Chapter 14 Chemical Equilibrium

Forward reaction

\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g}) \]

Reverse reaction

\[ 2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \]

At equilibrium

\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \]

Chemical equilibrium is reached when reactants combine to form products at the same rate as the products react to form reactants

\[ \text{forward} \quad \text{rate}_f = k_f[A] \]

\[ \text{reverse} \quad \text{rate}_r = k_r[B] \]

at equilibrium, \( \text{rate}_f = \text{rate}_r \), \( k_f[A] = k_r[B] \)
**Reaction Quotient, Q, and Equilibrium Constant, K**

In general,

\[ aA + bB \rightleftharpoons cC + dD \]

\[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

\[ Q = \frac{\text{Products}}{\text{Reactants}} \]

Generally use Q when a reaction has not reached equilibrium. At **equilibrium**, all [ ] do not change over time, and \( Q = K \)

\[ 3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \]

Whatever effects rates, effects equilibrium - Temp, concentration

\[ aA + bB \rightleftharpoons cC + dD \]

At equilibrium: \( \text{rate}_f = \text{rate}_r \)

if \( \text{rate}_f = k_f [A][B] \) and \( \text{rate}_r = k_r [C][D] \)

and \( k_f [A][B] = k_r [C][D] \)

and \[ \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r} = K \]

The first quotient is known at the equilibrium constant expression.
\[ K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

Law of Mass Action

- Products in the numerator and reactants in the denominator, "Products over Reactants"
- Raise each concentration to the power of the stoichiometric coefficient in the balanced equation

- \( K \ll 1 \) favors reactants \((10^{-3})\)
- \( K \gg 1 \) favors products \((10^3)\)
- If \( 10^{-3} < K < 10^3 \), products and reactants present

Note: For the reaction

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

at 400K \( K = 2.89 \)

For

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

\( K = \frac{1}{2.89} = 0.346 \)

The equilibrium constant is dependent on the direction of the reaction.
If a chemical equation can be expressed as the sum of two or more chemical equations, the equilibrium constant for the overall reaction is the product of the equilibrium constants for the component reactions.

\[2 \text{P(g)} + 3 \text{Cl}_2(g) \leftrightarrow 2 \text{PCl}_3(g) \quad K_1 = \frac{[\text{PCl}_3]^2}{[\text{P}]^2[\text{Cl}_2]^3}\]

\[\text{PCl}_3(g) + \text{Cl}_2(g) \leftrightarrow \text{PCl}_5(g) \quad K_2 = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}\]

\[2 \text{P(g)} + 5 \text{Cl}_2(g) \leftrightarrow 2 \text{PCl}_5(g) \quad K_3 = \frac{[\text{PCl}_5]^2}{[\text{P}]^2[\text{Cl}_2]^5}\]

\[\begin{align*}
2 \text{P(g)} + 3 \text{Cl}_2(g) & \leftrightarrow 2 \text{PCl}_3(g) \\
2 \text{PCl}_3(g) + 2 \text{Cl}_2(g) & \leftrightarrow 2 \text{PCl}_5(g) \\
2 \text{P(g)} + 5 \text{Cl}_2(g) & \leftrightarrow 2 \text{PCl}_5(g)
\end{align*}\]

\[K_3 = \frac{[\text{PCl}_5]^2}{[\text{P}]^2[\text{Cl}_2]^5} = \frac{[\text{PCl}_3]^2}{[\text{P}]^2[\text{Cl}_2]^3} \times \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} \times \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = K_1 \times K_2 \times K_2 = K_1 K_2^2\]

### Relations Between Equilibrium Constants

<table>
<thead>
<tr>
<th>Chemical Equation</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(aA + bB \leftrightarrow cC + dD)</td>
<td>(K_1)</td>
</tr>
<tr>
<td>(cC + dD \leftrightarrow aA + bB)</td>
<td>(K_2 = \frac{1}{K_1} = K_1^{-1})</td>
</tr>
<tr>
<td>(naA + nbB \leftrightarrow ncC + ndD)</td>
<td>(K_3 = K_1^n)</td>
</tr>
</tbody>
</table>

\(\text{H}_2\text{S}, \ Ka_1 = 9.5 \times 10^{-8}, \ Ka_2 = 1 \times 10^{-19}\)
Be aware of $K_c$ and $K_p$

$K_c$ is used with concentration expressed in molarity or moles per liter.

