Oxidation - Reduction Reactions

Oxidation and Reduction

I.   Oxidation States
    A. The oxidation rules (as summarized by Mr. Allan)
            1. In compounds, hydrogen has an oxidation # of +1
            2. In compounds, oxygen has an oxidation # of –2
            3. The sum of the oxidation #'s in anything is equal to its charge
    B. See Table 19-1 for a More Thorough Summary of Oxidation #'s

II.   Oxidation and Reduction Processes
    A. Oxidation
            1. Loss of Electrons
            2. Rxns in which atoms or ions attain a more positive or less negative oxidation state
            3. Na $\rightarrow$ Na^{+1} + e-
    B. Reduction
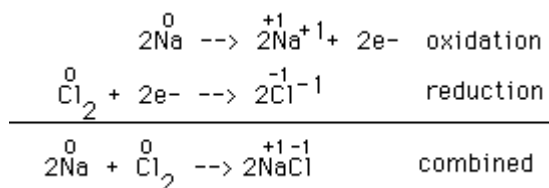   1. Gaining Electrons
            2. Rxns in which atoms or ions attain a more negative or less positive oxidation state
            3. Cl + e- $\rightarrow$ Cl^{-1}
    C. Redox rxns
            1. Any chemical process in which elements undergo a change in oxidation number
            2. Ox. cannot occur without red. occuring simultaneously
            3. number of electrons lost = number of electrons gained
            4. If none of the atoms in a reaction change oxidation state, then it is NOT a redox reaction
    D. Half-reactions
            1. The part of the reaction involving oxidation or reduction alone can be written as a half-reaction:

$$2\overset{0}{Na} \longrightarrow 2\overset{+1}{Na}{}^{+1} + 2e^- \quad \text{oxidation}$$

$$\overset{0}{Cl}_2 + 2e^- \longrightarrow 2\overset{-1}{Cl}{}^{-1} \quad \text{reduction}$$

$$\overline{2\overset{0}{Na} + \overset{0}{Cl}_2 \longrightarrow 2\overset{+1\,-1}{NaCl} \quad \text{combined}}$$

    E. Oxidation Numbers in Compounds
            1. Compounds are neutral
            2. Sum of the ox #'s = zero

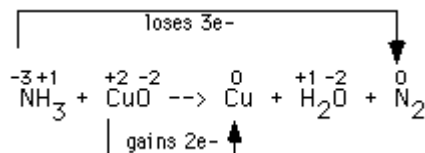|	
H_2SO_4	hydrogen is +1 2(+1) = +2
	oxygen is -2 4(-2) = -8
	sulfur must be +6 [-8 + (+6) + (+2) = 0]

Balancing Redox Equations

I.   Electron Transfer Method (***This is a different method than in your book)
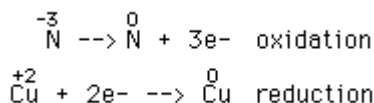
  A. Write the skeleton equation for the rxn

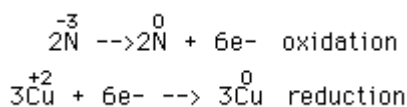$$NH_3 + CuO \rightarrow Cu + H_2O + N_2$$
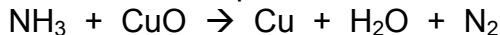
  B. Assign oxidation #'s to all elements and determine what is oxidized and what is reduced

 C. Write the electronic eqns for both the oxidation and reduction processes

$$\overset{-3}{N} \rightarrow \overset{0}{N} + 3e^- \quad \text{oxidation}$$

$$\overset{+2}{Cu} + 2e^- \rightarrow \overset{0}{Cu} \quad \text{reduction}$$

  D. Adjust the coefficients in both electronic eqns so that the number of electrons lost equals the number of electrons gained

$$2\overset{-3}{N} \rightarrow 2\overset{0}{N} + 6e^- \quad \text{oxidation}$$

$$3\overset{+2}{Cu} + 6e^- \rightarrow 3\overset{0}{Cu} \quad \text{reduction}$$

  E. Place these coefficients in the skeleton eqn.

$$2NH_3 + 3CuO \rightarrow 3Cu + H_2O + N_2$$
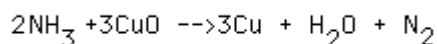
  F. Supply the proper coefficients for the rest of the eqn to satisfy conservation of atoms

$$2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2$$
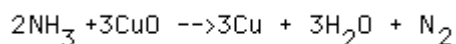
Oxidizing and Reducing Agents

