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

\[ \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (s)} \]

---

**Chemical Equilibrium**

*Balance of two or more chemical reactions*

- **Forward reaction:** Decomposition
- **Reverse reaction:** Dimerization

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

- Colorless gas
- Yucky-brown

*Decomposition is exactly balanced by dimerization at equilibrium.*

*Concentrations of NO\(_2\) and N\(_2\)O\(_4\) do not change with time.*

---

**Is Equilibrium Common?**

*Exchange: mass & energy*  
(open)  
(closed)  
(isolated)  

*Energy*  

*Nothing*  

*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 (O₃) in the stratosphere:
- **Stratosphere**: \([\text{O}_3]/[\text{O}_2] \approx \text{5x10}^{-6}\)
- **Surface**: \([\text{O}_3]/[\text{O}_2] \approx 10^{-8}\)

Equilibrium treatment predicts:
- Surface: \([\text{O}_3]/[\text{O}_2] \approx 10^{-38}\)
- 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 the 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:
- \(\text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{SO}_2 + \ldots\)
- Thermodynamics strongly favors the right side of this equilibrium: \(\Delta H_{rxn} \ll 0\)

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**

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

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

**Law of Mass Action**

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

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

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

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

However, the units are often used 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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B ⇒ AB</td>
<td>( K = \frac{[AB]}{[A][B]} ) = ( \frac{2}{2 \times 2} = \frac{1}{2} )</td>
</tr>
<tr>
<td>A + C ⇒ AC</td>
<td>( K = \frac{[AC]}{[A][C]} ) = ( \frac{3}{1 \times 1} = 3 )</td>
</tr>
<tr>
<td>A + D ⇒ AD</td>
<td>( K = \frac{[AD]}{[A][D]} ) = ( \frac{1}{3 \times 3} = \frac{1}{9} )</td>
</tr>
</tbody>
</table>

### Chemical Equilibrium

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

Estimate the equilibrium constant: \( K_c = \frac{7}{13} \).

### 14.2 – Writing Equilibrium Constants

**Homogenous equilibrium** applies to reactions in which all reacting species are in the same phase.

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

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

In most cases

\[
K_c \neq K_p
\]

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

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

\( \Delta n = \) moles of gaseous products – 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 \([\text{CO}] = 0.012 \text{ M} \), \([\text{Cl}_2] = 0.054 \text{ M} \), and \([\text{COCl}_2] = 0.14 \text{ M} \). Calculate the equilibrium constants \( K_c \) and \( K_p \) (\( R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \)).

\[
\text{CO (g) + Cl}_2 (g) \rightleftharpoons \text{COCl}_2 (g)
\]

\[
K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{0.14 \text{ M}}{0.012 \text{ M} \times 0.054 \text{ M}} = 220 \text{ M}^{-1}
\]

\[
\Delta n = -1
\]

\[T = (273 + 74) \text{ K} = 347 \text{ K}
\]

\[
K_p = K_c(RT)^{\Delta n} = 220 \text{ M}^{-1} \times (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 347 \text{ K})^{-1} = 7.7 \text{ atm}^{-1}
\]

### Equilibria Involving Condensed Phases

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

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

\[
K_p' = \frac{[\text{CaO(s)}][\text{CO}_2]}{[\text{CaCO}_3(s)]} = \text{constant} \quad [\text{CaO(s)}] = \text{constant}
\]

\[
K_c = [\text{CO}_2] = K_c' \quad \frac{[\text{CaCO}_3(s)]}{[\text{CaO(s)}]} \quad K_p = P_{\text{CO}_2}
\]

The concentration of solids and pure liquids are not included in the expression for the equilibrium constant.
Equilibrium Vapor Pressure

