Electrochemistry Ch. 19 Notes:

Homework: Read Chapter 19,
Bonus: 39, 41, 43, 45, 47, 51, 55, 61, 63, 65, 67, 71, 73, 77, 81, 87, 89, 91, 99, 109
Check MasteringChemistry Deadlines

Electrochemistry:

All chemistry is electrical in the sense it involves electrons and other charged ions. The term Electrochemistry is reserved for the study of the processes that convert chemical energy to electrical energy and vice versa.

Spontaneous reactions are labeled ***Voltaic Cells or Galvanic Cells***, derived from the names Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827). These cells use spontaneous redox reactions to produce electric current, electrons flow from one terminal (anode) to another (cathode) when connected by an external circuit and a salt bridge. Example cases of spontaneous electrochemical processes *include batteries, fuel cells* and *corrosion*.

Nonspontaneous reactions requiring electrical energy are called ***Electrolytic Cells;*** electric current removes electrons from one reactant and gives electrons to another. Example cases include *electrolysis*, used to decompose stable compounds such as H_2O or Fe_2O_3 into its elements, and *electroplating*.

For electrochemical reactions, a **redox reaction** can be separated in two, **oxidation** which occurs at the anode and **reduction** that occurs at the cathode.

Review Redox Reactions: (found in chapter 4.9)

Redox reactions exchange electrons. When balancing a reaction, remember to **balance**…

(1) the number of electrons lost = electrons gained

(2) the atoms on either side of the reaction must balance

(3) the total charge on either side of the reaction must balance.

Learn the half reaction method of balancing for electrochemistry reactions. This method splits apart the oxidation half reaction from the reduction half reaction.

Oxidation	**Reduction**
increases oxidation number	reduces oxidation number
lose electrons	gain electrons
occurs at anode	occurs at cathode
$2\ Cl^{-1} \rightarrow Cl_2 + 2\ e^-$	$K^+ + 1\ e^- \rightarrow K$
Oxidized substance, Cl^{-1}	Reduced substance, K^+
reductant/reducing agent	oxidant/ oxidizing agent
Oil- **O**xidation **i**s **l**osing e⁻'s	**Rig**- **R**eduction **i**s **g**aining
Leo	Ger
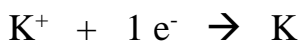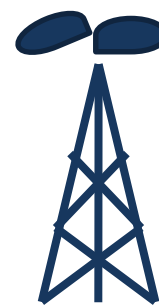
Oil

Rig

e⁻'s

Assigning Oxidation Numbers

1) elements   zero
2) monatomic ions   charge on ion
3) oxygen   mostly (-2) exceptions:
                          peroxide, O_2^{-2}, (-1) and
                          superoxides, O_2^{-1}, (-1/2)
4) hydrogen   mostly (+1)
                          exceptions: hydrides (-1)
5) halogens   mostly (-1)
                          Exceptions: (+1, +3, +5, +7)
                          when in a compound with lighter halogens or oxygen
6) Compounds   sum of oxidation numbers equal zero
7) polyatomic ions   sum of oxidation numbers equal charge of ion

Practice:
Determine the oxidation number of each element in the following list.

  a) Cl_2

  b) $MgCl_2$

  c) $Al(ClO)_3$

  d) $Ni(ClO_2)_2$

  e) $V(ClO_3)_5$

  f) $KClO_4$

  g) $K_2Cr_2O_7$

  h) C_2H_4O

  i) C_3H_8

Note: in most cases oxidation states are positive or negative integers. On occasion atoms within a compound may have an average fractional oxidation state. It is acceptable because the oxidation states are an imposed bookkeeping scheme, not an actual quantity.

Balancing Redox Rxns Using the Half Rxn Method

1) Assign oxidation numbers to each atom in the equation.
2) Determine what is oxidized and what is reduced.
3) Split the skeleton equation into two half reactions label appropriately as oxidation or reduction reactions.
4) Complete and balance each half reaction
   a) Balance atoms (except O and H) starting with the atom that changes oxidation state.
   b) Include electrons as products in the oxidation reaction and reactants in the reduction reaction
   c) If the solution is acidic: balance electric charges by adding H^{+1} ions, balance the O's by adding H_2O, verify all atoms balance
   d) If the solution is basic: balance electric charges by adding OH^{-1} ions, add H_2O to balance the O and H atoms, verify all atoms balance.
5) Combine the two half reactions to obtain overall equation
   a) Multiply each half reaction by the factor needed to have equivalent electrons lost and gained.
   b) Simplify and reduce to the lowest whole number ratio
6) Check balancing
   a) atoms
   b) sum of charges of reactants equal to those of products
   c) number on electrons lost and gained

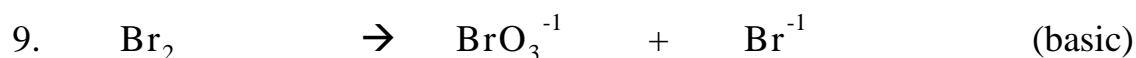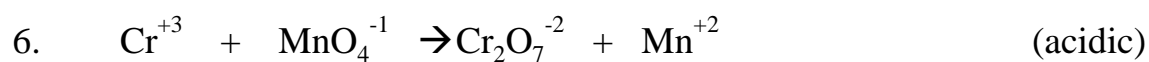*Example 1: Balance the following with the half reaction method.*

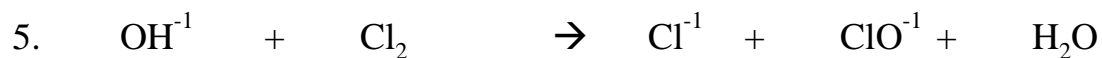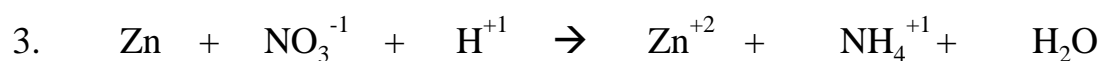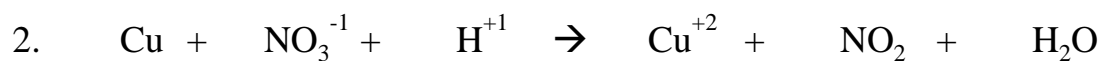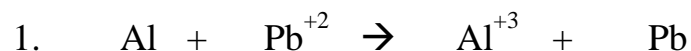a) I_2 (s) + $S_2O_3^{-2}$ (aq) → I^{-1} (aq) + $S_4O_6^{-2}$ (aq)
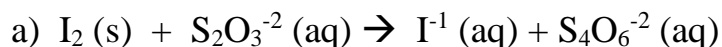
b) A breathalyzer detects ethanol in suspected drunk drivers. Ethanol oxidizes to acetaldehyde by dichromate ions in acidic solution. The *orange* dichromate turns to *green* Cr^{+3}. Balance the reaction using the half-reaction method.

$$Cr_2O_7^{-2} (aq) + C_2H_5OH (l) \rightarrow Cr^{+3} (aq) + C_2H_4O (l) \quad \text{(acidic conditions)}$$
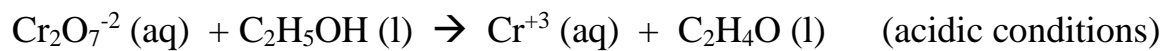
c) $I_2 (s) + H_2S (g) \rightarrow I^{-1} (aq) + S_8 (s)$ (acidic conditions)

d) $Al (s) + SO_4^{-2} (aq) \rightarrow Al^{+3} (aq) + SO_2 (g)$ (acidic conditions)

REDOX EQUATIONS: Answers to this additional practice found on website
Balance the following, identify species that oxidizes/reduces

1. $Al + Pb^{+2} \rightarrow Al^{+3} + Pb$

2. $Cu + NO_3^{-1} + H^{+1} \rightarrow Cu^{+2} + NO_2 + H_2O$

3. $Zn + NO_3^{-1} + H^{+1} \rightarrow Zn^{+2} + NH_4^{+1} + H_2O$

4. $HI + HNO_3 \rightarrow I_2 + NO + H_2O$

5. $OH^{-1} + Cl_2 \rightarrow Cl^{-1} + ClO^{-1} + H_2O$

6. $Cr^{+3} + MnO_4^{-1} \rightarrow Cr_2O_7^{-2} + Mn^{+2}$ (acidic)

7. $MnO_4^{-1} + Mn^{+2} \rightarrow MnO_2$ (acidic)

8. $MnO_4^{-1} + IO_3^{-1} \rightarrow Mn^{+2} + IO_4^{-1}$ (basic)

9. $Br_2 \rightarrow BrO_3^{-1} + Br^{-1}$ (basic)

Voltaic Cells: also known as Galvanic Cells, Spontaneous:

Conduction through metal, such as wires, involves the flow of electrons and no movement of atoms or obvious change in the metal.

