

Chem 103 lecture 7a Outline:

Monday: ΔG° vs ΔG ; ΔG° and work; ΔG° and coupled reactions; and stability.

Also: Redox reactions; oxidation numbers; balancing redox reactions.

Goal is to understand:

(0) relationship of ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (\text{this is used for variations of } Q \text{ usually})$$

The G vs reaction progress is analogous to a crater.



ΔG represents the slope of any position in the crater. If it's product favored at a certain Q value, then $\Delta G < 0$. If it's reactant-favored, then it's $\Delta G > 0$. At the very bottom of the crater, it's : $\Delta G = 0$, here $Q = K_{\text{equilibrium}}$. It's the most stable position. On the other hand, ΔG° represents a position in which $Q = 1$ (when does that happen? Think about it). Usually that would be somewhere on the side of the crater. Usually $\Delta G^\circ \neq 0$ for a reaction. It's some fixed point in the crater.

Example : to test your understanding!

Question: (This is like the classroom demonstration)

Consider the crystallization of sodium acetate trihydrate crystals ($\text{NaAc} \cdot 3\text{H}_2\text{O}$) from a supersaturated solution of sodium acetate. It's "melting point" is at 54°C .



What are the signs of ΔG and ΔG° for the cases below:

(a) A supersaturated solution of NaAc at 25°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$

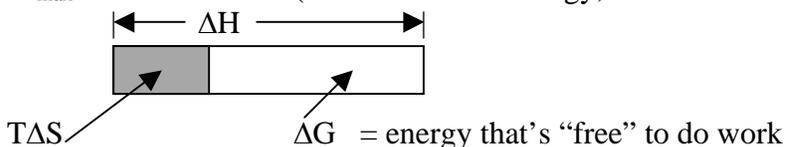
(b) An unsaturated solution of NaAc at 70°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$

(c) A saturated solution of NaAc at 54°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$

(d) Solid crystals of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ at 25°C $\Delta G^\circ = \underline{\hspace{2cm}}$, $\Delta G = \underline{\hspace{2cm}}$,

(1) relationship of ΔG to maximum work, W_{max} , a reaction can do:

$$W_{\text{max}} = -\Delta G \quad (\text{note: } \Delta G = \text{free energy, i.e. "free to do work".})$$



Example: How much energy would be available to do work for a reaction at standard conditions? Given: $\Delta H^\circ = -33 \text{ kJ/mol}$ and $\Delta S^\circ = -46 \text{ J/molK}$

(2) A reaction which is not product favored can be made so when coupled with product-favored reactions which have enough ΔG available to drive the former reaction.

The basic idea is that if a reaction $A \rightarrow B$ is not product favored ($\Delta G > 0$, *endergonic*) then it can be coupled to $C \rightarrow D$ which is product favored (i.e. $\Delta G < 0$, *exergonic*), so that the overall reaction is product favored. We can say that the exergonic reaction *drives* the endergonic reaction.



It's like a water wheel utilizing the exergonic process of water flowing downhill to drive endergonic process of grinding grain in a mill.

Example, suppose that $\Delta G^\circ = +23 \text{ kJ/mol}$ for (i) $A \rightarrow B$ and that $\Delta G^\circ = -33 \text{ kJ/mol}$ for (ii) $C \rightarrow D$. By what factor has the coupling of the two (i.e. (i) + (ii)) increased the equilibrium ratio, $\frac{[B]}{[A]}$, when compared to just the one (i)? (assume that the concentration of $[C] = [D]$).

