Terms to Know:

      Electrochemistry—the study of the interchange of chemical and electrical energy
      OIL RIG – oxidation is loss, reduction is gain (of electrons)
      Oxidation – the loss of electrons, increase in charge
      Reduction – the gain of electrons, reduction of charge
      Oxidation number – the assigned charge on an atom
      Oxidizing agent (OA) – the species that is reduced and thus *causes* oxidation
      Reducing agent (RA) – the species that is oxidized and thus *causes* reduction

ELECTROCHEMISTRY INVOLVES TWO MAIN TYPES OF PROCESSES:
    A. **Galvanic (voltaic) cells** – which are spontaneous chemical reactions (battery)
    B. **Electrolytic cells** – which are non-spontaneous and require external e^- source (DC power source)
    C. BOTH of these fit into the category entitled **Electrochemical** cells

GALVANIC CELLS

Parts of the voltaic or galvanic cell:
- Anode--the electrode where oxidation occurs. After a period of time, the anode may appear to become smaller as it falls into solution.
- Cathode-- the anode where reduction occurs. After a period of time it may appear larger, due to ions from solution plating onto it.
- inert electrodes—used when a gas is involved OR ion to ion involved such as Fe^{3+} being reduced to Fe^{2+} rather than Fe^0. Made of Pt or graphite.
- Salt bridge -- a device used to maintain electrical neutrality in a galvanic cell. This may be filled with agar which contains a neutral salt or it may be replaced with a porous cup.
- Electron flow -- always from anode to cathode. (through the wire)
- Standard cell notation (line notation) - anode/solution// cathode solution/ cathode   Ex. Zn/Zn^{2+} (1.0 *M*) // Cu^{2+} (1.0 *M*) / Cu
- Voltmeter - measures the cell potential (*emf*) . Usually is measured in volts.
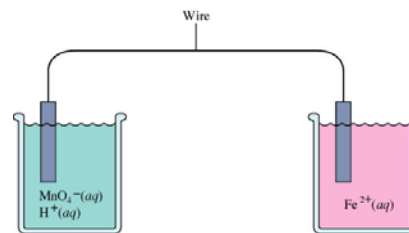
Balance this re-dox reaction:
MnO_4^- + Fe^{2+} → Mn^{2+} + Fe^{3+} [acidic]

RED:
OA:

OX:
RA

Overall rxn:

- If we place MnO_4^- and Fe^{2+} in the same container, the electrons are transferred directly when the reactants collide. No useful work is obtained from the chemical energy involved which is instead released as heat!
- We can harness this energy if we separate the oxidizing agent from the reducing agent, thus requiring the e^- transfer to occur through a wire! We can harness the energy that way to run a motor, light a bulb, etc.
- Sustained electron flow cannot occur in our first picture. Why not? As soon as electrons flow a separation of charge occurs which stops the flow of electrons. How do we fix it?
- **salt bridge**—it's job is to balance the charge using an electrolyte [usually in a U-shaped tube filled with agar that has the salt dissolved into it before it gels]. It connects the two compartments, ions flow from it, AND it keeps each "cell" neutral. Use KNO_3 as the salt when constructing your own diagram so that no precipitation occurs!
- **porous disk or cup**—also allows both cells to remain neutral by allowing ions to flow.
- **cell potential**—E_{cell}, *Emf*, or ε_{cell}—it is a measure of the electromotive force or the "pull" of the electrons as they travel from the anode to the cathode [more on that later!]
  - **volt (V)**—the unit of electrical potential; equal to 1 joule of work per coulomb of charge transferred
  - **voltmeter**—measures electrical potential; some energy is lost as heat [resistance] which keeps the voltmeter reading a tad lower than the actual or calculated voltage. Digital voltmeters have less resistance. If you want to get picky and eliminate the error introduced by resistance, you attach a variable-external-power source called a **potentiometer**. Adjust it so that zero current flows—the accurate voltage is then equal in magnitude but opposite in sign to the reading on the potentiometer.
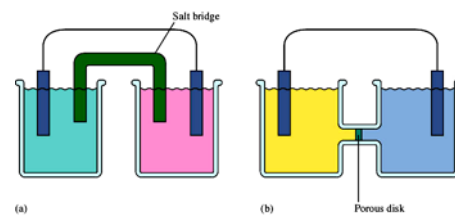
STANDARD REDUCTION POTENTIALS