Electrochemistry involves **ionic conduction**, the motion of ions through liquid, anions spontaneously move toward the anode and cations spontaneous move toward the cathode. The **electrodes** are connected externally by a metal wire in which electrons move from the anode (-) to the cathode (+). Metal electrodes are often part of the redox reaction. **Inert electrodes** do not react with reactants or products; they just provide a surface for the reaction to occur. Common inert electrodes are made of platinum metal or graphite (carbon).

In Voltaic Cells a spontaneous oxidation-reduction reaction produces electrical energy if...

1) The two half cells are physically separated, internally by a salt bridge and externally by a metal conduction wire.

2) Electron transfer is forced to occur along the external wire circuit.

3) A potential difference (voltage) is created making useful electrical energy.

Construction of Simple Galvanic Cell:

Half-cell: consists of oxidized and reduced forms of an element or more complex species in contact with each other. Commonly, this is a metal electrode immersed in a solution of its metal ions.

Two half cells are connected by a wire with a voltmeter inserted in the circuit to measure the potential difference. Complete the circuit with a salt bridge.

Salt bridge: median through which ions slowly pass, filled with a nonreactive salt and a substance to keep the salt solution from flowing out, this can be 5% agar solution (gelatin from algae) or as in our lab, cotton yarn. A semipermeable porous membrane often replaces the need for agar. The salt bridge serves 3 functions: 1) makes electrical contact completing the circuit, 2) maintains electrical neutrality, 3) prevents the spontaneous mixing of the half cells

Standard Cell: all reactants and products are in their standard states: pure liquid or solid, 1M concentration of solutions, 1 atm pressure of gas, all at 25°C. A standard cell is hard to maintain since the concentrations change as the reaction proceeds. The initial voltage value gives us information on a standard cell. Slowly equilibrium will be reached at which point the potential difference = 0 Volts.

Electromotive force = Emf = E_{cell} = Voltage, V = Joules/Coulomb (J/C).

1 electron has a charge of 1.60×10^{-19} C.

E_{cell} is positive for spontaneous reactions.

Shorthand Notation for Galvanic Cells: Drawing a diagram or using many words and half reactions to describe the Galvanic cell becomes tedious.

Shorthand: Ni (s) | Ni $^{+2}$ [0.180 M] || Cu^{+2} (? M) | Cu (s)

Anode | oxidation half cell || reduction half cell | Cathode.

The anode and cathode may be metals in the half reactions or inert electrodes. Double line represents salt bridge. Vertical line is a phase barrier. If two species in a half reaction are the same phase, comma may be used in place of vertical line.
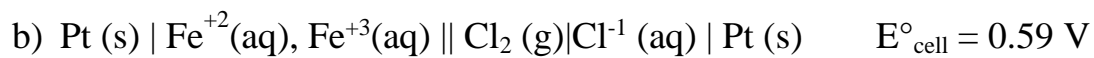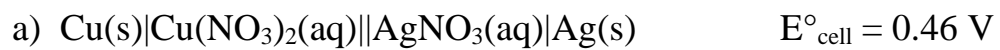
Standard Galvanic Cells:

Zn (s)|Zn(NO$_3$)$_2$(aq) ||Cu(NO$_3$)$_2$ (aq)| Cu(s) $E°_{cell}$= 1.10 V


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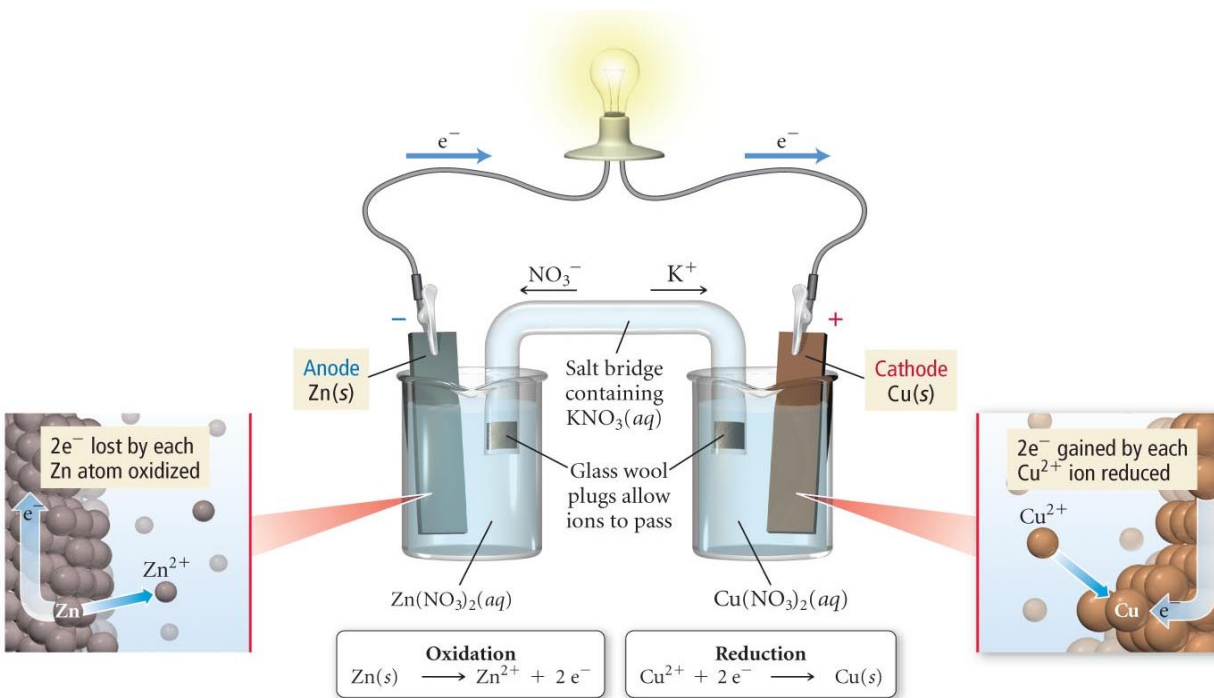
Example 2: **Examples of Standard Galvanic Cells:**

Draw and label the following standard galvanic cells in the complete form:

a) $Cu(s)|Cu(NO_3)_2(aq)||AgNO_3(aq)|Ag(s)$ $E°_{cell} = 0.46$ V

b) $Pt\ (s)\ |\ Fe^{+2}(aq),\ Fe^{+3}(aq)\ ||\ Cl_2\ (g)|Cl^{-1}\ (aq)\ |\ Pt\ (s)$ $E°_{cell} = 0.59$ V
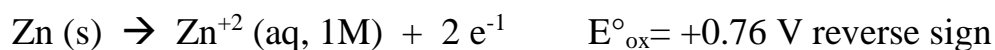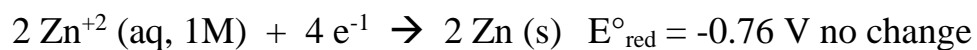
Standard Hydrogen Electrode and Standard Reduction Potentials:

