



Melvin Calvin

## Chemistry BC2001x: General Chemistry I



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Lecture 23: Thursday December 10, 2009

Topic: **Thermodynamics III:  
Summary and Applications in Biology**

Hand in problem set 11

You may pick up graded problem 11 in  
my office starting next Tuesday, December 15.

Once I have entered all the problem set grades,  
I will post them (by ID) on the web. Please check that  
your grades are all correctly recorded.

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## $\Delta G^\circ$ and equilibria: the key equations

From  $S^\circ$  values, calculate  $\Delta S^\circ$  for reaction.

From  $\Delta H_f^\circ$  values, calculate  $\Delta H^\circ$  for reaction.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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

$$\Delta G^\circ = -RT \ln K_{eq} = -2.303 RT \log K_{eq}$$

$$\log K_{eq} = -\Delta G^\circ / (2.303 RT)$$

At 25°C, 2.303 RT = 5.70804 kJ/mole

(this will be given in data tables for final.)

$$\Delta G = -n \mathcal{F} \Delta \mathcal{E}$$

$$-n \mathcal{F} \Delta \mathcal{E} = -n \mathcal{F} \Delta \mathcal{E}^\circ + RT \ln Q$$

$$\Delta \mathcal{E} = \Delta \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln Q \quad \text{Nernst Equation}$$

$$\log K_{eq} = n \Delta \mathcal{E}^\circ / k_N$$

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## $\Delta G^\circ$ and equilibria: An example

Consider  $\text{Hg}(\ell) \rightarrow \text{Hg}(\text{g})$        $K = P_{\text{Hg}}$

Previously:  $\Delta H^\circ = 61.317 \text{ kJ/mole}$

$$\Delta S^\circ = S^\circ(\text{g}) - S^\circ(\ell) = 174.85 - 76.02 = 98.83 \text{ J/K-mole}$$

enthalpy change favors the liquid, entropy the gas.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= (61.317 \text{ kJ/mole}) - (298.15 \text{ K})(98.83 \text{ J/K-mole}) / (1000 \text{ J/kJ})$$

$$= 61.317 - 29.46 = 31.85 \text{ kJ/mole}$$

$$\log K = -\Delta G^\circ / (2.303RT)$$

$$= -(31.15 \text{ kJ/mole}) / (5.708 \text{ kJ/mole}) = -5.58$$

$$K = 10^{-5.58} = 2.6 \times 10^{-6}$$

If spilled liquid mercury has come to equilibrium with vapor,

$$P_{\text{Hg}} = 2.6 \times 10^{-6} \text{ atm.}$$

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## $\Delta G^\circ$ and equilibria: Hg(g)

$\text{Hg}(\ell) \rightarrow \text{Hg}(\text{g})$       at 25°C,  $P_{\text{Hg}} = 2.6 \times 10^{-6} \text{ atm.}$

NIOSH lists toxic levels of gases.

For Hg, 0.05 mg/m<sup>3</sup> is dangerous for long-time exposure.

$PV = nRT$ , so  $n/V = P/RT$

$$n/V = (2.6 \times 10^{-6} \text{ atm}) / (0.0820578 \text{ L-atm/K-mole})(298.15 \text{ K})$$

$$= 1.1 \times 10^{-7} \text{ mole/L.}$$

But 1 mole of Hg weighs 200.58 grams,

and there are 1000 L per m<sup>3</sup> and 1000 mg per g, so

$$w/V = (1.1 \times 10^{-7} \text{ mole/L})(200.58 \text{ g/mole})(1000 \text{ mg/g})(1000 \text{ L/m}^3)$$

$$= 22 \text{ mg/m}^3$$

Moral: clean up mercury spills!



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## ΔE and ΔH: How are they related?

Bomb calorimeters measure ΔE

Constant pressure calorimeters measure ΔH

$H \equiv E + PV$  so  $\Delta H = \Delta E + \Delta(PV)$

How much does PV change during a reaction?

If P is constant,  $\Delta(PV) = P\Delta V$

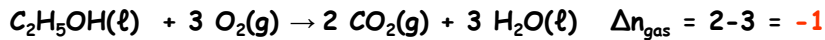
How much does V change during a reaction?

for liquids (including solutions) and solids, V's are small, and ΔV's are small fractions of V's.

but if gases are created or destroyed, ΔV's may be large.

We can treat the gases as ideal: thus  $\Delta(PV) = \Delta(nRT) = RT\Delta n_{\text{gas}}$

Consider the combustion of ethanol



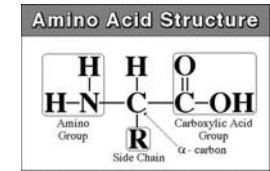
$$\Delta H - \Delta E = \Delta(PV) = RT\Delta n_{\text{gas}} = -2.47 \text{ kJ/mole}$$

So if  $\Delta H = -1366.85 \text{ kJ/mole}$ , then  $\Delta E = -1364.37 \text{ kJ/mole}$

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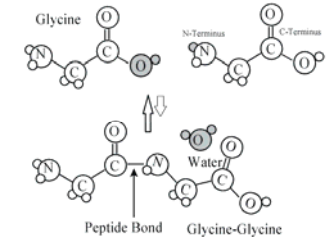
## Thermodynamics and biochemical reactions 1) protein formation

**Amino acids:** 20 in nature, differ by group R  
R=H is AA glycine.



**Proteins** are linear polymers of AA's connected by **peptide bonds**.

Formation of a peptide bond eliminates water.



