected with an electrically conductive wire and a separate pathway for ions. When connected, the two sets of chemicals will have an attraction to the electrons of the wire. The two half-cells then undergo a reduction tug of war. The relative reduction strengths of the substances determine the winner in the tug of war for the electrons and, as a result, the electrons are moved through the wire.



Reduction tug of war

Skipping ahead to 19.3

19.3 Standard Reduction Potentials

In the tug of war for electrons, substances are ranked according to their ability to reduce (gain electrons). The method used to rank the substance reduction potential is a comparative one where the substances are pitted against a standard 1 M $H^+(aq)$ solution and where the hydrogen ions in the standard half-cell cell attempt to gain electrons from the substance to become hydrogen gas.

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

The substances can be solids, liquids, gases, cations, anions, and even polyatomic ions.

Either the hydrogen ion in the standard cell or the substance being evaluated will reduce, thus gaining electrons. The "winner" of the reduction tug of war will cause the weaker substance to oxidize and lose electrons.

Hydrogen ion reduces and other substance oxidizes Substance loses the electron tug of war		Substance reduces and hydrogen gas oxidizes Substance wins the electron tug of war
Wins electron2: $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$ Loses electron2: $X^{2+}(aq) + 2\ e^- \leftarrow X(s)$ Reaction of X^{2+} has a negative potential (voltage)	or	Wins electron2: $2\ Y^+(aq) + 2\ e^- \rightarrow 2\ Y(s)$ Loses electrons: $2\ H^+(aq) + 2\ e^- \leftarrow H_2(g)$ Reaction of Y^+ has a positive potential (voltage)

The reduction potential, E^o_{red}, is measured in joules per coulomb[1] of electrons, **J/C**, which is called the volt[2], **V**.

---

[1] 96,485 coulombs of electrons are equal to 1 mol of electrons.

[2] The volt is the potential energy change in joules for one coulomb of electrons.

Here are some examples of reduction potentials.

Half-Reaction	*Relative Reduction Potential* E^o (V)
$F_2(g) + 3\ e^- \rightarrow\ 2\ F^-(aq)$	2.87
$Au^{3+} + 3\ e^- \rightarrow Au(s)$	1.50
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$	0.96
$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$	0.00
$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$	-2.37
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.05

When any two half-reactions are combined,

(1) The **higher reduction potential half-reaction will reduce** → to form the products in the half-reaction.
(2) The **lower reduction potential half-reaction will have its products oxidized** ← back into its reactants.

A reduction table will allow you to predict the reaction and standard potential between any two substances listed on the table.
This is how to predict the reaction between acidified nitrate ions and magnesium:

Half-Reaction	*Relative Reduction Potential* E^o (V)
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$	0.96
$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$	-2.37

The **higher voltage** reduction reaction will occur as written →, a reduction.
The lower reaction will be reversed since it is oxidized.

Reduction: $NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$
Oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$

The electrons are balanced so that reduction equals oxidation and the two half- reactions are added to show the net reaction. IMPORTANT! When **multiplying reactions** to balance electrons, the **voltage will not change**[3].

$$2\ NO_3^-(aq) + 8\ H^+(aq) + 6\ e^- \rightarrow 2\ NO(g) + 4\ H_2O(l)$$

$$3\ Mg(s) \rightarrow 3\ Mg^{2+}(aq) + 6\ e^-$$

$$3\ Mg(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Mg^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$$

Magnesium metal reacts with nitric acid by being oxidized as the nitric acid[4] reduces. The drop in potential energy in this reaction is the difference between the two reduction potentials.

$E°_{rxn}$ = $E°$ higher reduction potential - $E°$ lower reduction potential
$E°_{rxn} = 0.96\ V - (-2.37\ V)$
$E°_{rxn} = 3.33\ V$

This potential is valid at standard conditions when the concentration of the solutions are 1 *M* and the pressure of the gas is 1 atm.

---

[3] Voltage is defined as energy per coulomb not per mol as written in the balanced reaction.

[4] Nitric acid is one of the most dangerous oxidizing agents. It will oxidize almost any substance that is capable of oxidization. If you spill it on your skin, you will lose electrons. It also produces a poisonous gas as it reduces.

NOTE! **When calculating $E°_{rxn}$, use the above equation with the reduction potentials in the table:**

(1) **Do not change the sign of the reduction potential.**

In some textbooks, the procedure for finding $E°_{rxn}$ or $E°_{cell}$ involves changing the sign of the oxidized reaction's voltage and adding the two potentials. I follow the convention that Chang and the AP Chem solutions show where the net voltage is found by subtracting the oxidized substance's reduction voltage from the reduced substance's reduction voltage.

(2) **Voltages are never multiplied in electrochemical calculations**.

The volt is defined as energy per coulomb of electrons, so $E°$ does not change if the coefficients in the balanced reaction change. Even if the half-reaction is tripled, the voltage stays the same.

Here is a more extensive reduction table.