An arbitrary zero standard reduction cell potential has been chosen by scientists to be the SHE, Standard Hydrogen Electrode. In which the half cell has 1M H^{+1}, 1 atm H_2 (g) and an inert Pt electrode.

$$2\ H^+\ (aq,\ 1\ M) + 2\ e^{-1} \rightarrow H_2\ (g,\ 1\ atm)\quad E°_{red} = 0\ V$$
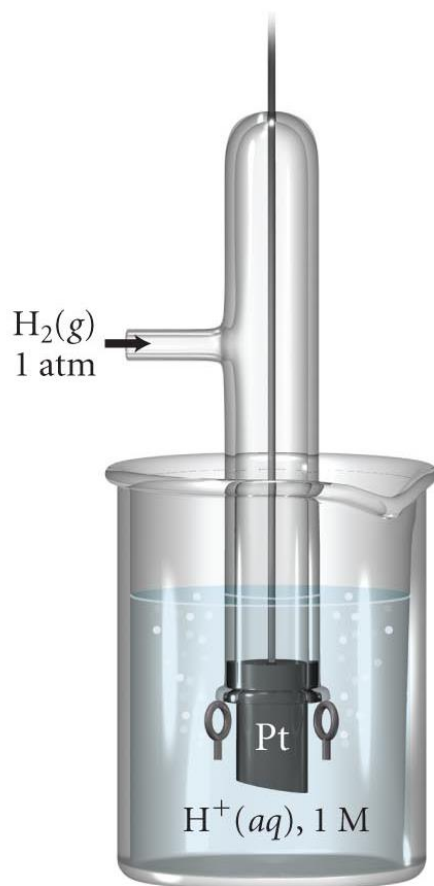
Cell potentials :

A) Dependent on concentrations and based on SHE arbitrary voltage assignment
B) Never change when a reaction is doubled, tripled, or halved
C) Sign will reverse when the reaction is reversed

$$Zn^{+2}\ (aq,\ 1M)\ +\ 2\ e^{-1} \rightarrow Zn\ (s)\qquad E°_{red} = -0.76\ V$$

$$2\ Zn^{+2}\ (aq,\ 1M)\ +\ 4\ e^{-1} \rightarrow 2\ Zn\ (s)\quad E°_{red} = -0.76\ V\ no\ change$$

$$Zn\ (s)\ \rightarrow\ Zn^{+2}\ (aq,\ 1M)\ +\ 2\ e^{-1}\qquad E°_{ox} = +0.76\ V\ reverse\ sign$$

Standard Reduction Cell Potential values are found in the appendix.

The Equation to solve for the standard cell potential of a reaction…

$$E°_{cell} = E°_{red\ (cathode)} - E°_{red\ (anode)} \quad \text{or} \quad E°_{cell} = E°_{ox} + E°_{red}$$

The cell potential must be positive to be spontaneous. That which is most easily oxidized has the lower (greater negative) reduction potential. That which is most easily reduced has the larger (greatest positive) reduction potential

TABLE 18.1 Standard Electrode Potentials at 25 °C

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78
$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^-$	$\longrightarrow PbSO_4(s) + 2\,H_2O(l)$	1.69
$MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow MnO_2(s) + 2\,H_2O(l)$	1.68
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51
$Au^{3+}(aq) + 3\,e^-$	$\longrightarrow Au(s)$	1.50
$PbO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	1.46
$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23
$MnO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	1.21
$IO_3^-(aq) + 6\,H^+(aq) + 5\,e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3\,H_2O(l)$	1.20
$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09
$VO_2^+(aq) + 2\,H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow NO(g) + 2\,H_2O(l)$	0.96
$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52
$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40

Stronger oxidizing agent ↑

Weaker reducing agent

$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34
$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16
$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0
$Fe^{3+}(aq) + 3\,e^-$	$\longrightarrow Fe(s)$	−0.036
$Pb^{2+}(aq) + 2\,e^-$	$\longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2\,e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.23
$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50
$Cr^{3+}(aq) + 3\,e^-$	$\longrightarrow Cr(s)$	−0.73
$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76
$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2\,e^-$	$\longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2\,e^-$	$\longrightarrow Ca(s)$	−2.76
$Ba^{2+}(aq) + 2\,e^-$	$\longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent (left)   Stronger reducing agent (right)

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Example 3:

   Given that $E°_{red}\ Cu^{+2} = 0.34\ V$,

      Write out the balanced half reactions and solve for the $E°_{red}$ for Zn^{+2} and Ag^{+1}

      a) $Zn|Zn(NO_3)_2||Cu(NO_3)_2|Cu$ $E°_{cell} = 1.10\ V$

      b) $Cu|Cu(NO_3)_2||AgNO_3|Ag$ $E°_{cell} = 0.46\ V$
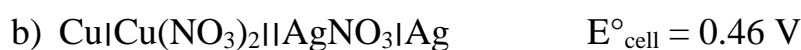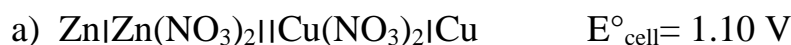
Example 4:

Order the ***oxidation*** half reactions by increasing strength under standard conditions. Half cells are as follows: Cu/Cu^{+2}, Zn/Zn^{+2}, H_2/H^+

a)   Write the balanced oxidation half reactions and standard half-cell potentials for each.

b)   Identify the species that is
      1)   the easiest to be oxidize
      2)   strongest reducing agent
      3)   strongest oxidizing agent
      4)   easiest to be reduced

Example 5:

Silver tarnish is mainly Ag_2S solid coating silver metal objects

$$Ag_2S\ (s)\ +\ 2e^-\ \rightarrow\ 2\ Ag\ (s)\ +\ S^{-2}\ (aq)\qquad E°_{red} = -0.691\ V$$

A tarnished silver spoon is placed in contact with a commercially available metal product in a glass-baking dish. Boiling water, to which some baking soda (salt bridge) has been added, is poured into the dish, and the metal product and spoon are completely covered. Within a short time, the spontaneous removal of tarnish from the spoon begins.

Is this commercially available metal product Al or Cu? Explain by writing out the oxidation half reaction and solve for the overall spontaneous $E°_{cell}$ value.

Free Energy and Redox Reactions:

Remember that Free Energy, ΔG, is related to the equilibrium constant K.