I.   Oxidizing and Reducing Agents

  A. Oxidizing agents

      1. A substance that has the potential to cause another substance to be oxidized

      2. The substance that is reduced in a redox rxn

      3. The halogens and oxygen are active oxidizing agents

  B. Reducing agents

      1. A substance that has the potential to cause another substance to be reduced

      2. The substance that is oxidized in a redox rxn

      3. Group I and II metals are active reducing agents

II. Strengths of Oxidizing and Reducing Agents
   A. Strong Oxidizing Agents
      1. Substances that readily gain electrons are strong oxidizing agents
         a. Halogens and oxygen
      2. Once reduced, the strong oxidizing agent makes a poor reducing agent
   a. It doesn't want to give up the electron(s) it gained (why not?)
   B. Strong Reducing Agents
      1. Substances that readily lose electrons are strong reducing agents
         a. Group I and Group II metals
      2. Once oxidized, the strong reducing agent makes a poor oxidizing agent
         a. It doesn't want to gain back the electrons it lost (why not?)

Relative Strength of Oxidizing and Reducing Agents	
Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$Cr_2O_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing Strength (left column, upward)

Increasing Strength (right column, downward)

C. Auto-oxidation
1. Redox process in which the substance acts as both the oxidizing agent and the reducing agent
2. Decomposition of hydrogen peroxide:

$$\overset{+1}{H_2}\overset{-1}{O_2} \rightarrow 2\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{O_2}$$
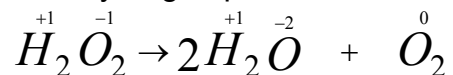
    a. Hydrogen is unchanged
    b. Oxygen is both oxidized and reduced

Electrochemistry
Electrochemistry is the branch of chemistry that deals with electricity-related applications of oxidation –reduction reactions

I.   <u>Electrochemical Cells</u>
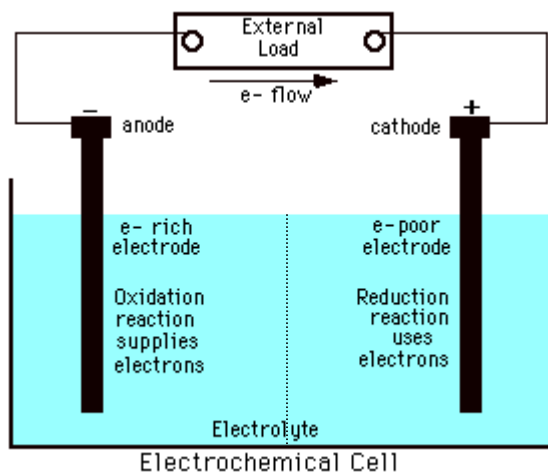   A. Electrochemical Cell
        1. A system of electrodes and electrolytes in which either chemical reactions produce electrical energy or an electric current produces chemical change
    B. Redox Energy Production
        1. Spontaneous redox rxns produce energy
            a. Heat if reactants are in contact
            b. If reactants are separated, electrons flow through the wire
    C. Electrochemical Terminology
   1. Electrode
            a. A conductor used to establish contact with a nonmetallic part of a circuit, such as an electrolyte
        2. Half-Cell
            a. A single electrode immersed in a solution of its ions
        3. Anode
            a. electrode where oxidation occurs
        2. Cathode
            a. electrode where reduction occurs

External Load
e- flow
anode   cathode
e- rich electrode   e-poor electrode
Oxidation reaction supplies electrons   Reduction reaction uses electrons
Electrolyte
Electrochemical Cell

II.   Voltaic Cells
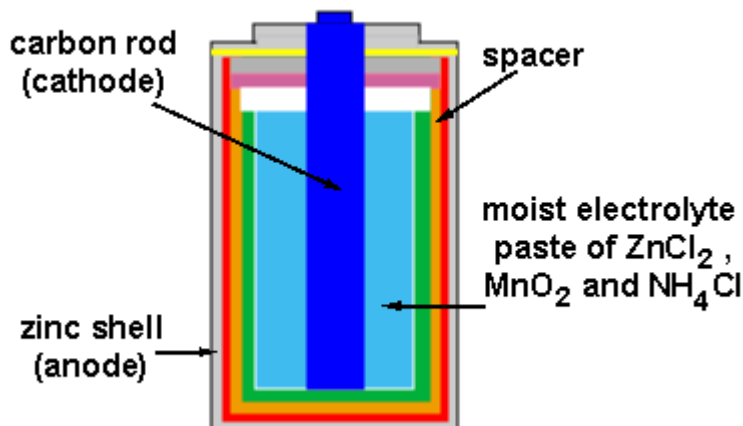   A. Voltaic Cells
        1. An electrochemical cell in which the redox rxn takes place spontaneously and produces electrical energy