Substance	ΔH <sub>f</sub> <sup>o</sup> (kJ/mole)	S <sup>o</sup> (J/K-mole)
glycine	-528.1	103.5
gly-gly	-746.9	180.3
H <sub>2</sub> O(l)	-285.9	70.0

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## Thermodynamics and biochemical reactions 1) proteins

Formation of a di-peptide:



Substance	ΔH <sub>f</sub> <sup>o</sup> (kJ/mole)	S <sup>o</sup> (J/K-mole)
glycine	-528.1	103.5
gly-gly	-746.9	180.3
H <sub>2</sub> O(l)	-285.9	70.0

$$\Delta H^{\circ} = (-746.9) + (-285.9) - 2(-528.1) = +23.4 \text{ kJ/mole}$$

$$\Delta S^{\circ} = (180.3) + (70.0) - 2(103.5) = +43.3 \text{ J/K-mole}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 23.4 - 12.9 = 10.5 \text{ kJ/mole. Not favored.}$$

$$\ln K = - (10,500 \text{ J/mole}) / [(8.31451 \text{ J/K-mole})(298.15 \text{ K})]$$

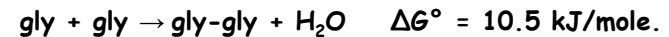
$$\ln K = - 4.235; K = 0.014$$

Reaction does not happen spontaneously at standard conditions.  
So how does this happen? How are proteins formed?

Must couple this unfavorable reaction with a favorable one.

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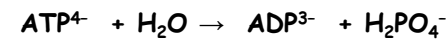
## Thermodynamics and biochemical reactions 1) proteins



Need a driving reaction!

Nature often uses **ATP**  
(adenosine triphosphate)

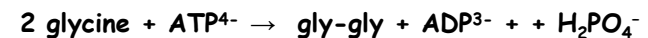
adenosine = adenine + ribose



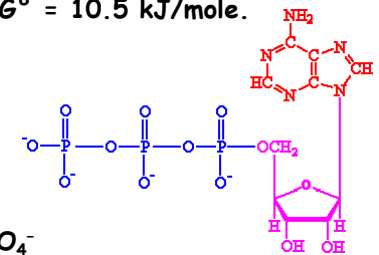
$$\Delta G^{\circ} = -37.64 \text{ kJ/mole}$$

often just written  $ATP + H_2O \rightarrow ADP + P_i$

So together (coupled by the common species water)



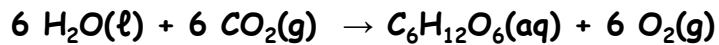
$$\Delta G^{\circ} = -27.1 \text{ kJ/mole}$$



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## Thermodynamics and biochemical reactions 2) photosynthesis

Formation of glucose in plants:



redox! **24 electrons transferred overall.**

Many many steps, worked out by Melvin Calvin  
(Nobel Prize for this in 1961).

Energetics of the overall process:

$$\Delta S^\circ = -223.3 \text{ J/K-mole} \quad \Delta H^\circ = 2806.85 \text{ kJ/mole}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \mathbf{2873.4 \text{ kJ/mole}}$$

Driven mainly by two exothermic reactions:

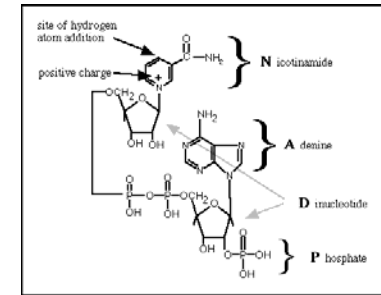
ATP to ADP (18 times in cycle)  
and NADPH to NADP (12 times)

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## Thermodynamics and biochemical reactions 2) photosynthesis

NADPH to NADP is an **oxidation**.

NADPH is both a source of energy and  
a reducing agent (the 24 electrons!)