$\Delta G = \Delta G° + RT\ln Q_{eq}$ and $\Delta G° = -RT\ln K_{eq}$

$\Delta G°$ is also related to cell potential…

$\Delta G° = -nFE°$

Where **n is the moles of electrons** transferred and F is Faraday's constant, the electrical charge on one mole of electrons, **F = 96,500 C/mol**.
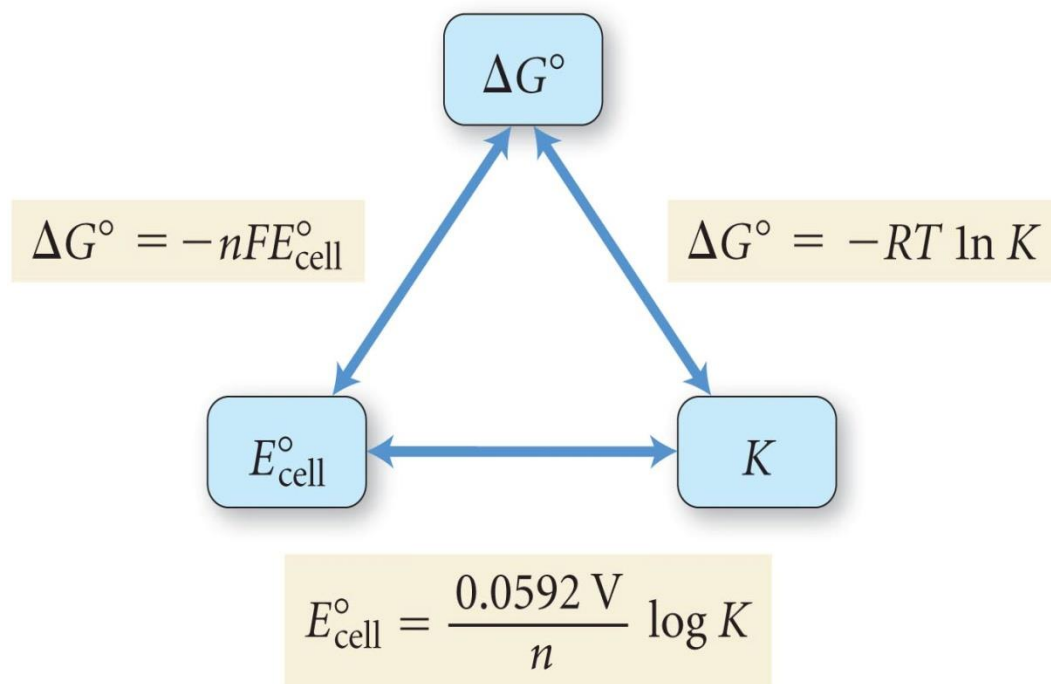
Remember that a Coulomb = J/V, E is in V, so ΔG in J converted to kJ.

We can rearrange the equations above to relate cell potential to the equilibrium constant and get…

$nFE° = RT\ln K_{eq}$ and $E°_{cell} = \left(\dfrac{RT}{nF}\right)\ln K_{eq}$

An older form of the equation used logs under standard temperature conditions (25°C)… $E°_{cell} = [(2.303 * 8.314 J/mol\ K * 298K)/n(96485C)]\log K_{eq}$

$E°_{cell} = (0.0592\ Volts/n)\log K_{eq}$

or $E°_{cell} = (0.0257/n)\ln K_{eq}$ at 25°C

Example 6:

Consider a reaction where tin (II) ions and solid tin is one half reaction and cadmium ions and cadmium solid are the other half reaction in a spontaneous voltaic cell under standard conditions and temperature.

a) Write out the shortened cell notation and determine $E°_{cell}$

b) Write out the overall reaction and determine the number of electrons transferred.

c) Calculate $\Delta G°$

d) Calculate, K_{eq}

Cell EMF under Nonstandard Conditions, Nernst Equation:

Not all reactions occur under standard conditions. Even if a reaction starts with standard conditions, over time the concentrations will change.

Manipulate the equations… $\Delta G° = -nFE°$ and $\Delta G = \Delta G° + RT\ln Q_{eq}$

to create the Nernst equation which allows us to calculate the cell potential under all conditions.

Nernst equation: $E = E° - (RT/nF)\ln Q$ or $E = E° - (2.303RT/nF)\log Q$

This allows us to calculate the electromotive force under nonstandard conditions. Generally, the reaction is assumed at 25°C (298K), R = 8.314 J/mol K, and F = 96500J/V. Replacing the constants leads to…

$E = E° - (0.0257/n)\ln Q$ or $E = E° - (0.0592/n)\log Q$ (at 298K)

Example 7:

Electrochemical Cells can be used to **determine unknown concentrations**. This may be useful in determining K_{sp} and molar solubility values or just any unknown concentration in a balanced equation if others are known and the E_{cell} is experimentally determined.

Given: E_{cell} = 1.075 V in the following reaction…

$$Cl_2 \text{ (g)} + Cu \text{ (s)} \rightarrow Cu^{+2} \text{ (aq)} + 2\ Cl^{-1} \text{ (aq)}$$

the anode mass is 15.0 g Cu (s),

Cl_2 (g) partial pressure is 0.75 atm,

and 0.080 M Cu^{+2} (aq)

$E°_{red} Cu^{+2}/Cu$ = 0.34 V, $E°_{red} Cl_2/Cl^{-1}$ = 1.36 V.

What is the concentration in molarity of Cl^{-1} ions in this problem?

Example 8:

The voltaic cell: Ni (s) | Ni^{+2} [0.180 M] || Cu^{+2} (? M) | Cu (s) has a cell potential of 0.575V at 25°C. Diagram the voltaic cell. Use the Appendix to solve for $E_{cell}°$. Solve for the concentration of copper ions.

Concentration Cell:

A concentration cell is a special case voltaic cell in which both half-cells have the same species but different concentrations. The two cells will spontaneously react when connected until equilibrium is reached. That equilibrium occurs when the concentrations become equal and the $E_{cell} = 0$, this is the same equilibrium that would be established if the two solutions are mixed directly. $E°_{cell} = 0$ for a concentration cell since $E°_{ox}$ and $E°_{red}$ are equal but opposite sign.

$E_{cell} = 0 - (0.0592/n)\log Q$

Nonstandard conditions

0.068

Voltmeter

Anode −   + Cathode

Salt bridge

$[Cu^{2+}] = 0.010\,M$

Cu(s)   Cu(s)

$[Cu^{2+}] = 2.0\,M$

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$	$Cu^{2+} + 2\,e^- \longrightarrow Cu(s)$
Solution becomes *more* concentrated with flow of current.	Solution becomes *less* concentrated with flow of current.

Standard conditions

0.00

Voltmeter

Anode −   + Cathode

Salt bridge

$[Cu^{2+}] = 1\ M$

Cu(s)

$[Cu^{2+}] = 1\ M$

Cu(s)
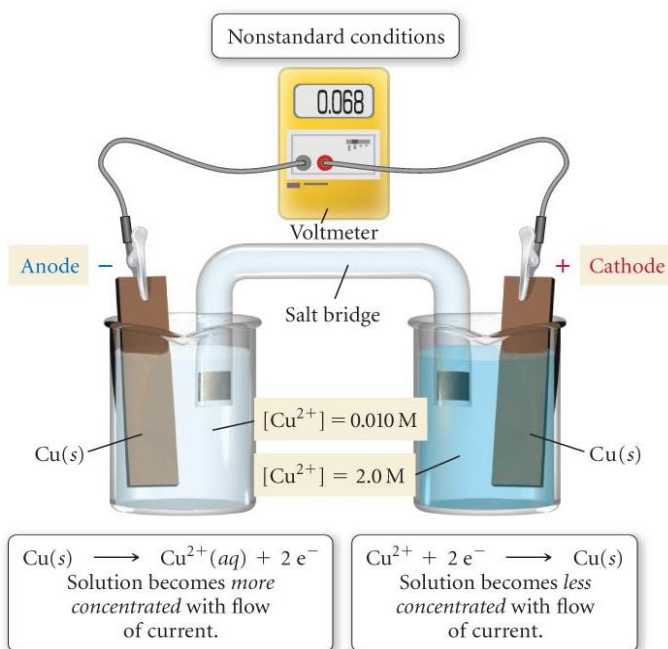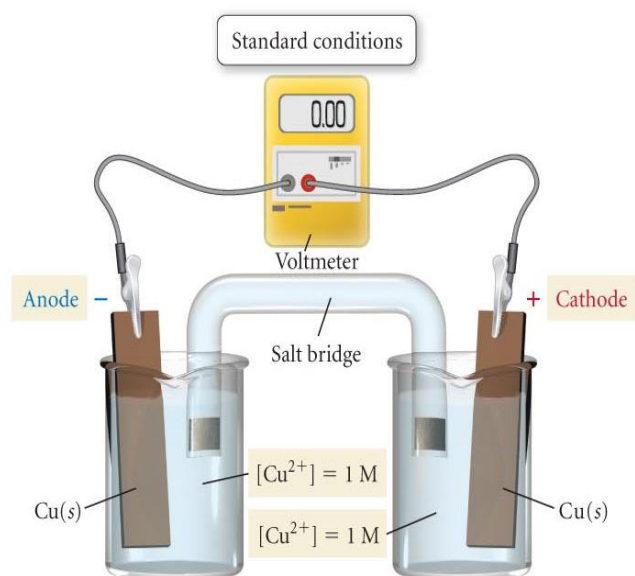
Example 9:

Solid zinc electrodes are in two half-reaction cells. One contains 0.500 M Zn^{+2} ions and the other 0.0020 M Zn^{+2} ions. An exterior circuit and a salt bridge complete the cells.

