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14.1 – Equilibrium

State in which competing processes are balanced so that there are no observable changes as time goes by.

Apparent lack of change is a consequence of an equilibrium but not a proof that there is an equilibrium in the system:

Equilibrium ≠ Steady State
Physical Equilibrium

Balance of competing physical processes

• Evaporation vs condensation
• Freezing vs melting

H₂O (l) ⇌ H₂O (s)
Chemical Equilibrium

Balance of two or more chemical reactions

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

Forward reaction: Decomposition

Reverse reaction: Dimerization

Colorless gas

Yucky-brown

Decomposition is exactly balanced by dimerization at equilibrium

Concentrations of NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} do not change with time
• *Equilibrium is not achieved instantaneously*

• *Concentrations stop changing at equilibrium but reactions do not stop*
Is Equilibrium Common?

Equilibrium is common in closed and isolated systems. However, chemical equilibria in open systems (atmosphere, ocean, etc.) are exceedingly rare.
Example: Atmospheric Ozone

*Ozone layer* refers to enhanced mixing ratio of ozone \((O_3)\) in the stratosphere:

**Stratosphere:** \([O_3]/[O_2] \sim 5 \times 10^{-6}\)

**Surface:** \([O_3]/[O_2] \sim 10^{-8}\)

Equilibrium treatment predicts:

\([O_3]/[O_2] \sim 10^{-38}\)

A factor of

\(~1,000,000,000,000,000,000,000,000,000,000\) different from the equilibrium!

*Photochemistry* keeps the ozone level away from equilibrium in the stratosphere

*Air-pollution chemistry* keeps it away from equilibrium near in air above big cities (ozone = major component of smog)
Kinetic Constraints (Chem 1C)

Equilibrium in biological systems is also quite uncommon.

Fluffy should be in equilibrium with air:

\[
\text{↔ } \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{SO}_2 + \ldots
\]

Thermodynamics strongly favors the right side of this equilibrium: \( \Delta H_{\text{rxn}} << 0 \)

However, at room temperature, Fluffy-the-Destroyer does NOT disintegrate into a bunch of gases!

Fluffy decomposition is thermodynamically allowed but fortunately for his owner it is VERY slow.

Fluffy's stability is kinetically constrained.
Contrary to equilibrium, Fluffies are common in nature

"Pusha" – Russian for "Fluffy" – professor's dog. (Also not in any kind of equilibrium with the surroundings).
Equilibrium Constant

\[ a A + b B \rightleftharpoons c C + d D \]

\[ K_C = \frac{[C]_eq^c[D]_eq^d}{[A]_eq^a[B]_eq^b} = \text{constant} \]

Law of Mass Action
Law of Mass-Action

\[ a\,A + b\,B \Leftrightarrow c\,C + d\,D \]

\[ K_C = \frac{[C]_\text{eq}^c [D]_\text{eq}^d}{[A]_\text{eq}^a [B]_\text{eq}^b} = \text{constant} \]

The statement in the textbook that \( K_C \) is a "dimensionless quantity" is not entirely correct.

Dimension of \( K_C \) = (dimension of concentrations used)\( ^{\Delta n} \)
\[ \Delta n = (c + d) - (a + b) \]

However, the units are often used \textit{implicitly} and not explicitly written. Examples will be given in problems as we go along.
Law of Mass-Action

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

\[ K_C = \frac{[C]_\text{eq}^c[D]_\text{eq}^d}{[A]_\text{eq}^a[B]_\text{eq}^b} \]

Equilibrium Will

- \( K_C \gg 1 \) Lie to the right Favor products
- \( K_C \ll 1 \) Lie to the left Favor reactants
Equilibrium Constant

A + B ⇌ AB

\[ K = \frac{[AB]}{[A][B]} = \frac{2}{2 \times 2} = \frac{1}{2} \]

A + C ⇌ AC

\[ K = \frac{[AC]}{[A][C]} = \frac{3}{1 \times 1} = 3 \]

A + D ⇌ AD

\[ K = \frac{[AD]}{[A][D]} = \frac{1}{3 \times 3} = \frac{1}{9} \]
Chemical Equilibrium

At what time is the equilibrium achieved in this system? – about 30 seconds or so

Estimate the equilibrium constant: $K_c = [white]/[red] \sim 7/13.$
Homogenous equilibrium applies to reactions in which all reacting species are in the same phase.

