Galvanic Cells Review

- **Broad idea:** Separate two redox half-reactions into two cells
  - One is half-cell is anode, one is the cathode

- Voltage (potential difference) between half-cells is governed by the Nernst equation:

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{nF}\ln Q$$

- Positive voltage is a spontaneous process, since $\Delta\bar{G}^0 = -m\mathcal{E}$

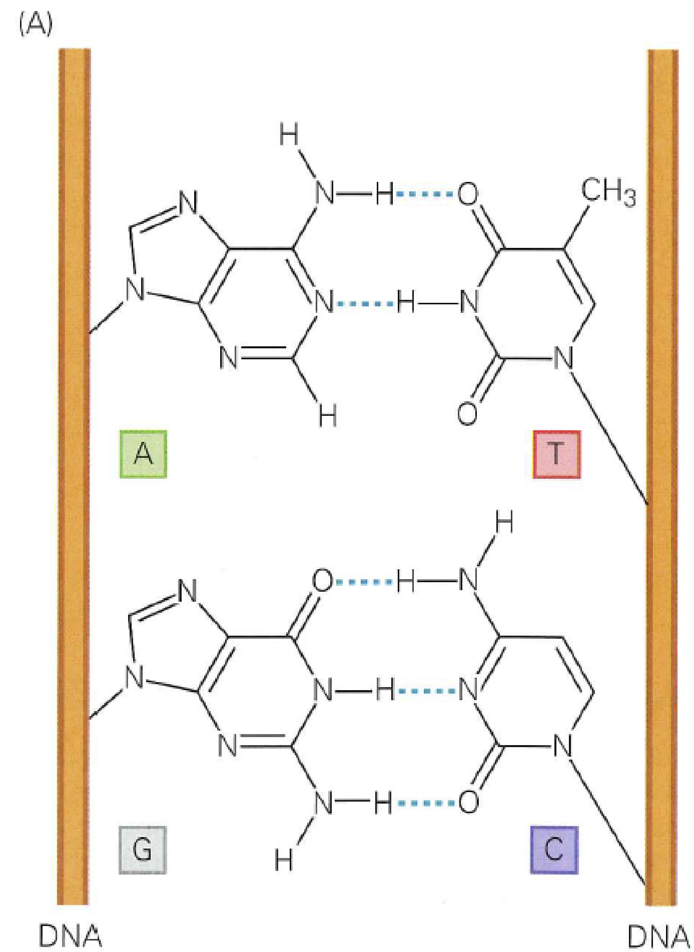
- **Remember:**
  - Do not multiply redox potentials by the electrons transferred! This is included in the Nernst equation (as *n*)
  - Leave pure materials out of reaction quotients!

Final Example: DNA Hybridization

- DNA "hybridizes" to form pairs of complementary strands
  - A pairs with T (2 H-bonds)
  - G pairs with C (3 H-bonds)

- Given ΔG for short strands, can we predict hybridization free energy for long strands?

- High salt concentrations favor hybridization. Why?



Molecules of Life, p. 23.

DNA Hybridization

- Simple-minded solution *doesn't* work:

$$\Delta\bar{G} \neq n_{AT}\Delta\bar{G}_{AT} + n_{GC}\Delta\bar{G}_{GC}$$

- **Smarter solution:** what if we account for initial unfavorable pairing?
  - First ΔG is less favorable because of entropic penalty
  - This still doesn't work, but it's closer

DNA Hybridization: What Works

- Energy requires initiation energy *plus* a context: what was the previous base pair?

$$\Delta\bar{G} = \Delta\bar{G}_{initiation} + \Delta\bar{G}_{12} + \Delta\bar{G}_{23} + \cdots$$

- Similar expressions exist for $\Delta\bar{S}$, $\Delta\bar{H}$
- **DNA hybridization energies are more than hydrogen bond energies!**
  - Stacking planar, aromatic groups on top of each other is energetically favorable

DNA Hybridization Example

- Consider this simple DNA sequence:

5’-GCAG-3’

3’-CGTC-5’

- Sum initiation energy with each combination down the sequence:

$$\Delta\bar{G}^0 = \Delta\bar{G}^0_{init} + \Delta\bar{G}^0\left(\begin{array}{ccccc} & C & & & \\ G & & & G & C \\ & & \rightarrow & & \\ C & & & C & G \\ & G & & & \end{array}\right) + \Delta\bar{G}^0\left(\begin{array}{ccccc} & A & & & \\ C & & & C & T \\ & & \rightarrow & & \\ G & & & G & T \\ & T & & & \end{array}\right) + \cdots$$

Coupled Free Energies

- Suppose we have two reactions:

$$A+B \rightarrow C$$
$$C \rightarrow D+E$$

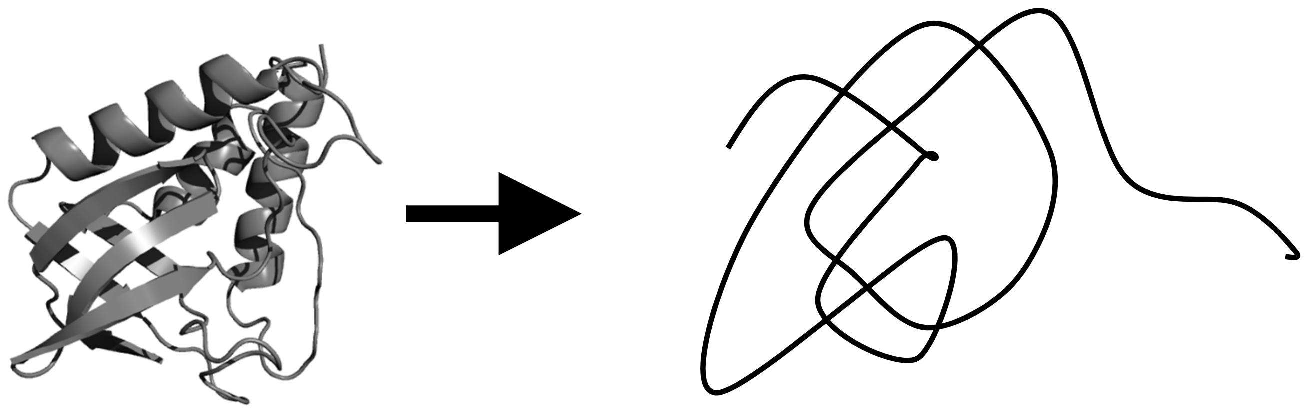
- **Hess's Law:** Free energies add

$$\Delta\bar{G} = \Delta\bar{G}_1^0 + RT\ln\frac{[C]}{[A][B]} + \Delta\bar{G}_2^0 + RT\ln\frac{[D][E]}{[C]}$$

- What does this mean about detecting intermediates with ΔG and K alone?
  - Thermodynamics is great, but there are limitations

Probabilities: Moving toward statistical thermodynamics

- Protein folding:



- What does $\Delta \bar{G}^0$ tell us about this system *at equilibrium?*

Folding vs. ΔG^0

$\Delta \overline{G}^0$ (kcal mol^{-1})	$\Delta \overline{G}^0$ (kJ mol^{-1})	K (at 298 K)	% Folded
15	63	1×10^{-11}	~100
10	42	5×10^{-8}	99.999995
5	21	2×10^{-4}	99.98
0	0	1	50
-5	-21	5×10^{3}	0.02

- What does it mean if a protein is 50% folded?