(a) Which concentration of Zn^{+2} ions will be reduced, (on the reactant side)?

(b) What is the initial spontaneous E_{cell}?

(c) What are the equilibrium concentrations of the Zn^{+2} ions in the cells?

Example 10:

A cell is constructed in which identical iron electrodes are placed in two solutions. Solution A contains 0.880 M $Fe(NO_3)_2$. Solution B contains Fe^{+2} ions of a **lower** concentration. A salt bridge and exterior wire circuit connect the two solutions. The initial cell potential of the cell is observed to be 0.051 V.
a) Draw a diagram of the cell described above and label well.

b) Which solution, A or B, is changing the iron ions to solid iron?

c) What is the initial $[Fe^{+2}]$ in solution B?

d) What is E_{cell} and the concentration of $[Fe^{+2}]$ in each of the solutions when the system reaches equilibrium?

Batteries and Fuel Cells: Types include Primary, Secondary and Fuel Cells…

Primary Galvanic Cells are irreversible. These are common store bought batteries.

The patent in 1866 for a Leclanche Cell also known as a Dry Cell has the **anode** as a **zinc** outer casing,

$$Zn \rightarrow Zn^{+2} + 2e^- \qquad E°_{ox}\, 0.76V$$

inside is a moist paste separated by a paper acting as a salt bridge
the **cathode** is **inert graphite** in the center touching moist NH_4Cl and MnO_2
Reduction cell reaction is

$$2NH_4^+ + 2e^- \rightarrow 2\,NH_3 + H_2 \quad E°_{red}\, 0.84V$$

$$E_{cell} = E_{ox} + E_{red} = 1.60\ V(\text{decreases as}$$
the cell is used)

MnO_2 is needed to prevent build up of H_2. Zn^{+2} reacts with the NH_3 to form a complex ion. Side reactions eliminate products to prevent a decrease in cell potential.

$$H_2 + 2\,MnO_2 \rightarrow Mn_2O_3\ (s) + H_2O\ (l)$$
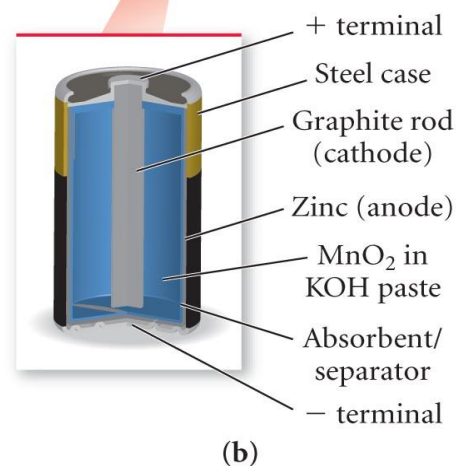
$$Zn^{+2} + 4\,NH_3 \rightarrow Zn(NH_3)_4^{+2}$$
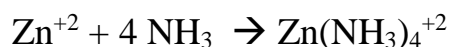
Alkaline Dry cell batteries are similar to the1866 patent except a more basic environment (KOH) is used giving the battery a longer shelf life.

Modern batteries last longer under heavy use.
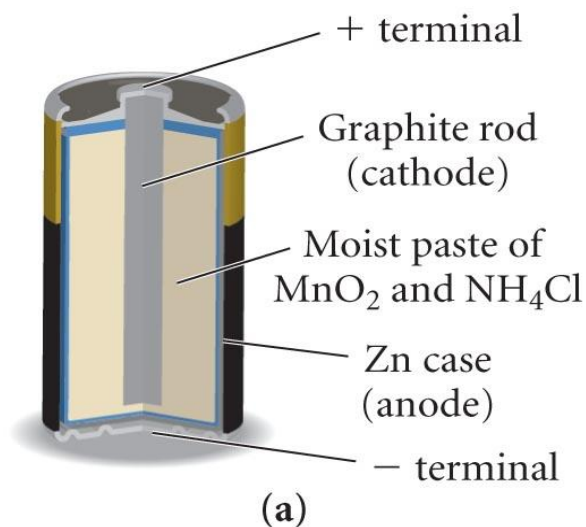
Secondary Galvanic Cells are rechargeable. During discharge the forward reactions occur and when direct current passes through the cell to recharge the reverse reactions occur**.**

Lead acid storage batteries used in cars batteries are a typical example.

Anode (−):
Lead grid packed with finely divided spongy lead
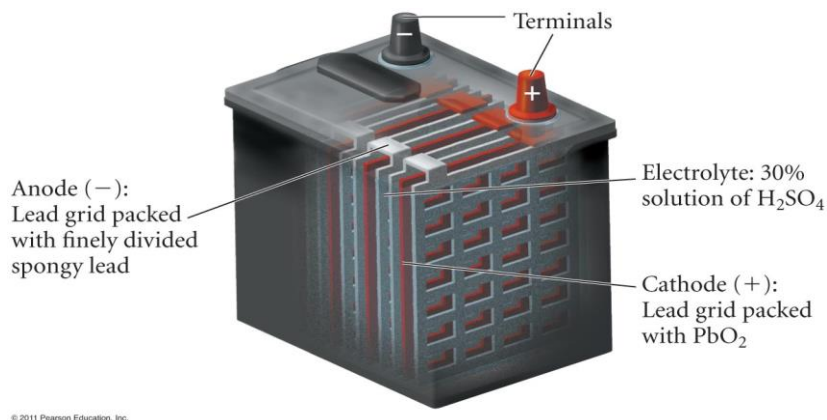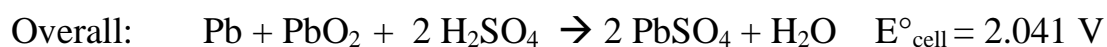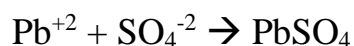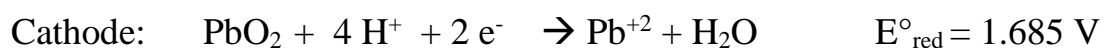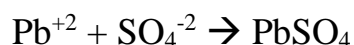
Cathode (+):
Lead grid packed with PbO_2

Electrolyte: 30% solution of H_2SO_4

Terminals

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The following reactions occur during discharge...

Anode: $Pb \rightarrow Pb^{+2} + 2\ e^-$ $E°_{ox} = 0.356$ V

$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$

Cathode: $PbO_2 + 4\ H^+ + 2\ e^- \rightarrow Pb^{+2} + H_2O$ $E°_{red} = 1.685$ V

$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$

Overall: $Pb + PbO_2 + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + H_2O$ $E°_{cell} = 2.041$ V

This is set up in a series of 6 cells in order to make a 12V battery.

Other common rechargeable batteries include Nickel-Cadmium (nicad). Nickel-Metal Hydride, Lithium and Lithium Ion batteries.

Example 11:

Nickel-cadmium batteries are more expensive than alkaline batteries but they are light, rechargeable, and can be sealed to prevent leakage.
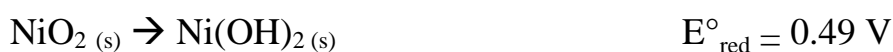The batteries in many calculators and in cordless tools are nickel-cadmium batteries.
In a NiCad battery the unbalanced half reactions are $Cd(s) \rightarrow Cd(OH)_2(s)$ and $NiO_2\ (s) \rightarrow Ni(OH)_2\ (s)$, which take place in basic solution.

a) *Balance the half reactions* in basic solution.