Zn-Cu Electrochemical Cell
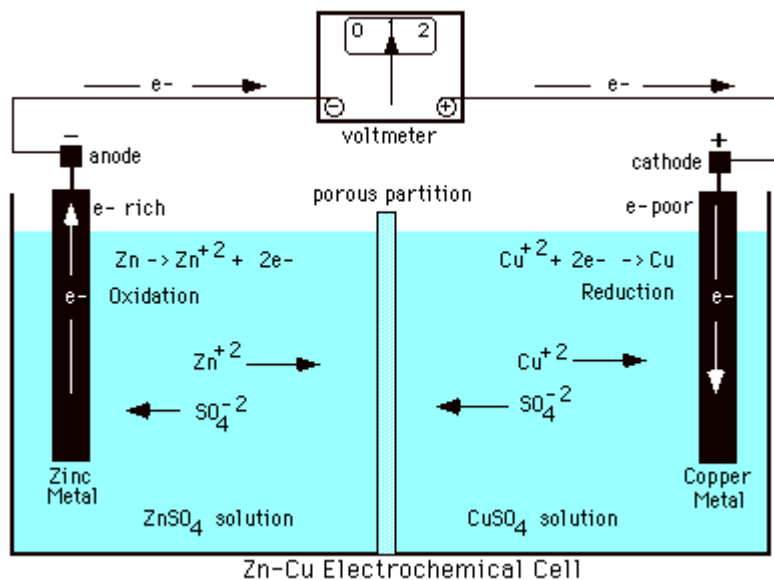
B. Zinc-Carbon Dry Cells (Flashlight batteries)

1. Anode reaction: $\overset{0}{Zn}(s) \rightarrow \overset{+2}{Zn^{2+}}(aq) + 2e^-$

2. Cathode reaction: $2\overset{+4}{Mn}O_2(s) + H_2O(l) + 2e^- \rightarrow \overset{+3}{Mn_2}O_3(s) + 2OH^-(aq)$

carbon rod (cathode)

spacer

zinc shell (anode)

moist electrolyte paste of $ZnCl_2$, MnO_2 and NH_4Cl

C. Alkaline Batteries

1. Anode reaction: $\overset{0}{Zn}(s) + 2OH^-(aq) \rightarrow \overset{+2}{Zn}(OH)_2(s) + 2e^-$

2. Cathode reaction $2\overset{+4}{Mn}O_2(s) + H_2O(l) + 2e^- \rightarrow \overset{+3}{Mn_2}O_3(s) + 2OH^-(aq)$

D. Mercury Batteries

   1. Anode reaction: $\overset{0}{Zn}(s) + 2OH^-(aq) \rightarrow \overset{+2}{Zn}(OH)_2(s) + 2e^-$

   2. Cathode reaction: $\overset{+2}{Hg}O(s) + H_2O(l) + 2e^- \rightarrow \overset{0}{Hg}(l) + 2OH^-(aq)$
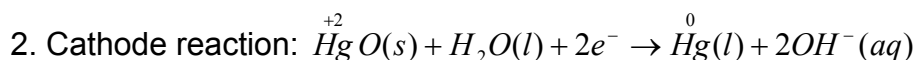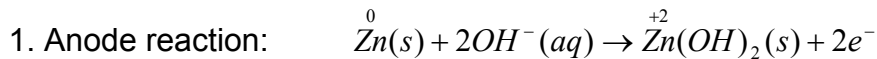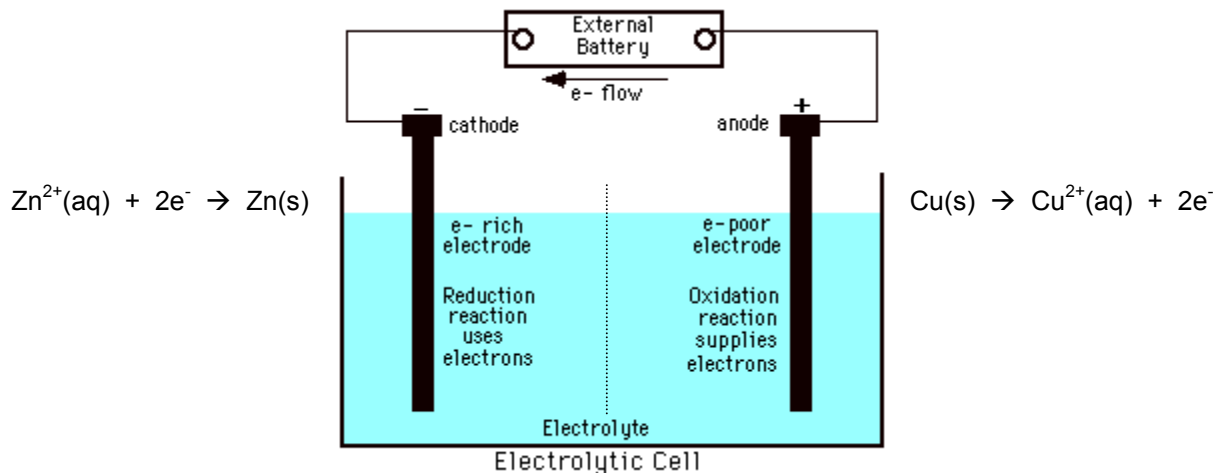
III.   Electrolytic Cells