Half-Reaction			
Cathode (Capable of Reducing →)		Anode (← Capable of Oxidizing)	$E°_{red}$ (V)
best at reducing → $F_2(g) + 2\,e^-$	→	$2\,F^-(aq)$	2.87
$Au^{3+}(aq) + 3\,e^-$	→	$Au(s)$	1.50
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	→	$2\,H_2O(l)$	1.23
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	→	$NO(g) + 2\,H_2O(l)$	0.96
$Ag^+(aq) + e^-$	→	$Ag(s)$	0.80
$Cu^{2+}(aq) + 2\,e^-$	→	$Cu(s)$	0.34
$2\,H^+(aq) + 2\,e^-$	→	$H_2(g)$	0.00
$Zn^{2+}(aq) + 2\,e^-$	→	$Zn(s)$	-0.76
$H_2O(l) + 2\,e^-$	→	$H_2(g) + 2\,OH^-(aq)$	-0.83
$Mg^{2+}(aq) + 2\,e^-$	→	$Mg(s)$	-2.37
$Li^+(aq) + e^-$	→	$Li(s)$ **best at oxidizing ←**	-3.05

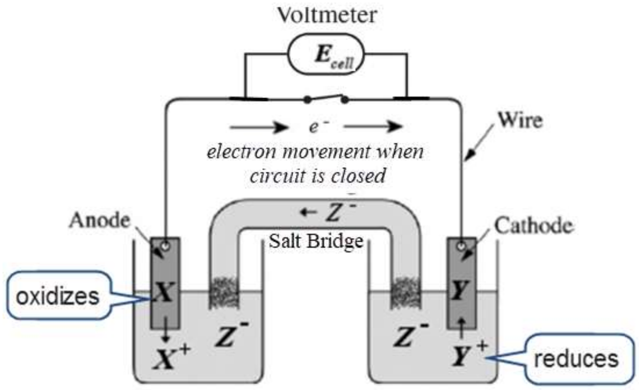
The higher half reaction will always go forward →
The lower half reaction will always reverse ←
The difference between the voltages in the reactions will be the net voltage of the reaction.

Now back to section 9.02

In a thermodynamically favored oxidation reduction reaction when the reactants are mixed, the reaction releases kinetic energy. The heat released can be used to do work. But if the reactants are kept separate and only allowed to react by losing and gaining electrons through an electrically conductive pathway such as a wire, the work of the reaction can be harnessed as electrical energy rather than heat.

A galvanic cell forces the electrons in redox reactions to go through a wire producing a current of electrons.

You must know every item in this diagram of a galvanic cell.

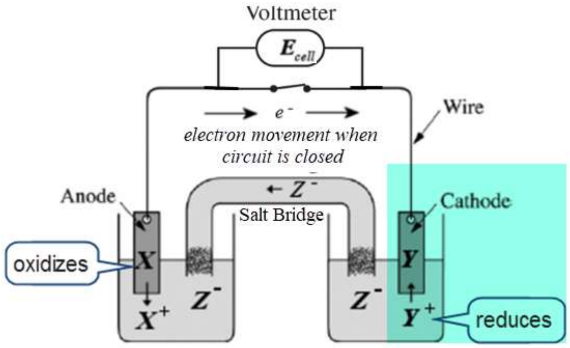


$X^+ + e^- \leftarrow X$ **Anode Oxidizes** (Z^- is a spectator ion) **Cathode Reduces** $Y^+ + e^- \rightarrow Y$

Net reaction: $X + Y^+ \rightarrow X^+ + Y$
The wire allows electrons to move toward the cathode.

The cathode is always the site of reduction.

- Mnemonic: fat cats must reduce
- The cathode's half-reaction always has the greater reduction potential.
- The cathode's reaction is the reduction reaction → on the reduction table.
- To reduce (gain electrons), electrons must flow through the wire toward the cathode.
- Typically, the cathode is shown as the reduced metal. In this case Y. However, the cathode can be any nonreactive conductive substance. The cathode is merely a surface for the Y^+ to reduce into Y.



For example, a cell that is made using gold ions and silver ions would result in a tug of war for the electrons. The gold ions with a greater reduction potential (pull) will win the tug of war and reduce to metallic gold at the cathode. Since only the gold ions in the cathode half-cell solution in this reaction are reducing, the cathode merely needs to be a conductive, nonreactive substance such as a graphite rod which will conduct electrons. As the reaction progresses, the cathode will be covered with metallic gold[5] atoms that were previously gold ions in solution.

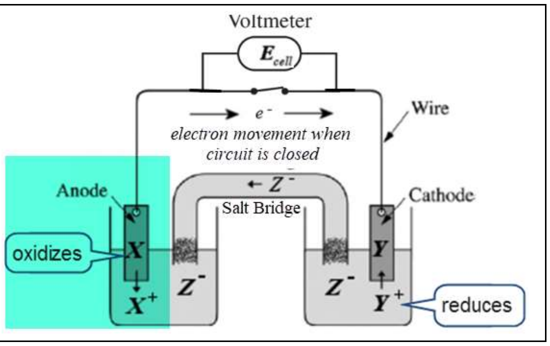
	Half-Reaction	E°_{red} (V)
Reduction at cathode	$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	1.50

---

[5] Reactions like this are used in plating substances in metals by reducing the metal ions to the metal on the cathode.

The anode is always the site of oxidation.

- Mnemonic: an-ox
- The anode's half-reaction always has the lower reduction potential.
- The anode's reaction is the oxidation reaction ← on the reduction table.
- To for the product of this half-reaction to oxidize (lose electrons), electrons must flow away from the anode through the wire.



