Electrochemistry

For any two metals in an activity series, the more active metal is the more readily oxidized.

Table 21.1
Activity Series of Metals, with Half-Reactions for Oxidation Process

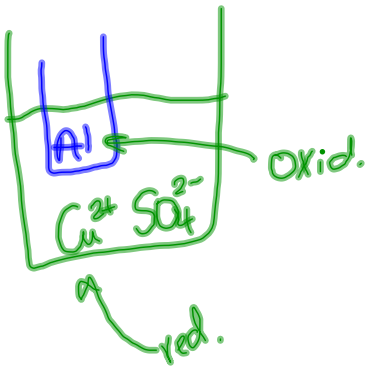
	Element	Oxidation half-reactions
Most active and most easily oxidized	Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
	Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
	Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
	Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Decreasing activity ↓	Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
	Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
	Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
	Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
	Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
	Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
	Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
	Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
	Hydrogen*	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
	Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
	Mercury	$Hg(s) \longrightarrow Hg^{2+}(aq) + 2e^-$
	Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Least active and least easily oxidized	Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

Cu^{2+}

Example: zinc metal in a solution of copper (II) sulfate

$Zn \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$



Electrochemical process - any conversion between chemical energy and electrical.

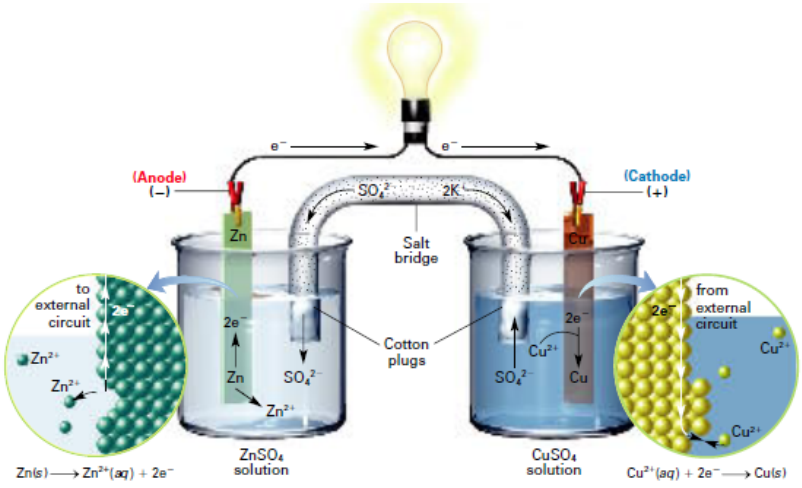
- all involve redox reactions
- half reactions must be physically separated if reaction is to be used as a source of electrical energy
- an electrochemical cell is any device that converts between electrical energy and chemical energy

Voltaic Cells

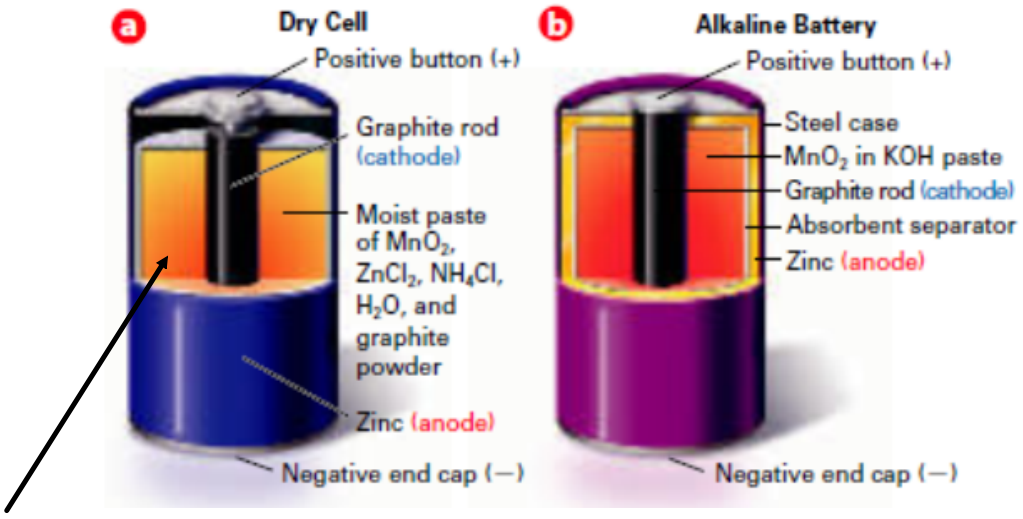
- electrochemical cells used to convert chemical energy into electrical energy
- electrical energy is produced in a voltaic cell by spontaneous redox reactions within the cell
- A half-cell is one part of a voltaic cell in which either oxidation or reduction occurs.
    - normally consists of a metal immersed in a solution of its ions
    - half-cells are connected by a salt bridge - a tube containing a strong electrolyte

- electrode - a conductor in a circuit that carries electrons to or from a substance other than a metal
    anode - the electrode at which the oxidation occurs (labeled the negative electrode because electrons are produced)
    cathode - the end at which reduction occurs (labeled the positive electrode because electrons are consumed)

- always remains balanced in terms of charge because of the salt bridge



Using Voltaic Cells as Energy Sources



electrolyte is a paste

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (anode reaction)

Reduction: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ (cathode reaction)

