

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

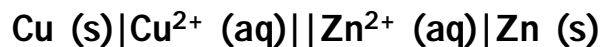
✓ **Sunday, 4/14 Review Session: 4:30 - 6:00 pm, B203 Angell**

✓ Email me *today* if you need to take exam at an alternate time

1

Another system

➤ Now, consider this cell:



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

➤ What does a *negative* potential mean?

✓ Electrons *want* to flow from Cathode (Zn) to Anode (Cu)

✓ So, reaction is *spontaneous* in the "reverse" direction:



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Pulling Rank

- Rank Ag, Cu and Zn based on their ability to *cause reduction*:
 - ✓ Cu reduces Ag⁺
 - ✓ Zn reduces Cu²⁺
- So, as reducing agents:

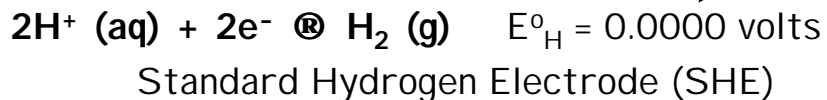


How can we *quantify* this?

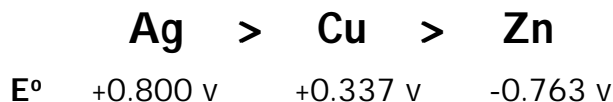
3

Quantifying Reduction

- Measure E°_{cell} for *reduction* ½-cells with a **reference ½-cell**:



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

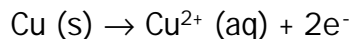


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Calculating E°_{cell}

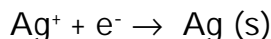


Anode (oxidation)

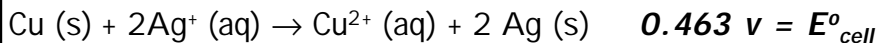
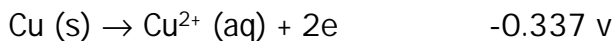
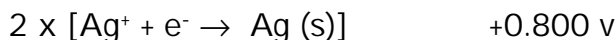


$$E^{\circ}_{\text{ox}} = -E^{\circ}_{\text{Cu}} = -0.337 \text{ v}$$

Cathode (reduction)



$$E^{\circ}_{\text{red}} = E^{\circ}_{\text{Ag}} = +0.800 \text{ v}$$



Or:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cathode (right)}} - E^{\circ}_{\text{Anode (left)}}$$

reduction potentials

The Thermodynamics Connection!

Recall that:

work = charge x potential

Which gives:

$$W_{\text{electr}} = n F E_{\text{cell}}$$

mol e⁻/mol rxn

Faraday's Constant = $9.6487 \times 10^4 \text{ C/mol e}^{-}$

For a reversible system at constant Temp and Pressure:

$$W_{\text{max}} = -\mathbf{DG}$$

So:

$$\mathbf{DG^{\circ} = -n F E^{\circ}_{\text{cell}}}$$

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What about K?

Simple!

$$\Delta G^\circ = -RT \ln K = -n F E^\circ_{\text{cell}}$$

Rearranging gives:

$$E^\circ_{\text{cell}} = \frac{RT \ln K}{n F}$$

At 298.15K:

$$E^\circ_{\text{cell}} = (0.0592/n) \text{Log}K$$