Reaction at anode

$Cd_{(s)} \rightarrow Cd(OH)_{2\ (s)}$ $E°_{ox} = 0.81$ V

Reaction at cathode

$NiO_{2\ (s)} \rightarrow Ni(OH)_{2\ (s)}$ $E°_{red} = 0.49$ V
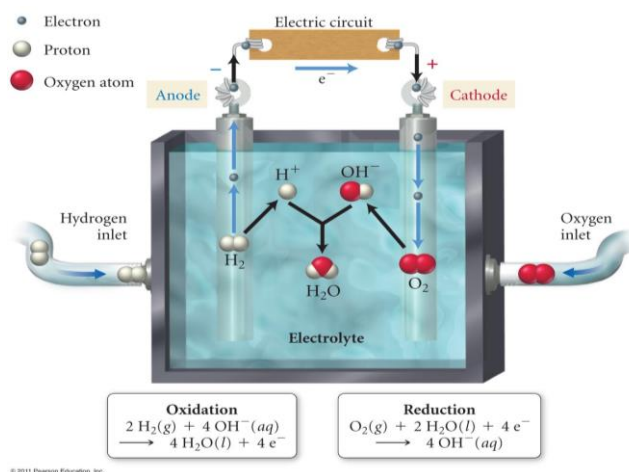
b) *Write the overall reaction and include the $E°_{cell}$ under standard conditions for the nickel-cadmium battery as it spontaneously discharges?*

c) In some batteries the power continually decreases toward zero volts in cell potential as the reactants are used up and products formed, in others the cell voltage remains fairly constant during discharge. Explain the reason for the difference and determine what is expected for the NiCad battery above.

Fuel Cells have a continuous supply of reactants and removal of product and are 50-70% efficient. A H_2 and O_2 fuel cell that creates water has been used in space crafts for power for decades. Now fuel cell batteries are being made to fuel alternative vehicles, equipment, buildings and some day residential homes.
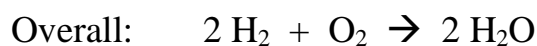
Anode: (H_2 + 2 OH^{-1} → 2 H_2O + 2 e⁻) x 2

Cathode: O_2 + 2 H_2O + 4 e⁻ →   4 OH^-

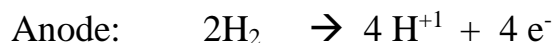Overall: 2 H_2 + O_2 → 2 H_2O
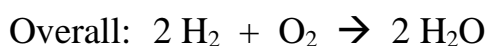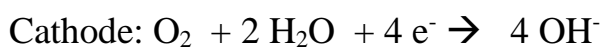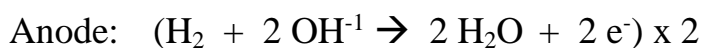
with catalyst Ag, Pt, CoO

Newer fuel cells replaced the strong OH^{-1} electrolyte with a special proton exchange membrane (PEM).

The PEM is a plastic membrane that conducts protons, not electrons.

Anode: $2H_2$ → 4 H^{+1} + 4 e⁻

Cathode: O_2 + 4 H^{+1} + 4 e⁻ →   4 H_2O

Overall: 2 H_2 + O_2 → 2 H_2O

Corrosion:

Corrosion is an unwanted problem associated with spontaneous electrochemical reactions. **Corrosion** is the spontaneous oxidation of a metal by chemicals in the environment, mainly O_2.

Because many materials we use are active metals, corrosion can be a very big problem
> Metals are often used for their strength and malleability, but these properties are lost when the metal corrodes.
> For many metals, the product of corrosion also does not adhere to the metal, and as it flakes off more metal can corrode.

Rusting:
- At the anodic regions, Fe(s) is oxidized to Fe^{2+}
- The electrons travel through the metal to a cathodic region where O_2 is reduced
  > in acidic solution from gases dissolved in the moisture
- The Fe^{2+} ions migrate through the moisture to the cathodic region where they are further oxidized to Fe^{3+} which combines with the oxygen and water to form **rust**
  > rust is hydrated iron(III) oxide, $Fe_2O_3 \bullet nH_2O$
  >> the exact composition depends on the conditions
  > moisture must be present
  >> water is a reactant
  >> required for ion flow between cathodic and anodic regions
- Electrolytes promote rusting
  > enhances current flow
- Acids promote rusting
  > lowering pH will lower E°_{red} of O_2

The Rusting of Iron
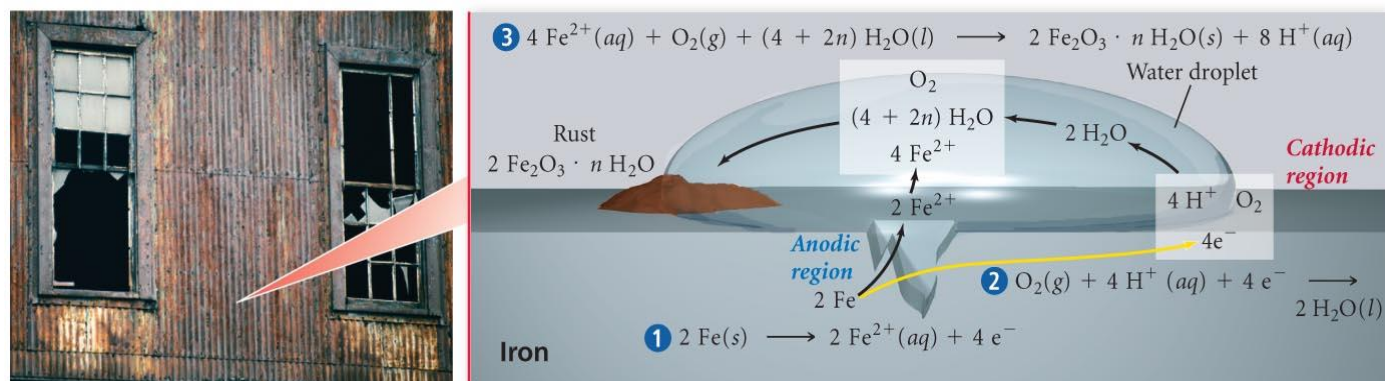
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A great deal of money is spent every year trying to prevent or replace corrosion problems. Five ways of reducing corrosion follows.

Reducing and Preventing Corrosion.

a) Plating a metal with a thin layer of less easily oxidized metal. Example: tin can to store food. Tin coated iron works since $Sn \rightarrow Sn^{+2} + 2e^-$ has $E°_{ox} = 0.14$ V and is less easily oxidized compared to iron, $Fe \rightarrow Fe^{+2} + 2e^-$ has $E°_{ox} = 0.44$ V Problem: If the container is dented and the iron layer is exposed, corrosion occurs faster than an unprotected iron container by the new electrochemical cell made with Sn and Fe.

b) Connecting the metal directly to a "sacrificial anode" which is more easily oxidized. Example: underground iron pipe, bridges, or ships. When Zn is attached to Fe the Zn is preferentially oxidized protection the Fe since $Zn \rightarrow Zn^{+2} + 2e^-$ has $E°_{ox} = 0.763$ V which is higher than Fe.