Writing the Cell Reaction

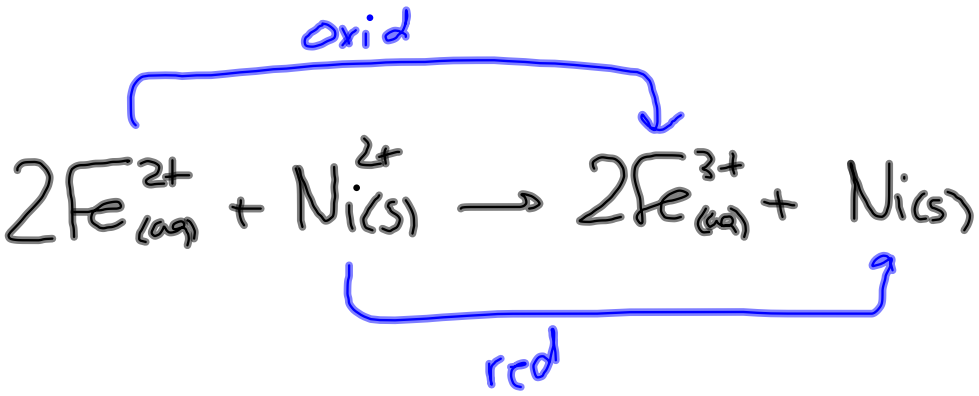
$Fe^{3+}_{(aq)} + e^- \Rightarrow Fe^{2+}_{(aq)}$ $\quad E^0_{Fe3+} = 0.77\ V$

$Ni^{2+}_{(aq)} + 2e^- \Rightarrow Ni_{(s)}$ $\quad E^0_{Ni2+} = -0.25\ V$

Reduction: $2Fe^{3+}_{(aq)} + 2e^- \rightarrow 2Fe^{2+}_{(aq)}$

Oxidation: $Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

$2Fe^{3+}_{(aq)} + Ni_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Ni^{2+}_{(s)}$


oxid
2Fe(aq)2+ + Ni(s) → 2Fe(aq)3+ + Ni(s)
red

Half-Cells and Cell Potentials

Electrical Potential
- measure of the cell's ability to produce an electric current
- measured in volts (V)
- results from a competition for electrons between two half-cells

reduction potential - tendency of a half-reaction to occur as reduction

cell potential - difference in reduction potentials of the two half-cells

$$E^0_{cell} = E^0_{red} - E^0_{oxid}$$

Calculating the Standard Cell Potential

Red.

$Fe^{3+}_{(aq)} + e^- \Rightarrow Fe^{2+}_{(aq)}$ $\quad E^0_{Fe3+} = 0.77\ V$

Oxid.

$Ni^{2+}_{(aq)} + 2e^- \Rightarrow Ni_{(s)}$ $\quad E^0_{Ni2+} = -0.25\ V$

$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxid.}$$

$$= (0.77V) - (-0.25V)$$

$$= \boxed{1.02V}$$

Calculating Standard Cell Potentials

- If the cell potential for a given redox reaction is positive, then the reaction is **spontaneous**.

- If the cell potential is negative then the reaction is **nonspontaneous**.

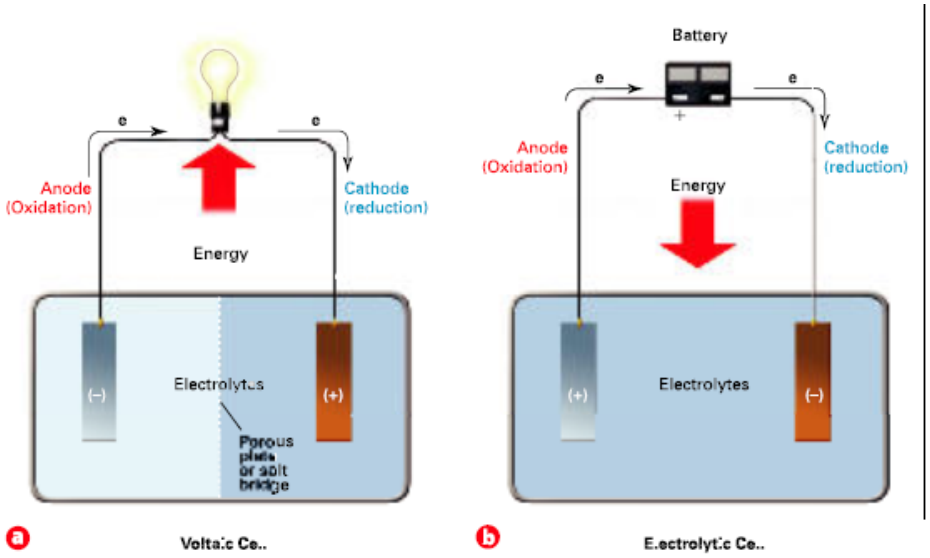
$$Zn_{(s)} + 2Ag^{+}_{(aq)} \quad Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Electrolysis

Electrolysis - electrical energy is used to bring about a chemical energy

Electrolytic cell - electrochemical cell used to cause a chemical change through
the application of electrical energy

- uses electrical energy to make a nonspontaneous reaction go to completion.


e
e
Anode
(Oxidation)
Cathode
(reduction)
Energy
(–)
Electrolytes
(+)
Porous
plate
or salt
bridge
a
Battery
e
e
Anode
(Oxidation)
Cathode
(reduction)
Energy
(+)
Electrolytes
(–)
b

Electrolysis of Water

The products of the electrolysis of water are hydrogen and oxygen gas.

Reduction: $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Oxidation: $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$

Electrolysis of Brine

If electrolyte in solution is more easily oxidized or reduced than water, the products of electrolysis will be substances other than hydrogen and oxygen.

brine - concentrated aqueous solution of sodium chloride

During electrolysis of brine, chloride ions are oxidized at the anode, and water is reduced at the cathode.

Reduction: $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Oxidation: $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

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#37-42
#45-49 (omit 47)
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