- Vapor pressure of a pure liquid (solid) at equilibrium: $A(s) \rightleftharpoons A(g)$ and $B(l) \rightleftharpoons B(g)$ does NOT depend on the amount of liquid (solid)!
- vapor pressure increases with temperature $A(s) \Delta A(g)$

$$P_{eq} = K_P$$

<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>1.6x10^{-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 sublimes when its $P_{eq}$ exceeds the ambient vapor pressure of that substance (its partial pressure)

Dry ice (solid CO$_2$) at 20°C: $P_{eq} = K_P = 56.5$ atm

Partial pressure of CO$_2$ in air: $P_{CO2} = 0.00037$ atm

Conclusion: dry ice will sublime in open air at 20°C

Reactions Involving Solvents

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad K_w = \frac{[H^+][OH^-]}{[H_2O]}$

$[H_2O]$ ~ 55.6 M in dilute solutions and can be treated as a constant

$$K_w = K[H_2O] = [H^+] [OH^-]$$

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°C
- $[H^+] = [OH^-]$ neutral
- $[H^+] > [OH^-]$ acidic
- $[H^+] < [OH^-]$ basic

Solubility and Equilibrium

- Equilibrium concentration of a solute dissolved in a solvent: $A(s) \rightleftharpoons A(aq)$ does NOT depend on the amount of excess solute
- Tabulated for many compounds

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solubility (g/100g H$_2$O)</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>

Looking Ahead to Chem 1C: Ionization Constants of Acids

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

$K_a = \frac{[H^+][A^-]}{[HA][H_2O]}$

$K_w = K[H_2O] = [H^+] [OH^-]$ is NOT included in the equilibrium constant for the acid ionization

$K_a$ is called the 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

$$aA + bB \rightleftharpoons cC + dD$$

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

- 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.

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

\[ K_C = K_P (RT) \]

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

\[ K_C = 0.0702 \text{ atm}^2 \times (0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 295 \text{ K})^{-2} = 1.20 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2} \]

**Sample Problem**

Carbonic acid ionizes in water in two steps:

1. \( \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \)

\[ K_{C1} = 4.3 \times 10^{-7} \text{ M} \]

2. \( \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \)

\[ K_{C2} = 5.6 \times 10^{-11} \text{ M} \]

What is the equilibrium constant for the full reaction:

3. \( \text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-} \)

\[ K_{C3} = ??? \]

**Sample Problem**

You know equilibrium constants for the following reactions:

1. \( \text{S(s)} + \text{O}_2 (g) \rightleftharpoons \text{SO}_2 (g) \quad K_{C1} = 10^{52} \)

2. \( 2\text{S(s)} + 3\text{O}_2 (g) \rightleftharpoons 2\text{SO}_3 (g) \quad K_{C2} = 10^{129} \text{ M}^{-1} \)

What is the equilibrium constant for reaction:

3. \( 2\text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{SO}_3 (g) \quad K_{C3} = ??? \)

**Multiple Equilibria**

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.

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

\[ K_{C3} = \frac{[C][D]}{[A][B]} \]

\[ K_{C1} (RT)^{\Delta n} \]

\[ K_{C2} (RT)^{\Delta n} \]

\[ K_{C3} (RT)^{\Delta n} \]

**Equilibrium Constants for the Forward and Reverse Reactions**

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

\[ K_C' = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{K_C} = 216 \text{ M}^{-1} \]

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

**14.4 – Reaction Quotient**

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

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

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

- \( Q_C > K_C \) 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 $H_2O$, 0.050M $CH_4$, 0.15M $CO$ and 0.20M $H_2$?

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. Treat units either implicitly (without writing them down) or explicitly.

Isomerization equilibrium constant for the following reaction is $K_c = 9.0$.

Calculate the equilibrium concentrations for the case when only $[A]_0 = 0.010$ M and $[B]_0 = 0.0$.

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>$-x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>$0.010 - x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

$$K_c = 9.0 = \frac{[B]_0}{[A]_0} = \frac{x}{0.010 - x} \Rightarrow 0.090 - 9.0x = x \Rightarrow x = 0.0090$$

Therefore, $[B] = 0.0090$ M and $[A] = 0.0010$ M at equilibrium.