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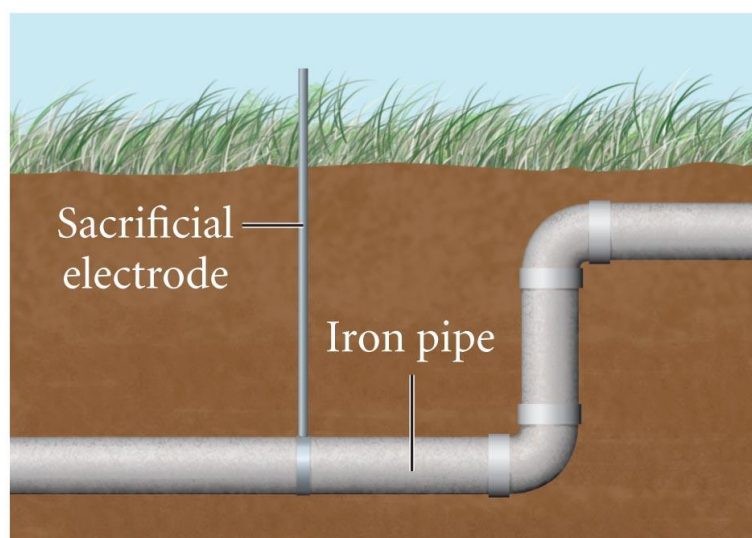
Problem: Over time the sacrificial anode corrodes and will need to be replaced.

c) Allow a protective film to naturally form on metal surface. Example: 1) the green copper patina on the statue of liberty in which Cu exposed to the environment forms $CuCO_3 \cdot Cu(OH)_2$ 2) Al reacts to form Al_2O_3. In both cases a tough hard inert surface forms over the metal and prevents further damage. Problem: Acid rain will dissolve the protective coatings that have been established.

d) Galvanizing, or coating an object with a more easily oxidized metal. This is similar to the "sacrificial anode"; only the entire object is coated. Example: galvanized nails in which the Fe nail is coated with a thin layer of Zn. The iron stays protected and strong even when bent and exposed since the Zn will oxidize preferentially.

e) Apply a protective coating over the metal. Example: paint, wax or a sealant.

Example 11:

Give a minimum of three useful ways to protect an ocean-going ship from corrosion. Identify the pro's and con's. Which methods are most beneficial?

Electrolysis or Electrolytic Cells, Nonspontaneous:

Electrolytic Cells are nonspontaneous and need power to react. E_{cell} is a negative value. Aluminum was once a very expensive metal to refine since it was originally isolated by electrolysis methods. No salt bridge is necessary since the reaction will not spontaneously occur. You must separate the products to avoid them spontaneously returning to the reactants. Anode (+) and cathode (−)

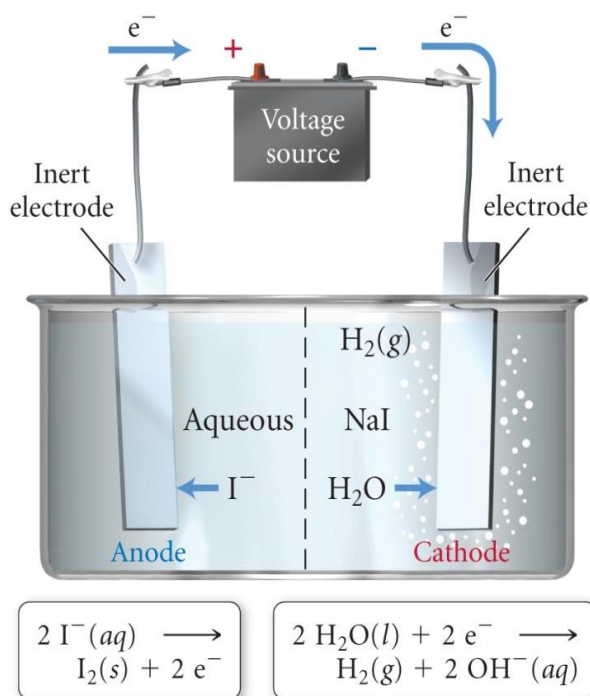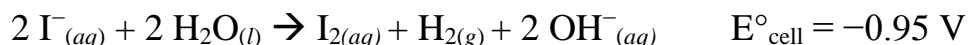*Examples of electrolysis:*

Aqueous NaI produces I_2 (s) and H_2 (g)

possible oxidations

$$2\ I^- \rightarrow I_2 + 2\ e^- \qquad E°_{ox} = -0.54\ V$$

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad E°_{ox} = -0.82\ V$$

possible reductions

$$Na^+ + 1e^- \rightarrow Na^0 \qquad E°_{red} = -2.71\ V$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E°_{red} = -0.41\ V$$

overall reaction

$$2\ I^-_{(aq)} + 2\ H_2O_{(l)} \rightarrow I_{2(aq)} + H_{2(g)} + 2\ OH^-_{(aq)} \qquad E°_{cell} = -0.95\ V$$

That which is easier to accomplish will occur.

When more than one cation is present, the cation that is easiest to reduce will be reduced first at the cathode
   least negative or most positive $E°_{red}$

When more than one anion is present, the anion that is easiest to oxidize will be oxidized first at the anode
        least negative or most positive $E°_{ox}$

Molten NaCl (l) produces Cl₂ gas and solid Na

Electrolysis of pure compounds:

- The compound must be in molten (liquid) state
- Electrodes normally graphite
- Cations are reduced at the cathode to metal element
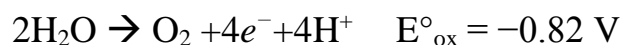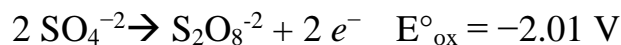- Anions oxidized at anode to nonmetal element

$$2\ Cl^-(l) \longrightarrow Cl_2^-(g) + 2\ e^-$$

$$2\ Na^+(l) + 2\ e^- \longrightarrow 2\ Na(s)$$
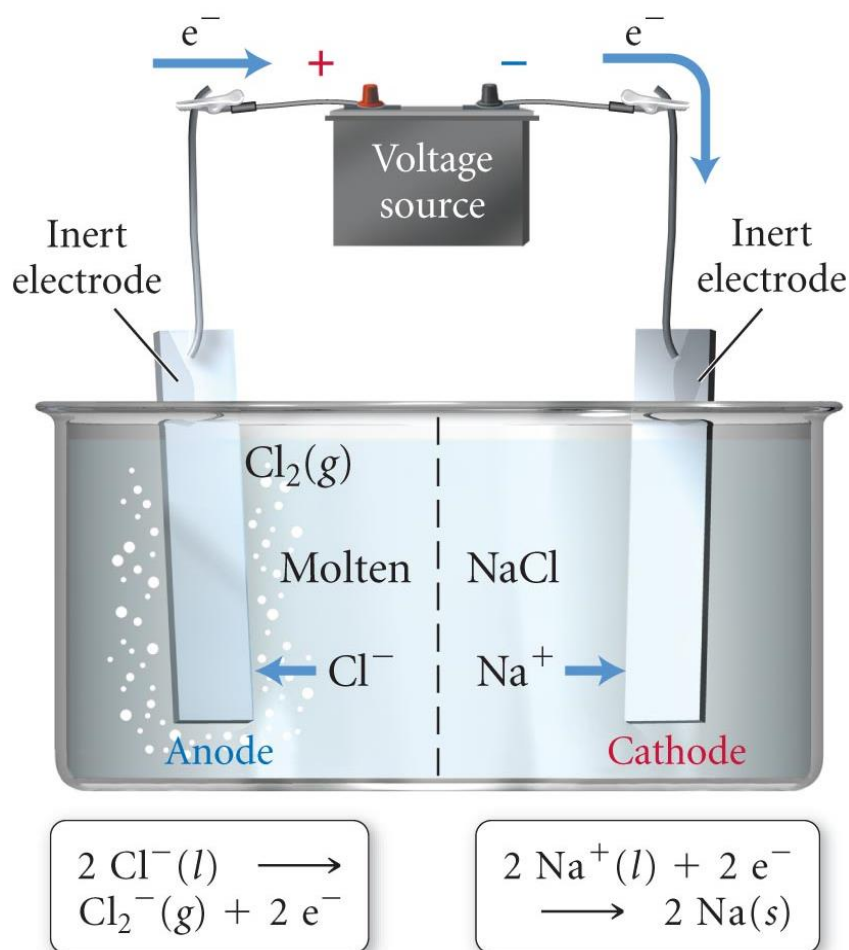
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Aqueous NaCl (aq) produces H₂ and Cl₂ gases

Write out the possible reactions and predict the expected products…

The actual reaction requires a greater voltage for the oxidation of water to oxygen than the predicted 0.82V at pH = 7 (overvoltage occurs). The overvoltage increases the value to about 1.4V causing Cl₂ to oxidize more easily.