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

\[
K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}
\]

\[
K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}
\]

In most cases

\[
K_c \neq K_p
\]

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

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

\[
\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}
\]

\[
= (c + d) - (a + b)
\]
Sample Problem

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form COCl₂ (g) at 74°C are [CO] = 0.012 M, [Cl₂] = 0.054 M, and [COCl₂] = 0.14 M. Calculate the equilibrium constants $K_c$ and $K_p$ ($R = 0.082\ L\ atm\ K^{-1}\ mol^{-1}$)

\[
\begin{align*}
K_c &= \frac{[COCl_2]}{[CO][Cl_2]} \\
&= \frac{0.14\ M}{0.012\ M \times 0.054\ M} \\
&= 220\ M^{-1}
\end{align*}
\]

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

\[
\Delta n = 1 - 2 = -1 \\
T = (273 + 74)\ K = 347\ K
\]

\[
K_p = 220\ M^{-1} \times (0.0821\ L\ atm\ K^{-1}\ mol^{-1} \times 347\ K)^{-1} = 7.7\ atm^{-1}
\]
**Equilibria Involving Condensed Phases**

*Heterogenous equilibrium* applies to reactions in which reactants and products are in different phases.

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)
\]

**Chemical Equilibrium:**

\[
K'_c = \frac{[\text{CaO}(s)][\text{CO}_2]}{[\text{CaCO}_3(s)]}
\]

\[
K_c = [\text{CO}_2] = K'_c \times \frac{[\text{CaCO}_3(s)]}{[\text{CaO}(s)]}
\]

**Pressure Equilibrium:**

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

The concentration of *solids* and *pure liquids* are **not included** in the expression for the equilibrium constant.
\[
\text{CaCO}_3 (s) \rightleftharpoons \text{CaO (s)} + \text{CO}_2 (g)
\]

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

\[P_{\text{CO}_2} \text{ does not depend on the amount of CaCO}_3 \text{ or CaO!}\]
Equilibrium Vapor Pressure

- Vapor pressure of a pure liquid (solid) at equilibrium: does NOT depend on the amount of liquid (solid)!
- Increases with temperature

$$A(s) \rightleftharpoons A(g)$$
$$B(l) \rightleftharpoons B(g)$$

$$P_{eq} = K_P$$

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temperature</th>
<th>$P_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20°C</td>
<td>0.023 atm</td>
</tr>
<tr>
<td>Water</td>
<td>100°C</td>
<td>1 atm (boiling)</td>
</tr>
<tr>
<td>Hg</td>
<td>20°C</td>
<td>$1.6 \times 10^{-9}$ atm</td>
</tr>
<tr>
<td>Chloroform</td>
<td>20°C</td>
<td>0.21 atm</td>
</tr>
</tbody>
</table>

- Liquid **boils** when its $P_{eq}$ exceeds the ambient pressure

$$P_{eq} \geq P_{ambient}$$
Sublimation

Solid **sublimates** when its $P_{eq}$ exceeds the ambient vapor pressure of that substance (its partial pressure)

Dry ice (solid CO$_2$) at 20ºC:  

$$P_{eq} = K_P = 56.5 \text{ atm}$$

Partial pressure of CO$_2$ in air:  

$$P_{CO_2} = 0.00037 \text{ atm}$$

**Conclusion**: dry ice will sublime in open air at 20ºC

$CO_2(s) \rightarrow CO_2(g)$

NOT at equilibrium!  

