THE REAL Q

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{Q}{Q_0} \right) \] always

For IDEAL gases and solutions:

the reaction \( n_A \ A + n_B \ B \rightarrow n_C \ C + n_D \ D \)

\[ Q = \frac{\frac{n_C}{C_C} \frac{n_D}{C_D}}{\frac{n_A}{C_A} \frac{n_B}{C_B}} \]

\( \gamma = \) activity coeff.

\( \gamma_C = \) activity = \( a \)

\[ Q_{\text{real}} = \frac{\frac{\gamma_C^{n_C}}{a_C^{n_C}} \frac{\gamma_D^{n_D}}{a_D^{n_D}}}{\frac{\gamma_A^{n_A}}{a_A^{n_A}} \frac{\gamma_B^{n_B}}{a_B^{n_B}}} = \left( \frac{\gamma_C}{a_C} \right)^{n_C} \left( \frac{\gamma_D}{a_D} \right)^{n_D} \]

If \( \gamma_A < 1 \), \( \Delta G_A \) i.e., \( M_A \) is more neg. than expected from Conc. i.e., more stable

If \( \gamma_A > 1 \), \( M_A \) is less stable

STANDARD STATE: \( C = 1 \), \( \gamma = 1 \)

So \( Q^\circ = 1 \) (in this course.)
Activity \(= a = \gamma C\)

where \(C = \text{concentration}\)

and \(\gamma = \text{activity coefficient}\)

Consider the “reaction” of changing the concentration of substance A from standard state, \(C^0\), to any concentration \(C\),

\[A(C^0) \rightarrow A(C)\]
Now, do several steps of NOTHING

\[ \Delta H = RT \frac{\Delta H}{RT} \]

\[ \Delta H = RT \ln \left( e^{\frac{\Delta H}{RT}} \right) \]

\[ = RT \ln \gamma \]

\[ \gamma = e^{\frac{\Delta H}{RT}} \text{ by definition for convenience} \]

\[ \therefore \Delta G = RT \ln \gamma + RT \ln \frac{C}{C_0} \]

\[ = RT \ln \gamma \frac{C}{C_0} = RT \ln \frac{a}{C_0} \]
Activity coefficient of ions in solution:
is about ion atmospheres:
crystal: perfect correlation

Real solution: good correlation

strong negative terms
weak positive terms

Net negative $\Delta G$ interaction
<table>
<thead>
<tr>
<th>Table 23-4</th>
<th>Mean-activity coefficients for electrolytes in water at 25°C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molality</td>
<td>0.001 0.005 0.01 0.05 0.10 0.50 1.00 2.00</td>
</tr>
<tr>
<td></td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>AB → A⁺ + B⁻</td>
<td>0.965 0.920 0.890 0.770</td>
</tr>
<tr>
<td>HCl</td>
<td>0.965 0.929 0.905 0.830 0.794 0.757 0.809 1.009</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.965 0.927 0.902 0.819 0.778 0.681 0.657 0.668</td>
</tr>
<tr>
<td>AB ⇌ A⁺⁺ + B⁻</td>
<td>0.744 0.515</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>0.700 0.477 0.387 0.202 (0.150) 0.063 0.043 0.035</td>
</tr>
<tr>
<td>CdSO₄</td>
<td>0.697 0.476 0.383 0.199 (0.150) 0.061 0.041 0.032</td>
</tr>
</tbody>
</table>

Example using activities:

Weak acid: $HA(aq) \rightarrow H^+(aq) + A^-(aq)$

Suppose $\Delta G^0 = +11.4 \frac{kJ}{mol} = 2 \times 5.7$

$$K_a = 1 \times 10^{-2} \ (a^+ = 298 K)$$

If assume ideal at $[HA] = 1 M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 0.01$$

$$[H^+] = [A^-] = 0.1 M \ at \ equilibrium.$$

But attraction of $H^+ \parallel A^-$ at 0.1M makes them more stable

$$\gamma \equiv 0.5 \ for \ both \ H^+ \parallel A^-$$

$$\gamma_{HA} \equiv 1$$

So:

$$K = \frac{a_{H^+}a_{A^-}}{1} = a^2 = 0.01$$

$$a = \gamma C = (0.5)C = 0.1$$

$$[C] = 0.2 M \ for \ H^+ \parallel A^-$$

Electrostatic attraction makes $\Delta G$ more negative; The reaction goes further right than expected from ideal behavior. Actual concentration is 0.2M for each ion.

