Chemistry 132 NT

It's easy to sit there and say you'd like to have more money. And I guess that's what I like about it. It's easy. Just sitting there, rocking back and forth, wanting that money.

Jack Handey

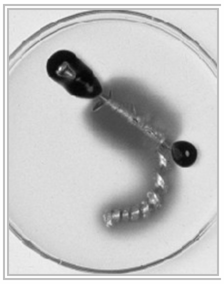
Chem 132 NT

Electrochemistry

Module 2

Voltaic Cells

- **Standard Cell emf's and Standard Electrode Potentials**
- **Equilibrium Constants from emf's**



An experiment in corrosion of an iron nail and magnesium ribbon. Corrosion is an electrochemical process.

Review

- Balancing oxidation-reduction reactions
- Sketching and labeling a voltaic cell
- Writing the cell reaction from the cell notation
- Calculating the quantity of work from a given amount of cell reactant

Standard Cell emf’s and Standard Electrode Potentials

- A **cell emf** is a measure of the driving force of the cell reaction.
  - The reaction at the anode has a definite **oxidation potential**, while the reaction at the cathode has a definite **reduction potential**.
  - Thus, the overall cell emf is a combination of these two potentials.

E_{cell} = oxidation potential + reduction potential

Standard Cell emf’s and Standard Electrode Potentials

- A **cell emf** is a measure of the driving force of the cell reaction.
  - A **reduction potential** is a measure of the tendency to gain electrons in the reduction half-reaction.
  - You can look at the oxidation half-reaction as the reverse of a corresponding reduction reaction.

Standard Cell emf’s and Standard Electrode Potentials

- A **cell emf** is a measure of the driving force of the cell reaction.
  - A **reduction potential** is a measure of the tendency to gain electrons in the reduction half-reaction.
  - The **oxidation potential** for an oxidation half-reaction is the negative of the reduction potential for the reverse reaction.

Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - Consider the zinc-copper cell described earlier.

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

  - The two half-reactions are

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

Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - The zinc half-reaction is an oxidation.
  - If you write E_{Zn} for the reduction potential of zinc, then $-E_{Zn}$ is the oxidation potential of zinc.

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad (E_{Zn})$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad -(E_{Zn})$$

Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - The copper half-reaction is a reduction..
  - Write E_{Cu} for the electrode potential.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad (E_{Cu})$$

Standard Cell emf’s and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - For this cell, the cell emf is the sum of the **reduction potential for the copper** half-cell and the **oxidation potential for the zinc** half-cell.

$$E_{cell} = E_{Cu} + (-E_{Zn})$$

$$E_{cell} = E_{Cu} - E_{Zn}$$

Standard Cell emf’s and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - Note that the cell emf is the **difference** between the two electrode potentials.
  - In general, E_{cell} is obtained by subtracting the **anode potential from the cathode potential**.

$$E_{cell} = E_{cathode} - E_{anode}$$

Standard Cell emf’s and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - The electrode potential is an **intensive property** whose **value is independent of the amount** of species in the reaction.

Standard Cell emf’s and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (in your text) are tabulated as <u>reduction</u> potentials.
  - Thus, the electrode potential for the half-reaction

$$\mathbf{2Cu^{2+}(aq) + 4e^{-} \;\text{®}\; 2Cu(s)}$$

is the same as for

$$\mathbf{Cu^{2+}(aq) + 2e^{-} \;\text{®}\; Cu(s)}$$

Tabulating Standard Electrode Potentials

- The **standard emf, E^{o}_{cell}**, is the emf of a cell operating under standard conditions of concentration (1 M), pressure (1 atm), and temperature (25 ^{o}C).
  - Note that individual electrode potentials require that we choose a **reference electrode**.
  - You arbitrarily <u>assign this reference electrode a potential of zero</u> and obtain the potentials of the other electrodes by measuring the emf’s.

Tabulating Standard Electrode Potentials

- The **standard emf, E^{o}_{cell}**, is the emf of a cell operating under standard conditions of concentration (1 M), pressure (1 atm), and temperature (25 ^{o}C).
  - By convention, the reference chosen for comparing electrode potentials is the **standard hydrogen electrode.**
  - **Standard electrode potentials** (in your text) are measured relative to <u>this hydrogen reference</u>.

Tabulating Standard Electrode Potentials

- The **standard emf, E^o_{cell}**, is the emf of a cell operating under standard conditions of concentration (1 M), pressure (1 atm), and temperature (25 ^oC).
  - For example, when you measure the emf of a cell composed of a **zinc electrode connected to a hydrogen electrode**, you obtain 0.76 V.
  - Since zinc acts as the anode (oxidation) in this cell, **its <u>reduction</u> potential is listed as –0.76 V.**

Strengths of Oxidizing and Reducing Agents

- Standard electrode potentials are useful in determining the strengths of **oxidizing and reducing agents** under standard-state conditions.
  - A reduction half-reaction has the general form

$$\textbf{oxidized species} + \textbf{ne}^- \rightarrow \textbf{reduced species}$$

  - The oxidized species acts as an oxidizing agent.

