IV. Chemical Equilibrium

A) Law of Chemical Equilibrium
Concentration expressed as molarity

\[
Molarity\ of\ A = [A] = \frac{\text{moles of } A}{\text{volume in liters}} \quad \text{units: } \frac{\text{mole}}{L} = M
\]

Consider the hypothetical reaction

\[\text{A} (g) + \text{B} (g) \rightarrow \text{C} (g) + \text{D} (g)\]

Compound A is allowed to react with B and the concentrations of the reactants and products are plotted as a function of time.

Note: After eleven seconds the concentrations do not change with time.

Chemical equilibrium is the condition that exists when the concentrations of the reactants and products no longer change with time. Chemical equilibrium is a dynamic state. It occurs when the rate of the forward reaction (A + B \rightarrow C + D) equals the rate of the reverse reaction (A + B \leftrightarrow C + D).

\[\text{A} (g) + \text{B} (g) \leftrightarrow \text{C} (g) + \text{D} (g)\]

indicates equilibrium
At equilibrium there is a specific relationship between the concentrations of the reactants and products.

Consider three experiments for the reaction

\[ A(g) + B(g) \rightleftharpoons C(g) + D(g) \]

in which the initial concentrations of A and B vary from experiment to experiment.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>[A]_{eq}</th>
<th>[B]_{eq}</th>
<th>[C]_{eq}</th>
<th>[D]_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.00</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>9.60</td>
<td>10.0</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>3</td>
<td>0.500</td>
<td>3.00</td>
<td>0.500</td>
<td>0.500</td>
</tr>
</tbody>
</table>

The following relationship fits the data in each experiment.

\[
\frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} = 0.167 = \text{constant} = K_c
\]

For the general reaction

\[ m A(g) + n B(g) + \cdots \rightleftharpoons p C(g) + q D(g) + \cdots \]

\( K_c \) is defined

\[
\frac{[C]^p_{eq} [D]^q_{eq} \cdots}{[A]^m_{eq} [B]^n_{eq} \cdots} = K_c
\]

The magnitude of the constant \( K_c \) depends on the nature of the reaction and the temperature.

The units of \( K_c \) depend on the specific reaction.

**Example:** \( A + 3 B \rightleftharpoons 2 C \)

\[
K_c = \frac{[C]^2_{eq}}{[A]_{eq} [B]^3_{eq}} \quad \text{units:} \quad \frac{\text{mole}^2}{\text{L}^3} = \left[ \frac{\text{L}}{\text{mole}} \right]^2
\]

**Example:** \( A + B \rightleftharpoons C + D \)
\[ K_c = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} \quad \text{units:} \quad \frac{\text{mole}^2}{\text{L}} = \text{unitless} \]

Terms:
When \( K < 1 \), then the equilibrium is said to lie to the left.
When \( K > 1 \), then the equilibrium is said to lie to the right.

B) Equilibrium Calculations

**Example #1:** Initially, 0.2660 mole of PCl\(_3\) and 0.3340 mole of Cl\(_2\) are placed in a 2.00 L container at 300\(^\circ\)C. If the moles of PCl\(_3\) are found experimentally to be 0.0660 at equilibrium, calculate \( K_c \) for the reaction

\[ \text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5 \]

at 300\(^\circ\)C.

**Plot of the Concentrations of PCl\(_3\), Cl\(_2\), and PCl\(_5\) versus Time**

![Plot](image)

where \([A]_i\) is the initial (at time = 0) molarity of A and \([A]_{eq}\) is the equilibrium molarity of A

**Important observations from the above plot**

3
• Initial moles of a substance + change in moles of substance = equilibrium moles of substance

Example:
initial moles of PCl₃ + change in moles of PCl₃ = equilibrium moles of PCl₃

0.0 moles of PCl₃ + 0.0660 moles of PCl₃ = 0.0660 moles of PCl₃

• The changes in number of moles of reactants and products are related by mole ratios.

These observations can be utilized in an Equilibrium Table to solve equilibrium problems.