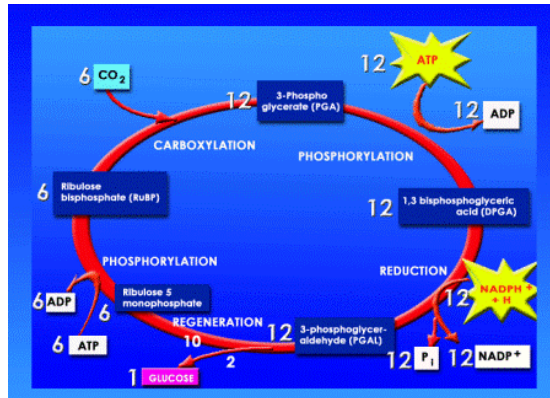


$$\Delta H^\circ = -113.0 \text{ kJ/mole} \text{ and } \Delta S^\circ = 105.9 \text{ J/K-mole},$$

$$\Delta G^\circ \text{ per NADPH} = \mathbf{-114.58 \text{ kJ/mole}}$$

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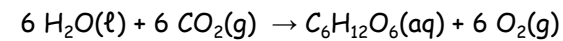
## Thermodynamics and biochemical reactions 2) photosynthesis



Calvin cycle, making one molecule of glucose.  
This diagram actually simplifies the process!

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## Thermodynamics and biochemical reactions 2) photosynthesis



$$18 \{ \text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{P}_i \} \quad \Delta G^\circ = 2805.85 \text{ kJ/mole}$$

$$\Delta G^\circ = 18(-37.64 \text{ kJ/mole})$$

$$12 \{ \text{NADPH} + \text{H}^+ \rightarrow \text{NADP}^+ + \frac{1}{2} \text{H}_2\text{O} \} \quad \Delta G^\circ = 12(-114.58 \text{ kJ/mole})$$

$$\text{net: } \Delta G^\circ = \mathbf{460.9 \text{ kJ/mole.}}$$

So this is not the whole story!

(and the reaction does not occur at standard conditions and 25°C)

Additional steps to get to glucose.

These coupled reactions  
occur on a large enzyme  
called **rubisco**  
M = 55 kDaltons!

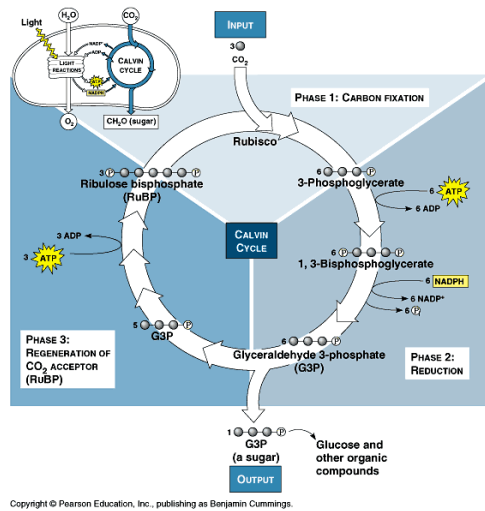


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## Thermodynamics and biochemical reactions 2) photosynthesis

How are the  
18 ATP's and the  
12 NADPH's  
produced for the  
Calvin cycle?

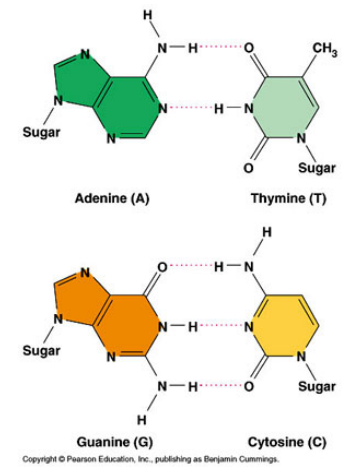
From sunlight, in a  
different cycle



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## Thermodynamics and biochemical reactions 3) base pairing in DNA



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## Thermodynamics and biochemical reactions 3) base pairing in DNA

Detailed energetics depends not just on which base pair is being formed (C-G) or (A-T), but also on the neighbors, due to non-bonding (**dipole-dipole** and **van der Waals**) interactions in the stacks. Adding a G-C adjacent and parallel to another G-C gives  $\Delta H^\circ = -12.7 \text{ kJ/mole}$ ,  $\Delta S^\circ = -124.3 \text{ J/K-mole}$ , so at 25°C,  $\Delta G^\circ = -14.0 \text{ kJ/mole}$ . An A-T adjacent and parallel to another A-T gives  $\Delta H^\circ = -35.1 \text{ kJ/mole}$ ,  $\Delta S^\circ = -98.7 \text{ J/K-mole}$ , so at 25°C,  $\Delta G^\circ = -5.9 \text{ kJ/mole}$ . Base pairing energetically favored, but entropically disfavored. Need to have  $\Delta G^\circ$  **negative** for stability, but **small** so transcription can occur!

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## Reprise: demonstration from early class

Throw K(s) into water: what happens?

- 1) the metal dissolves vigorously
- 2) flames!
- 3) the solution becomes basic.

What is happening?

Active metal, K(s), is being oxidized

Reaction generates H<sub>2</sub>(g): H is being reduced

The redox reaction also produces base OH<sup>-</sup>

Reaction is exothermic: heat ignites H<sub>2</sub>

H<sub>2</sub> reacts vigorously (burns) with O<sub>2</sub> makes H<sub>2</sub>O

Acid-base chemistry, oxidation-reduction chemistry, combustion, gas properties, thermodynamics, and understanding why K<sup>+</sup> and H<sub>2</sub>O are stable (Lewis theory) are all part of understanding this story.

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