- Each half-reaction has a cell potential
- Each potential is measured against a standard which is the standard hydrogen electrode [consists of a piece of inert Platinum that is bathed by hydrogen gas at 1 atm]. **The hydrogen electrode is assigned a value of ZERO volts**.
- **standard conditions**—1 atm for gases, 1.0M for solutions and 25°C for all (298 K)
- **naught, °**--we use the naught to symbolize standard conditions [Experiencing a thermo flashback?] That means E_{cell}, *Emf*, or ε_{cell} become E_{cell}°, *Emf*$^{\circ}$, or $\varepsilon_{cell}^{\circ}$ when measurements are taken at standard conditions. You'll soon learn how these change when the conditions are non-standard!
- The diagram to the right illustrates what really happens when a Galvanic cell is constructed from zinc sulfate and copper(II) sulfate using the respective metals as electrodes.
  - Notice that 1.0 M solutions of each salt are used
  - Notice an overall voltage of 1.10 V for the process
  - Reading the reduction potential chart
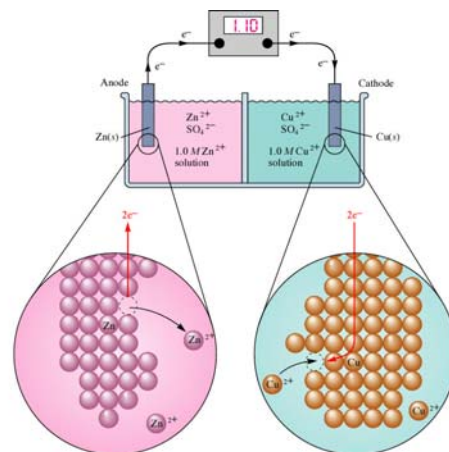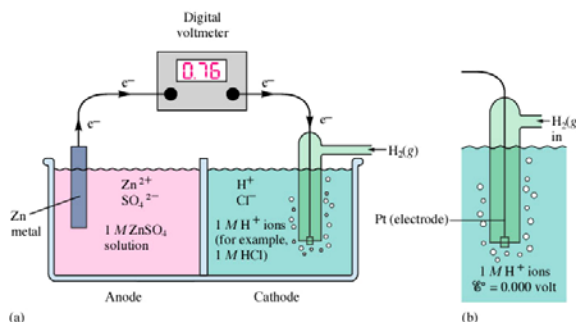
☞ elements that have the *most positive reduction potentials are easily reduced* (in general, non-metals)
☞ elements that have the least positive reduction potentials are easily oxidized (in general, metals)
☞ The table can also be used to tell the strength of various oxidizing and reducing agents.
☞ Can also be used as an activity series. Metals having less positive reduction potentials are more active and will replace metals with more positive potentials.

HOW CAN WE DETERMINE WHICH SUBSTANCE IS BEING REDUCED AND WHICH IS BEING OXIDIZED??

The MORE POSITIVE reduction potential gets to indeed be reduced IF you are trying to set up a cell that can act as a battery.

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°(V)$
$F_2(g) + 2\,e^-$	→	$2\,F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3\,e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2\,e^-$	→	$2\,Cl^-$	1.36
$O_2(g) + 4\,H^+ + 4\,e^-$	→	$2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	→	$2\,Br^-$	1.07
$2\,Hg^{2+} + 2\,e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2\,e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2\,e^-$	→	$2\,Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2\,e^-$	→	$2\,I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2\,e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2\,e^-$	→	Sn^{2+}	0.15
$S(s) + 2\,H^+ + 2\,e^-$	→	$H_2S(g)$	0.14
$2\,H^+ + 2\,e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2\,e^-$	→	$Pb(s)$	−0.13
$Sn^{2+} + 2\,e^-$	→	$Sn(s)$	−0.14
$Ni^{2+} + 2\,e^-$	→	$Ni(s)$	−0.25
$Co^{2+} + 2\,e^-$	→	$Co(s)$	−0.28
$Tl^+ + e^-$	→	$Tl(s)$	−0.34
$Cd^{2+} + 2\,e^-$	→	$Cd(s)$	−0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	−0.41
$Fe^{2+} + 2\,e^-$	→	$Fe(s)$	−0.44
$Cr^{3+} + 3\,e^-$	→	$Cr(s)$	−0.74
$Zn^{2+} + 2\,e^-$	→	$Zn(s)$	−0.76
$Mn^{2+} + 2\,e^-$	→	$Mn(s)$	−1.18
$Al^{3+} + 3\,e^-$	→	$Al(s)$	−1.66
$Be^{2+} + 2\,e^-$	→	$Be(s)$	−1.70
$Mg^{2+} + 2\,e^-$	→	$Mg(s)$	−2.37
$Na^+ + e^-$	→	$Na(s)$	−2.71
$Ca^{2+} + 2\,e^-$	→	$Ca(s)$	−2.87
$Sr^{2+} + 2\,e^-$	→	$Sr(s)$	−2.89
$Ba^{2+} + 2\,e^-$	→	$Ba(s)$	−2.90
$Rb^+ + e^-$	→	$Rb(s)$	−2.92
$K^+ + e^-$	→	$K(s)$	−2.92
$Cs^+ + e^-$	→	$Cs(s)$	−2.92
$Li^+ + e^-$	→	$Li(s)$	−3.05