**Equilibrium Table**

<table>
<thead>
<tr>
<th>Substances</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCl₃</td>
<td>0.2660</td>
<td>-0.0660</td>
<td>0.2000</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.3340</td>
<td>-0.0660</td>
<td>0.2680</td>
</tr>
<tr>
<td>PCl₅</td>
<td>0.0000</td>
<td>+0.0660</td>
<td>0.0660</td>
</tr>
</tbody>
</table>

Change in moles of Cl₂ = (equilibrium moles of Cl₂) - (initial moles of Cl₂)

Change in moles of PCl₅ = (equilibrium moles of PCl₅) - (initial moles of PCl₅)

Equilibrium moles of Cl₂ = (initial moles Cl₂) + (change in moles Cl₂)

Substituting the equilibrium moles into the equilibrium expression

\[
K_c = \frac{[PCl_5]_{eq}}{[PCl_3]_{eq} [Cl_2]_{eq}} = \frac{0.0660 \text{ mole}}{0.200 \text{ L}} = \frac{0.268 \text{ mole}}{0.268 \text{ L}} = 2.46 \frac{L}{\text{mole}}
\]

**Example #2:** Initially, 3.00 moles of PCl₃ and 3.00 moles of Cl₂ are placed in a 5.00 L container at 300°C. Calculate the equilibrium concentration of PCl₅, \([PCl_5]_{eq}\). \(K_c\) is 2.46 L/mole.

Unknown: \([PCl_3]_{eq}\). Let \(x = \) moles of PCl₃ at equilibrium.

Knowns: initial moles of PCl₃ = 3.00 mole, initial moles of Cl₂ = 3.00 mole, volume of container =
5.00L, \( K_c = 2.46 \text{ L/mole} \)

Concepts: chemical equilibrium, molarity

Substitute known values into equilibrium table.

<table>
<thead>
<tr>
<th></th>
<th>( \text{PCl}_3 )</th>
<th>+</th>
<th>( \text{Cl}_2 )</th>
<th>( \rightleftharpoons )</th>
<th>( \text{PCl}_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>3.00</td>
<td>+</td>
<td>3.00</td>
<td>0 mol</td>
<td></td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>-x</td>
<td>x</td>
<td>x mol</td>
<td></td>
</tr>
<tr>
<td>equil</td>
<td>3.00-x</td>
<td>3.00-x</td>
<td>x</td>
<td>x mol</td>
<td></td>
</tr>
</tbody>
</table>

Use the concepts presented above to fill in the table.

Substituting equilibrium moles into the equilibrium expression

\[
K_c = \frac{[\text{PCl}_5]_{eq}}{[\text{PCl}_3]_{eq} \cdot [\text{Cl}_2]_{eq}} = \frac{\frac{x}{5.00L}}{\frac{3.00-x}{5.00L} \cdot \frac{3.00-x}{5.00L}} = \frac{2.46L}{\text{mole}}
\]

\[
2.46x^2 - 19.76x + 22.14 = 0
\]

For the quadratic equation

\[
a x^2 + b x + c = 0
\]

the solutions are

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

Substituting

\[
x = \frac{-(-19.76) \pm \sqrt{(-19.76)^2 - 4(2.46)(22.14)}}{2(2.46)}
\]

\[
x = 1.35, \ 6.67
\]

Although both roots (1.35 and 6.67) are mathematically correct, only one root satisfies the physical constraints of the problem and that root is 1.35. If root 6.67 is used, then the moles of \( \text{PCl}_3 \) and \( \text{Cl}_2 \) at equilibrium would be -3.67 (3.00 - 6.67) and the equilibrium concentrations of \( \text{PCl}_3 \) and \( \text{Cl}_2 \) would be -0.734 M. A negative or zero equilibrium concentration for reactants or products is physically impossible.
\[ x = 1.35 \text{ mole} = \text{ moles of } PCl_5 \text{ at equilibrium} \]

\[ [PCl_5]_{eq} = \frac{x}{5.00L} = \frac{1.35\text{mole}}{5.00L} \]

\[ [PCl_3]_{eq} = \frac{(3.00-x)}{5.00L} = \frac{(3.00-1.35)}{5.00L} = \frac{1.65\text{mole}}{5.00L} \]

\[ [Cl_2]_{eq} = \frac{1.65\text{mole}}{5.00L} \]

The degree of dissociation, \( \alpha \), of B

\[ B \rightleftharpoons 2 \text{ A} \]

is defined as

\[ \alpha = \frac{\text{change in moles of } B}{\text{initial moles of } B} \]

and the percent dissociation is \( (\alpha)(100) \).

**Example #3:** If 3.00 moles of B are placed in a 1.00 L flask at 25°C, calculate the degree of dissociation, \( \alpha \), of B. \( K_c \) for B at 25°C is 0.100 mole/L.

Unknown: change in moles of B. Let \( x = \text{change in moles of B} \)

Knowns: initial moles of B = 3.00 mole, volume of flask = 1.00 L, \( K_c = 0.100 \text{ mole/L} \)

Concepts: chemical equilibrium, degree of dissociation

Substitute known values into the equilibrium table.