$\gamma = 0.5$ is like saying the concentrations of $H^+$ and $A^-$ are less. LeChateliers says this will shift the equilibrium to the right.
Hydrolysis of diphosphate bond.

\[
\text{ATP} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{ADP} + \text{P}_i + \text{H}^+ \\
\begin{align*}
\Delta G^0 &= \Delta H^0 - T\Delta S^0 \\
&= -21,000 \text{ J} - 298(-100 \text{ J/K}) \\
&= 21 + 30 \\
&= +9 \text{ kJ/mol}
\end{align*}
\]

Equally "high energy" phosphate bonds

But \( \Delta G^0 \) means \( [\text{H}^+] = 1 \) \( \text{pH} = 0 \)

Biological Standard State: \( [\text{H}^+] = 10^{-7} \) (usual)
ATP + H₂O → ADP + H⁺ + Pᵢ

What does LeChatelier say if we are at pH 7?

\[ \Delta G = \Delta G^0 + RT \ln \frac{Q}{Q^0} = +9 + RT \ln \frac{[\text{ADP}][H^+][\text{P}_i]}{[\text{ATP}][X_{\text{H}_2\text{O}}]} \]

\[
\frac{[\text{ADP}][H^+][\text{P}_i]}{[\text{ATP}][X_{\text{H}_2\text{O}}]} \frac{1}{1} = \frac{\frac{1}{1 \times 10^{-7}}}{(1)(1)(1)(1)(1)} \]

Use **biological** standard state = pH 7

\[ \Delta G = \Delta G^0 + RT \ln \frac{Q}{Q^0} = -31 + RT \ln \frac{[\text{ADP}][H^+][\text{P}_i]}{[\text{ATP}][X_{\text{H}_2\text{O}}]} \frac{1}{1} \]

\[
\frac{[\text{ADP}][H^+][\text{P}_i]}{[\text{ATP}][X_{\text{H}_2\text{O}}]} \frac{1}{1 \times 10^{-7}} = \frac{(1)(1)(1)}{(1)(1)} \]

\[ \Delta G^0 = \Delta G^0 + RT \ln \frac{Q^0}{Q^0} = \Delta G^0 + RT \ln \frac{1}{1} \]

\[
= +9 + 5.7 \times (-7) = +9 - 39.9 = -31 \]
The famed “high energy phosphate bond” yields little more free energy than a **hydrogen bond**!

What is $K$ when $\Delta G^0' = -31 \text{ kJ/mol}$?

$$K = 10^{\Delta G^0'/5.7} = 10^{-31/5.7} = 2.7 \times 10^5$$

i.e., enough but not too much.
LeChatlier:

adding heat (raising temperature) shifts equilibrium (changes K) in the direction that uses the heat (lowers temperature).

Endothermic ($\Delta H = +$) absorbs heat; rxn will therefore use heat and lower the T, i.e., will shift to the right (K increases with rising T)

Exothermic ($\Delta H = \text{negative}$) gives off heat and raise the T; therefore shift to the left (K decreases with rising T)
Saying the same thing with $\Delta G^0$

\begin{align*}
\text{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}{RT_2} + \frac{\Delta S^0}{R} \\
\ln K_1 &= -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \\
\ln K_2 - \ln K_1 &= -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\
\ln \frac{K_2}{K_1} &= \ln \frac{K_2}{K_1} \\
\text{Van't Hoff equation} \quad \text{(one of several)}
\end{align*}

You will do this for the Lab experiment on the dissolving of butanol in water.

divide by $-RT$ and call it $T_2$
do same for $T_1$