Strengths of Oxidizing and Reducing Agents

- Standard electrode potentials are useful in determining the strengths of **oxidizing and reducing agents** under standard-state conditions.
  - Consequently, the **strongest oxidizing agents** in a table of standard electrode potentials are the **oxidized species** corresponding to the half-reactions **with the largest (most positive) E^o values**. (For example $F_2(g)$)

Strengths of Oxidizing and Reducing Agents

- Standard electrode potentials are useful in determining the strengths of **oxidizing and reducing agents** under standard-state conditions.
  - An oxidation half-reaction has the general form

$$\textbf{reduced species} \rightarrow \textbf{oxidized species} + \textbf{ne}^-$$

  - The reduced species acts as a reducing agent.

Strengths of Oxidizing and Reducing Agents

- Standard electrode potentials are useful in determining the strengths of **oxidizing and reducing agents** under standard-state conditions.
  - Consequently, the **strongest reducing agents** in a table of standard electrode potentials are the **reduced species** corresponding to the half-reactions **with the smallest (most negative) E^o values**. (for example, Li(s))

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Consider a cell constructed of the following two half-reactions.

$$\mathbf{Cd^{2+}(aq) + 2e^- \rightarrow Cd(s);\ E^o = -0.40\,V}$$

$$\mathbf{Ag^{+}(aq) + 1e^- \rightarrow Ag(s);\ E^o = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - You will need to **reverse** one of these reactions to obtain the oxidation part of the cell reaction.

$$\mathrm{Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s);\ E^{o} = -0.40\,V}$$

$$\mathrm{Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - This will be Cd, because it has the more negative electrode potential.

$$\mathrm{Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s);\ E^{o} = -0.40\,V}$$

$$\mathrm{Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Therefore, you reverse the half-reaction and change the sign of the half-cell potential.

$$\mathrm{Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-};\ E^{o} = 0.40\,V}$$

$$\mathrm{Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - We must double the silver half-reaction so that when the reactions are added, the electrons cancel.

$$\mathbf{Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-};\ E^{o} = 0.40\,V}$$

$$\mathbf{Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - This does not affect the half-cell potentials, which do not depend on the amount of substance.

$$\mathbf{Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-};\ E^{o} = 0.40\,V}$$

$$\mathbf{2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Now we can add the two half-reactions to obtain the overall cell reaction and cell emf.

$$\mathbf{Cd(s) \rightarrow Cd^{2+}(aq) + 2e^{-};\ E^{o} = 0.40\,V}$$

$$\mathbf{2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s);\ E^{o} = 0.80\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Now we can add the two half-reactions to obtain the overall cell reaction and cell emf.

$$\mathbf{Cd(s) \rightarrow Cd^{2+}(aq) + \cancel{2e^-};\quad E^o = 0.40\,V}$$

$$\mathbf{2Ag^+(aq) + \cancel{2e^-} \rightarrow 2Ag(s);\quad E^o = 0.80\,V}$$

$$\mathbf{Cd(s) + 2Ag^+(aq) \rightarrow Cd^{2+}(aq) + 2Ag(s);\quad E^o_{cell} = 1.20\,V}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - The corresponding cell notation would be

$$\mathbf{Cd(s)\,|\,Cd^{2+}(1M)\,||\,Ag^+(1M)\,|\,Ag(s)}$$

Calculating Cell emf's from Standard Potentials

- The **emf of a voltaic** cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Note that the emf of the cell equals the standard electrode potential of the cathode minus the standard electrode potential of the anode.

$$\mathbf{E^o_{cell} = E^o_{cathode} - E^o_{anode}}$$

A Problem To Consider

- Calculate the standard emf for the following voltaic cell at 25 °C using standard electrode potentials. What is the overall reaction?

$$Al(s)\,|\,Al^{3+}(aq)\,||\,Fe^{2+}(aq)\,|\,Fe(s)$$

  - The reduction half-reactions and standard potentials are

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s);\ E^o = -1.66\ V$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\ E^o = -0.41\ V$$

A Problem To Consider

- Calculate the standard emf for the following voltaic cell at 25 °C using standard electrode potentials. What is the overall reaction?

$$Al(s)\,|\,Al^{3+}(aq)\,||\,Fe^{2+}(aq)\,|\,Fe(s)$$

  - You <u>reverse the first half-reaction</u> and its half-cell potential to obtain