<table>
<thead>
<tr>
<th>( B \rightleftharpoons 2 \text{ A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
</tr>
<tr>
<td>change</td>
</tr>
<tr>
<td>equil</td>
</tr>
</tbody>
</table>

The reaction must go to the right in order to produce A. Moles of B will be consumed and thus, the change in moles of B will be \(-x\).

Use the concepts presented above to fill in the table.

<table>
<thead>
<tr>
<th>( B \rightleftharpoons 2 \text{ A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
</tr>
<tr>
<td>change</td>
</tr>
<tr>
<td>equil</td>
</tr>
</tbody>
</table>

Substitute equilibrium moles into the equilibrium expression.
\[
K_c = \frac{[A]_\text{eq}^2}{[B]_\text{eq}} = \frac{\left(\frac{2x}{1.00 \text{ L}}\right)^2}{\left(\frac{3.00-x}{1.00 \text{ L}}\right)} = 0.100 \frac{\text{mole}}{L}
\]

\[4.00x^2 + 0.100x - 0.300 = 0\]

\[x = 0.261, -0.287\]

\[x = 0.261 \text{ mole} = \text{change in moles of B}\]

\[\alpha = \frac{\text{change in moles of B}}{\text{initial moles of B}} = \frac{x}{3.00 \text{mole}} = \frac{0.261 \text{mole}}{3.00 \text{mole}} = 8.70 \times 10^{-2}\]

C) Factors Affecting Equilibrium Concentrations at Constant Temperature

Le Châtelier’s principle - when a system is in equilibrium, a change in any one of the factors upon which the equilibrium depends will cause the equilibrium to shift in such a way as to diminish the effect of the change.

To determine if the reaction

\[a \text{ A (g)} + b \text{ B (g)} \rightleftharpoons c \text{ C (g)} + d \text{ D (g)}\]

will go to the left or to the right to reestablish the equilibrium, \(Q\) is defined as

\[Q = \frac{[C]^c_{\text{in}} [D]^d_{\text{in}}}{[A]^a_{\text{in}} [B]^b_{\text{in}}}\]

If \(Q < K_c\), then the reaction will go to the right to reestablish the equilibrium. Moles of reactants A and B will be consumed and moles of products C and D will be produced.

If \(Q > K_c\), then the reaction will go to the left to reestablish the equilibrium. Moles of products C and D will be consumed and moles of reactants A and B will be produced.

1) Addition or Removal of Moles of Reactants or Products

**Example #4:** If 1.00 mole of PCl₅ is added to the equilibrium in Example #2, what will be the NEW equilibrium concentration of PCl₅?

Unknown: new equilibrium molarity of PCl₅ after the addition of 1.00 mole of PCl₅

Knowns: *equilibrium* moles of PCl₅, Cl₂, and PCl₃ (1.65, 1.65, and 1.35 mole) before the addition of 1.00 mole of PCl₅ (see Example #2); \(K_c = 2.46 \text{ L/mole; volume of the container} = 5.00 \text{ L}\)
Concepts: chemical equilibrium, Q, molarity

Step #1: Evaluate Q and determine whether the reaction will go to the left or right to reestablish the equilibrium.

\[ \text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5 \]

Initial: \[ \begin{align*} \text{PCl}_3 & : 1.65 \\ \text{Cl}_2 & : 1.65 \\ \text{PCl}_5 & : 1.35 + 1.00 \text{ mole} \end{align*} \]

The moles in the table are the equilibrium values from Example #2 and the 1.00 mole of PCl\(_5\) added.

\[ Q = \frac{[\text{PCl}_5]_{\text{eq}}}{[\text{PCl}_3]_{\text{in}} [\text{Cl}_2]_{\text{in}}} = \frac{\frac{2.35 \text{ mole}}{5.00 \text{ L}}}{\frac{1.65 \text{ mole}}{5.00 \text{ L}} \cdot \frac{1.65 \text{ mole}}{5.00 \text{ L}}} = \frac{4.31 \text{ L}}{\text{mole}} \]

\[ Q = 4.31 \frac{\text{L}}{\text{mole}} > 2.46 \frac{\text{L}}{\text{mole}} = K_c \]

Since \( Q > K_c \), the reaction will go to the left to reestablish the equilibrium. Moles of PCl\(_3\) will be consumed and moles of PCl\(_5\) and Cl\(_2\) will be produced.