Table 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathcal{E}°$ (V)	Half-Reaction	$\mathcal{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Calculating Standard Cell Potential Symbolized by $E°_{cell}$ OR *Emf°* OR$\varepsilon_{cell}°$ [I'll mix and match!]
1. Decide which element is oxidized or reduced using the table of reduction potentials. Remember: **THE MORE POSITIVE REDUCTION POTENITAL GETS TO BE REDUCED**.
2. Write both equations AS IS from the chart with their voltages.
3. Reverse the equation that will be oxidized **and change the sign of the voltage** [this is now $E°_{oxidation}$]
4. Balance the two half reactions **do not multiply voltage values**
5. Add the two half reactions and the voltages together.
6. $E°_{cell} = E°_{oxidation} + E°_{reduction}$ ° means standard conditions: 1atm, 1M, 25°C

Neumonic Devices that come in handy when constructing spontaneous cell--one that can act as a battery:

    AN OX – oxidation occurs at the anode (may show mass decrease)

    RED CAT – reduction occurs at the cathode (may show mass increase)

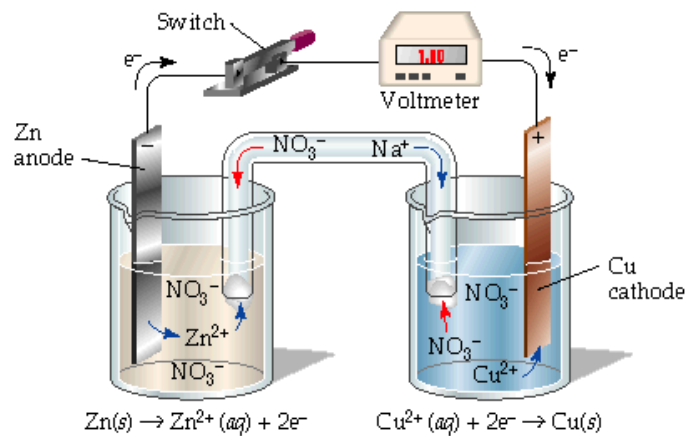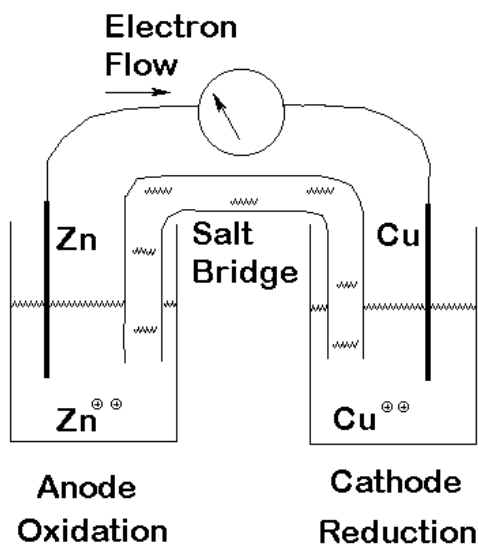   **FAT CAT** – The electrons in a voltaic or galvanic cell ALWAYS flow
                From the **A**node **T**o the **CAT**hode

    Ca⁺hode – the cathode is + in galvanic (voltaic) cells

    Salt Bridge – bridge between cells whose purpose is **to provide ions to balance the charge**.
   Usually made of a salt filled agar (KNO_3) or a porous cup.

EPA--in an **e**lectrolytic cell, there is a **p**ositive **a**node.

Electron Flow

Zn | Salt Bridge | Cu

Zn ⊕ ⊕

Anode
Oxidation

Cathode
Reduction

Switch

Voltmeter 1.10

Zn anode

NO_3^- Na^+

NO_3^-
Zn^{2+}
NO_3^-

NO_3^-
NO_3^-
Cu^{2+}

Cu cathode

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

ANIONS from the salt move to the anode while CATIONS from the salt move to the cathode!