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-;\ E^o = 1.66\ V$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\ E^o = -0.41\ V$$

A Problem To Consider

- Calculate the standard emf for the following voltaic cell at 25 °C using standard electrode potentials. What is the overall reaction?

$$Al(s)\,|\,Al^{3+}(aq)\,||\,Fe^{2+}(aq)\,|\,Fe(s)$$

  - To obtain the overall reaction we must balance the electrons.

$$2Al(s) \rightarrow 2Al^{3+}(aq) + \boxed{6e^-};\ E^o = 1.66\ V$$

$$3Fe^{2+}(aq) + \boxed{6e^-} \rightarrow 3Fe(s);\ E^o = -0.41\ V$$

A Problem To Consider

- Calculate the standard emf for the following voltaic cell at 25 °C using standard electrode potentials. What is the overall reaction?

$$\text{Al}(s)\,|\,\text{Al}^{3+}(aq)\,||\,\text{Fe}^{2+}(aq)\,|\,\text{Fe}(s)$$

  - Now we add the reactions to get the overall cell reaction and cell emf.

$$2\text{Al}(s) \text{ ® } 2\text{Al}^{3+}(aq) + \cancel{6e^-};\ E^o = 1.66\ \text{V}$$

$$3\text{Fe}^{2+}(aq) + \cancel{6e^-} \text{ ® } 3\text{Fe}(s);\ E^o = -0.41\ \text{V}$$

$$2\text{Al}(s) + 3\text{Fe}^{2+}(aq) \text{ ® } 2\text{Al}^{3+}(aq) + 3\text{Fe}(s);\ E^o = 1.25\ \text{V}$$

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among **E^o_{cell}, free energy, and equilibrium constant.**
  - In our thermodynamics chapter, we saw that ΔG equals the maximum useful **work** of a reaction.
  - For a voltaic cell, **work = $-nFE^o$**, so when reactants are in their standard states

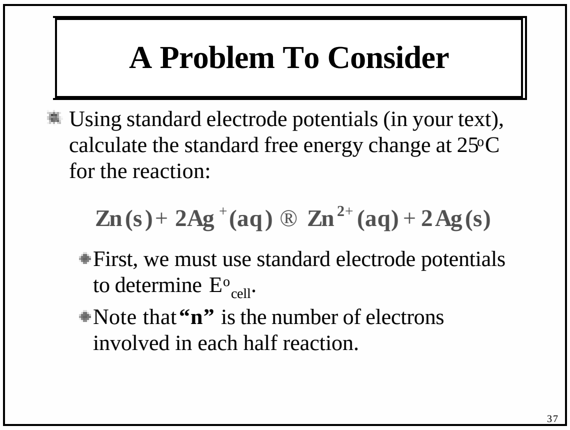
$$\text{D}G^o = -nFE^o$$

A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

$$\text{Zn}(s) + 2\text{Ag}^+(aq) \text{ ® } \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$$

  - First, we must use standard electrode potentials to determine E^o_{cell}.
  - The cell reaction equals the sum of the half-reactions after they have been multiplied by factors so that the electrons cancel in the summation.

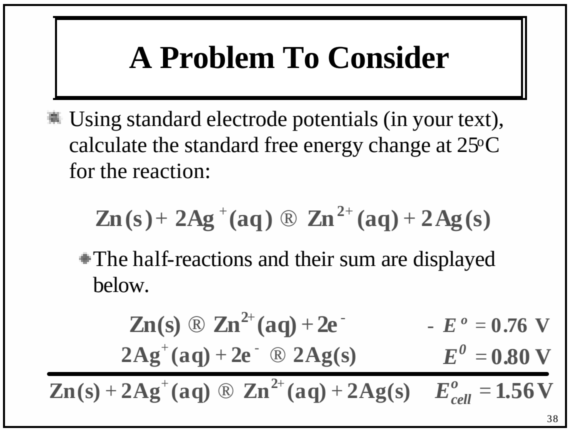


A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

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

  - First, we must use standard electrode potentials to determine E^{o}_{cell}.
  - Note that **"n"** is the number of electrons involved in each half reaction.