$P_{CO_2} \neq P_{eq}$
Solubility and Equilibrium

- Equilibrium concentration of a solute dissolved in a solvent: does NOT depend on the amount of excess solute
- Tabulated for many compounds

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solubility (g/100g H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>35.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>36.0</td>
</tr>
<tr>
<td>LiCl</td>
<td>84.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.00029</td>
</tr>
</tbody>
</table>
Reactions Involving Solvents

\[ \text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (aq) + \text{OH}^- (aq) \quad K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \]

\[ [\text{H}_2\text{O}] \sim 55.6 \text{ M in dilute solutions and can be treated as a constant} \]

\[ K_w = K_c[H_2O] = [H^+][OH^-] \]

The *ion-product constant* \((K_w)\) is the product of the molar concentrations of \(H^+\) and \(OH^-\) ions at a particular temperature.

*Solution Is*

At 25\(^0\)C
\[ K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \]

- \([H^+] = [OH^-]\) neutral
- \([H^+] > [OH^-]\) acidic
- \([H^+] < [OH^-]\) basic
Looking Ahead to Chem 1C: Ionization Constants of Acids

\[
\text{HA (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq)
\]

\[
\text{HA (aq)} \rightleftharpoons \text{H}^+ (aq) + \text{A}^- (aq)
\]

\[
K_a = K_c \times [\text{H}_2\text{O}] = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}
\]

\([\text{H}_2\text{O}]\) is NOT included in the equilibrium constant for the acid ionization

\(K_a\) is called the \textit{acid ionization constant}

- \(K_a\) is small for weak acids
- \(K_a\) is large for strong acids
Summary of Concepts

• **Equilibrium is a delicate balance between competing processes**

• **Chemical equilibria can be homogeneous or heterogeneous**

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

\[
K_C = \frac{[C]_e^c[D]_e^d}{[A]_e^a[B]_e^b} = \text{constant} \\
K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} = K_C (RT)^{\Delta n} \neq K_C
\]

• **Concentrations of solids of solvents are not included in** $K_C$ (or $K_P$)
Consider the following equilibrium at 295 K:

\[
\text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 (g) + \text{H}_2\text{S (g)}
\]

The partial pressure of each gas is 0.265 atm. Calculate \( K_P \) and \( K_C \) for the reaction.

\[
K_P = P_{\text{NH}_3} P_{\text{H}_2\text{S}} = 0.265 \text{ atm} \times 0.265 \text{ atm} = 0.0702 \text{ atm}^2
\]

\[
K_P = K_c(RT)^{\Delta n}
\]

\[
K_C = K_p(RT)^{-\Delta n}
\]

\[
\Delta n = 2 - 0 = 2 \quad T = 295 \text{ K}
\]

\[
K_C = 0.0702 \text{ atm}^2 \times (0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 295 \text{ K})^{-2}
\]

\[
= 1.20 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2}
\]
If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.
Carbonic acid ionizes in water in two steps:

1. \( H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad K_{C1} = 4.3 \times 10^{-7} \text{ M} \)

2. \( HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_{C2} = 5.6 \times 10^{-11} \text{ M} \)

What is the equilibrium constant for the full reaction:

3. \( H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \quad K_{C3} = ??? \)

Reaction 1, 2, and 3 are related as follows:

\{Reaction 1\} + \{Reaction 2\} = \{Reaction 3\}

Therefore:

\[ K_{C3} = K_{C1} \times K_{C2} \]

\[ K_{C3} = (4.3 \times 10^{-7} \text{ M}) \times (5.6 \times 10^{-11} \text{ M}) = 2.4 \times 10^{-17} \text{ M}^2 \]
Sample Problem

You know equilibrium constants for the following reactions:

1. $S(s) + O_2(g) \rightleftharpoons SO_2(g) \quad K_{C1} = 10^{52}$
2. $2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g) \quad K_{C2} = 10^{129} \text{ M}^{-1}$

What is the equilibrium constant for reaction:

3. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad K_{C3} = ???$

Reaction 1, 2, and 3 are related as follows:

$2 \times \{\text{Reaction 1}\} + \{\text{Reaction 3}\} = \{\text{Reaction 2}\}$

Therefore:

$$K_{C1} \times K_{C1} \times K_{C3} = K_2$$

Rearranging:

$$K_{C3} = K_{C2} \times (K_{C1})^{-2} = (10^{129} \text{ M}^{-1})/(10^{52})^2 = 10^{25} \text{ M}^{-1}$$
When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