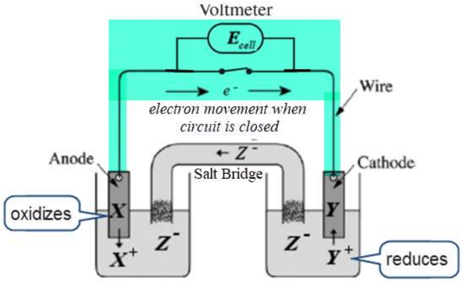
In the example of a gold-silver cell, metallic silver is the loser in the tug of war and oxidizes into silver ions at the anode. In contrast to the metallic gold plating on the cathode, the silver anode erodes as the metallic silver changes into silver ions. While the cathode can be used to metal plate, the anode can be used to etch or carve the metal at the anode.

	Half-Reaction	$E°_{red}$ (V)
Reduction at cathode	$Au^{3+}(aq) + 3\ e^-$ winner → $Au(s)$	1.50
Oxidation at anode	$Ag^+(aq) + e^-$ ← $Ag(s)$ loser	0.80

Net Reaction: $Au^{3+}(aq) + 3\ Ag(s) \rightarrow Au(s) + 3\ Ag^+(aq)$

Wire = external circuit where electron movement is always toward the cathode

- The external circuit allows electrons to move from the anode (oxidation) to the cathode (reduction).[6]
- A closed circuit is one where the switch is closed, and the electrons can flow through the circuit.
- An open circuit is one where the switch is open, and the electrons cannot flow.

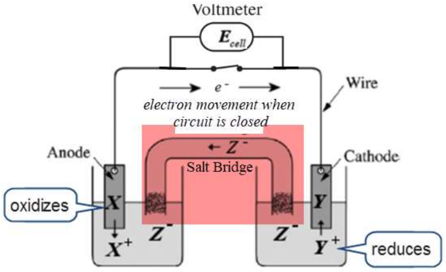


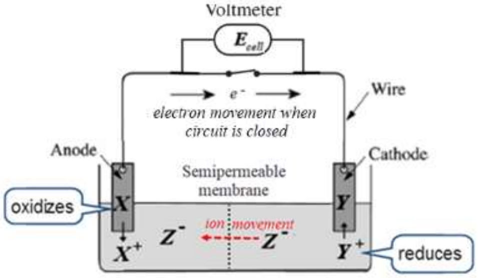
Salt Bridge = internal circuit for ion movement

- In a galvanic cell, the reacting substances are separated forcing the electrons to move through the wire rather than reacting directly with one another.
- The salt bridge allows for the movement of ions which balances the movement of electrons and balances the changes of the ion concentrations of the solutions.

A cell will not operate without a salt bridge.

- The direction of ion movement in a salt bridge is logical. Spectator anions are attracted to the anode, and spectator cations are attracted to the cathode.
- The salt bridge is usually shown as a tube with a conductive solution, but it can be a paste or a semipermeable membrane that keeps the two half-reactions separate, yet still allows the movement of ions.
- A salt bridge must be able to allow (*aq*) ions to move. A solid, electrically conductive wire cannot replace a salt bridge as only electrons move in a metal.





---

[6] Curiously, the convention for current direction, *I*, is defined as the opposite of the flow of electrons. You will not have to worry about that contradiction in chemistry.

As in all electrochemical reactions, the standard electrical potential, voltage, is the difference in the tug of war for the electrons. The values for the reduction potentials are subtracted, and the net potential will be the voltage for the cell.

	Half-Reaction	E^o_{red} (V)
Reduction at cathode	$Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$	1.50
Oxidation at anode	$Ag^{+}(aq) + e^- \leftarrow Ag(s)$	0.80

When the solutions are 1.0 *M* $Au^{3+}(aq) + 3\,Ag(s) \rightarrow Au(s) + 3\,Ag^{+}(aq)$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = 1.50\text{ V} - 0.80\text{ V}$$

$$E^\circ_{cell} = 1.50\text{ V} - 0.80\text{ V}$$

$$E^\circ_{cell} = 0.70\text{ V}$$

Caution! By far, the most common error in electrochemistry calculations involves signs.

The degree symbol with the voltage symbol, $E°$, which is used on the reduction tables means the voltage values of these reductions are based on standard conditions: 1 *M* solutions and 1 atm pressures for gases at 25°C. Changes in these concentrations are covered later in the unit.

All galvanic electrochemical cells have a positive voltage.

The **positive voltage, E^o_{cell}, represents a spontaneous (thermodynamically favored) reaction**.

A positive E^o_{cell} means that the cell can do work, ΔG = -, as the electrons go “downhill.”

A reaction with **a negative value E^o_{cell} will not take place unless it is forced** by an applied outside voltage. Cells that are forced to react push the electrons “uphill.” This type of electrochemical cell is called an electrolytic cell, the opposite of a galvanic cell. Electrolytic cells are covered in section 19.08.

In these examples cells are simply separate jars or solutions separated by a membrane. Modern batteries and cells keep the reducing and oxidizing species separate using sophisticated materials such as carbon nanotubes. Developing these new materials which were Nobel prize winning achievements have made batteries capable of become practical replacements for external oxidation reduction reactions. Without these materials the oxidation and reduction reactions would mix and spontaneous release potential their energy as heat. Battery fires are usually the result of failures of salt bridges.

Summarizing:

When calculating the standard potential of a galvanic cell using a reduction table:

1. Sort the half-reactions of the reduction table from high reduction voltage-top to low reduction voltage-bottom. Caution, reduction tables on the AP test may have an incorrect order.

