Quantitative LeChatelier regarding adding HEAT

**Effect of Temperature on K**

\[ \Delta G^0 = -RT \ln K = \Delta H^0 - T \Delta S^0 \]

\[ \ln K_2 = \frac{-\Delta H^0 + \Delta S^0}{RT_2} \]

\[ \ln K_1 = \frac{-\Delta H^0 + \Delta S^0}{RT_1} \]

\[ \ln K_2 - \ln K_1 = \frac{-\Delta H^0 \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}{R} \]

\[ = \ln \frac{K_2}{K_1} = \text{Van't Hoff equation (one of several)} \]

Plot \( \ln K \) vs. \( \frac{1}{T} \)

Slope = \(-\frac{\Delta H^0}{R}\)

Intercept = \(\frac{\Delta S^0}{R}\)

We assume \(\Delta H^0\) and \(\Delta S^0\) are independent of \(T\) (approximation)

IMPORTANT for HW prob
\[ \Delta G^0 = -RT \log(K) \]

\[ K(T) = e^{-\Delta G^0/RT} \]

Do NOT assume \( \Delta G^0 \) is independent of \( T \) !!!

\[ K(T) = e^{-\Delta G^0/RT} = e^{-(\Delta H^0 - T \Delta S^0)/RT} \]

Temperature dependence of \( K \) depends only on \( \Delta H^0 \) by the Van’t Hoff equation
\[ \Delta G^0 \text{ for forming a base pair} \]
But, 5’ A-C is *accidently* = 5’ C-A

and 5’ A-G is *accidently* = 5’ G-A

Independent of which pairs first!
Independent of site of initiation and direction of zipping.

Because, ultimately, 1 initiation and ALL pairing are made, \textit{regardless} of starting point and direction.
Table 4.4

Initiation Fees

\[ \Delta G_{\text{init}} = +8.1 \text{ kJ/mol} \]

\[ \Delta H_{\text{init}} = +0.8 \text{ kJ/mol} \]

Independent of site of initiation and direction of zipping

Because, ultimately, 1 initiation and ALL pairing are made, regardless of starting point and direction.
Might expect $4 \times 4 = 16$ entries in Table 4.4

but: 6 cases of equivalence

$\begin{align*}
5' - G - T \\
C - A - 5' 
\end{align*}$

$= 5' - A - C \\
\frac{4 \times 3}{2}$

Just a 180° Rotation

But

$\begin{align*}
5' - G - C \\
G - C - 5' 
\end{align*}$

and

$\begin{align*}
5' - A - T \\
T - A - 5' 
\end{align*}$

← Go into themselves

and

$C - C$

and

$5' - T - A \\
A - T - 5'$
5’...-A-A-...3’
3’...-T -T-...5’
180 degree rotation

5’...-T-A-...3’
3’...-A-T-...5’

NOT 5’...-T-A-...3’
3’...-A-T-...5’
\[ \Delta G^0 \]

\[ \begin{array}{cccc}
5' & 3' \\
\text{init} +8.1 & A \cdots T & +0.8 \\
-3.7 & T \cdots A & -30.2 \\
-2.4 & A \cdots T & -30.2 \\
-5.4 & G \cdots C & -32.7 \\
-9.3 & C \cdots G & -41.0 \\
-6.0 & A \cdots T & -35.6 \\
3' & 5' & -168.9 \text{ for Single Strand} \Rightarrow \Delta G, \\
\end{array} \]

\[ \ln K_z = -\frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{5} \right) \]

\[ K = 10 \frac{18.7}{5.9} = 1416 \]

37°C = 310 K

\[ \Delta G^0 \]

\[ \begin{array}{cccc}
5' & 3' \\
\text{init} & A \cdots T & -4.2 \\
-3.7 & T \cdots A & -3.7 \\
-2.4 & A \cdots T & -2.4 \\
-5.4 & G \cdots C & -6.0 \\
-9.3 & C \cdots G & -6.0 \\
-6.0 & A \cdots T & -5.4 \\
3' & 5' & -168.9 \text{ for Single Strand} \Rightarrow \Delta G, \\
\end{array} \]

\[ \Delta G^0(\text{initiation}) = -23.4 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta H^0(\text{initiation}) = +0.8 \text{ kJ mol}^{-1} \]

*Data are from H. T. Allawi and J. Santalucia Jr., 1997, Biochemistry.
\[ \text{TP} \rightarrow \text{P} + \text{T} \]

\[ \text{HA} \rightarrow \text{A}^- \quad + \quad \text{H}^+ \]
\[ HA \rightleftharpoons H^+ + A^- \]

\[ K_a = K_d = \frac{[H^+][A^-]}{[HA]} \]