  A. Electrolysis

     1. Process by which an electric current is used to drive redox rxns (nonspontaneous redox)

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

Electrolytic Cell

  B. Electroplating

     1. An electrolytic process in which a metal ion is reduced and a solid metal is deposited on a surface

     2. Inactive metals form ions that are more easily reduced than hydrogen

        a. Solution contains a salt of the plating metal

        b. Cathode is object to be plated

        c. Anode is a piece of the plating metal

Silver ato

Silver ions are reduced
(and plated)
at the cathode
$Ag^{+1} + e^- \rightarrow Ag$ $Ag \rightarrow Ag^{+1} + e^-$

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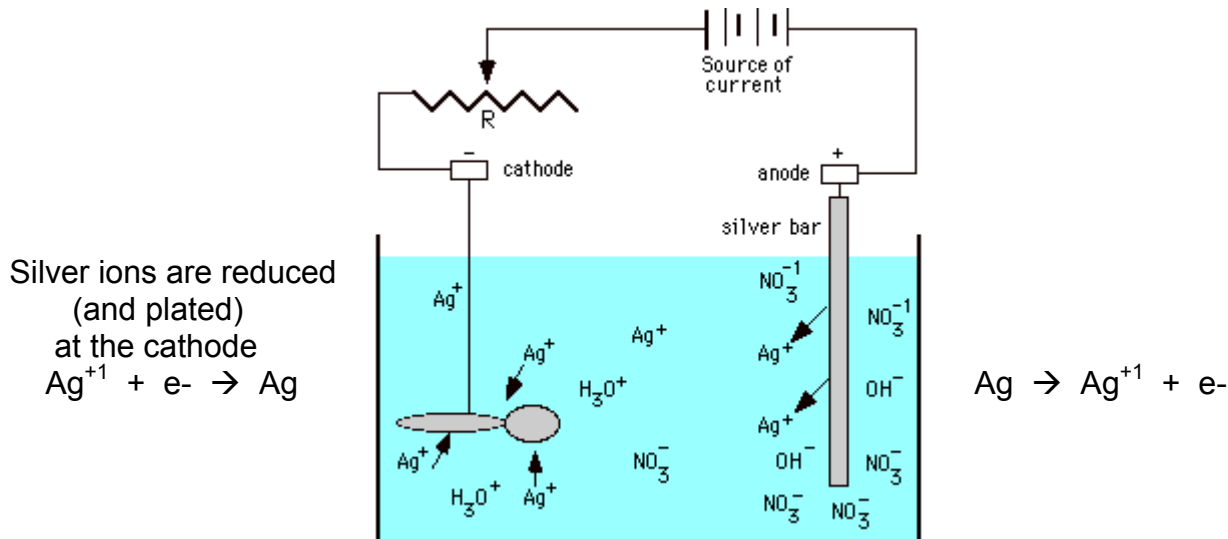
C. Rechargeable Cells
1. Voltaic Cells
a. Source of energy on its discharge cycle
2. Electrolytic Cell
a. Requires energy input
b. Stores chemical energy of its recharge cycle
3. Automobile Lead Storage battery
a. Six two-volt cells in series (2 x 6 volts = 12 volts)
b. Anode - Metallic lead
c. Cathode - PbO_2
d. H_2SO_4 serves as the electrolyte
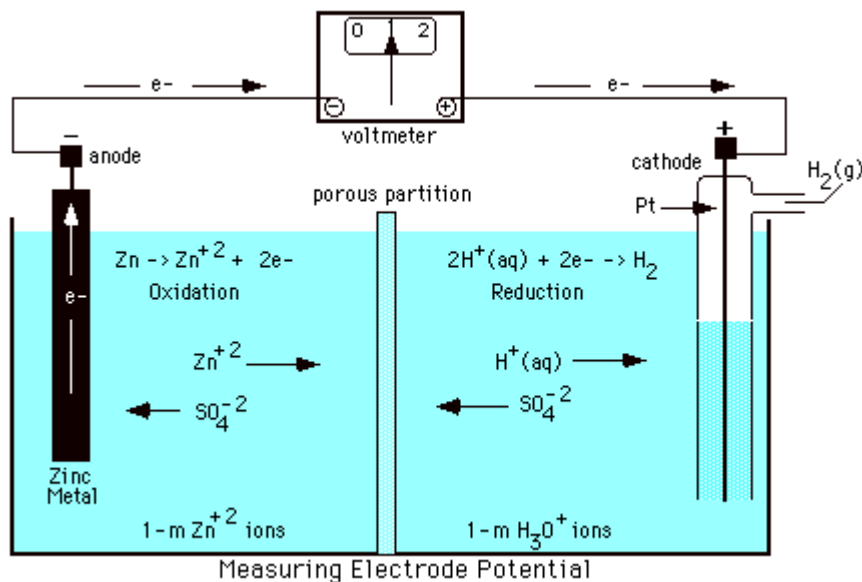D. Electrode Potential
1. Potential Difference
a. Difference in electric potential between two electrodes
b. Energy required to move a certain electric charge between electrodes
c. Measured in volts
2. Electrode Potential (Reduction Potential)
a. The potential difference between an electrode and its solution in a half reaction