2. The top rxn reduces →, the lower rxn oxidizes ←.

3. The reduced substance is the **reactant** of reaction shown on the reduction table (***<u>upper left</u>***).
   It reacts at the cathode as shown on the reduction table.

4. The oxidized substance is the **product** of the reaction shown on the reduction table **(*lower right*)**.
   It reacts at the anode in the opposite direction shown on the reduction table.

	Half-Reaction	E°_{red} (V)
Reduction at cathode	$Y^+ + e^- \rightarrow Y$	higher reduction potential
Oxidation at anode	$X^+ + e^- \leftarrow X$	lower reduction potential

5. The electromotive force is calculated using the listed reduction potentials with the equation:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$E^\circ_{cell} > 0$ is a galvanic cell which is thermodynamically favored.
If on balancing the redox reaction, you change the coefficients of a reduction or oxidation, E°_{cell} is not changed.
E°_{cell} is based on all the solutions being at 1 *M* and the gases at 1 atm.
E_{cell} decreases as [reactants] decreases and [products] increases.
Eventually the voltage will drop to zero when the reaction quotient, *Q*, equals the equilibrium constant, *K*.
E_{cell} is **not dependent** on of the size of the solid electrodes or the volume of the solutions used.

Every AP Chemistry exam has a question where you must determine the reaction from a reduction table. Typically, the reduction table given in the problem will not be sorted in order of reduction potential.

e.g.

Half-Reaction	E° at 25°C (V)
$Br_2 + 2e- \rightarrow 2\ Br^-$	1.07
$Cl_2 + 2e- \rightarrow 2\ Cl^-$	1.36
$I_2 + 2e- \rightarrow 2I^-$	0.53

Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2. Justify that the reaction is thermodynamically favorable by calculating the value of E° for the reaction.

To answer this FRQ you would first resort the table with the reduction values in descending order

Half-Reaction	E° at 25°C (V)
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	1.36
$Br_2 + 2\ e^- \rightarrow 2\ Br^-$	1.07
$I_2 + 2\ e^- \rightarrow 2I^-$	0.53

Highlight the desired substance, Br_2.

Half-Reaction	E° at 25°C (V)
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	1.36
$Br_2 + 2\ e^- \rightarrow 2\ Br^-$	1.07
$I_2 + 2\ e^- \rightarrow 2I^-$	0.53

Determine the direction of the reaction to make the desired substance.

Half-Reaction	E° at 25°C (V)
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	1.36
$Br_2 + 2\ e^- \leftarrow 2\ Br^-$	1.07
$I_2 + 2\ e^- \rightarrow 2I^-$	0.53

Then identify the reaction that would cause that reaction.

Half-Reaction	$E°$ at 25°C (V)
reduction rxn: $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	1.36
oxidation rxn: $Br_2 + 2\ e^- \leftarrow 2\ Br^-$	1.07
$I_2 + 2\ e^- \rightarrow 2I^-$	0.53

Combine the two half-reactions:

$$\begin{array}{rcl} Cl_2 + 2\ e^- & \rightarrow & 2\ Cl^- \\ 2\ Br^- & \rightarrow & Br_2 + 2\ e^- \\ \hline Cl_2 + 2\ Br^- & \rightarrow & 2\ Cl^- + Br_2 \end{array}$$

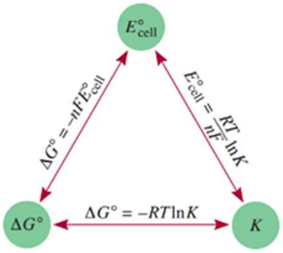
The reduction potential would be $E°_{rxn} = E°$ higher reduction potential - $E°$ lower reduction potential

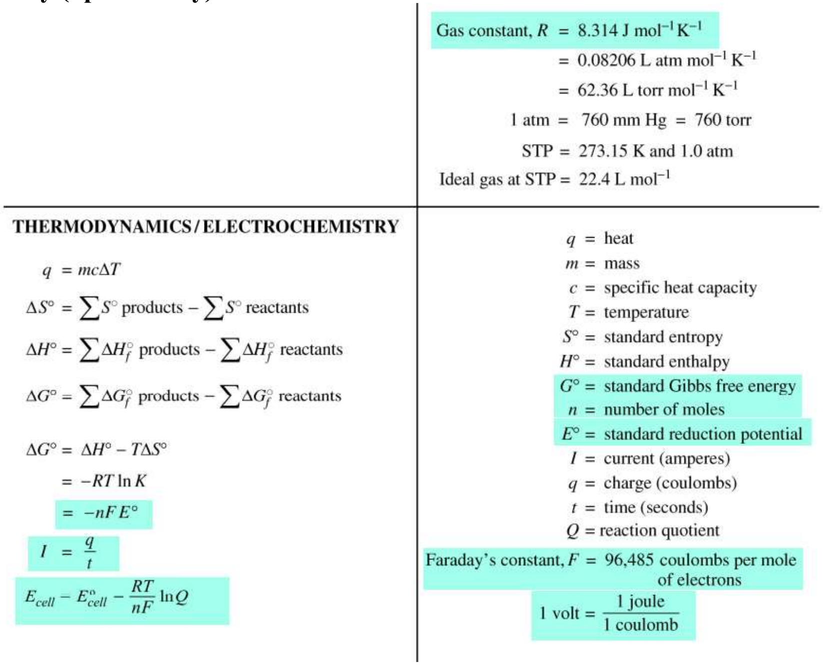
$$E°_{rxn} = 1.36\ \text{V} - 1.07\ \text{V}$$

$$E°_{rxn} = 0.30\ \text{V}$$

Next you will learn how to find the Gibbs free energy and equilibrium constant for this reaction.