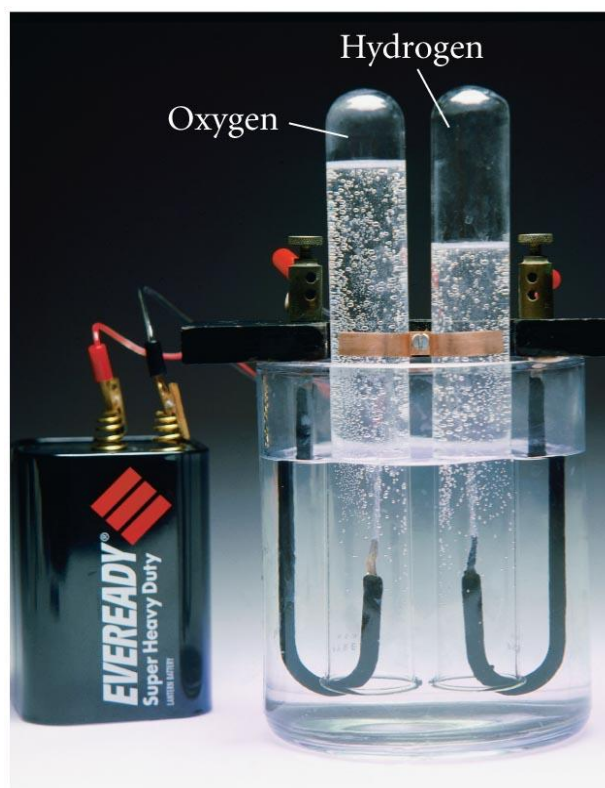**Electrolysis of water in Na$_2$SO$_4$ (aq) solution produces O$_2$ and H$_2$ gases**

possible oxidations

$2 \ SO_4^{-2} \rightarrow S_2O_8^{-2} + 2 \ e^-$ $E°_{ox} = -2.01$ V

$2H_2O \rightarrow O_2 + 4e^- + 4H^+$ $E°_{ox} = -0.82$ V

possible reductions

$Na^+ + 1e^- \rightarrow Na^0$ $E°_{red} = -2.71$ V

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E°_{red} = -0.41$ V

Predict the overall reaction:

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Electrolysis of Aqueous Solutions:
- Possible cathode reactions
  - reduction of cation to metal
  - reduction of water to H$_2$
    - $2 \ H_2O + 2 \ e^- \rightarrow H_2 + 2 \ OH^-$ $E° = -0.83$ v @ stand. cond.
    - $E° = -0.41$ v @ pH 7

- Possible anode reactions
  - oxidation of anion to element
  - oxidation of H$_2$O to O$_2$
    - $2 \ H_2O \rightarrow O_2 + 4 \ e^- + 4H^+$ $E° = -1.23$ v @ stand. cond.
    - $E° = -0.82$ v @ pH 7

- Half-reactions that lead to least negative E_{cell} will generally occur unless overvoltage changes the conditions
  - **Overvoltage** often occurs for the oxidation of water to O$_2$ in aqueous solutions due to the large number of electrons and H$^+$ ions involved as well as other kinetic factors. With the overvoltage the oxidation of water requires about 1.4V. *The underlying kinetic factors that cause this are beyond the scope of this class.*
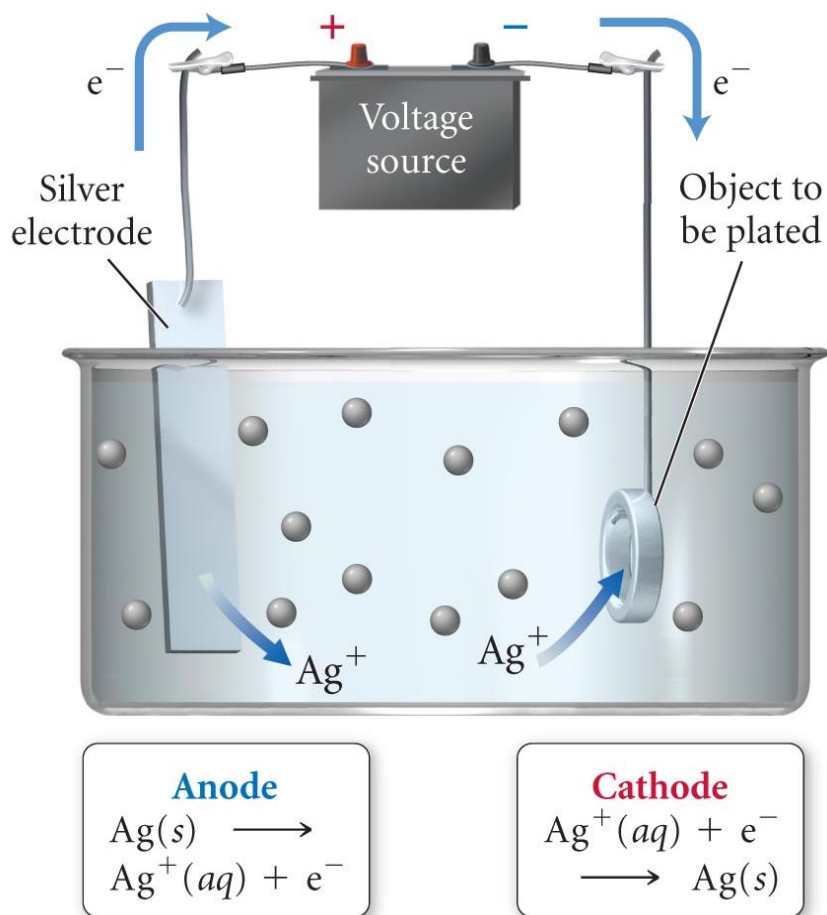
Applications of Electrolysis:

Electrolytic Refining is the most practical, but expensive method to isolate active metals like Na. Chemical reactions can separate many less active metals from their ores. Usually further refining is still needed for purification. Example: the anode contains impure copper and the cathode is purified Cu. As power is forced through the system the pure Cu thickens and grows and the impure Cu thins and drops off a sludge of impurities to the bottom of the vessel.

Electroplating of Metals uses the same method as the refining by electroplating a thin layer of a metal such as Ag or Au on jewelry.

In electroplating, the work piece is the cathode

Cations are reduced at cathode and plate to the surface of the work piece
The anode is made of the plate metal. The anode oxidizes and replaces the metal cations in the solution.

Voltage source

Silver electrode

Object to be plated

Ag^+

Ag^+

Anode

$Ag(s) \longrightarrow$
$Ag^+(aq) + e^-$

Cathode

$Ag^+(aq) + e^-$
$\longrightarrow Ag(s)$

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Quantitative Aspects of Electrolysis:

Volt = Joule/Coulomb

Current is the number of electrons that flow through the system per second, Ampere

Coulomb = Amp · sec (C = A· s) and Faraday's constant = 96500 C/mole e⁻

Electrical work is generally measured in watts. 1 W = 1 J/s.

One kilowatt hour (kWh) = (1000W) (3600s/hr) = 3.6 x 10^6 J

Example 12:

An unknown aqueous iron salt is electrolyzed by a current of 2.75 A for 45 minutes producing 1.43 g of solid Fe. Solve for the oxidation number for Fe in the salt?

Example 13:

Solve for the grams of Cr (s) that will be deposited from CrO_4^{-2} (aq) using 6.00 amps current for 3 ¹/₂ hours.   Assume the theoretical yield of Cr (s) is obtained.

Example 14:

How many kWh are required to produce 5.00 kg of Mg from the electrolysis of molten $MgCl_2$ if the applied cell potential is 5.00 V. Assume 100% efficiency.