$K_p$ is used with pressures, if you are given partial pressures in atmospheres.

$$P = \left( \frac{n}{V} \right)RT$$

is a measure of concentration

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

$$K_p = \frac{P_{NH_3}^2}{P_{H_2}^3P_{N_2}} = \frac{([NH_3]RT)^2}{([H_2]RT)^3([N_2]RT)} = K_c \frac{(RT)^2}{(RT)^3(RT)} = K_c(RT)^{-2}$$

$$K_p = K_c( RT )^{\Delta n} \quad \Delta n = \text{moles products} - \text{moles reactants}$$

For above reaction, $\Delta n = 2 - (3 + 1) = -2 \quad K_p = K_c( RT )^{-2}$

Ex: In the synthesis of ammonia from nitrogen and hydrogen, $K_c = 9.60$ at 300°C. Calculate $K_p$ for this reaction at this temperature.
Heterogeneous Equilibrium

CaCO$_3$(s) $\rightleftharpoons$ CaO(s) + CO$_2$(g)

The concentration of a solid is proportional to its density and remains constant as long as the temperature does not change.

\[
\text{Density} = \frac{\text{g/cm}^3}{\text{g/mol}} = \frac{\text{mol}}{\text{cm}^3}
\]

Since concentrations of solids are constant, they are included in the equilibrium constant and don't appear in the reaction quotient.

\[
K = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \quad [\text{CO}_2] = K_x \frac{[\text{CaCO}_3]}{[\text{CaO}]}
\]

\[
[\text{CO}_2] = K \quad P_{\text{CO}_2} = K_p
\]

Write the equilibrium-constant expression for Kc and Kp for each of the following reactions.

CO$_2$(g) + H$_2$(g) $\rightleftharpoons$ CO(g) + H$_2$O(l)

SnO$_2$(s) + 2CO (g) $\rightleftharpoons$ Sn(s) + 2CO$_2$(g)
Calculating Equilibrium Constants
Substitute the equilibrium concentrations into the equilibrium concentrations.

Ex: Nitryl chloride, NO₂Cl, is in equilibrium with NO₂ and Cl₂,

\[ 2 \text{NO}_2\text{Cl}(g) \rightleftharpoons 2 \text{NO}_2(g) + \text{Cl}_2(g) \]

At equilibrium the concentrations of the substances are [NO₂Cl] = 0.00106 M, [NO₂] = 0.0108 M, and [Cl₂] = 0.00538 M. From these data calculate the equilibrium constant, \( K_c \).

Predicting the Direction of a Reaction.
- \( Q < K \), not equilibrium, reactants will be converted to products
- \( Q = K \), equilibrium
- \( Q > K \), no equilibrium, products will be converted to reactants

Ex: At 448°C the equilibrium constant, \( K_c \) for the reaction,

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

is 51. Predict how the reaction will proceed to reach equilibrium at 448°C if we start with \( 2.0 \times 10^{-2} \) mol of HI, \( 1.0 \times 10^{-2} \) mol of H₂, and \( 3.0 \times 10^{-2} \) mol of I₂ in a 2.0 L container.
Calculating Equilibrium Concentrations

Follow flow chart on page 580

- Balanced Equation
- Difference Table: include initial conc., change in conc. $\Delta[\]$ and equilibrium conc.
- Substitute equilibrium conc. into equilibrium equation and solve for x. If you use quadratic equation, use the root that makes sense.
- Calculate equilibrium concentrations by inserting value of x.
- Check your results by substituting your answer into equilibrium equation.

