### **Oxidation States**

Redox reactions are identified by taking inventory of the oxidation states of each substance throughout a reaction.

 $Cd(s) + NiO_{2}(s) + 2H_{2}O(l) -> Cd(OH)_{2}(s) + Ni(OH)_{2}(s)$ 

The oxidizing agent removes electrons from another substance. The reducing agent is the substance that gives up electrons.

# Rules for oxidation numbers

- 1) An atom in its elemental form has a oxidation number of zero.
- 2) Alkali metals = +1. Alkali Earth metals = +2, Aluminum = +3
- 3) Oxygen: usually -2, except in peroxide  $(O_2^{-2})$  where it is 1.
- 4) Hydrogen: +1 with a nonmetal, -1 with a metal
- 5) Halogens: -1 in a binary compound, when combined with oxygen in a polyatomic ion, the charge will be positive.
- Sum of oxidation numbers: For a neutral compound is zero. The sum of oxidation numbers for a polyatomic ion is equal to its charge.

#### **Balancing Redox**

- When balancing redox reactions, it is necessary to balance the number of electrons as well as the elements.
- Many times, redox reactions are written as two half reactions: one reaction for the oxidation, one for the reduction.
- When balancing two half reactions to put them together, a series of steps will be used.

# Balancing Redox (in acid soln)

- 1. Divide into one oxidation and one reduction half reaction.
- 2. Balance the reaction:
  - 1. Balance elements other than H and O.
  - 2. Balance O by adding  $H_2O$
  - 3. Balance H by adding H<sup>+</sup>
  - 4. Balance charge by adding e<sup>-</sup>.
- 3. Multiply each half reaction by an integer to make the numbers of electrons equal.
- 4. Add the two half reactions and simplify.

### Balancing Redox (in base soln)

Divide into one oxidation and one reduction half reaction.

- 2. Balance the reaction:
  - 1. Balance elements other than H and O.
  - 2. Balance O by adding  $H_2O$
  - 3. Balance H by adding H<sup>+</sup>
  - 4. Balance charge by adding e<sup>-</sup>.
- 3. Multiply each half reaction by an integer to make the numbers of electrons equal.
- 4. Add the two half reactions and simplify.
- 5. Add enough  $OH^{-}$  to both sides to neutralize all  $H^{+}$  and form water. Re-simplify the water!

#### **Redox Reactions**

In a redox reaction, one element will lose electrons (oxidation) while another element gains the lost electrons (reduction).

Ex:  $Zn(s) + Cu^{+2}(aq) -> Zn^{+2}(aq) + Cu(s)$ 

The transfer of electrons in this way can produce energy in the form of electricity. This is called electrochemistry.

# Voltaic Cells

The energy released by a spontaneous redox reaction can be used to perform electrical work. In a voltaic cell, the transfer of electrons is done through an external pathway rather than directly through reactants



### Definitions

Cathode - electrode at which reduction occurs Anode - electrode at which oxidation occurs Salt Bridge - tube that contains an electrolyte solution that does not react with ions in either cell Electrons flow across the wire from the anode to the cathode. Completing the circuit, anions and cations move through the salt bridge to maintain balance of charge between the two compartments.

#### Voltage

An electron has more potential energy on the anode than at the cathode and will spontaneously "fall" toward the cathode.

The difference between the potential energies per electric charge is measured in volts:

1 Volt = 1 J/Coulomb

The potential difference creates a force that pushes electrons through the circuit, creating an electromotive force, or emf.

# Standard Cell Potential

- The electromotive force of a voltaic cell is called the cell potential or cell emf (Ecell).
- Under standard conditions, the emf is called the standard cell potential or standard emf (E<sup>o</sup>cell)
- Standard cell potential is given through the following equation:
  - $E^{o}_{cell} = E^{o}_{red}(cathode) E^{o}_{red}(anode)$
- $E^{o}_{\mbox{\rm red}}$  are the potential for reduction to happen on the electrode. The more positive the value, the more likely that reduction will take place.

# Tips for determining E<sup>o</sup>cell

- The more positive half reaction will occur at the cathode. The more negative at the anode.
- The stoichiometric coefficient for a half reaction does not affect the E<sup>o</sup><sub>red</sub>. (It is not necessary to multiply by molar coefficients)

# The Nernst Equation

Batteries "die" because the concentration of reactants are consumed as the battery produces energy. When the chemicals run out, the E = 0.

- Since concentration changes throughout a battery's life, nonstandard conditions are always possible.
- Nernst rearranged and modified the nonstandard free energy equation to become:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

### Nernst Equation

Most Nernst calculations are done at 298 K, so the equation can be simplified to:

$$E = E^{\circ} - \frac{0.0592 V}{n} \log Q \ (T = 298 K)$$

#### **Redox Spontaneity**

One of our previous equations can be generalized to apply to all redox reactions:  $E^{o} = E^{o}_{red}(reduction) - E^{o}_{red}(oxidation)$ 

Using this equation, we can determine the spontaneity of a redox reaction through its emf:

+ E = spontaneous process

- E = nonspontaneous process

### EMF and Free Energy

Because redox reactions can be classified as spontaneous or not, there must be a relationship between EMF and free energy:

$$\Delta G^{o} = -nFE^{o}$$

Since both n and F are positive numbers, if  $E^{\rm o}$  is positive, then  $\Delta G^{\rm o}$  is negative, which both indicate a spontaneous reaction.

At equilibrium for a redox reaction, the  $\Delta G$  and EMF = 0, so the equilibrium constant can be calculated using the equation:  $\mathbf{nE}^{\circ}$ 

$$\log K = \frac{nE^6}{0.0592}$$
 (T = 298 K)

# Stoichiometry & Current

- Electrolysis is the process in which electrons are run through a compound for the process of decomposition, or to separate the compound into elements.
- The movement of electron charge through a circuit in one second is called a current. Current is measured in amps (A). Current is related to electron charge through the equation: Charge = Amps • seconds
- Once the coulombs of charge is known, the moles of electrons can be determined through Faraday's constant (1 mol  $e^- = 96,500 \text{ C}$ )

#### Example

The electrolysis of molten copper (II) chloride can be conducted by a current of 15 A. How many grams of copper metal can be created by this current running through the copper (II) chloride for 30 minutes?