19.04 Thermodynamically Favorability (Spontaneity) of Redox Reactions





Gas constant, $R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$
$= 0.08206\ \text{L atm mol}^{-1}\text{K}^{-1}$
$= 62.36\ \text{L torr mol}^{-1}\text{K}^{-1}$
1 atm = 760 mm Hg = 760 torr
STP = 273.15 K and 1.0 atm
Ideal gas at STP = $22.4\ \text{L mol}^{-1}$

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S° = \sum S° \text{ products} - \sum S° \text{ reactants}$$

$$\Delta H° = \sum \Delta H_f° \text{ products} - \sum \Delta H_f° \text{ reactants}$$

$$\Delta G° = \sum \Delta G_f° \text{ products} - \sum \Delta G_f° \text{ reactants}$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= -RT\ln K$$

$$= -nFE°$$

$$I = \frac{q}{t}$$

$$E_{cell} = E°_{cell} - \frac{RT}{nF}\ln Q$$

q = heat
m = mass
c = specific heat capacity
T = temperature
$S°$ = standard entropy
$H°$ = standard enthalpy
$G°$ = standard Gibbs free energy
n = number of moles
$E°$ = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
Q = reaction quotient
Faraday's constant, F = 96,485 coulombs per mole of electrons
$1\ \text{volt} = \frac{1\ \text{joule}}{1\ \text{coulomb}}$

The thermodynamic favorability of a galvanic cell can be calculated directly from the standard voltage of a reaction. The equation and Faraday's constant are both on the AP Chemistry equation sheet.

$$\Delta G° = -\ n\ F\ E°_{cell}$$

(1) Don't forget the negative sign in this equation.
(2) n is the number of moles of electrons exchanged in the balanced redox equation[7].
(3) F, Faraday's constant 96,485 coulombs per mole of e^-.
(4) $E°_{cell}$ is the standard voltage of the cell. A volt has the base units of J/C. **As a result, the calculated answer will be in J not kJ.**

---

[7] The multiplication by the moles of electrons is needed because the voltage does not include the coefficients of the rxn.

What is the standard Gibbs free energy of the reaction between the lithium and fluorine?

$$\mathrm{Li}(s) + \mathrm{F_2}(g) \rightarrow \mathrm{Li^+}(aq) + 2\mathrm{F^-}(aq)$$

		Half-Reactions	E^o_{red} (V)	
Cathode	F_2 is reducing	$F_2(g) + 2\,e^- \rightarrow 2\,F^-$	+2.87	
Anode		$Li^+ + e^- \leftarrow Li$	-3.05	Li is oxidizing

$$E°_{cell} = 2.87\text{ V} – (-3.05\text{ V}) = 5.92\text{ V}$$

The two half reactions $2\,e^- + F_2 \rightarrow 2\,F^-$
$2\,Li \rightarrow 2\,Li^+ + 2\,e^-$

Overall electron exchange of 2 electrons, $n = 2$

Net Reaction $2\,Li + F_2 \rightarrow 2\,Li^+ + 2\,F^-$

$\Delta G° = -\,n\,F\,E°_{cell}$
$\Delta G° = -\,2\,(96{,}485\text{ C/mol}) \times 5.92\text{ J/C} = 1140{,}000\text{ J/mol}$
$\Delta G° = -1140\text{ kJ/mol}$ notice how the units work out.

This is a large Gibbs free energy, far in excess of the rule of -25 kJ. Even a small standard voltage can produce large equilibrium constant.

KNOW and UNDERSTAND THIS TABLE which is premised on all species staring at 1 *M*.

$\Delta G°$	*K*	$E°_{cell}$	Starting with reactants and products as 1 *M* solutions and 1 atm pressures
Negative	Greater than 1	Positive	Thermodynamically favored reaction Reaction progresses forward → to increase the concentration of the products.
Zero	1	0	Reaction is at equilibrium No work can be done ⇆
Positive	Less than 1 (greater than 0)	Negative	Forward reaction not thermodynamically favored. Reaction progresses in reverse direction ← to decrease the product concentrations.

19.05 The Effect of Concentration of Cell *Emf*

Voltages on a reduction table are for standard conditions $E°$ (1 atm , 1.0 *M* , 25°C) and the potentials will change as a cell operates and the solution concentrations increase at the anode and decrease at the cathode.

Nonstandard E_{cell} voltages occur when the concentration of the reactants and products are not 1 *M* or 1 atm.

You will be expected to predict and justify the change in standard voltage for a cell that is not at standard conditions.

Since cathodes and anodes are most often solids, you can ignore them for changes in voltages. Solid amounts will change, but their concentration does not. Just like in equilibrium problems, solids are ignored.

The best method of explaining changes from the standard voltage is based on the Nernst equation which is on the AP Equation sheet.

How to predict and justify nonstandard conditions for Galvanic cells using the Nernst Equation.

