Applications of Chemical Equilibrium

- Van't Hoff Equation (Temperature dependence of K_{eq})
- Calculations of Equilibrium
  - Charge and mass balance
  - Applications to pH: Henderson-Hasselbalch
- Electrochemistry and Free Energy
- Application: DNA Melting

Van’t Hoff Equation

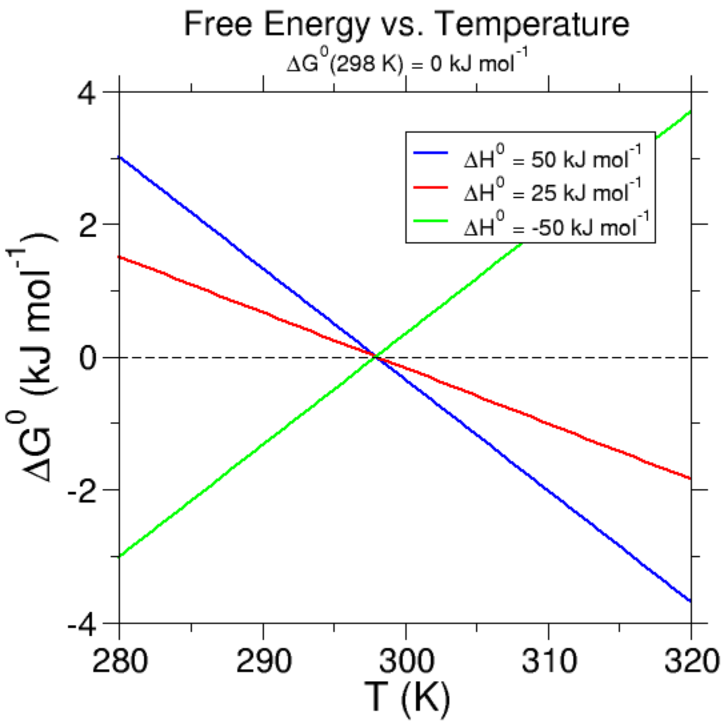
- Temperature dependence of ΔG:

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H(T_2^{-1} - T_1^{-1})$$

- If this is true for *any* ΔG, it must be true for $\Delta\bar{G}^0$, too: express $\Delta\bar{G}^0$ in terms of K_eq

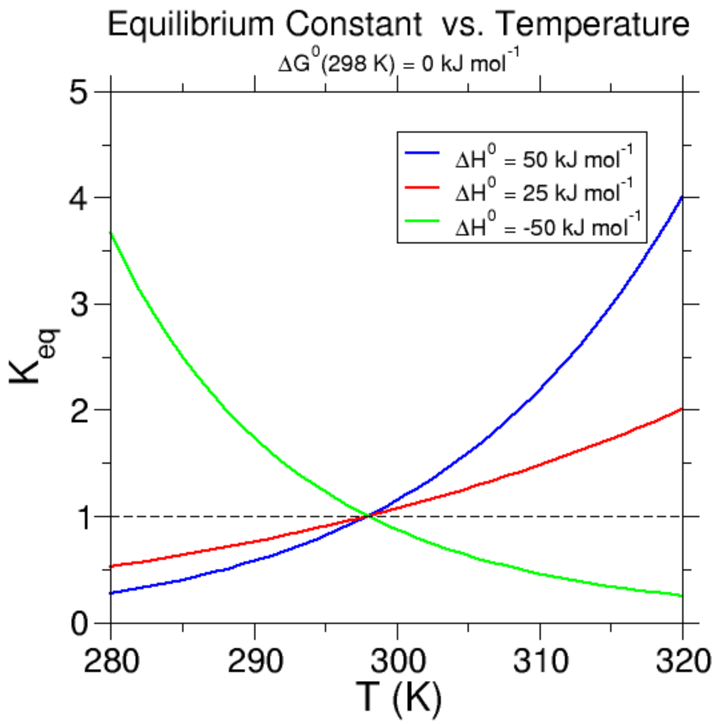
$$\ln\frac{K_2}{K_1} = -\frac{\Delta H}{R}(T_2^{-1} - T_1^{-1})$$

Van’t Hoff Equation



Free Energy vs. Temperature

ΔG^0(298 K) = 0 kJ mol^{-1}



Equilibrium Constant vs. Temperature

ΔG^0(298 K) = 0 kJ mol^{-1}

- Since $K = \frac{[\text{products}]}{[\text{reactants}]}$, bigger K favors products

Solving Equilibrium Problems

- Model System: Sodium Acetate Buffer

$$HOAc \rightarrow H^+ + OAc^-$$

- Useful constants:

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$K_A = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

(alternatively, $pK_A = 4.74$)