Equilibrium Constants for the Forward and Reverse Reactions

\[
\begin{align*}
\text{N}_2\text{O}_4 (g) & \rightleftharpoons 2\text{NO}_2 (g) \\
K_C &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3} \text{ M} \\

2\text{NO}_2 (g) & \rightleftharpoons \text{N}_2\text{O}_4 (g) \\
K_C' &= \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{K_C} = 216 \text{ M}^{-1}
\end{align*}
\]
14.4 – Reaction Quotient

\[ a \, A + b \, B \rightleftharpoons c \, C + d \, D \]

\[ K_C = \frac{[C]_\text{eq}^c [D]_\text{eq}^d}{[A]_\text{eq}^a [B]_\text{eq}^b} \]

\[ Q_C = \frac{[C]_{\text{initial}}^c [D]_{\text{initial}}^d}{[A]_{\text{initial}}^a [B]_{\text{initial}}^b} \]

- \( Q_C > K_C \) system proceeds from right to left to reach equilibrium
- \( Q_C = K_C \) the system is at equilibrium
- \( Q_C < K_C \) system proceeds from left to right to reach equilibrium
Sample Problem

At 1400K, $K_C = 4.7$ for reaction (we will omit the units of M$^2$ for simplicity but remember that units are implied)

$$H_2O(g) + CH_4(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Which direction will the reaction proceed in a mixture containing 0.035M H$_2$O, 0.050M CH$_4$, 0.15M CO and 0.20M H$_2$?

This mixture is:

Reaction quotient for this mixture is:

$$Q = \frac{[CO][H_2]^3}{[H_2O][CH_4]} = \frac{0.15 \times 0.20^3}{0.035 \times 0.050} = 0.69$$

The reaction will proceed to the right (towards the products) because $Q < K_C$
14.4 – Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown $x$, which represents the *change in concentration*.

2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for $x$.

3. Having solved for $x$, calculate the equilibrium concentrations of all species.

4. Treats units either implicitly (without writing them down) or explicitly
Sample Problem

Isomerization equilibrium constant for the following reaction is $K_C = 9.0$. Calculate the equilibrium concentrations for the case when only $[A]_0 = 0.010 \text{ M}$ and $[B]_0 = 0$.

Let $x$ be the change in concentration of isomer A in mol/L

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M)</td>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>Change (M)</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>0.010 - x</td>
<td>x</td>
</tr>
</tbody>
</table>

$$K_C = 9.0 = \frac{[B]}{[A]} = \frac{x}{0.010 - x}$$

$$0.090 - 9.0x = x$$

$x = 0.0090$

Therefore, $[B] = 0.0090 \text{ M}$ and $[A] = 0.0010 \text{ M}$ at equilibrium.
Sample Problem

Equilibrium constant for the decomposition of solid NH$_4$Cl is $K_p = 0.0100$ atm$^2$ at a certain high temperature. Calculate the equilibrium vapor pressures of NH$_3$(g) and HCl(g) starting from pure NH$_4$Cl(s).

Let $x$ be the equilibrium NH$_3$ pressure in atm. HCl pressure will have to be the same based on reaction stoichiometry.

\[
\begin{align*}
\text{NH}_4\text{Cl}(s) & \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g) \\
\text{Initial (P)} & = 0.00 \text{ atm} \quad 0.00 \text{ atm} \\
\text{Change (P)} & = +x \quad +x \\
\text{Equilibrium (P)} & = x \quad x \\
\end{align*}
\]

\[K_p = 0.0100 = P_{\text{NH}_3} P_{\text{HCl}} = x^2 \quad \Rightarrow \quad x^2 = 0.0100 \quad x = 0.100\]

Therefore, $P_{\text{NH}_3} = P_{\text{HCl}} = 0.1$ atm at equilibrium.
Sample Problem

At 1280° C the equilibrium constant \( K_c \) for the reaction

\[
\text{Br}_2 (g) \rightleftharpoons 2\text{Br} (g)
\]

is \(1.1 \times 10^{-3} \text{ M} \). If the initial concentrations are \([\text{Br}_2] = 0.063 \text{ M} \) and \([\text{Br}] = 0.012 \text{ M} \), calculate the concentrations of these species at equilibrium.

