Chapter 14 – Fundamentals of Electrochemistry
continued

Vocabulary:

Oxidation - Loss of electrons (increase oxidation state)
Reduction – Gain of electrons (decrease oxidation state)
Oxidizing agent – Substance that takes electrons (Standard reduction potential is more positive.)
Reducing agent – Substance that gives up electrons (Standard reduction potential is more negative.)
Anode – Electrode that oxidation takes place (positive polarity)
Cathode – Electrode that reduction takes place (negative polarity)
Coulombs – unit of charge
Volt – unit of potential
Ampere – unit of current (coulomb/sec)
Joule – unit of work
Watt – unit of power (work/sec)

Standard Potentials

- **Standardized potentials (E^o), listed as reductions, for all half-reactions**
- **Measured versus the S.H.E (0)**
- **Used in predicting the action in either a galvanic cell or how much energy would be needed to force a specific reaction in a non-spontaneous cell**
- **Assumes an activity of one for the species of interest (usually a fair approximation) at a known temperature in a cell with the S.H.E.**
- **Assumes that the cell of interest is connected to the (+) terminal of the potentiometer (voltmeter) and the S.H.E. is connected to the (-) terminal**

TABLE 22-1 Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.010
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

*See Appendix 3 for a more extensive list.

Better Oxidizing Agents in upper left hand corner.

Better Reducing Agents in lower Right hand corner

Nernst Equation

The Nernst equation allows you to determine the cell potential when the activities of the species involved $\neq 1$ ***(i.e. non-standard conditions, more typical to real-life)***

For $$aA + ne^- \Leftrightarrow bB$$

$$E = E° - (RT/nF) \ln (\mathcal{A}_b^{\ b} / \mathcal{A}_a^{\ a})$$

At 25° C:

$$E = E° - (0.05916/n) \log (\mathcal{A}_b^{\ b} / \mathcal{A}_a^{\ a})$$

Nernst Equation

- **Accounts for potentials of cells where the reagents are not at an activity of 1**
  - **Remember that standard potentials are at $\mathcal{A}$=1**
- **Accounts for the number of electrons transferred in a reaction, the temperature of the reaction, LeChatelier's Principle and a variety of other factors**
- **Used to calculate E_+ and E_- under non-standard conditions**
  - **Most real cases!**

The Nernst Equation for Complete Reactions…..

- **Setup two Nernst equations**
  - **One for E_+**
  - **One for E_-**

- **Solve each Nernst equation to get E_+ and E_-**

- **Solve for E_{cell} ($E_{cell} = E_+ - E_-$)**

What is E°'??

- **E°' is used in biochemistry to express the standard reduction potentials (E°) for conditions at pH 7.**
- **E°' is more useful for biochemists since most biological systems are near pH 7.**
- **Many redox reactions involved H^+ -- by expressing E° as E°', then it is understood that the $[H^+] = 10^{-7}$ M.**
- **Table 14-2 (pg. 303) lists the E° and E°' for various reduction reactions of interest in biochemistry.**

A galvanic cell is assembled in which the left cell is the anode where cadmium metal electrode is oxidized to cadmium ion in 0.010 M cadmium nitrate. In the right cell, the cathode, silver ion is reduced to silver metal on a silver metal electrode in 0.50 M silver nitrate.

1. Draw the cell (both a picture and a schematic diagram)
2. Write the half and net cell reactions
3. Calculate the net cell voltage
4. Indicate in which direction the cell is spontaneous

Using the Nernst Equation to Solve for a Species Concentration
(Chemical Sensor)

The cell is described as follows. Solve for the concentration of chloride if the measured cell voltage is 0.485 V

$$Pt_{(s)}\,|\,H_{2(g,\,1.00\,atm)}\,|\,H^{+}_{(aq,\,pH=3.6)}\,||\,Cl^{-}_{(aq,\,?M)}\,|\,AgCl_{(s)}\,|\,Ag_{(s)}$$

Problem - Calculate the E_{cell} for the following:

$Fe_{(s)} \mid FeBr_2(0.010M) \mid\mid NaBr\ (0.050\ M) \mid Br_{2(\ell)} \mid Pt_{(s)}$

Problem - A mercury cell used to power pacemakers runs on the following reaction:

$Zn_{(s)} + HgO_{(s)} = ZnO_{(s)} + Hg_{(l)}$ $\quad E° = 1.35$ V

If the power required to operate the pacemaker is 0.0100 W, how many kilograms of HgO (FM 216.59) will be consumed in 365 days? How many pounds of HgO is this (1 lb = 453.6 g)?

Applications of electrochemistry in analytical chem:
http://www.env.plymouth.ac.uk/eim/eat_home.htm