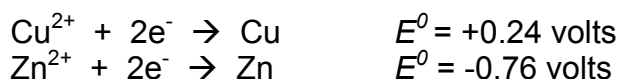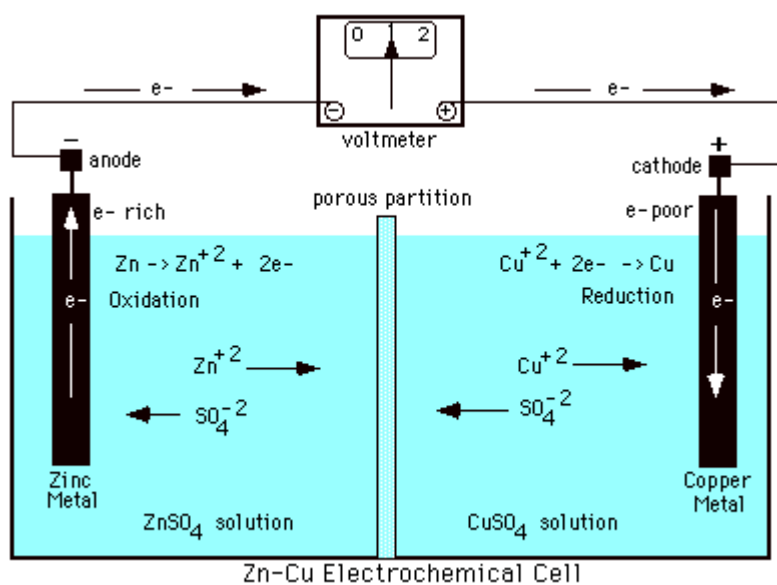b. The sum of the two electrode potentials is the potential difference for the complete cell
3. Measuring Electrode Potentials
a. Hydrogen standard electrode (SHE) is assigned a potential of zero volts
b. Other electrodes are compared to hydrogen

Measuring Electrode Potential

4. Determining Potential Difference from Electrode Potentials (Table 19-4)
    a. Half reactions with positive potentials occur spontaneously to the right reductions
    b. the more (+) the reduction potential, the greater its tendency to occur as a reduction
    c. Half reactions with negative potentials occur spontaneously to the left as oxidations
    d. the more (-) the reduction potential, the greater its tendency to occur as an oxidation
5. Calculating Cell Potential
    a. $E^0{}_{cell} = E^o{}_{cathode} - E^0{}_{anode}$

Example: For a Zn-Cu cell

Zn-Cu Electrochemical Cell

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.24 \text{ volts}$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^0 = -0.76 \text{ volts}$$

- The copper reduction will occur at the cathode, and proceed as written.
- Zinc will be oxidized at the anode, and the reaction will be written:

$$Zn \rightarrow Zn^{2+} + e^- \qquad E^0 = +0.76 \text{ volts}$$
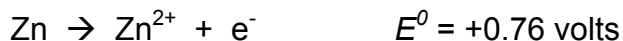
The sign on the potential changes changes when the direction of the reaction is changed, so:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.24 \text{ volts}$$
$$\underline{Zn \rightarrow Zn^{2+} + e^- \qquad E^0 = +0.76 \text{ volts}}$$
$$E^0{}_{cell} = +1.00 \text{ volts}$$