Oxidation-Reduction (Redox) Reactions (4.4)

"Redox" reactions: reactions in which electrons are transferred from one species to another

Oxidation & reduction always occur simultaneously

We use **OXIDATION NUMBERS** to keep track of electron transfers

Rules for Assigning Oxidation Numbers:

1) the ox. state of any free (uncombined) element is zero.
   Ex: $Na, S, O_2, H_2, Cl_2, O_3$

2) The ox. state of an element in a simple ion is the charge of the ion.
   Ex: Mg^{2+} → oxidation of Mg is +2

3) the ox. # for hydrogen is +1
   (unless combined with a metal, then it has an ox. # of -1)
   Ex: NaH Ex: NaOH (H bonded to O)

4) the ox. # of fluorine is always -1.

5) the ox. # of oxygen is usually -2.
   exception: peroxides, H_2O_2

6) in any neutral compound, the sum of the oxidation #'s = zero. Ex: $MgSO_4$

7) in a polyatomic ion, the sum of the oxidation #'s = the overall charge of the ion.

8) more electronegative = −
   more electropositive = +
   Ex = CN^- (+2, -3)

use these rules to assign oxidation #'s; ***assign known #'s first, then fill in the #'s for the remaining elements:*

Examples: Assign oxidation #'s to each element:

a) $NaNO_3$ (+1, +5, -2)

b) SO_3^{2-} (+4, -2)

c) HCO_3^- (+1, +4, -2)

d) H_3PO_4 (+1, +5, -2)

e) $Cr_2O_7^{2-}$ (+6, -2)

f) $K_2Sn(OH)_6$ (+1, +4, -2, +1)

Oxidation
Is
Loss
Reduction
Is
Gain

Oxidation-Reduction Reactions: oxidation & reduction always occur together (as one loses electrons, the other gains them)

- **oxidation**: the process of losing electrons (ox # increases)
- **reduction**: the process of gaining electrons (ox # decreases)
- **oxidizing agents**: species that cause oxidation (they are reduced)
- **reducing agents**: species that cause reduction (they are oxidized

Honors text: 4.4, 18.1-18.6

A reaction is "**redox**" if a change in oxidation # happens; if no change in oxidation # occurs, the reaction is **nonredox.**

Examples:

$MgCO_3 \rightarrow MgO + CO_2$ NONREDOX

(+2) ox

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$ OA = Cu, RA = Zn

(-2) red

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$ NONREDOX

(+2) ox

$CO_2 + H_2O \rightarrow C_6H_{12}O_6 + O_2$ OA = C, RA = O

(-4) red

Balancing Redox Equations (4.4)

- In balancing redox equations, the # of electrons lost in oxidation (the increase in ox. #) must equal the # of electrons gained in reduction (the decrease in ox. #)
- There are 2 methods for balancing redox equations:

1. Change in Oxidation-Number Method: based on equal total increases and decreases in oxidation #'s

Steps:

1) Write equation and assign oxidation #'s.
2) Determine which element is oxidized and which is reduced, and determine the change in oxidation # for each.
3) Connect the atoms that change ox. #'s using a bracket; write the change in ox. # at the midpoint of each bracket.
4) Choose coefficients that make the total increase in ox. # = the total decrease in ox. #.
5) Balance the remaining elements by inspection.

Example:

3(+4) ox

$3\,S + 4\,HNO_3 \rightarrow 3\,SO_2 + 4\,NO + 2\,H_2O$

4(-3) red

If needed, reactions that take place in acidic or basic solutions can be balanced as follows:

Acidic:	Basic:
• add H_2O to the side needing oxygen	• add 2 OH^- to the side needing oxygen; and add 1 H_2O to the other side
• then add H^+ to balance the hydrogen	• then add 1 H_2O to the side needing hydrogen, and 1 OH^- to the other side

Example: Balance the following equation, assuming it takes place in acidic solution.

$8H^+ + ClO_4^- + 8I^- \rightarrow Cl^- + 4I_2 + 4H_2O$

8(+1) ox

1(-8) red

Honors text: 4.4, 18.1-18.6

2. The Half-Reaction Method: separate and balance the oxidation and reduction half-reactions.

Steps:

1) write equation and assign oxidation #'s.
2) Determine which element is oxidized and which is reduced, and determine the change in oxidation # for each.
3) Construct unbalanced oxidation and reduction half reactions.
4) Balance the elements and the charges (by adding electrons as reactants or products) in each half-reaction.
5) Balance the electron transfer by multiplying the balanced half-reaction by appropriate integers.
6) Add the resulting half-reaction and eliminate any common terms to obtain the balanced equation.

