5.111 Lecture Summary #26
Oxidation/Reduction Lecture 3
and Nernst Equation

Topics: Adding and Subtracting Half-Cell Reactions,
Chapter 12

From Friday’s handout

Standard States and Cell Potentials

$$\Delta G^\circ_{cell} = -nF\Delta E^\circ_{cell}$$

$$\Delta E^\circ_{cell} = \text{cell potential (cell voltage) in which products and reactants are in their standard states}$$

Units for $\Delta E$ is volts.

Example - Calculate $\Delta E^\circ_{cell}$ for

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

anode \quad Zn (s) \rightarrow Zn^{2+} (aq) + 2e^- \rightarrow Zn (s) \ (oxidation)

cathode \quad Cu^{2+} (aq) + 2e^- \rightarrow Cu (s) \ (reduction)

$$\Delta E^\circ_{(\text{cell})} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Look up Standard REDUCTION Potentials ($E^\circ$) in back of book (measured against S.H.E)

$$\text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn} (s) \quad E^\circ = -0.7628 \text{ volts}$$
$$\text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \quad E^\circ = +0.3402 \text{ volts}$$

$$\Delta E^\circ_{(\text{cell})} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
$$= E^\circ (\text{Cu}^{2+}/\text{Cu}(s)) - E^\circ (\text{Zn}^{2+}/\text{Zn}(s))$$
$$= 0.3402 - (-0.7628) = 1.103 \text{ volts}$$

Is the flow of electrons spontaneous?

$$\Delta G^\circ_{cell} = -nF\Delta E^\circ_{cell}$$

So, if $\Delta E^\circ_{cell}$ is positive, $\Delta G^\circ_{cell}$ will be negative.

Is a reaction spontaneous when $\Delta G^\circ$ is negative?
Galvanic Cell is an electrochemical cell in which a _________________ chemical reaction is used to generate an electric current.

Electrolytic Cell uses electrical energy provided by an external circuit to carry out _________________ reactions.

Summary

Whether the cell operates spontaneously can be determined by $\Delta E_{\text{cell}}$. ($\langle + \rangle = \text{spontaneous}$)

$\Delta E_{\text{cell}}$ can be calculated from the Standard Reduction Potentials ($E^\circ$) of half-cell reactions.

Meaning of standard reduction potential $E^\circ$

A large positive $E^\circ$ means the element or compound is easy to reduce

ex. $\text{F}_2 (g) + 2e^- \rightarrow 2\text{F}^- \quad E^\circ = +2.87$ volts (easy to add electrons to $\text{F}_2$)

positive $E^\circ$, negative $\Delta G^\circ$, favorable

Is $\text{F}_2$ a good oxidizing agent?

A large positive $E^\circ$ means the oxidized species of the couple is very oxidizing.

A large negative $E^\circ$ means the element or compound is hard to reduce

ex. $\text{Li}^{+1} + e^- \rightarrow \text{Li} (s) \quad E^\circ = -3.045$ volts (hard to add electrons to $\text{Li}^{+1}$)

negative $E^\circ$, positive $\Delta G^\circ$, not favorable

Is $\text{Li}^{+1}$ a good oxidizing agent?

A large negative $E^\circ$ means the reduced species of the couple is very reducing.

Example: What is $\Delta E^\circ$ for the cell reaction: $2\text{Fe}^{3+} (aq) + 2\text{I}^- (aq) \rightarrow 2\text{Fe}^{2+} (aq) + \text{I}_2 (s)$?

balanced reaction at the cathode:

balanced reaction at the anode:
Standard Reduction Potentials are:

\( E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.770 \text{ V} \)
\( E^\circ (\text{I}_2/\text{I}^-) = +0.535 \text{ V} \)

\( \Delta E^\circ (\text{cell}) = E^\circ (\text{cathode}) - E^\circ (\text{anode}) \)

Is the reaction spontaneous?

Which is the better oxidizing agent: \( \text{Fe}^{3+}, \text{I}_2 \)?

Which is the better reducing agent: \( \text{I}^-, \text{Fe}^{2+} \)?

**Question:** Vitamin \( \text{B}_{12} \) has a large negative reduction potential, so how is it reduced in the body? Vitamin \( \text{B}_{12} \) needs to be reduced to be active. Proper functioning of an enzyme that requires vitamin \( \text{B}_{12} \) and folic acid is thought to be necessary for preventing heart disease and birth defects.

Where do you get vitamin \( \text{B}_{12} \) and folic acid in your diet? and how is the vitamin \( \text{B}_{12} \) reduced?

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**Today’s material**

**Adding and Subtracting Half-Cell Reactions to Calculate \( \Delta E^\circ \) for a New Half-Cell Reaction**

What if you need to know \( E^\circ \) for the half-cell reaction: \( \text{Cu}^{2+} (\text{aq}) + e^- \rightarrow \text{Cu}^+ (\text{aq}) \), but it is not available in the Table in the book? However, values of \( E^\circ \) for other reactions involving Cu are available.