Step #2: Solve the equilibrium problem.

Let \( x \) = change in moles of PCl\(_3\). Since the reaction goes to the left to reestablish the equilibrium, moles of PCl\(_3\) will be consumed and the entry for PCl\(_3\) in the row labeled “change” of the equilibrium table will be \(-x\).

\[ \begin{align*} \text{PCl}_3 & + \text{Cl}_2 \rightleftharpoons \text{PCl}_5 \\ \text{initial} & : 1.65 & 1.65 & 2.35 & 1.00 \text{ mole} \\ \text{change} & : x & x & -x & \text{mole} \\ \text{equil} & : 1.65 + x & 1.65 + x & 2.35 - x & \text{mole} \end{align*} \]

\[ K_c = \frac{[\text{PCl}_5]_{\text{eq}}}{[\text{PCl}_3]_{\text{eq}} [\text{Cl}_2]_{\text{eq}}} = \frac{\frac{2.35 - x}{5.00 \text{ L}}}{\frac{1.65 + x}{5.00 \text{ L}} \cdot \frac{1.65 + x}{5.00 \text{ L}}} = \frac{2.46 \text{ L}}{\text{mole}} \]

\[ 0.492x^2 - 2.624x + 1.010 = 0 \]

\[ x = 0.361 \text{ mole} = \text{change in moles of PCl}_3 \]
\[ [\text{PCl}_3]_{eq} = \frac{(2.35 \text{ mole} - x)}{5.00 \text{ L}} = \frac{(2.35 \text{ mole} - 0.36 \text{ mole})}{5.00 \text{ L}} = \frac{1.99 \text{ mole}}{5.00 \text{ L}} \]

2) Change in Volume of the Container

**Example #5:** If the volume of the container in Example #2 is decreased from 5.00 L to 2.00 L, will the moles of PCl₃ at the NEW equilibrium be greater or less than the moles of PCl₃ in Example #2?

Unknown: new equilibrium moles of PCl₃ after the volume of the container in Example #2 is reduced to 2.00 L.

Knowns: equilibrium moles of PCl₃, Cl₂, and PCl₃ in Example #2, new volume = 2.00 L, \( K_c = 2.46 \text{ L/mole} \).

Concept: Q, molarity

Step #1

\[
\begin{align*}
\text{PCl}_3 + \text{Cl}_2 & \rightleftharpoons \text{PCl}_5 \\
\text{initial} & \quad 1.65 \quad 1.65 \quad 1.35 \quad \text{mole} \\
\end{align*}
\]

\[
Q = \frac{[\text{PCl}_5]_{in}}{[\text{PCl}_3]_{in} [\text{Cl}_2]_{in}} = \frac{\frac{(1.35 \text{ mole})}{2.00 \text{ L}}}{\frac{(1.65 \text{ mole})}{2.00 \text{ L}} \frac{(1.65 \text{ mole})}{2.00 \text{ L}}} = 0.992 \frac{L}{\text{mole}}
\]

\[
Q = 0.992 \frac{L}{\text{mole}} < 2.46 \frac{L}{\text{mole}} = K_c
\]

Since Q < \( K_c \), the reaction will go to the right to reestablish the equilibrium. Moles of PCl₃ and Cl₂ will be consumed and moles of PCl₅ will be produced. The moles of PCl₅ at the NEW equilibrium will be greater than the moles of PCl₃ in Example #2.

D) Dependency of K on Temperature

Plot of ln(K_p) versus 1/T for the reaction

\[
\text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g)
\]
Equation for a straight line is
\[ y = (slope)x + (intercept) \]
\[ \ln(K_p) = \left[ \frac{-\Delta H}{R} \right] \frac{1}{T} + C \]

where C is a constant.

Consider \( K_2 \) at \( T_2 \) and \( K_1 \) at \( T_1 \) for a specific reaction, then
\[
\ln(K_p)_2 = \left[ \frac{-\Delta H}{R} \right] \frac{1}{T_2} + C
\]

\[
\ln(K_p)_1 = \left[ \frac{-\Delta H}{R} \right] \frac{1}{T_1} + C
\]

\[
\ln(K_p)_2 - \ln(K_p)_1 = \left[ \frac{-\Delta H}{R} \right] \frac{1}{T_2} - \frac{1}{T_1}
\]

Rearranging

\[
\ln(K_p)_2 = \left[ \frac{\Delta H}{R} \right] \frac{T_2 - T_1}{T_2 T_1} + \ln(K_p)_1
\]

When \(\Delta H > 0\), heat is absorbed and the reaction is said to be \textit{endothermic}.