Exercise 1

a. Consider a galvanic cell based on the reaction

$$Al^{3+}(aq) + Mg(s) \rightarrow Al(s) + Mg^{2+}(aq)$$
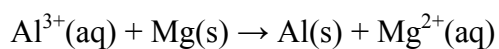
Give the balanced cell reaction and calculate $E°$ for the cell.

b. A galvanic cell is based on the reaction [you'll need a more complete table of reduction potentials!]

$$MnO_4^-(aq) + H^+(aq) + ClO_3^-(aq) \rightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$
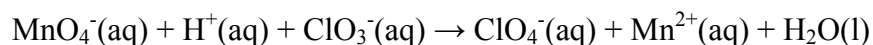
Give the balanced cell reaction and calculate $E°$ for the cell.

A: 0.71 V
B: 0.32 V

LINE NOTATION

Standard cell notation (line notation) – "Ion sandwich" in alphabetical order

Anode metal/anode ion//cathode ion//**C**athode metal
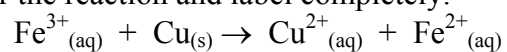
For Reaction: $M + N^+ \rightarrow N + M^+$

      Anode || Cathode   (alphabetical order!)

M(electrode)|M^+ (solution)|| N^+ (solution)|N(electrode)

| - indicates phase boundary

|| - indicates salt bridge

EX: Zn / Zn^{2+} (1.0 *M*)// Cu^{2+} (1.0 *M*) / Cu

Sample Problem: Calculate the cell voltage for the following reaction. Draw a diagram of the galvanic cell for the reaction and label completely.

       $Fe^{3+}_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + Fe^{2+}_{(aq)}$

Exercise 2
Calculate the cell voltage for the galvanic cell that would utilize silver metal and involve iron(II) ion and iron(III) ion. Draw a diagram of the galvanic cell for the reaction and label completely.

$E°_{cell}= 0.03$ V

CELL POTENTIAL, ELECTRICAL WORK & FREE ENERGY

Combining the thermodynamics and the electrochemistry, not to mention a bit of physics:
- The work that can be accomplished when electrons are transferred through a wire depends on the "push" or *emf* which is defined in terms of a potential difference [in volts] between two points in the circuit.

$$emf(V) = \varepsilon = \frac{work(J)}{charge(C)}$$

   - Thus one joule of work is produced [or required] when one coulomb of charge is transferred between two points in the circuit that differ by a potential of one volt
     - ➢ IF work flows OUT it is assigned a MINUS sign
     - ➢ When a cell produces a current, the cell potential is positive and the current can be used to do work THEREFORE ε and work have opposite signs!

$$\varepsilon = -\frac{work(J)}{charge(C)} = \frac{-w}{q} \therefore -w = \varepsilon q$$

   - ➢ **faraday(F)**—the charge on one MOLE of electrons = 96,485 coulombs (AP Exam uses 96,500)
   - ➢ q = # moles of electrons × F
   - For a process carried out at constant temperature and pressure, w_{max} [neglecting the very small amount of energy that is lost as friction or heat] is equal to ΔG, therefore….

$$\Delta G° = -nFE°$$

G = Gibb's free energy
n = number of moles of electrons
F = Faraday constant 9.6485309×10^4 J/V • mol

So it follows that:

$-E^o$ implies **non**spontaneous.

$+E^o$ implies spontaneous (would be a good battery!)
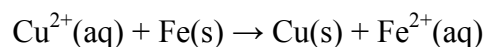
Strongest Oxidizers are weakest reducers.

As $E^o \downarrow$ reducing strength $\uparrow$.

As $E^o \uparrow$ oxidizing strength $\uparrow$.

Exercise 3

Using the table of standard reduction potentials, calculate ΔG° for the reaction

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

Is this reaction spontaneous?

= **yes**

Exercise 4

Using the table of standard reduction potentials, predict whether 1 M HNO_3 will dissolve gold metal to form a 1 M Au^{3+} solution.
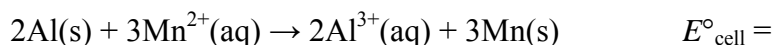
= **no**

DEPENDENCE OF CELL POTENTIAL ON CONCENTRATION

   Voltaic cells at NONstandard conditions: LeChatlier's principle can be applied. An increase in the concentration of a reactant will favor the forward reaction and the cell potential will increase. The converse is also true!