One can add or subtract half-cell reactions with known \( E^\circ \) to form the new half-cell reaction:

**Half-cell reactions:**

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

**Standard Reduction Potentials are:**

\( E^\circ (\text{Cu}^{2+}/\text{Cu} (\text{s})) = +0.340 \text{ V} \)
\( E^\circ (\text{Cu}^+/\text{Cu} (\text{s})) = +0.522 \text{ V} \)
and calculate the $E^\circ$ for that new half-cell reaction as follows:

$$\Delta G_{\text{new}}^\circ = \Delta G_{\text{reduction}}^\circ - \Delta G_{\text{oxidation}}^\circ$$

or

$$-n_3 E^\circ_3 (\text{new}) = -n_1 E^\circ_1(\text{reduction}) + n_2 E^\circ_2(\text{oxidation})$$

$$E^\circ_3 = \frac{n_1 E^\circ_1(\text{reduction}) - n_2 E^\circ_2(\text{oxidation})}{n_3}$$

$$E^\circ_3 = (2)(0.340V) - (1)(0.522V) = 0.158 \ V = E^\circ (\text{Cu}^{2+}/\text{Cu}^+)$$

**NERNST EQUATION**

An exhausted battery is a sign that the cell reaction has reached equilibrium. At equilibrium, a cell generates zero potential difference across its electrodes.

To understand this, we need to know how the cell potential changes with cell composition.

What do we know already about equilibrium and the components of a reaction?

We know that $\Delta G$ changes as the concentrations of the components change until equilibrium is reached, then $\Delta G = 0$.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

What do we know about the relationship between $\Delta G^\circ$ and $\Delta E^\circ$?

$$\Delta G^\circ = -n_3 \Delta E^\circ$$

Combining:

$$-n_3 \Delta E = -n_3 \Delta E^\circ + RT \ln Q$$

Dividing by $-n_3$:

$$\Delta E = \frac{\Delta E^\circ - RT \ln Q}{n_3} \quad \text{(NERNST EQ.)}$$

**Example:** Calculate $\Delta E$ (the cell potential, potential difference, emf) at 25 °C of a cell in which the concentration of Zn$^{2+}$ ions is 0.10 M and Cu$^{2+}$ is 0.0010 M.

$$\text{Cu}^{2+} (\text{aq}) + \text{Zn} (s) \Rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu} (s)$$
Step 1: Calculate $\Delta E^\circ$ (Cell) from the $E^\circ$ for the half-reactions.

\begin{align*}
\text{Cu}^{2+} (aq) + 2e^- &\Rightarrow \text{Cu} (s) \quad E^\circ (\text{Cu}^{2+}/\text{Cu}(s)) = +0.340 \text{ V} \\
\text{Zn} (s) &\Rightarrow \text{Zn}^{2+} (aq) + 2e^- \quad E^\circ (\text{Zn}^{2+}/\text{Zn}(s)) = -0.7628 \text{ V}
\end{align*}

$\Delta E^\circ (\text{cell}) = E^\circ (\text{cathode}) - E^\circ (\text{anode})$

Step 2: Calculate Q for $\text{Cu}^{2+} (aq) + \text{Zn} (s) \Rightarrow \text{Zn}^{2+} (aq) + \text{Cu} (s)$

$Q = \ldots$

Step 3: Find n

Step 4: Use the Nernst Eq.

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

$\Delta E = 1.103 \text{ V} - \frac{(8.315 \text{ J K}^{-1}\text{mol}^{-1})(298 \text{ K}) \ln (1.0 \times 10^2)}{(2)(96485 \text{ Cmol}^{-1})}$

$\Delta E = 1.103 \text{ V} - 0.0592 = +1.044 \text{ V}$

**NOTE: UNITS and CONSTANTS**

$1 \text{ JC}^{-1} = 1 \text{ V}$

At 25.00°C, $\frac{RT}{\mathcal{N}} = \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K})}{96485 \text{ Cmol}^{-1}} = 0.025693 \text{ V}$

If you use log instead of ln

$\Delta E = \Delta E^\circ - \frac{RT}{nF} \log Q$ \quad Use $(2.303)(0.025693) = 0.0592 \text{ V}$

$\Delta E = \frac{\Delta E^\circ - 0.025693 \text{ V}}{n} \ln Q$ \quad OR \quad $\Delta E = \frac{\Delta E^\circ - 0.0592 \text{ V}}{n} \log Q$
What about at EQUILIBRIUM?

Q = ?

\( \Delta G = ? \)

\[
\Delta G = \Delta G^\circ + RT \ln Q \\
\Delta G^\circ = -RT \ln K \\
\Delta G^\circ = -n \Delta E^\circ
\]

Combining:

\[-RT \ln K = -n \Delta E^\circ\]

OR:

\[
\ln K = \frac{n \Delta E^\circ}{RT}
\]

Can calculate K from standard potentials!

Now the answer to the biochemical question:

How is vitamin B\(_{12}\) reduced in the body? Vitamin B\(_{12}\) is reduced by a protein called flavodoxin.

\( E^\circ \) for vitamin B\(_{12}\) is -0.526 V

\( E^\circ \) for flavodoxin is -0.230 V

Is the reduction of vitamin B\(_{12}\) by flavodoxin spontaneous?

\[
\Delta E^\circ(\text{cell}) = E^\circ(\text{reduction}) - E^\circ(\text{oxidation}) \\
= E^\circ(\text{vitamin } B_{12}) - E^\circ(\text{flavodoxin}) \\
= -0.526 \text{ V} - (-0.230 \text{ V}) = -0.296 \text{ V}
\]

\[
\Delta G^\circ = -n \Delta E^\circ = -(1)(96485 \text{ Cmol}^{-1})(-0.296 \text{ V}) = +28.6 \text{ kJ/mol}
\]

Vitamin B\(_{12}\) is a better reducing agent than flavodoxin. Vitamin B\(_{12}\) should reduce flavodoxin not the other way around. So why don't we all have heart disease and megaloblastic anemia?

Answer: S-adenosylmethionine provides the energy to drive the reaction. The \( \Delta G^\circ \) for the cleavage of S-adenosylmethionine is -37.6 kJ/mol