When \(\Delta H < 0\), heat is evolved and the reaction is said to be \textit{exothermic}.

**Example:** If \(K_p = 0.09823\) at 20°C and 0.4554 at 40°C, calculate \(\Delta H\) for the reaction.

\[
\text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g)
\]

\[
\ln(K_p)_2 = \left[ \frac{\Delta H}{R} \right] \frac{T_2 - T_1}{T_2 T_1} + \ln(K_p)_1
\]

Rearranging

\[
\Delta H = R \ln \left( \frac{(K_p)_2}{(K_p)_1} \right) \frac{T_2 T_1}{T_2 - T_1} = (8.314 J/K) \ln \left( \frac{(0.09823)}{0.4554} \right) \frac{(313 K)(293 K)}{(20 K)} = 5.85 \cdot 10^4 J
\]

E) Entropy and Free Energy
The thermodynamic function entropy, $S$, is a measure of the disorder or randomness of a system. Entropy is a state function.

The second law of thermodynamics states that an increase in entropy of the universe is associated with every spontaneous process. The change in entropy of the universe is the sum of the changes in the entropy of the system and surroundings.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (1)$$

For a process to proceed spontaneously $\Delta S_{\text{univ}}$ must be a positive number. If $\Delta S_{\text{univ}}$ is a negative number, then the process will proceed spontaneously in the reverse direction and when $\Delta S_{\text{univ}} = 0$, then the system is at equilibrium.

The change in the entropy of the surroundings, $\Delta S_{\text{surr}}$, is dependent on the heat that is transferred between the system and the surroundings. For a constant pressure and constant temperature process

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-(q_p)_{\text{sys}}}{T} = \frac{-\Delta H}{T} \quad (2)$$

As an example consider the reaction

$$\text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g) \quad \Delta H^\circ = -92.4 \text{kJ}, \quad \Delta S^\circ = -198.5 \text{ J/K}$$

The change in the entropy of the surroundings with the formation of two moles of NH$_3$ is

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{(-92.4 \text{kJ})}{298 \text{K}} = 310 \frac{\text{J}}{\text{K}}$$

and the change in the entropy of the universe is

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -198.5 \frac{\text{J}}{\text{K}} + 310 \frac{\text{J}}{\text{K}} = 111 \frac{\text{J}}{\text{K}}$$

The entropy of the system, $\Delta S^\circ = -198.5 \text{ J/K}$, decreases primarily because there are fewer product molecules than reactant molecules. The reduction in number of molecules results in a lowering of the positional disorder. Although $\Delta S^\circ$ for the reaction is a negative number, $\Delta S_{\text{univ}} > 0$ due to the large increase in the entropy of the surroundings and the reaction proceeds spontaneously to the right.

For a constant pressure and constant temperature process, eq 2 can be substituted into eq 1.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{-\Delta H}{T} = \Delta S + \frac{-\Delta H}{T} \quad (3)$$

Multiply eq 3 by $-T$ and rearrange.
\[-T \Delta S_{\text{univ}} = \Delta H - T \Delta S\]  \hspace{1cm} (4)

*Gibbs free energy, $G$, is defined as*

$$G = H - TS$$

For a constant pressure and constant temperature process

$$\Delta G = \Delta H - T \Delta S \hspace{1cm} (5)$$

Comparing eqs 4 and 5

$$\Delta G = -T \Delta S_{\text{univ}}$$

A constant pressure and constant temperature process will be spontaneous when $\Delta S_{\text{univ}} > 0$ or $\Delta G < 0$.

**Example:** Calculate $\Delta G^\circ$ at $25^\circ C$ for the following reaction?

$$\text{H}_2(\text{g}) \rightarrow 2 \text{H}(\text{g})$$

$\Delta H^\circ = 436 \text{ kJ}$, $\Delta S^\circ = 98.5 \text{ J/K}$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 436 \text{kJ} - (298 \text{K})(98.5 \frac{\text{J}}{1000 \text{J}}) = 407 \text{kJ}$$

F) Reaction Free Energy

For the generic reaction

$$a \text{A}(\text{g}) + b \text{B}(\text{g}) \rightarrow c \text{C}(\text{g}) + d \text{D}(\text{g})$$

the reaction free energy, $\Delta G$, is defined as

$$\Delta G = \Delta G^0 + RT \ln \left( \frac{P_c P_d}{P_a P_b} \right)$$

A plot of $G$ for the above reaction versus the extent of reaction yields...
The degree of reaction is a measure of the extent to which the reaction has advanced from the left to right.