Exercise 5
For the cell reaction

$$2Al(s) + 3Mn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Mn(s) \qquad E°_{cell} =$$

predict whether E_{cell} is larger or smaller than $E°_{cell}$ for the following cases.

a. $[Al^{3+}] = 2.0\ M$, $[Mn^{2+}] = 1.0\ M$
b. $[Al^{3+}] = 1.0\ M$, $[Mn^{2+}] = 3.0\ M$

A: <
B: >

For a more quantitative approach…..
When cell is not at standard conditions, use **Nernst Equation**:

$$E = E° - \frac{RT}{nF}\ln Q$$

R = Gas constant 8.315 J/K• mol
F = Faraday constant
Q = reaction quotient $[products]^{coefficient}/[reactants]^{coefficient}$
E = Energy produced by reaction
T = Temperature in Kelvins
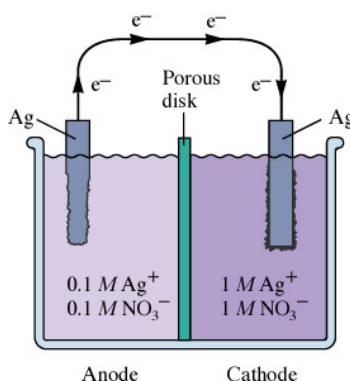n = # of electrons exchanged in BALANCED redox equation

Rearranged, another useful form

NERNST EQUATION: $E = E° - \dfrac{0.0592}{n}\log Q$ @ 25°C (298K)

As E declines with reactants converting to products, E eventually reaches zero.
Zero potential means reaction is at equilibrium [dead battery]. Also, $Q = K$ AND $\Delta G = 0$ as well.


0.1 M Ag⁺
0.1 M NO₃⁻ | 1 M Ag⁺
1 M NO₃⁻

Anode   Cathode

CONCENTRATION CELLS
We can construct a cell where both compartments contain the same components BUT at different concentrations

Notice the difference in the concentrations pictured at left. Because the right compartment contains 1.0 M Ag^+ and the left compartment contains 0.10 M Ag^+, there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves [producing Ag^+ ions] to raise the concentration of Ag^+ in solution.
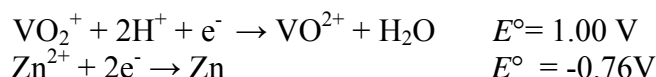
Exercise 6
Determine the direction of electron flow and designate the anode and cathode for the cell represented here.
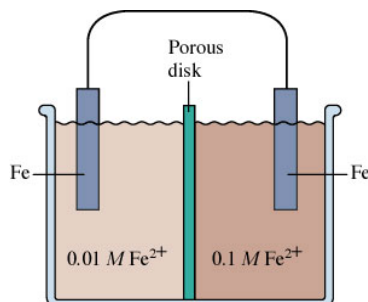
left → right

Exercise 7
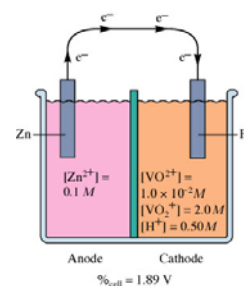Determine $E^o{}_{cell}$ and E_{cell} based on the following half-reactions:

$$VO_2{}^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \qquad E^o = 1.00 \text{ V}$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad\qquad E^o = -0.76 \text{V}$$

Where
$T = 25°C$
$[VO_2{}^+] = 2.0 \ M$
$[H^+] = 0.50 \ M$
$[VO^{2+}] = 1.0 \times 10^{-2} \ M$
$[Zn^{2+}] = 1.0 \times 10^{-1} \ M$

$E^o{}_{cell} = \mathbf{1.76 \ V}$
$E_{cell} = \mathbf{1.89 \ V}$

SUMMARY OF GIBB'S FREE ENERGY AND CELLS

☞ $-E^o$ implies NONspontaneous.
☞ $+E^o$ implies spontaneous (would be a good battery!)
☞ $E = 0$, equilibrium reached (dead battery)
☞ larger the voltage, more spontaneous the reaction
☞ ΔG will be negative in spontaneous reactions
☞ $K > 1$ are favored

Two important equations:
$\Delta G = -nFE^o$ ["minus nunfe"]
$\Delta G = -RT\ln K$ ["ratlink"]

G = Gibbs free energy [Reaction is spontaneous if ΔG is *negative*]
n = number of moles of electrons.
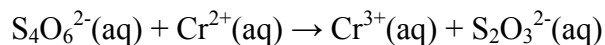F = Faraday constant 9.6485309×10^4 J/V (1 mol of electrons carries 96,500C)
E = cell potential

$R = 8.31$ J/mol•K
T = Kelvin temperature
K = equilibrium constant $[products]^{coeff.}$ /$[reactants]^{coeff}$

Favored conditions: $E_{cell} > 0$ $\Delta G < 0$ $K > 1$

Exercise 8
For the oxidation-reduction reaction

$$S_4O_6^{2-}(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$$

The appropriate half-reactions are

$$S_4O_6^{2-} + 2\ e^- \rightarrow 2\ S_2O_3^{2-} \qquad E° = \ \ 0.17V \qquad (1)$$
$$Cr^{3+} + e^- \rightarrow Cr^{2+} \qquad E° = -0.50\ V \qquad (2)$$

Balance the redox reaction, and calculate $E°$ and K (at 25°C).