Let \( x \) be the change in concentration of \( \text{Br}_2 \) in the units of \( M \)

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.063</th>
<th>0.012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>-x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>0.063 - x</td>
<td>0.012 + 2x</td>
</tr>
</tbody>
</table>

\[ K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} \]

\[ K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3} \]

Solve for \( x \)
\[ K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3} \]

\[ 4x^2 + 0.048x + 0.000144 = 0.0000693 - 0.0011x \]

\[ 4x^2 + 0.0491x + 0.0000747 = 0 \]

\[ ax^2 + bx + c = 0 \quad \quad \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ x = -0.0105 \quad x = -0.00178 \]

\[ \text{Br}_2 (g) \rightleftharpoons 2\text{Br} (g) \]

Initial (M) \quad 0.063 \quad 0.012

Change (M) \quad -x \quad +2x

Equilibrium (M) \quad 0.063 - x \quad 0.012 + 2x

At equilibrium, \([\text{Br}] = 0.012 + 2x = -0.009\ M\ or\ 0.00844\ M\]

At equilibrium, \([\text{Br}_2] = 0.062 - x = 0.0648\ M\]
If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

**14.5 – Le Châtelier’s Principle**

- **Changes in Concentration**

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

Equilibrium shifts left to offset stress

Add \( \text{NH}_3 \)
Sample Problem

Equilibrium pressures for the following reaction

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

are: \( P_A = 1.00 \text{ atm} \); \( P_B = 2.00 \text{ atm} \); \( P_C = 2.00 \text{ atm} \). All “A” molecules are suddenly removed from the mixture. What are the pressures after the system re-equilibrates?

The equilibrium constant \( K_P \) is: \( K_P = \frac{P_B \times P_C}{P_A} = 4.00 \text{ atm} \).

Let \( x \) be the new pressure of A after re-equilibration. Pressures of B and C will have to be reduced by \( x \).

<table>
<thead>
<tr>
<th>( P_A )</th>
<th>( P_B )</th>
<th>( P_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>After “A” removal</td>
<td>0.00</td>
<td>2.00</td>
</tr>
<tr>
<td>After re-equilibration</td>
<td>( x )</td>
<td>2.00-( x )</td>
</tr>
</tbody>
</table>

\[
K_P = 4 = \frac{(2-x)^2}{x} \quad \text{or} \quad x^2 - 8x + 4 = 0 \quad x_1 = 7.46 \quad x_2 = 0.536
\]

Only the second solution makes physical sense leading to:

\( P_A = 0.536 \text{ atm} \); \( P_B = 1.46 \text{ atm} \); \( P_C = 1.46 \text{ atm} \)
Concentration Effects

Change Shifts the Equilibrium

- Increase concentration of product(s) left
- Decrease concentration of product(s) right
- Decrease concentration of reactant(s) left
- Increase concentration of reactant(s) right
Sample Problem

Will the equilibrium concentration of NO$_2$ increase, decrease or stay constant if we:

$$\text{NO}_2\text{Cl}(g) + \text{NO}(g) \rightleftharpoons \text{NO}_2(g) + \text{NOCl}(g)$$

- Increase [NOCl]?
  - [NO$_2$] decreases
- Increase [NO]?
  - [NO$_2$] increases
- Decrease [NO]?
  - [NO$_2$] decreases
- Increase [NO$_2$Cl]?
  - [NO$_2$] increases
Effects of Volume and Pressure

A \( (g) + B \ (g) \rightleftharpoons C \ (g) \)

<table>
<thead>
<tr>
<th>Change</th>
<th>Shifts the Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase all partial pressures</td>
<td>Side with fewest moles of gas</td>
</tr>
<tr>
<td>Decrease all partial pressures</td>
<td>Side with most moles of gas</td>
</tr>
<tr>
<td>Increase volume of reactor</td>
<td>Side with most moles of gas</td>
</tr>
<tr>
<td>Decrease volume of reactor</td>
<td>Side with fewest moles of gas</td>
</tr>
</tbody>
</table>

Example: decrease the reactor volume by a factor of 2.