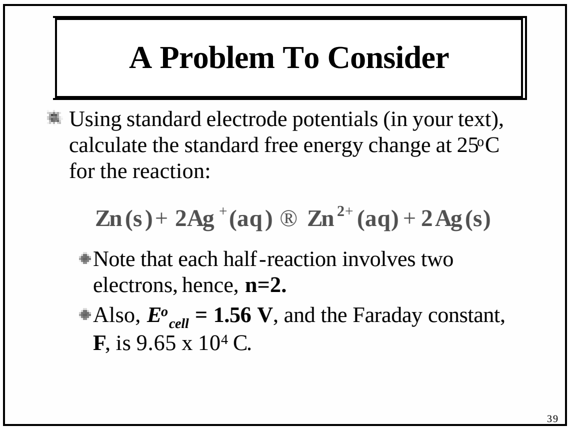
A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

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

  - The half-reactions and their sum are displayed below.

$$\begin{array}{lr} Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} & -E^{o} = 0.76\ V \\ 2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s) & E^{0} = 0.80\ V \\ \hline Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s) & E^{o}_{cell} = 1.56\ V \end{array}$$



A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

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

  - Note that each half-reaction involves two electrons, hence, **n=2.**
  - Also, E^{o}_{cell} **= 1.56 V**, and the Faraday constant, **F**, is 9.65×10^{4} C.

A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

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

  - Therefore:

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

$$\Delta G^{o} = -(2) \times (9.65 \times 10^{4} C) \times (1.56 \tfrac{J}{C})$$

$$\Delta G^{o} = -3.01 \times 10^{5} J$$

A Problem To Consider

- Using standard electrode potentials (in your text), calculate the standard free energy change at 25°C for the reaction:

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

  - Thus the standard free energy change is –301 kJ.

Equilibrium Constants from emf’s

- Some of the most important results from electrochemistry are the relationships among **E^{o}_{cell}, free energy, and equilibrium constant.**
  - The measurement of cell emf’s gives you yet another way of calculating equilibrium constants.

Equilibrium Constants from emf’s

- Some of the most important results from electrochemistry are the relationships among **E^o_{cell}, free energy, and equilibrium constant.**
  - Combining the previous equation, $\Delta G^o = -nFE^o_{cell}$, with the equation $\Delta G^o = -RT\ln K$, we get

$$nFE^o_{cell} = RT\ln K$$

Equilibrium Constants from emf’s

- Some of the most important results from electrochemistry are the relationships among **E^o_{cell}, free energy, and equilibrium constant.**
  - Or, rearranging, we get

$$E^o_{cell} = \frac{2.303RT}{nF}\log K$$

Equilibrium Constants from emf’s

- Some of the most important results from electrochemistry are the relationships among **E^o_{cell}, free energy, and equilibrium constant.**
  - Substituting values for the constants R and F at 25 °C gives the equation

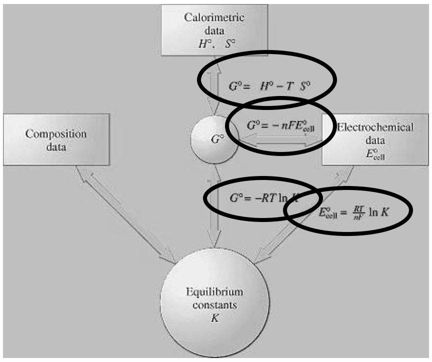
$$E^o_{cell} = \frac{0.0592}{n}\log K$$

(values in volts at 25 °C)

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among **E^o_{cell}, free energy, and equilibrium constant.**
  - The figure on the next slide summarizes the various relationships among K, ΔG^o, and E^o_{cell}.

The relationships among K, DG º, and E^o_{cell}.



A Problem To Consider

- The standard emf for the following cell is 1.10 V.
  $Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$
  Calculate the equilibrium constant K_c for the reaction
  $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$
  - Note that n=2. Substituting into the equation relating E^o_{cell} and K gives

$$1.10\ V = \frac{0.0592}{2} \log K$$

A Problem To Consider

- The standard emf for the following cell is 1.10 V.

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

  Calculate the equilibrium constant K_c for the reaction

  $$\mathrm{Zn\,(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)}$$

  - Solving for log K_c, you find

$$\log K = 37.2$$

A Problem To Consider

- The standard emf for the following cell is 1.10 V.

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

  Calculate the equilibrium constant K_c for the reaction

  $$\mathrm{Zn\,(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)}$$

  - Now take the antilog of both sides:

$$K_c = \text{antilog}(37.2) = 1.6 \times 10^{37}$$

A Problem To Consider

- The standard emf for the following cell is 1.10 V.

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

  Calculate the equilibrium constant K_c for the reaction

  $$\mathrm{Zn\,(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)}$$

  - The number of significant figures in the answer equals the number of decimal places in 37.2 (one). Thus

$$K_c = 2 \times 10^{37}$$

Operational Skills

- Determining the relative strengths of oxidizing and reducing agents
- Determining the direction of spontaneity from electrode potentials
- Calculating the emf from standard potentials
- Calculating the free-energy change from electrode potentials
- Calculating the cell emf from free-energy change
- Calculating the equilibrium constant from cell emf

Time for a few review questions