$E° = 0.67$ V
$K = 10^{22.6} = 4 \times 10^{22}$

Applications of Galvanic Cells
Batteries: cells connected in series; potentials add together to give a total voltage.
Examples:
  Lead-storage batteries (car)--Pb anode, PbO_2 cathode, H_2SO_4 electrolyte
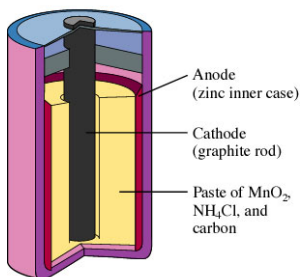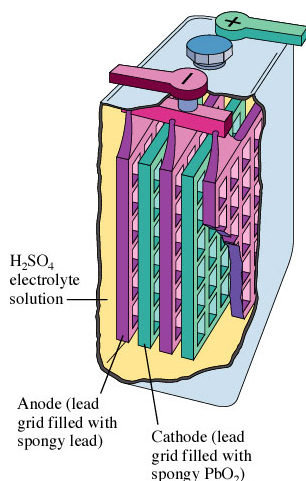 Dry cell batteries
    Acid versions: Zn anode, C cathode; MnO_2 and NH_4Cl paste
    Alkaline versions: some type of basic paste, ex. KOH
    Nickel-cadmium – anode and cathode can be recharged
  Fuel cells
    Reactants continuously supplied (spacecraft –hydrogen and oxygen)

H_2SO_4 electrolyte solution

Anode (lead grid filled with spongy lead)

Cathode (lead grid filled with spongy PbO_2)

Anode (zinc inner case)

Cathode (graphite rod)

Paste of MnO_2, NH_4Cl, and carbon

Batteries for electronic watches are, by necessity, very tiny.

Insulation
Cathode (steel)
Anode (zinc container)
Solution of H_2O (oxidizing agent) in a basic medium (KOH and $Zn(OH)_2$)
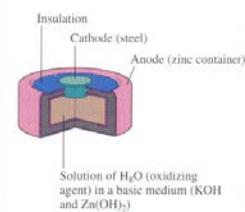
Figure 17.15
A mercury battery of the type used in small calculators.

ELECTROLYSIS AND ELECTROLYTIC CELLS

Electrolysis- the use of electricity to bring about chemical change. Literal translation "split with electricity"

Electrolytic cells [NON spontaneous cells]:

☞Used to separate ores or plate out metals.

☞Important differences between a voltaic/galvanic cell and an electrolytic cell:

1) Voltaic cells are spontaneous and electrolytic cells are forced to occur by using an electron pump or battery or any DC source.
2) A voltaic cell is separated into two half cells to generate electricity; an electrolytic cell occurs in a single container.
3) A voltaic [or galvanic] cell IS a battery, an electrolytic cell NEEDS a battery
4) AN OX and RED CAT still apply BUT the polarity of the electrodes is reversed. The cathode is Negative and the anode is Positive (remember **E.P.A – electrolytic positive anode**). Electrons still flow FATCAT.
5) Usually use inert electrodes

Predicting the Products of Electrolysis:

**If there is no water present and you have a pure molten ionic compound, then:**

☞the cation will be reduced (gain electrons/go down in charge)

☞the anion will be oxidized (lose electrons/go up in charge)

**If water is present and you have an aqueous solution of the ionic compound, then:**

☞ you'll need to figure out if the ions are reacting or the water is reacting.