(1) Find the standard voltage of the cell, E^o, based on 1 M solution concentrations and 1 atm gas pressures using data from a standard reduction table.

$$E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}}$$

(2) Determine the net reaction by combining the reduction and oxidation half- reactions.

(3) Determine which substances are in the equilibrium quotient, Q, from the net reaction. Only include the substances (solutions and gases) whose concentrations can be changed. **Solids (usually the cathode and anode) are not included in the quotient ratio.**

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Typically, [Products] will be the anode solution and the [Reactants] will be the cathode solution.

(4) Use Q in the Nernst equation to show the direction of change from the standard voltage.
The equation sheet uses RT as the numerator of the log multiplier. Since these cells are almost always run at standard conditions RT will be the same value for 99% of the problems.

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

$$E_{cell} = E^\circ_{cell} - \frac{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{\text{n} \times 96{,}485 \text{ C/mol}} \ln Q$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0257 \text{ V}}{n} \ln Q$$

n is the number of moles of electrons exchanged in the balanced reaction.

Therefore, the multiplier of the natural log, $\frac{0.0257 \text{ V}}{n}$, will always be positive.

You will not have to calculate the new voltage for the AP Chem exam.
However, the equation can be used as the explanation for justifying an answer for predicting the increase or decrease of a voltage because of nonstandard concentrations.

If Q is less than 1, the reactants are supercharged.
Therefore, ln Q will be negative, and the voltage will increase.

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{REACTANTS}]}$$

$$E_{cell} = E^\circ_{cell} - (\text{negative number})$$

$$E_{cell} = \textit{increases}$$

Or if Q is greater than 1, the products dominate.
Therefore, log Q will be positive, and the voltage will decrease.

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[\text{PRODUCTS}]}{[\text{reactants}]}$$

$$E_{cell} = E^\circ_{cell} - (\text{positive number})$$

$$E_{cell} = \textit{decreases}$$

If you understand logs and can remember the Nernst equation, you’re all set.

Alternately, you can justify changes in nonstandard voltages using the reaction quotient, Q and K_{eq}.

This will require a longer explanation. Use a pen because you will be writing a lot.

A galvanic cell has a positive E° which produces a very large K_{eq}. For example, a voltage of just 1 V will have a $K_{eq} \approx 10^{16}$.

As the cell operates, the voltage of a cell will decrease. This is because the decrease in concentration of the reactants and the simultaneous increase in concentrations of the products causes the reaction quotient to approach the equilibrium constant. As the reaction quotient, Q, approaches the K_{eq}, the electromotive potential, the voltage, will gradually drop and become zero when $Q = K_{eq}$.

Description of Concentrations	Equilibrium Quotient		Voltage Compared to Standard E°
High concentration of reactants with very little product. Lots of reactant.	$Q = \frac{[\text{Products}]}{\mathbf{[REACTANTS]}} < 1$	Q is less than standard conditions and voltage is increased since Q is even farther from K than standard voltage.	$E > E^{\circ}$
Equal concentrations of reactant and products. **Standard Conditions**	$Q = \frac{[\text{Products}]}{[\text{Reactants}]} = 1$	The ratio of 1 for Q is the basis for the standard voltage. So you get what you expect from the table	$E = E^{\circ}$
Concentration of reactants is less than that of products. You are running out of reactant.	$Q = \frac{\mathbf{[PRODUCTS]}}{[\text{Reactants}]} > 1$	Q is approaching the equilibrium and voltage is decreased since Q is closer to K than standard voltage.	$E < E^{\circ}$
The concentration of reactants is low enough and products high enough that **equilibrium** has been reached.	$Q = \frac{\Large[\text{PRODUCTS}]}{\small[\text{reactants}]} = K_{eq}$	Equilibrium has been reached and no work can be done.	$E = 0$ V

Summarizing

If $Q = \frac{[\text{\scriptsize Products}]}{[\text{Reactants}]}$ *causes* E_{cell} *to have higher voltages* $\rightarrow\rightarrow$ *until* $Q = 1$ *resulting in* $E_{cell} = E^{\circ}$ (standard voltage)

If $Q == \frac{[\text{Products}]}{[\text{\scriptsize Reactants}]}$ *causes* E_{cell} *to have lower voltages* $\rightarrow\rightarrow$ *until* $Q = K_{eq}$ *resulting resulting in equilibrium and* $E_{cell} = 0$ V

In multiple choice questions where you only pick an answer, you can quickly and accurately predict the shift in the reaction by using the deviations in concentration and Le Châtlier's principle.

Reactants greater than 1 M or products less than 1 M result in a forward shift, →, increasing voltage
Reactants less than 1 M or products more than 1 M result in a reverse shift , ←, decreasing voltage

If all that is required is an answer for a voltage prediction, Le Châtlier's principle is a fast, reliable way of predicting voltage changes.

CAVEAT !

You cannot use Le Châtlier's principle to justify or explain changes in voltage on FRQ's!
AP refuses to allow Le Châtlier's principle for an explanation. Instead, you must use the Nernst equation or Q's relationship with K.

Concentration cells

So far there have never been any questions on concentration shells, but they are listed in the curriculum. So, you should at least know the principles involved.

