5.111 Lecture Summary #26 **Wednesday, November 12, 2014**

Reading for Today: 13.6-13.12 in 5th (4th ed: 12.6-12.12)
Reading For Lecture #27: 16.5-16.7 in 5th and 4th

Topic: I. Relationship between Cell Potential and Gibbs Free Energy
II. Meaning of Standard Reduction Potentials
III. Nernst Equation

I. Relationship between Cell Potential (ΔE_{cell}) and Gibbs Free Energy (ΔG)

The flow of electrons arises from a potential difference, ΔE_{cell}, between the electrodes in the circuit.

ΔE_{cell} is known as cell____________________, cell voltage, and electromotive force (emf)

The overall free energy of the cell is related to the cell potential by

$\Delta G_{\text{cell}} = -n\Im\Delta E_{\text{cell}}$ n = number of electrons
$\Im$ = Faraday's constant

For Standard State

$\Delta G°_{\text{cell}} = -n\Im\Delta E°_{\text{cell}}$

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

Units for ΔE is ____________.

Example - Calculate $\Delta E°_{\text{cell}}$ for $\text{Zn (s)} \mid \text{Zn}^{2+}\text{ (aq)} \mid\mid \text{Cu}^{2+}\text{ (aq)} \mid \text{Cu (s)}$

anode $\text{Zn (s)} \Rightarrow \text{Zn}^{2+}\text{ (aq)} + 2e^-$

cathode $\text{Cu}^{2+}\text{ (aq)} + 2e^- \Rightarrow \text{Cu (s)}$

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

$\Delta E°$(cell) = **standard reduction** potential for the couple at cathode minus **standard reduction** potential for the couple at anode

Look up Standard **REDUCTION** Potentials ($E°$) in back of book

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

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

Is the flow of electrons spontaneous?

$$\Delta G^\circ_{cell} \quad = \quad -n\Im\Delta E^\circ_{cell}$$

So, if ΔE°_{cell} is positive, ΔG°_{cell} will be negative.

Is a reaction spontaneous when ΔG° is negative?

What is the name of an electrochemical cell in which a **spontaneous** chemical reaction is used to generate an electric current?

What is the name of an electrochemical cell in which electrical energy provided by an external circuit is used to carry out **nonspontaneous** reactions?

Summary
Whether the cell operates spontaneously can be determined by ΔE_{cell}.
$((+\Delta E^\circ)$ = spontaneous, since $+\Delta E^\circ$ *means* $-\Delta G^\circ)$

ΔE_{cell} can be calculated from t**Standard Reduction** Potentials (E°) of half-cell reactions.

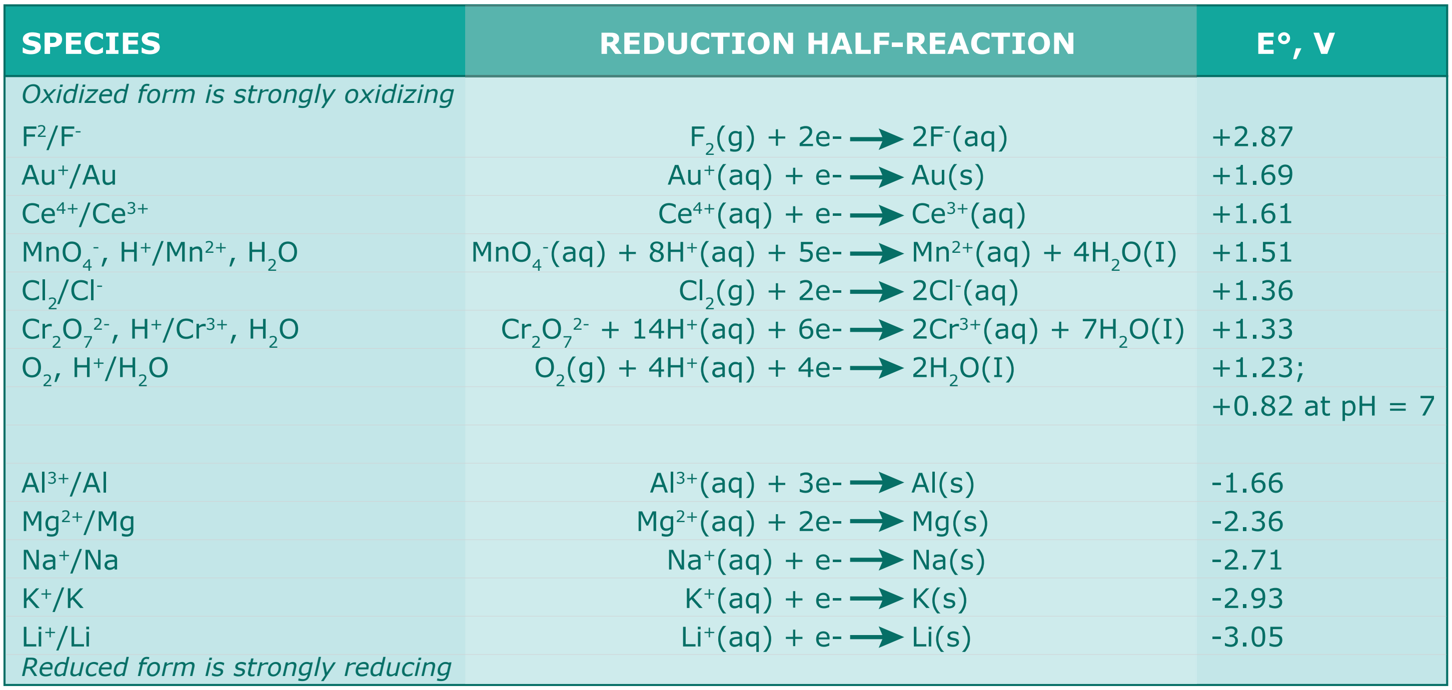
II. Meaning of standard reduction potential E°