☞ you can always look at a reduction potential table to figure it out but, as a rule of thumb:

☞ **no group IA or IIA metal will be reduced in an aqueous solution – water will be reduced instead.**

☞ **no polyatomic will be oxidized in an aqueous solution – water will be oxidized instead.**

*Since water has the more positive potential, we would expect to see oxygen gas produced at the anode because it is easier to oxidize than water or chloride ion. Actually, chloride ion is the first to be oxidized. The voltage required in excess of the expected value (called the overvoltage) is much greater for the production of oxygen than chlorine, which explains why chlorine is produced first. Causes of overvoltage are very complex. Basically, it is caused by difficulties in transferring electrons from the species in the solution to the atoms on the electrode across the electrode-solution interface. Therefore, E values must be used cautiously in predicting the actual order of oxidation or reduction of species in an electrolytic cell.
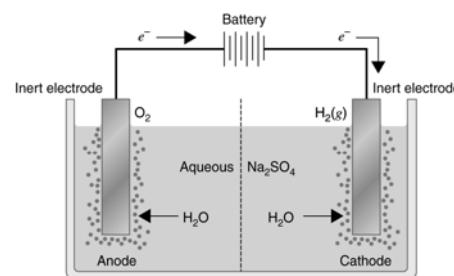
Half Reactions for the electrolysis of water

If Oxidized: $2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^-$

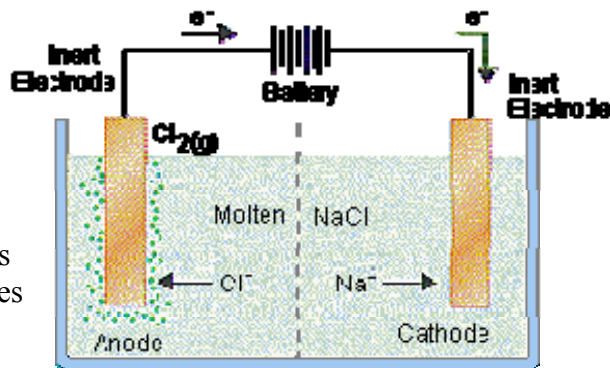If Reduced: $2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$
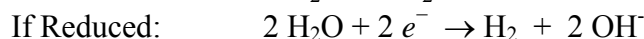
Calculating the Electrical Energy of Electrolysis
How much metal could be plated out?
How long would it take to plate out?

Faraday's Law: The amount of a substance being oxidized or reduced at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

Use dimensional analysis for these calculations, remembering: **# coulombs = *It***

---

1 Volt = 1 Joule/Coulomb
1 Amp = 1 Coulomb/second (current is measured in amp, but symbolized by *I*)
Faraday = 96,500 Coulombs/mole of electrons
Balanced redox equation gives #moles of e^-/mole of substance
Formula weight gives grams/mole

Exercise 9
How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?

= 31.3 min

Exercise 10
An acidic solution contains the ions Ce^{4+}, VO_2^+, and Fe^{3+}. Using the $E°$ values listed in Table 17.1 [Zumdahl], give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.

$Ce^{4+} > VO_2^+ > Fe^{3+}$

.
Electrochemistry

Applications of electrolytic cells:
☞ production of pure forms of elements from mined ores
   Aluminum from Hall-Heroult process
   Separation of sodium and chlorine (Down's cell)
   Purify copper for wiring

Downs cell

Hall-Heroult process for producing Aluminum
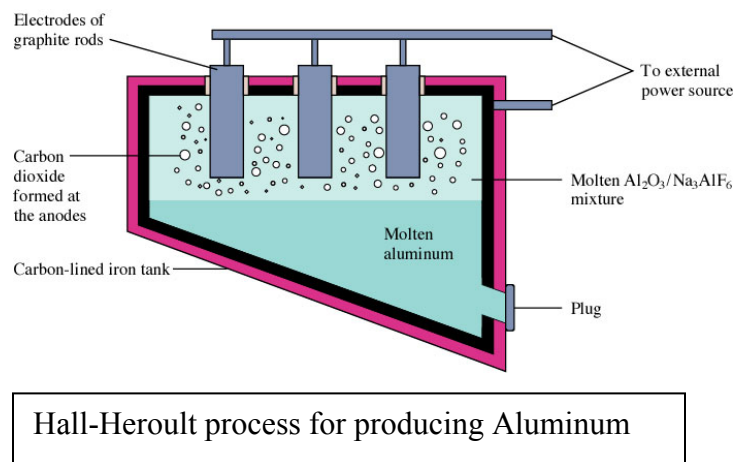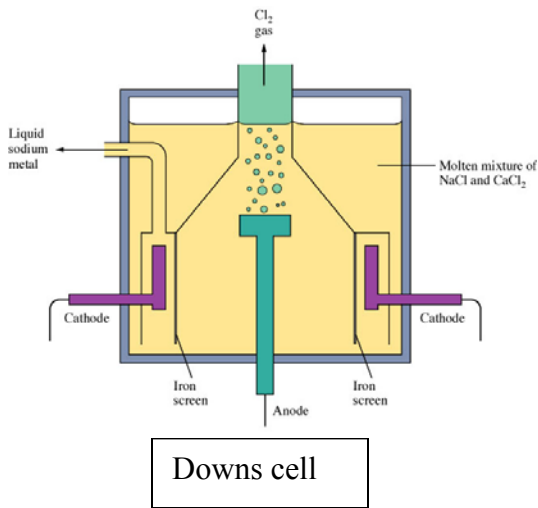
☞ electroplating—applying a thin layer of an expensive metal to a less expensive one
   Jewelry --- 14 K gold plated
   Bumpers on cars --- Chromium plated
☞ Charging a battery --- i.e. your car battery when the alternator functions