The slope of the above curve at any point is equal to the reaction free energy, $\Delta G$. When the degree of reaction is 0, only the reactants A and B are present, $\Delta G < 0$, and the reaction will proceed spontaneously to the right. When the degree of reaction is 1.0, only the products are present, $\Delta G > 0$, and the reaction will proceed spontaneously to the left. When the degree of reaction is 0.16, $\Delta G = 0$ and the reaction is at equilibrium.

At equilibrium, $\Delta G = 0$ and

$$\Delta G = 0 = \Delta G^\circ + RT \ln \frac{(P_C)_e^{eq} (P_D)_e^{eq}}{(P_A)_e^{eq} (P_B)_e^{eq}}$$

(6)

$K_p$ is defined as
\[ K_p = \left[ \frac{(P_C)^c_{eq}(P_D)^d_{eq}}{(P_A)^a_{eq}(P_B)^b_{eq}} \right] \quad (7) \]

Substituting eq 7 into eq 6 and rearranging

\[ \Delta G^\circ = -RT\ln(K_p) \quad \text{or} \quad K_p = \exp\left[ \frac{-\Delta G^\circ}{RT} \right] \]

Relationship between \( K_c \) and \( K_p \)

For the generic reaction

\[ a \text{ A (g)} + b \text{ B (g)} \rightarrow c \text{ C (g)} + d \text{ D (g)} \]

Assuming ideal gas behavior

\[ P_A = \left[ \frac{n_A}{V} \right] RT = [A]RT; \quad P_B = [B]RT; \quad P_C = [C]RT; \quad P_D = [D]RT \]

Substituting

\[ K_p = \left[ \frac{(P_C)^c_{eq}(P_D)^d_{eq}}{(P_A)^a_{eq}(P_B)^b_{eq}} \right] = \left[ \frac{([C]RT)^c_{eq}([D]RT)^d_{eq}}{([A]RT)^a_{eq}([B]RT)^b_{eq}} \right] = \left[ \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}} \right] (RT)^{c+d-a-b} \]

and

\[ K_p = K_c (RT)^\Delta n \]

where \( \Delta n = c + d - a - b \).

G) Standard Reaction Free Energy and Standard Absolute Entropy

1) \( \Delta G^\circ \)
The free energy change for the formation of a compound in its standard state from its elements (most stable form) in their standard states is called the standard free energy of formation, \( \Delta G^\circ_f \).

**Example:**

\[
\text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g) \quad \Delta G^\circ_f = -33.2 \text{ kJ}
\]

By definition \( \Delta G^\circ_f \) for elements in their most stable form is zero.

A table of \( \Delta G^\circ_f \) is found in the text. See example below.

To calculate the standard reaction free energy, \( \Delta G^\circ \), from the standard free energies of formation

\[
\Delta G^\circ_{\text{reaction}} = \sum n_{\text{product}} \Delta G^\circ_f (\text{product}) - \sum n_{\text{reactant}} \Delta G^\circ_f (\text{reactant})
\]

where \( n \), called the *mole number*, is the stoichiometric coefficient in the thermochemical equation.

2) \( \text{S}^\circ \)

The third law of thermodynamics states that the entropy for all pure, perfectly ordered, crystalline substances is zero at absolute zero \((0 \text{ K})\). Consequently the *absolute entropies*, \( \text{S}^\circ \), of all compounds and elements in their most stable form can be determined. Some of these entropies are listed in a table of thermodynamic data found in the text.

**Example:** Table of Selected Thermodynamic Data

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta G^\circ_f ) (kJ/mole)</th>
<th>( \text{S}^\circ ) (J/mole-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CO}_2 (g)</td>
<td>-394.4</td>
<td>213.6</td>
</tr>
<tr>
<td>\text{H}_2\text{O} (l)</td>
<td>-237.2</td>
<td>70.0</td>
</tr>
<tr>
<td>\text{H}_2 (g)</td>
<td>0.0</td>
<td>130.5</td>
</tr>
<tr>
<td>\text{H} (g)</td>
<td>203.3</td>
<td>115</td>
</tr>
</tbody>
</table>

To calculate the change in the standard entropy for a reaction

\[
\Delta S^\circ_{\text{reaction}} = \sum n_{\text{product}} \text{S}^\circ (\text{product}) - \sum n_{\text{reactant}} \text{S}^\circ (\text{reactant})
\]