A large positive E° means the element or compound is easy to reduce

e.g. $F_2\,(g) + 2e^- \Rightarrow 2F^-$ $\quad E^\circ = +\,2.87$ volts (easy to add electrons to F_2)
positive E°, negative ΔG°, favorable

Is F_2 a good oxidizing agent?

A large positive E° for F_2/F^- means the oxidized species of the couple is very oxidizing.



SPECIES	REDUCTION HALF-REACTION	E°, V
Oxidized form is strongly oxidizing		
F^2/F^-	$F_2(g) + 2e- \longrightarrow 2F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e- \longrightarrow Au(s)$	+1.69
Ce^{4+}/Ce^{3+}	$Ce^{4+}(aq) + e- \longrightarrow Ce^{3+}(aq)$	+1.61
MnO_4^-, H^+/Mn^{2+}, H_2O	$MnO_4^-(aq) + 8H^+(aq) + 5e- \longrightarrow Mn^{2+}(aq) + 4H_2O(I)$	+1.51
Cl_2/Cl^-	$Cl_2(g) + 2e- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}$, H^+/Cr^{3+}, H_2O	$Cr_2O_7^{2-} + 14H^+(aq) + 6e- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(I)$	+1.33
O_2, H^+/H_2O	$O_2(g) + 4H^+(aq) + 4e- \longrightarrow 2H_2O(I)$	+1.23;
		+0.82 at pH = 7
Al^{3+}/Al	$Al^{3+}(aq) + 3e- \longrightarrow Al(s)$	-1.66
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2e- \longrightarrow Mg(s)$	-2.36
Na^+/Na	$Na^+(aq) + e- \longrightarrow Na(s)$	-2.71
K^+/K	$K^+(aq) + e- \longrightarrow K(s)$	-2.93
Li^+/Li	$Li^+(aq) + e- \longrightarrow Li(s)$	-3.05
Reduced form is strongly reducing		

Figure by MIT OpenCourseWare.

A large negative $E°$ means the element or compound is hard to reduce

e.g. $Li^{+1} + e^- \Rightarrow Li\ (s)$ $E° = -\ 3.045$ volts

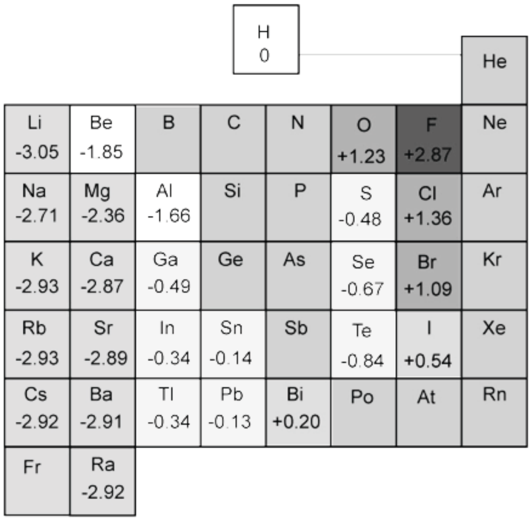
(hard to add electrons to Li^{+1})
negative $E°$, positive $\Delta G°$, not favorable

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

Li (s) is a good ________________.

Li (s) reduces other elements or compounds.
Li (s) gets oxidized.

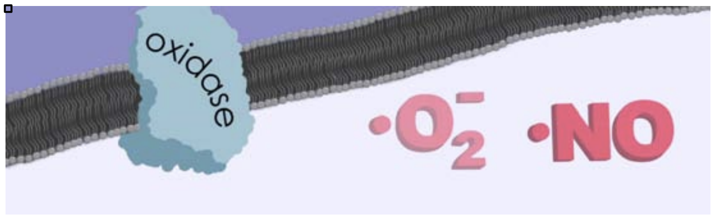
For Li+/Li with a large negative $E°$, the reduced species of the couple is very reducing.