Before the compression we have an equilibrium:

\[
\frac{[C]_0}{[A]_0 \times [B]_0} = K_C
\]

The compression doubles the concentrations initially, \( Q < K \), so equilibrium shifts to the products:

\[
[A] = 2[A]_0 \quad [B] = 2[B]_0 \quad [C] = 2[C]_0
\]

\[
Q = \frac{[C]}{[A] \times [B]} = \frac{2[C]_0}{2[A]_0 \times 2[B]_0} = \frac{K_C}{2}
\]
Sample Problem

Will the ratio of concentrations $[CO]/[COCl_2]$ in reaction

$$\text{Cl}_2(g) + \text{CO}(g) \rightleftharpoons \text{COCl}_2(g)$$
increase, decrease or stay constant if we:

1. Add Cl$_2$(g) at constant volume 
   
   $[CO]/[COCl_2]$ decreases

2. Add Ar at constant volume 

   No change

3. Compress the container 
   
   $[CO]/[COCl_2]$ decreases

4. Decompress the container 
   
   $[CO]/[COCl_2]$ increases
Temperature Effects

Treat the heat of reaction as a reactant: \[ A \Leftrightarrow B \pm \text{“heat”} \]

**Exothermic**
\[ A \Leftrightarrow B + \text{“heat”} \]
- Increase temperature \( \Rightarrow \) increase [“heat”]
- Decrease temperature \( \Rightarrow \) decrease [“heat”]
- \( K \) decreases

**Endothermic**
\[ A + \text{“heat”} \Leftrightarrow B \]
- \( K \) increases

\( 2\text{NO}_2 \) (brown) \( \Leftrightarrow \) \( \text{N}_2\text{O}_4 \) (colorless) + heat

room T

colder

hotter
Sample Problem

Use your intuition to predict whether “heat” will be released (“heat” = product) or consumed (“heat” = reactant) in the following reactions. Predict the effect of *temperature increase* on the equilibrium constant:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat?</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$</td>
<td>Consumed</td>
<td>$\uparrow$</td>
</tr>
<tr>
<td>$\text{NO}_2(g) + \text{NO}_3(g) \rightleftharpoons \text{N}_2\text{O}_5(g)$</td>
<td>Released</td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>$\text{Hem-O}_2 \rightleftharpoons \text{Hemoglobin} + \text{O}_2$</td>
<td>Consumed</td>
<td>$\uparrow$</td>
</tr>
</tbody>
</table>

Breaking bonds consumes heat, and making them releases it.
Equilibrium Thermodynamics

The equilibrium constant can be calculated from the standard Gibbs energy change for the reaction (more in Chapter 18):

\[
A + B \rightleftharpoons C + D
\]

\[
\Delta G_{rxn}^0 = \Delta H_{rxn}^0 - T \Delta S_{rxn}^0 = \left(\Delta G_f^0\right)_{\text{products}} - \left(\Delta G_f^0\right)_{\text{reactants}}
\]

\[
K = e^{-\frac{\Delta G_{rxn}^0}{RT}}
\]

Reaction is **thermodynamically**:  

- **Favored**  
  \(\Delta G^\circ < 0\)  
  - Increase T  
    - \(K\) decreases  
  - Decrease T  
    - \(K\) increases

- **Unfavored**  
  \(\Delta G^\circ > 0\)  
  - Increase T  
    - \(K\) increases  
  - Decrease T  
    - \(K\) decreases
Adding a Catalyst

- Does not change $K$
- Does not shift the position of an equilibrium system
- However, the system will reach equilibrium sooner!

Catalyst lowers $E_a$ for both forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.
## Le Châtelier’s Principle Summary

<table>
<thead>
<tr>
<th>Change</th>
<th>Shift Equilibrium</th>
<th>Change Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Pressure</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Volume</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Temperature</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Catalyst</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
The Haber-Bosch Process

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 2\text{NH}_3 (g) \quad \Delta H^0 = -92.6 \text{ kJ/mol} \]