Solving Equilibrium Problems: Tips

- Write out balanced chemical equation

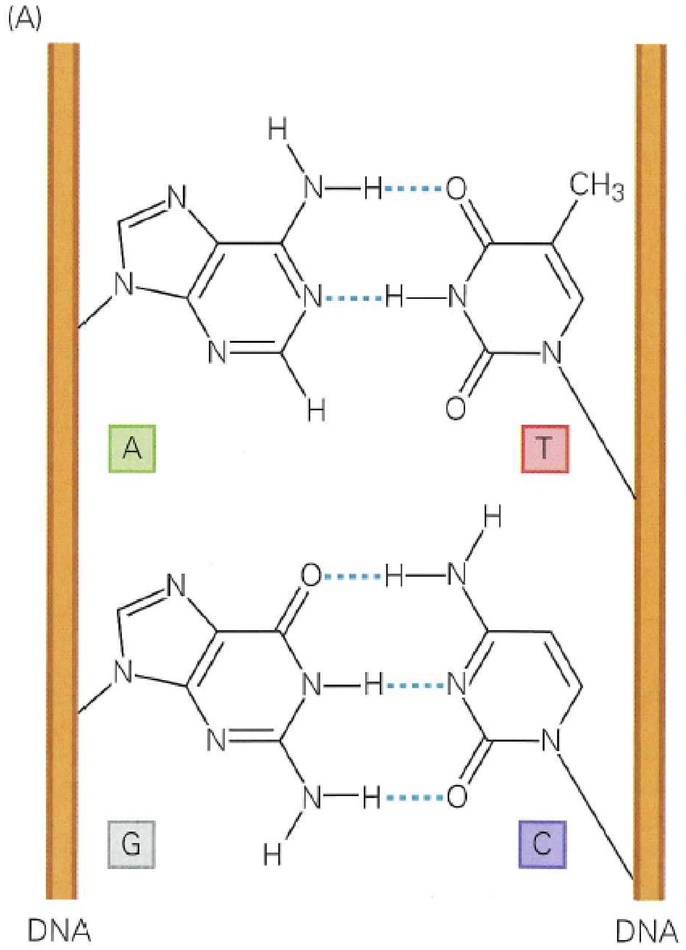
- Set up table:
  - Initial concentrations
  - Change (conserve mass & charge)
  - Final conditions → expression for K

- Check units and make sure you've answered the question

- If activities are needed (i.e. $a_A \neq [A]$), use them in the equilibrium expression instead of concentrations

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 $\Delta\bar{S}$, $\Delta\overline{H}$
- **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:

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

Coupled Free Energies

- Suppose we have two reactions:

A+B → C
C → D+E

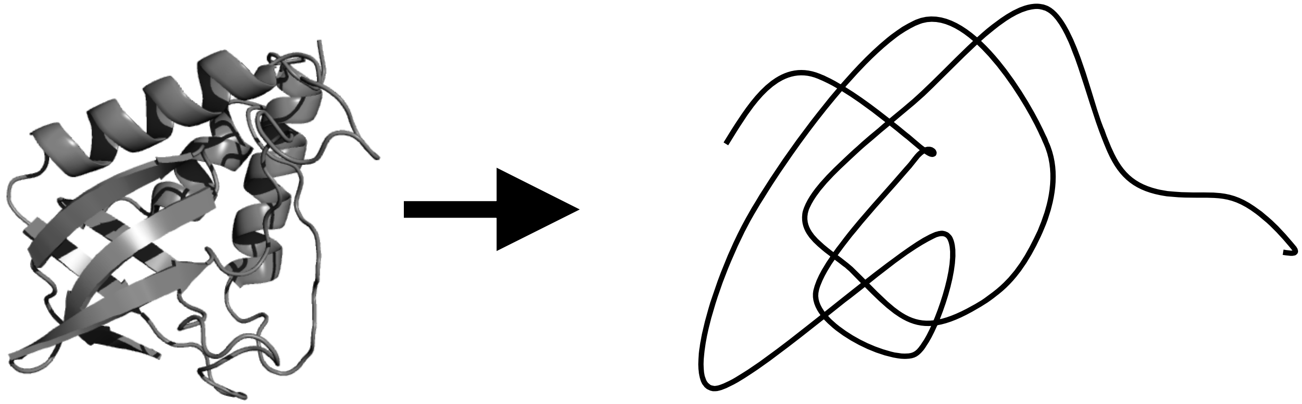
- **Hess's Law:** Free energies add

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

- 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

$\mathbf{\Delta\overline{G}^0}$ **(kcal mol^{-1})**	$\mathbf{\Delta\overline{G}^0}$ **(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?