EX: The equilibrium constant, $K_c$, for the reaction of $H_2$ with $I_2$ is 57.0 at 700 K:

$$H_2(g) + I_2(g) \rightleftharpoons 2 HI(g) \quad K_c = 57.0 \text{ at } 700 \text{ K}.$$

If 1.00 mol of $H_2$ is allowed to react with 1.00 mol of $I_2$ in a 10.0 L reaction vessel at 700 K, what are the concentrations of $H_2$, $I_2$ and HI at equilibrium? What is the equilibrium composition of the equilibrium mixture in moles?
EX: For the reaction \( \text{I}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{IBr}(g) \), \( K_c = 280 \) at 150°C.
Suppose that 0.500 mol of IBr in a 1.00 L flask is allowed to reach equilibrium at 150°C. What are the equilibrium concentrations of IBr, I\(_2\) and Br\(_2\).
**Factors that Effect Equilibrium**

- Concentrations change
- Pressures change
- Temperature changes

**Le Châtelier's Principle**

If a stress (such as a change in concentration, pressure, or temperature) is applied to a system in equilibrium, the equilibrium shifts in a way that tends to undo the effect of the stress.

Example

A change in concentration will effect the value of Q. The concentrations will shift until Q again equals K.

\[
3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)
\]
\[ K = \frac{[NH_3]^2}{[H_2]^3[N_2]} = 1.2 \] \text{ at } 375^\circ C

\[ H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \]

\[ K = \frac{[HI]^2}{[H_2][I_2]} = 50.0 \]

If H\textsubscript{2} is added, Q will decrease. The equilibrium will shift so that more HI is produced by consuming H\textsubscript{2} and I\textsubscript{2} until Q = K.

Endothermic: Reactants + heat = products
Increasing T results in increase in K.

Exothermic: Reactants = products + heat
Increasing T results in decrease in K.

Equilibrium shifts in the direction that absorbs heat.
### Effects of Disturbances on Equilibrium and K

<table>
<thead>
<tr>
<th>Disturbances</th>
<th>Change as Mixture Returns to Equilibrium</th>
<th>Effect on Equilibrium</th>
<th>Effect on K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of reactant</td>
<td>Some of added reactant is consumed</td>
<td>Shift to right</td>
<td>No Change</td>
</tr>
<tr>
<td>Addition of Product</td>
<td>Some of added product is consumed</td>
<td>Shift to left</td>
<td>No Change</td>
</tr>
<tr>
<td>Decrease in volume, increase in pressure</td>
<td>Pressure decreases</td>
<td>Shift toward fewer gas molecules</td>
<td>No change</td>
</tr>
<tr>
<td>Increase in volume, decrease in pressure</td>
<td>Pressure increases</td>
<td>Shift toward more gas molecules</td>
<td>No change</td>
</tr>
<tr>
<td>Rise in temperature</td>
<td>Heat energy is consumed</td>
<td>Shift in the endothermic direction</td>
<td>Change</td>
</tr>
<tr>
<td>Drop in temperature</td>
<td>Heat energy is generated</td>
<td>Shift in exothermic direction</td>
<td>Change</td>
</tr>
</tbody>
</table>

### The Effect of Catalyst

A catalyst increases the rate at which equilibrium is achieved, but it does not change the composition of the equilibrium mixture.
Le Châtelier's Examples

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H = +180.5 \text{ kJ} \]

<table>
<thead>
<tr>
<th>Equilibrium Constant, K</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 \times 10^{-31}</td>
<td>298 K</td>
</tr>
<tr>
<td>6.7 \times 10^{-10}</td>
<td>900 K</td>
</tr>
<tr>
<td>1.7 \times 10^{-3}</td>
<td>2300 K</td>
</tr>
</tbody>
</table>

\[ 2\text{ NO}_2 \rightleftharpoons \text{N}_2\text{O}_4(g) \quad \Delta H = -57.2 \text{ kJ} \]

<table>
<thead>
<tr>
<th>Equilibrium Constant, K</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>273 K</td>
</tr>
<tr>
<td>70</td>
<td>298 K</td>
</tr>
</tbody>
</table>

\[ 3\text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

Which way does equilibrium shift when:
- Add \text{H}_2?
- Add \text{NH}_3?
- Volume increased?
- Volume decreased?
The Link Between Chemical Equilibrium and Chemical Kinetics

\[ K = \frac{k_f}{k_r} \]

\[ k = Ae^{-\frac{E_a}{RT}} \quad \ln k = -\frac{E_a}{RT} \]

\[ \frac{\Delta \ln k}{\Delta \frac{1}{T}} = -\frac{E_a}{R} \]

\[ K = \frac{k_1}{k_{-1}} \]

Ch 14 Equilibrium 14