☞ **Corrosion**—process of returning metals to their natural state, the ores.
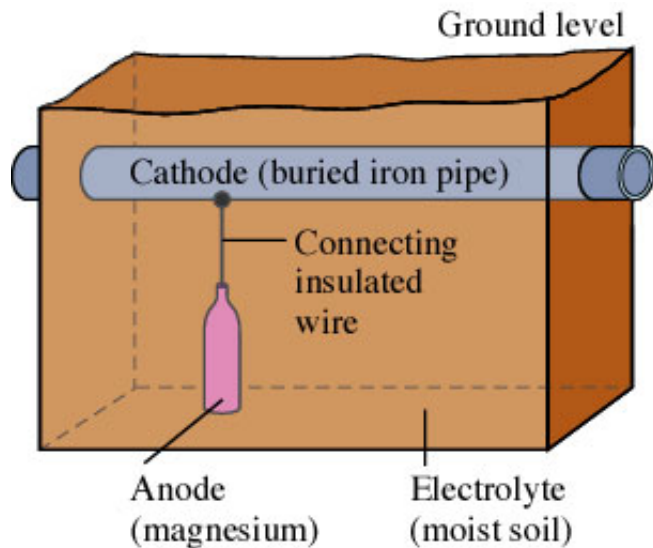
☞ Involves oxidation of the metal which causes it to lose its structural integrity and attractiveness.
☞ The main component of steel is iron.
☞ 20% of the iron and steel produced annually is used to replace rusted metal!
☞ most metals develop a thin oxide coating to protect them, patina's, tarnish, rust, etc.

CORROSION OF IRON
   o An electrochemical process!
   o Steel has a nonuniform surface since steel is not completely homogeneous. Physical strains leave stress points in the metal as well causing iron to be more easily oxidized (*anodic* regions) than it is at others (*cathodic* regions)
   o In the anodic region: $Fe \rightarrow Fe^{2+} + 2\,e^-$; the electrons released flow through the steel to a cathodic region where they react with oxygen
   o In the cathodic region: $O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$
   o The iron (II) ions travel to the cathodic regions through the moisture on the surface of the steel [just like ions travel through a salt bridge]. Another reaction occurs in the cathodic region:
   $$4\,Fe^{2+}\,(aq) + O_2\,(g) + (4+2n)\,H_2O\,(l) \rightarrow 2\,Fe_2O_3 \bullet n\,H_2O\,(s) + 8\,H^+\,(aq)$$
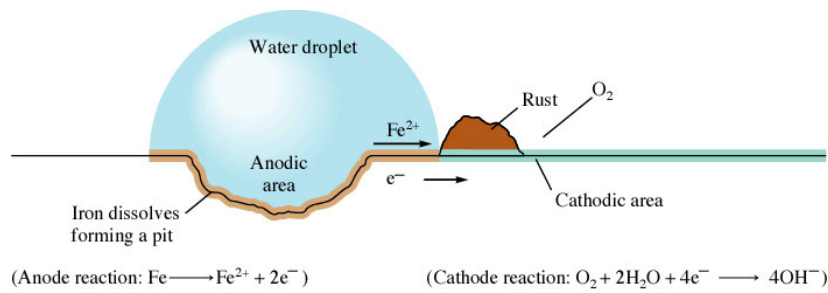
- o This means rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel
- o hydration of iron affects the color of the rust; black to yellow to the familiar reddish brown
- o Prevention: paint, coat with zinc [galvanizing], cathodic protection—insert an active metal like Mg connected by a wire to the tank or pipeline to be protected. Mg is a better reducing agent than iron [so is more readily oxidized] the Mg anode dissolves and must be replaced, BUT protects the steel in the meantime!

Ground level

Cathode (buried iron pipe)

Connecting insulated wire

Anode
(magnesium)

Electrolyte
(moist soil)

- o Ships hulls often have bars of titanium attached since in salt water, Ti acts as the anode and is oxidized instead of the steel hull.

Electrochemistry