April 12, 2002

- **Today:** *Demo a day finale!*
- **Exam #3**
  - ✓1999 Exam #3 Questions - answers to be posted this weekend
  - ✓Exam Info Page - final update this weekend
  - ✓**Sunday, 4/14 Review Session: 4:30 - 6:00 pm, B203 Angell**
  - ✓Email me *today* if you need to take exam at an alternate time

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Another system

- Now, consider this cell:

$$\mathbf{Cu\ (s)|Cu^{2+}\ (aq)||Zn^{2+}\ (aq)|Zn\ (s)}$$

$$E^{o}_{cell} = -1.100 \text{ volts}$$

- What does a *negative* potential mean?
  - ✓Electrons *want* to flow from Cathode (Zn) to Anode (Cu)
  - ✓So, reaction is *spontaneous* in the "reverse" direction:

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

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Pulling Rank

- Rank Ag, Cu and Zn based on their ability to *cause reduction:*
  - ✓ Cu reduces Ag^+
  - ✓ Zn reduces Cu^{2+}
- So, as reducing agents:

Zn > Cu > Ag

How can we ***quantify*** this?

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Quantifying Reduction

By definition

- Measure E^o_{cell} for *reduction ½-cells* with a **reference ½-cell**:

$2H^+$ (aq) + $2e^-$ ® H_2 (g) E^o_H = 0.0000 volts
Standard Hydrogen Electrode (SHE)

Tabulate as ***Standard Reduction Potentials*** (oxidizing power):

	Ag	**Cu**	**Zn**
E^o	+0.800 v	+0.337 v	-0.763 v

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Calculating E^o_{cell}

$Cu\ (s)|Cu^{2+}\ (aq)||Ag^+\ (aq)|Ag\ (s)$

Anode (oxidation)	**Cathode (reduction)**
$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$	$Ag^+ + e^- \rightarrow Ag\ (s)$
$E^o_{ox} = -E^o_{Cu} = -0.337$ v	$E^o_{red} = E^o_{Ag} = +0.800$ v

$2 \times [Ag^+ + e^- \rightarrow Ag\ (s)]$ +0.800 v

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e$ -0.337 v

$Cu\ (s) + 2Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$ ***0.463 v = E^o_{cell}***

Or: **$E^o_{cell} = E^o_{Cathode} - E^o_{Anode}$**

(right) (left)

reduction potentials

The Thermodynamics Connection!

Recall that:

work = charge x potential

Which gives:

$w_{electr} = n\ F E_{cell}$

mol e^-/mol rxn

Faraday's Constant = *9.6487 x 10^4 C/mol e^-*

For a reversible system at constant Temp and Pressure:

$w_{max} = -\Delta G$

So: **$\Delta G^o = -n\ F E^o_{cell}$**

What about K?

Simple!

$$\Delta G^o = -RTLnK = -n\,F E^o_{cell}$$

Rearranging gives:

$$E^o_{cell} = \frac{RTLnK}{n\,F}$$

At 298.15K:

$$E^o_{cell} = (0.0592/n)LogK$$

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