A concentration cell has the same substances in both cells. So, the standard voltage will be 0 V.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln\frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{cell} = 0.00\text{ V} - \frac{RT}{nF}\ln\frac{[\text{products}]}{[\text{reactants}]}$$

$$\text{if } [\text{products}] = [\text{reactants}],\ \ln\frac{[\text{products}]}{[\text{reactants}]} = \ln 1 = 0$$

$$E_{cell} = 0.00\text{ V} - 0.00\text{V}$$

However, if the concentrations of the reactant and product solutions are different, the ln of Q would not be zero and you will have the reactions progress to equalize their concentrations. For AP you will not have to calculate the voltage, just determine the direction of the reaction.

Concentration cells are responsible for nerve impulses. The sodium and potassium ions are pumped through channels in cell walls so that there are higher concentrations of one side of the cell wall than the other. This results in a potential difference which can be used to trigger an electrical nerve impulse. The concentrations of electrolytes are critical.
Here's the resting voltage of cell ready to discharge.

Reactant 140 n*M* K^+ inside of cell wall
Product 5 n*M* K^+ outside of cell wall

$$E_{cell} = -\frac{RT}{nF}\ln\frac{[5\text{ m}M]\text{ K}^+}{[140\text{ m}M]\text{ K}^+}$$

$$E_{cell} = 0.09\text{ V}$$

Reaction will proceed so ion concentrations are equal.

EEG's and EKG's are used to detect these impulses. Your thoughts are electrochemical cell reactions. You're thoughts electrochemical cells learning about electrochemical cells.

19.06 Batteries – not in curriculum

19.07 Corrosion – not in curriculum

19.08 Electrolysis in Electrolytic cells

Electrolytic cells use an outside electric current to produce substances through reduction and oxidation reactions.

Electrolysis is NOT thermodynamically favored.
An external force must move the electrons for these reactions.

Galvanic cells: E_{cell} is positive, the substance reducing has the higher reduction potential.
ΔG is negative.
K is greater than 1 (usually greater than 1000).

Electrolytic cells: E_{cell} is negative, the substance reducing has the lower reduction potential.
ΔG is positive.
K, while still a positive number, is less than 1 (usually smaller than 0.001)

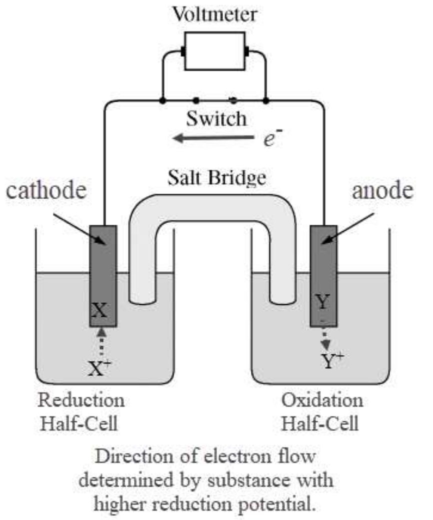
The cathode is still the site of reduction, the anode is still the site of oxidation, and the electrons move from the anode to the cathode.

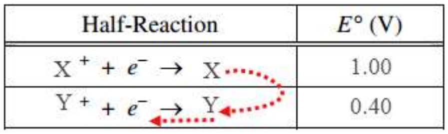
Electrolytic cells are not thermodynamically favored so an outside voltage (force) must be applied to make the electrons move from the anode to the cathode.

The lightbulb or ammeter in the cell diagram of a galvanic cell is replaced by a battery or other direct current power source that does work to electrolyze the substances in the cell.

Compare the two types of electrochemical cells.

Galvanic cells:

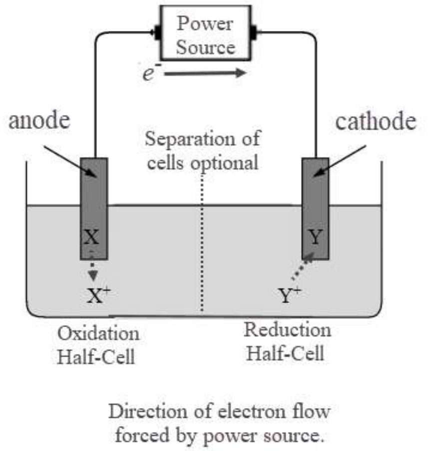


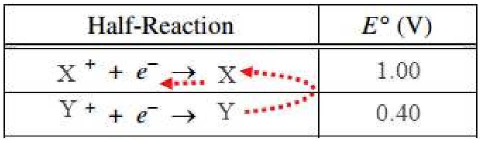


Half-Reaction	$E°$ (V)
$X^+ + e^- \rightarrow X$	1.00
$Y^+ + e^- \rightarrow Y$	0.40

$X^+ + Y \rightarrow X + Y^+$ $E°_{cell} = +0.60$ V

Electrolytic Cell





Half-Reaction	$E°$ (V)
$X^+ + e^- \rightarrow X$	1.00
$Y^+ + e^- \rightarrow Y$	0.40

$X + Y^+ \rightarrow X^+ + Y$ $E°_{cell} = -0.60$ V

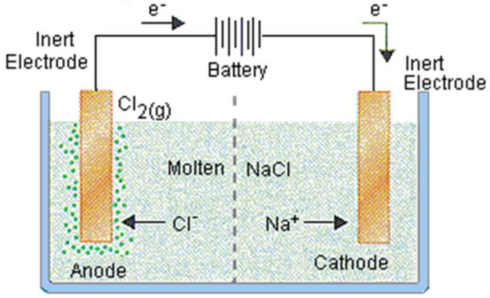
Electrolytic cells involving molten ionic substances (the most common electrolysis questions on the AP test)

Ionic salt melts can be converted into their elemental forms in an electrolytic cell.
The ionic compound must be molten to conduct electricity.
An electrolytic cell does not require a salt bridge.

