For ideal gases and solutions

$$\Delta G_r = +\Delta_r G^0$$

- $$- RT \ln \left( \frac{C_A}{C_A^0} \right)^{n_A}$$
- $$- RT \ln \left( \frac{C_B}{C_B^0} \right)^{n_B}$$
+ $$+ RT \ln \left( \frac{C_C}{C_C^0} \right)^{n_C}$$
+ $$+ RT \ln \left( \frac{C_D}{C_D^0} \right)^{n_D}$$

$$\Delta G_r = \Delta G_r^0 + RT \ln \left( \frac{Q}{Q^0} \right)$$, where:

$$Q = \frac{C_C^{n_C} C_D^{n_D}}{C_A^{n_A} C_B^{n_B}}$$

$$Q^0 = \frac{(C_C^0)^{n_C} (C_D^0)^{n_D}}{(C_A^0)^{n_A} (C_B^0)^{n_B}}$$

$$\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0$$

-$$T \Delta S$$ Entropy changes relative to the standard states.

High concentrations is the same as low volume per molecule:

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right) = -R \ln \left( \frac{C_2}{C_1} \right)^n$$

$$Q^0$$ is always 1:

- 1 bar, 1 molar, or X (molefraction) = 1 (pure liquid or solid)

except for the biochemical standard state where
$$C^0' (H^+) = 10^{-7} \text{ M}$$
Le Chatlier's Principle

A system at equilibrium will react to changes ("stresses") that destroy the equilibrium, so as to relieve the stress.

1. Increased concentrations will be reduced.
   Decreased concentrations will be increased.

2. Heat added will be used.
   Heat removed will be replaced.

3. Pressure applied causes volume decrease.
   Pressure decrease causes volume increase.

* If the system is able to.
Quantitative Le Chatelier

\[ n_A A + n_B B \rightarrow n_C C + n_D D \]

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

\[ \Delta G_r = \Delta G_r^0 + RT \ln\left( \frac{Q}{1} \right) \]

What happens if \( C_C \) or \( C_D \) (product conc.) is increased?
\[ \Delta G_r \text{ becomes more positive} = \text{LESS SPONTANEOUS (shifts LEFT)} \]

What happens if \( C_A \) or \( C_B \) (reactant conc.) is increased?
\[ \Delta G_r \text{ becomes more negative} = \text{MORE SPONTANEOUS (shifts RIGHT)} \]
At *equilibrium*: \[ \Delta G = \Delta G^0 + RT \ln \left( \frac{Q_{eq}}{Q_0} \right) = 0 \]
\[ \Delta G = \Delta G^0 + 2.3RT \log \left( \frac{Q_{eq}}{Q_0} \right) = 0 \]

What is this telling us?
\[ \Delta G^0 = -2.3RT \log \left( \frac{Q_{eq}}{Q_0} \right) \]

At 298 K:
\[ \Delta G^0 = - (2.3)(8.3145)(298) \log \left( \frac{Q_{eq}}{Q_0} \right) \]
\[ -5700 \log \left( \frac{Q_{eq}}{Q_0} \right) \text{ in J/mol} \]
\[ -5.7 \log \left( \frac{Q_{eq}}{Q_0} \right) \text{ in kJ/mol} \]

\[ Q_{eq}/Q_0 = K/1 = K \] , the equilibrium constant

Therefore:
\[ \Delta G^0 = -5.7 \log (K) \] at 298 K
\[ \Delta G^0 = -2.3RT \log \left( \frac{Q_{eq}}{Q_0} \right) = -5.7 \log (K) \]

\[ K = \frac{1}{10^{\Delta G^0/5.7}} \]

<table>
<thead>
<tr>
<th>\Delta G^0</th>
<th>10^{\Delta G^0/5.7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>+17.1</td>
<td>10^{-3} = 0.001</td>
</tr>
<tr>
<td>+11.4</td>
<td>10^{-2} = 0.01</td>
</tr>
<tr>
<td>+5.7</td>
<td>10^{-1} = 0.1</td>
</tr>
<tr>
<td>0.0</td>
<td>10^0 = 1.0</td>
</tr>
<tr>
<td>-5.7</td>
<td>10^1 = 10</td>
</tr>
<tr>
<td>-11.4</td>
<td>10^2 = 100</td>
</tr>
<tr>
<td>-17.1</td>
<td>10^3 = 1000</td>
</tr>
</tbody>
</table>
Standard States

**Gases:** 1 atm partial pressure (new convention is 1 bar) and *ideal.*

**Liquids and Solids:** 1 atm and pure (\( x = 1 \)), where \( x \) is the mole fraction of the liquid.

**Solutes:** 1 molar (sometimes 1 molal or \( x_{\text{solute}} = 1 \)) and *ideal.*

* The enthalpy is as if the gas is at such a low pressure that it behaves ideally, but the entropy is as if it is at 1 atm.

** The enthalpy is as if the solute concentration is so low that the solution is ideal (no significant solute-solute interactions) but the entropy corresponds to unit concentration.
Units in $Q$

The rule is to use concentration units that are 1 in the standard state.

If $A(g)$ use $P_A^{\text{bar}}$

If $A(l)$ use $X_A$, mole fraction

If $A(aq)$ use $\text{mol} \text{L}^{-1}$

For reaction $A(g) + B(aq) \rightarrow C(l)$

$$Q = \frac{X_C}{P_A^{\text{bar}}} \frac{[B(aq)]_M}{[A]_M}$$
For \( H_2O(l) \rightarrow H_2O(g) \)

\[
Q = \frac{P_{H_2O(g)}}{X_{H_2O}} = \frac{P_{H_2O(g)}}{1} \text{ for pure } H_2O(l)
\]

\[
K = (P_{H_2O(g)})_{eq} = \text{Vapor Pressure}
\]
\[ \Delta G^0 = -386 - (-137) = -249 \text{ kJ/mol (as written)} \]

Example: \( \frac{1}{2} \text{O}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(aq) \)

\[ Q = \frac{\text{CO}_2(aq)}{P_{\text{O}_2(g)} P_{\text{CO}(g)}} \]

What is \( \frac{[\text{CO}_2(aq)]}{P_{\text{CO}}} \) at equilibrium in air?

1st: Estimate: Large negative \( \Delta G^0 \) so \( K \gg 1 \)

\[ \approx \frac{249}{6} \approx 40 \]

K \approx 40

because \( (2.3)(8.3)(298) \)

\[ = 5700 \text{ J} = 5.7 \text{ kJ} \approx 6 \text{ mol} \]

at 298 K

Every 5.7 kJ gives 1 power of 10

\[ \log = \text{exponent of 10} \quad \ln = \text{exponent of e} \]

\[ \ln K = -\frac{\Delta G^0}{RT} \quad \text{so} \quad K = e^{-\frac{\Delta G^0}{RT}} = 10 \]

\[ K = \frac{-(-249000)}{(2.3)(8.3)(298)} = 10 \]

\[ = 10 \]

\[ = 4.4 \times 10^4 \]
\[ K = \frac{10^{-249,000}}{(2.3 \times 8.3)(298)} = 10^{\frac{249}{5.7}} = 4.4 \times 10^{43} \]