				H 0			He
Li -3.05	Be -1.85	B	C	N	O +1.23	F +2.87	Ne
Na -2.71	Mg -2.36	Al -1.66	Si	P	S -0.48	Cl +1.36	Ar
K -2.93	Ca -2.87	Ga -0.49	Ge	As	Se -0.67	Br +1.09	Kr
Rb -2.93	Sr -2.89	In -0.34	Sn -0.14	Sb	Te -0.84	I +0.54	Xe
Cs -2.92	Ba -2.91	Tl -0.34	Pb -0.13	Bi +0.20	Po	At	Rn
Fr	Ra -2.92						

IN THEIR OWN WORDS

Prof. John Essigmann describes how oxidation reactions in our bodies are both essential for life and responsible for cell damage that can potentially lead to cancer. Research in the Essigmann lab focuses on studying how cells respond to toxins that cause oxidative damage to DNA.



III. NERNST EQUATION

An exhausted battery is a sign that the cell reaction has reached ____________________.

At equilibrium, a cell generates ______________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 ΔG changes as the concentrations of the components change until equilibrium is reached, then ΔG = 0.

$$\Delta G = \Delta G° + RT \ln Q$$

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

$$\Delta G° \quad = \quad -n\Im\Delta E°$$

Combining:

$$-n\Im\Delta E \;=\; -n\Im\Delta E° + RT \ln Q$$

Dividing by $-n\Im$:

$$\Delta E = \Delta E° - \frac{RT}{n\Im} \ln Q \qquad \text{(NERNST EQ.)}$$

Example: Calculate ΔE (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.

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

Step 1: Calculate $\Delta E°$(Cell) from the $E°$ for the half-reactions.

We already did this on page 1.

$\Delta E°(\text{cell}) = 1.1030\ \text{V}$

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

Q =

Step 3: Find n

Step 4: Use the Nernst Eq.

$$\Delta E = \Delta E° - \frac{RT}{n\Im} \ln Q$$

$$\Delta E = 1.1030\ \text{V} - \frac{(8.315\ \text{J K}^{-1}\text{mol}^{-1})(298\ \text{K})}{(2)(96485\ \text{Cmol}^{-1})} \ln(1.0 \times 10^{2})$$

$$\Delta E = 1.1030\ \text{V} - 0.0592 = +1.0438\ \text{V}$$

NOTE: UNITS and CONSTANTS **$1\ \text{JC}^{-1} = 1\ \text{V}$**

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

If you use log instead of ln $\Delta E = \Delta E° - \frac{RT}{n\Im} \log Q$ Use $(2.303)(0.025693) = 0.0592$ V

$\Delta E = \Delta E° - \frac{0.025693\ \text{V}}{n} \ln Q$ OR $\Delta E = \Delta E° - \frac{0.0592\ \text{V}}{n} \log Q$

What about at EQUILIBRIUM?

Q = ?

ΔG = ?

$$\Delta G = \Delta G° + RT \ln Q$$
$$\Delta G° = -RT \ln K$$
$$\Delta G° = -n\Im\Delta E°$$

Combining:

$$-RT \ln K = -n\Im\Delta E°$$

OR:

$$\ln K = \frac{n\Im\Delta E°}{RT}$$

Can calculate ______ from standard potentials!

Reduction potentials are not just important for batteries. Reduction potentials are important in biology too.

Question: Vitamin B_{12} has a large negative reduction potential, so how is it reduced in the body?

Vitamin B_{12} needs to be reduced to be active. Proper functioning of an enzyme that requires vitamin B_{12} and folic acid is thought to be necessary for preventing heart disease and birth defects.

Where do you get vitamin B_{12} and folic acid in your diet?

Vitamin B_{12} is reduced by a protein called flavodoxin in a one electron process.

$E°$ for vitamin B_{12} is -0.526 V
$E°$ for flavodoxin is -0.230 V

Which is a better reducing agent?

Is the reduction of vitamin B_{12} by flavodoxin spontaneous?

Let's calculate $\Delta E°$ and $\Delta G°$ from the standard reduction potentials

$E°$ for vitamin B_{12} is -0.526 V
$E°$ for flavodoxin is -0.230 V

$\Delta E° = E°(\text{reduction}) - E°(\text{oxidation})$

$= E°(\text{vitamin } B_{12}) - E°(\text{flavodoxin})$

$= - 0.526 \text{ V} - (- 0.230 \text{ V}) =$

$\Delta G° = -n\Im\Delta E° = - (1)(96485 \text{ Cmol}^{-1})(- 0.296 \text{ V}) = + 28.6 \text{ kJ/mol}$

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?

How is the reaction driven forward? It is not spontaneous.

Answer: *S*-adenosylmethionine provides the energy to drive the reaction.

The $\Delta G°$ for the cleavage of *S*-adenosylmethionine is -37.6 kJ/mol, which is greater than the + 28.6 kJ/mol needed for the reduction reaction.

Net $\Delta G°$ for coupled reaction =

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