Anode attracts anions for oxidizing: $Cl_2 + 2\,e^- \leftarrow 2\,Cl^-$ $E^o_{ox} = +1.36$ V
Cathode attracts the cations for reducing: $2\,Na^+ + 2\,e^- \rightarrow 2\,Na$ $E^o_{red} = -2.71$ V

The net reaction is $2\,Na^+ + 2\,Cl^- \rightarrow 2\,Na + Cl_2$ $E^o_{cell} = -4.07$ V

Again, electrolytic cells have a negative voltage and are not thermodynamically favored.
So, the electrons are forced to move by a power source, a battery[8].
The direction of electron flow is the same as in a galvanic cell, from anode (oxidation) to cathode (reduction).



Electrolysis of Water

The redox equations for water for are complicated and all the half-reactions would be given in any question involving the electrolysis of water. You will just be responsible for manipulating them (reverse one and perhaps multiply to balance electrons.)

Anode : Oxidation of water $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^-$

Cathode Reduction of water $2\times(2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-)$

The addition of the two half-reactions $6\,H_2O \rightarrow 2\,H_2 + 4\,OH^- + O_2 + 4\,H^+$

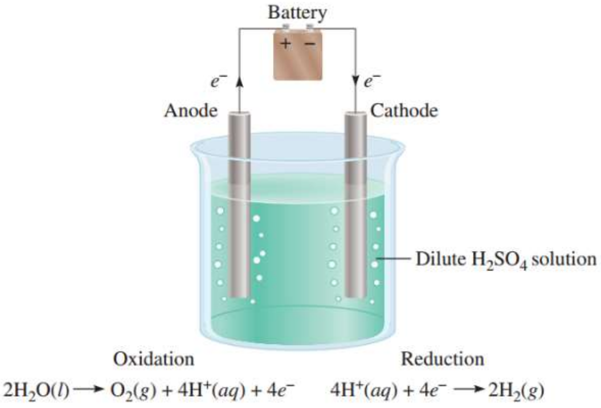
At the cathode where the hydrogen gas is produced (reduction), the solution becomes alkaline.

At the anode where the oxygen gas is produced (oxidation), the solution becomes acidic.

When mixed, $4\,OH^- + 4\,H^+ = 4\,H_2O$

Net Reaction: $6\,H_2O \rightarrow 2\,H_2 + O_2 + 4\,H_2O$

For the electrolysis of water to be effective, the reaction must occur in a conducting solution.



---

[8] While the E^o_{cell} can predict the thermodynamics of the reaction, the actual voltages that are required to force this reaction usually are in excess of the predicted voltage of the cell.

Electrolysis of Ionic Aqueous Solutions (you can skip this section)

The only electrolysis reactions involving aqueous solutions will be plating reactions where the oxidation and reduction reactions are simple. So, you will not have to know the complex reactions involved in aqueous electrolysis.

Quantitative Aspects of Electrolysis

$I = \frac{q}{t}$

I = current (amperes)
q = charge (coulombs)
t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$

These are very common on the FRQ's. So, even though this is at the end of the chapter, it is worth your attention.

q, coulombs are numbers of electrons, C.

F, 1 faraday = 96,485 C = 1 mole of electrons

Current, *I*, is tricky since amperes, A, are coulombs per second, C/*s*, which is not listed on the equation sheet.

I = amps whose symbol is A but is actually C/*s*

In most quantitative electrolytic problems, you are given time and current and need to find the moles of electrons:

$$\text{mol } e^- = \frac{I \times \text{seconds}}{96{,}485 \text{ C/mol}} \text{ is a useful equation to remember}$$

I must be in amps and *time* must be in seconds.

Note: In almost all AP questions, time is given in hours because it takes a long time to make an appreciable amount of product using electrolysis.

Once you know the moles of electrons used in the electrolysis, you can use the stoichiometry of the reaction (ratio of mol of electrons to mol of substance) to find the mol of substance produced.

The stoichiometry in most FRQ's is not 1:1. So you will need to divide the mole of electrons by a stoichiometric value of the number of electrons in the reduction reaction.

These are common FRQ problems because they combine stoichiometry with electrochemistry.
The next question is as complicated as these get. If you can do this problem, you are all set.

A gold(III) cyanide solution has 2.50 amps of current run through it for 3.00 hours. How much elemental gold would be produced at the cathode?

$$\text{Au}^{3+}(aq) + 3\,e^- \rightarrow \text{Au}(s)$$

$$\text{mol } e^- = \frac{I \times t}{96{,}485 \text{ C/mol}}$$

$$\frac{\left(\frac{2.50 \text{ C}}{\text{second}} \times 3.00 \text{ hour} \times \frac{3{,}600 \text{ seconds}}{\text{hour}}\right)}{96{,}485 \text{ C/mol } e^-} = 0.280 \text{ mol } e^-$$

$$0.280 \text{ mol } e^- \times \frac{1\text{Au}}{3\,e^-} = 0.0933 \text{ mol Au}$$

Three hours of electrolysis will only produce 18 g of gold (less than 1 cm^3)