Solution: (i) $A \rightarrow B$ $\Delta G^\circ = 23 \text{ kJ/mol}$

$$\Rightarrow K_{(i)} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{-23,000 \text{ J/mol}}{(8.314 \text{ J/molK})(298 \text{ K})}\right) = e^{-9.28} = 9.33 \times 10^{-5} = \frac{[B]}{[A]}$$

Whereas for the coupled case:

(i) + (ii): $A + C \rightleftharpoons B + D$ $\Delta G^\circ = +23 - 33 = -10. \text{ kJ/mol}$

$$K_{(i)+(ii)} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{10,000 \text{ J/mol}}{(8.314 \text{ J/molK})(298 \text{ K})}\right) = e^{+4.04} = 56.8 = \frac{[B][D]}{[A][C]} = \frac{[B]}{[A]}$$

The ratio of $\frac{[B]}{[A]}$ has increased by a factor of: $\frac{56.8}{9.33 \times 10^{-5}} = 6.1 \times 10^5$!

This is a huge increase due to the help of the second reaction. Now we see that it is very product favored! (Biological systems, i.e. living cells, use this all the time to manufacture large complex molecules like proteins, carbohydrates, fats and nucleic acids...)

Here's a biochemical example:

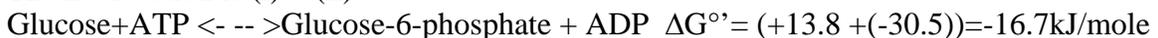


This reaction is an *endergonic* first step in the breakdown of glucose (via *glycolysis* – a central metabolic pathway in all cells)



This is an *exergonic* reaction that can help drive reaction (i) because it releases enough free energy. The cell just needs to have enough ATP to be able to do this step.

The net reaction is (i) + (ii)



(3) Understand the meaning of *stability*. Distinguish between *kinetic stability* and *thermodynamic stability*.

(4) Redox reactions (READ CHAPTER 5 SECTIONS 3 , 4 (and 5)).

Definitions: **reduction**: loss of electrons **Oxidation**: gain of electrons

Here's a mnemonic: **Oxidation = Loss of e⁻'s Reduction = Gain of e⁻'s. "OIL RiG"**

Example: $\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$

Na loses an electron to become a cation: Na^+ and Cl gains an electron to become an anion, Cl^- . The complete ionic compound product is Na^+Cl^- or just NaCl.

This can be viewed as occurring in two *half reactions*:

Oxidation half-reaction: $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ this is oxidation. (Na lost an electron)

Reduction half reaction: $\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightarrow \text{Cl}^-$ reduction (Cl gains an electron)

We call this an oxidation-reduction reaction, or *redox* reaction for short.

In the $\text{Na} + \text{Cl}_2$ reaction, which one is oxidized? **Na** Which is reduced? **Cl₂**

Which one is the **oxidizing agent** (or **oxidant**)? **Cl₂**

Which one is the **reducing agent** (or **reductant**)? **Na**

(Remember that the oxidizing and reducing agents are both *reactants*. Don't look for the oxidants and reductants among the products).

(5) Oxidation numbers (**ON**): Know how to determine the oxidation number of elements involved in a reaction.

Rules for oxidation numbers (ON): (5.4)

a) all monatomic ions: the charge is the ON

e.g. Na^+ : ON = 1 ; Cl^- : ON = -1

b) elements in elemental form: ON = 0

e.g. O_2 : ON = 0; S_8 : ON = 0

c) usually: O = -2, H = +1

e.g. H_2O : ON of O = -2; ON of H = +1

also: other common ON's: F : -1,

other halides except when bound to O or F

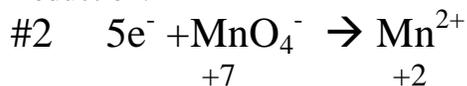
know exceptions: NaH; ON of H = -1

b) write the half rxns:

Oxidation:



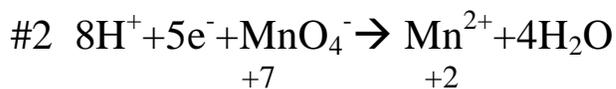
Reduction:



c) balance the H's and O's. check charges

Oxidation : already balanced

Reduction:



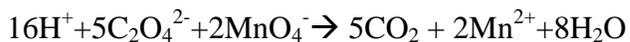
1st: add 4 H₂O on the right to balance the O's

2nd: add 8 H⁺'s on the left to balance the H's

balanced!

d) add the 2 half rxns so e's cancel out.