**50% Protonated (Bound)**

\[ \text{and} \quad [H^+] = K_d \quad [A^-] = [HA] \]

**50% Dissociated**

\[ PT \quad \frac{P}{m} \quad T \quad \rightarrow \quad \frac{m}{T} \quad + \quad \frac{P}{m} \]

\[ K_d = \frac{[P][T]}{[PT]} \]

When \([P] = K_d\), 50% bound.

\[ K_d = 1 \times 10^{-9} \text{ M} = 1 \text{ nM} \]

“\( P \) binds at the nM level”
Like Prob. 14 a (see Example 4.15 p. 133)

Using histidine as a buffer

If NaOH (or HCl) is added to 0.10 mol of HisH to make a total of 1 L of pH 7 buffer

Find the concentrations of all species:

\[ [H^+], [OH^-], [Na^+], [Cl^-], [HisH^+2], [HisH^+2][HisH][His] \]

7 unknowns need 7 equations

7th equation: Sum of the 4 His species = 0.10 mol
General

\[ HB \rightleftharpoons B^- + H^+ \]

or

\[ \frac{[HB]}{[B^-]} = \frac{[H^+]}{k_a} \]

\[ \text{and} \quad [H^+] = k_a \]

H\(B\) favored at high [\(H^+\)] or small \(k_a\).

Also note \(k_a = 10^{-pK_a}\), \(pK_a = -\log k_a\)

\(k_{a1} = 10^{-1.82}\), \(k_{a2} = 10^{-6}\), \(k_{a3} = 10^{-9.16}\)

Therefore:

\[ \frac{[\text{HisH}_3^{+2}]}{[\text{HisH}_3^{+}]} = \frac{[H^+]}{k_{a1}} = \frac{10^{-7}}{10^{-1.82}} = 0.66 \times 10^{-5} \]

\[ \text{ignore} \quad \text{HisH}_3^{2+} \]

Start here:

\[ \frac{[\text{HisH}_2^{+1}]}{[\text{HisH}]} = \frac{[H^+]}{k_{a2}} = \frac{10^{-7}}{10^{-6}} = 0.10 \]

This ratio is closest to 1

\[ \frac{[\text{HisH}^-]}{[\text{His}^-]} = \frac{[H^+]}{k_{a3}} = \frac{10^{-7}}{10^{-9.16}} = 145 \]

\[ \text{ignore} \quad \text{His}^- \]

\[ [\text{HisH}_2^{+}] = 0.10 \quad [\text{HisH}] \]

\[ [\text{HisH}_2^{+}] + [\text{HisH}] = 0.10 \]

ignoring \(\text{His}^{3+} \quad \text{HisH}_3^{+2} \)

\[ 0.10 \quad [\text{HisH}] + [\text{HisH}] = 0.10 \quad ; \quad [\text{HisH}] = \frac{0.10}{1.10} = 0.091 \]

Then \[ [\text{HisH}_2^{+}] = 0.10 \quad [\text{HisH}] = 0.091 \text{ M} \]
Now, go back and solve for the small concentrations that were temporarily ignored

Likewise: \[ \text{His}H_3^{+2} = [\text{His}H^+] \times 0.66 \times 10^{-5} = 0.0091 \times 0.66 \times 10^{-5} = 6 \times 10^{-8} \text{ M} \]

And \[ [\text{His}^-] = \frac{[\text{HisH}]}{145} = \frac{0.091}{145} = 6.3 \times 10^{-4} \text{ M} \]

CHARGE: \[ +1[\text{Na}^+] + 1[\text{H}^+] - 1[\text{OH}^-] + 2[\text{His}H_3^{+2}] + 1[\text{His}H^+] + 0[\text{His}^-] - 1[\text{His}^+] \]

\[ [\text{Na}^+] = -[10^{-7} - 10^{-7} + 2(6 \times 10^{-8}) + 0.009 + 0 - 6 \times 10^{-4}] = 0 \]

\[ [\text{Na}^+] = -0.0091 + 0.0006 = -0.0085 \quad \text{Whoa Nellie!} \]

\[ [\text{Cl}^-] = +0.0091 - 0.006 = +0.0085 \quad \text{That's better.} \]

(Substitute \(-[\text{Cl}^-]\) for \([\text{Na}^+]\) in above eq.)

(Hisz is a better base than acid)