Example: Balance the following using the half-reaction method:

(+2) ox

$2HNO_3 + 3H_2S \rightarrow 2NO + 3S + 4H_2O$

HNO_3: (+1)(+5)(-2), -6; H_2S: (+1)(-2), +2; NO: (+2)(-2); S: 0; H_2O: (+1)(-2), +2

(-3) red

reduction:

$2(N^{+5} + 3e^- \rightarrow N^{+2})$

$2N^{+5} + 6e^- \rightarrow 2N^{+2}$

oxidation:

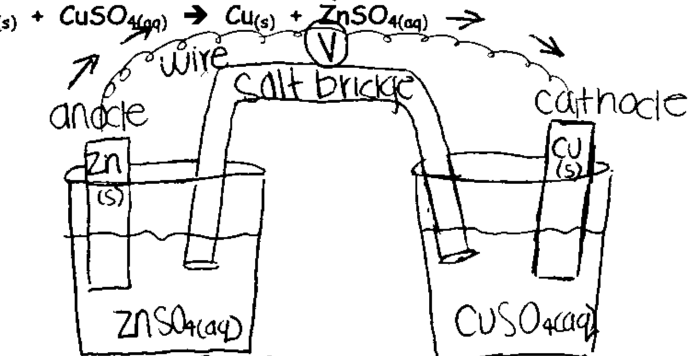
$3(S^{2-} \rightarrow S + 2e^-)$

$3S^{2-} \rightarrow 3S + 6e^-$

Electrochemical Cells (18.1-18.6)

Consider the reaction:

$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$



ox: $Zn \rightarrow Zn^{2+} + 2e^-$ red: $Cu^{2+} + 2e^- \rightarrow Cu$

- If the 2 solutions are not physically connected, but are connected by an external wire, electrons can still be transferred through the wire.
- Electrons flowing through a wire generate energy in the form of electricity.
- An electrochemical cell is a container in which chemical reactions produce electricity or an electric current produces chemical change.
- When an electrochemical cell produces electricity, it is also known as a **voltaic cell**.
- In the copper-zinc cell, the Cu and Zn electrodes (strips of each metal) are immersed in sulfate solutions of their respective ions ($CuSO_4$ and $ZnSO_4$)
- The solutions are separated by a porous barrier (prevents solutions from mixing, but allows ions to pass through), or a salt bridge (any medium through which ions can pass slowly).
- Cu^{2+} ions gain 2 electrons at the surface of the Cu strip, where they are deposited as Cu atoms:
  $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)
- Zn atoms in the Zn strip are losing electrons to become Zn^{2+} ions in solution:
  $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

- Voltaic cells are divided into 2 components called **HALF CELLS**: consist of a metal electrode in contact with a solution of its own ions.
- The **ANODE** is the half cell at which oxidation occurs; (a source of electrons)
- The **CATHODE** is the half cell at which reduction occurs (use up electrons)
  - ***electrons "flow" from left to right (anode to cathode)***
  - we can predict the "direction" of the electron flow in any given cell using the activity series and reduction potentials for metals (**see Table 18.1, p. ~~520~~)** 667
  - The more negative the **Standard Reduction Potential** value, the more likely a metal is to "give up" its electrons (become oxidized) and serve as the anode.
- The reaction in the cell will be spontaneous if the E° for the cell is positive; it is calculated as follows:

$$\boxed{E°\ \text{cell} = E°\ \text{cathode} - E°\ \text{anode}}$$

· consider the zinc-copper cell:

$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.7618\ V$

$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = 0.3419\ V$

-reduction of zinc has the lower value, so Zn is the anode

-what is the E° for the cell?

$E°_{cell} = 0.3419\ V - (-0.7618\ V)$

$E°_{cell} = 1.1037$

· consider a cell made from Al and Zn:

$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.7618$

$Al^{3+} + 3e^- \rightarrow Al \qquad E° = -1.662$

-what is the anode?

Al

-what is the E° for the cell?

$E°_{cell} = -0.7618 - (-1.662)$

$E°_{cell} = 0.9002\ V$

· Batteries are voltaic cells: a voltage is generated by a battery only if electrons continue to be removed from 1 substance and transferred to another; when equilibrium is reached between the 2 half cells, the battery is "dead."

· **Rechargeable batteries**: an external voltage source is applied to the battery's electrodes and reverses the half-reactions; this restores the electrodes to their original state.

· while the battery is being used, it operates as a voltaic cell (converts chemical energy into electric energy)

· while the battery is being charged, it operates as an electrolytic cell (converts electric energy into chemical energy)