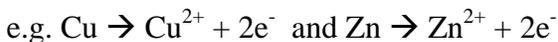
Multiply #1 by 5 and #2 by 2 and combine:



Balanced!

8) Electrochemical potential:

In general, metals placed in water tend to dissolve in the form of cations.



the tendency to oxidize can be represented by the *oxidation potential*, E°_{ox} .

From Table 19.1, page 927)

Standard reduction potentials, E°_{red}
(the more + E° is, the more spont the half rxn)

Reduction half rxn	E° (Volts)
$F_2(g) + 2e^- \rightarrow 2 F^-(aq)$	+2.87 V
$Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.05

a) Which is the most spontaneous reduction half rxn?

$F_2(g) + 2e^- \rightarrow 2 F^-(aq)$
(i.e. the one with the most positive E°)

b) Which is the least spontaneous redn half rxn?

$Li^+(aq) + e^- \rightarrow Li(s)$
(i.e. the one with the most negative E°)

c) Which is most spont oxidation half rxn?

$Li(s) \rightarrow Li^+(aq) + e^-$

Li is the “most active” metal

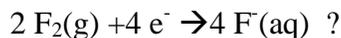
d) Which is the strongest oxidizing agent?

$F_2(g)$ (i.e. the most spontaneously reduced)

e) Which is the strongest reducing agent?

$Li(s)$ (i.e. the most spontaneously reduced)

f) What is the E°_{red} for:



$E^\circ_{red} = +2.87 \text{ V}$ (not $2(2.87 \text{ V})$). Note that E°_{red} is an intrinsic property not extrinsic. Doesn't depend on mass (like pressure or density).

g) What is the E°_{oxid} for $3 Li(s)$?



h) Write a possible redox reaction based on the following half rxns.

1	$Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$	+0.34V
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2	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
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One has to be reduced, the other oxidized, so
Reverse #2 and add to #1 :



1.10 V is the redox potential?

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = .34 + .76 = 1.10\text{V}$$

Electrochemical Cells:

2 types:

a) Voltaic Cells or Galvanic Cells (spontaneous)

b) Electrolysis cells (nonspontaneous)

Voltaic Cells

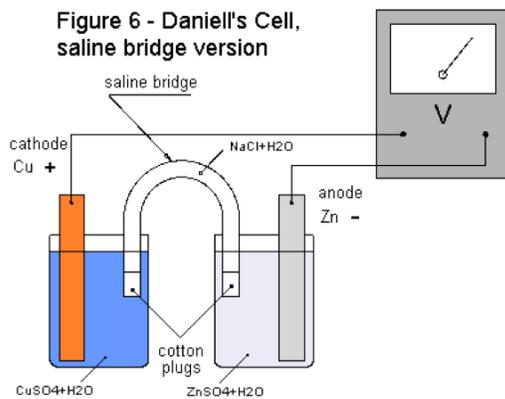
voltaic cells: One of the simplest is the Daniell Cell:

It uses: $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ 1.1 Volt output.

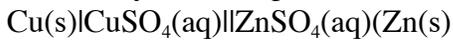
Zn supplies e^- and Cu(II) ion accepts electrons.

What if we can force the e^- to go thru wire?

Draw the Daniell cell and explain it.



this battery can be represented using the line diagram as:



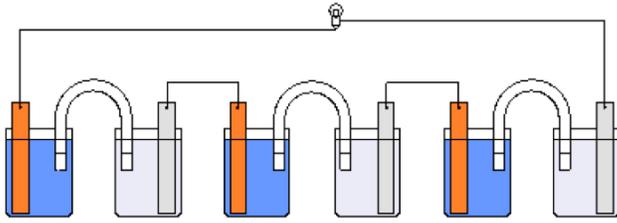


Figure 8 - Battery of three Daniell's Cells

This equivalent to 3 batteries in series