Equilibrium constant for the decomposition of solid NH₄Cl is $K_p = 0.0100$ atm² at a certain high temperature.

Calculate the equilibrium vapor pressures of NH₃(g) and HCl(g) starting from pure NH₄Cl(s).

Let $x$ be the equilibrium NH₃ pressure in atm. HCl pressure will have to be the same based on reaction stoichiometry.

<table>
<thead>
<tr>
<th>NH₄Cl(s)</th>
<th>NH₃(g)</th>
<th>HCl(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (P)</td>
<td>0.00 atm</td>
<td>0.00 atm</td>
</tr>
<tr>
<td>Change (P)</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium (P)</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

$$K_p = 0.0100 = P_{NH_3}P_{HCl} = x^2 \Rightarrow x^2 = 0.0100 \Rightarrow x = 0.100$$

Therefore, $P_{NH_3} = P_{HCl} = 0.1$ atm at equilibrium.

Sample Problem

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

$$Br_2 (g) \rightleftharpoons 2Br (g)$$

is $1.1 \times 10^{-3}$ M. If the initial concentrations are $[Br_2] = 0.063$ M and $[Br] = 0.012$ M, calculate the concentrations of these species at equilibrium.

Let $x$ be the change in concentration of $Br_2$ in the units of $M$

$$Br_2 (g) \rightleftharpoons 2Br (g)$$

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

$$K_c = \frac{[Br]^2}{[Br_2]} = \frac{0.012 + 2x^2}{0.063 - x} = 1.1 \times 10^{-3} \Rightarrow \text{Solve for } x$$
14.5 – Le Châtelier’s Principle
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.

- **Changes in Concentration**
  
  \[ N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g) \]
  
  Equilibrium shifts left to offset stress
  
  Add \( NH_3 \)

### Sample Problem
Equilibrium pressures for the following reaction

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

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?

Let \( x \) be the new pressure of \( A \) after re-equilibration

The equilibrium constant \( K_p \) is: \( K_p = P_B \cdot P_C / P_A = 4.00 \text{ atm} \).

Let \( x \) be the new pressure of \( A \) after re-equilibration.

Pressures of \( B \) and \( C \) will have to be reduced by \( x \).

\[
\begin{align*}
P_A &= 0.00 \\
P_B &= 2.00 \\
P_C &= 2.00
\end{align*}
\]

\[
K_p = \frac{(2-x)^2}{2.00-x} \quad \text{or} \quad x^2 - 8x + 4 = 0 \\
x_1 = 0.536, \quad x_2 = 3.46
\]

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

<table>
<thead>
<tr>
<th>Change</th>
<th>Shifts the Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase concentration of product(s)</td>
<td>left</td>
</tr>
<tr>
<td>Decrease concentration of product(s)</td>
<td>right</td>
</tr>
<tr>
<td>Increase concentration of reactant(s)</td>
<td>right</td>
</tr>
<tr>
<td>Decrease concentration of reactant(s)</td>
<td>left</td>
</tr>
</tbody>
</table>

### Sample Problem
Will the equilibrium concentration of \( \text{NO}_2 \) increase, decrease or stay constant if we:

- Increase \([\text{NOCl}]\)? \( [\text{NO}_2] \) decreases
- Decrease \([\text{NO}]\)? \( [\text{NO}_2] \) increases
- Increase \([\text{NO}_2\text{Cl}]\)? \( [\text{NO}_2] \) increases

### Effects of Volume and Pressure

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

- **Change**
  
  Increase all partial pressures
  Decrease all partial pressures
  Increase volume of reactor
  Decrease volume of reactor

- **Shifts the Equilibrium**
  
  Side with fewest moles of gas
  Side with most moles of gas

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

Before the compression we have an equilibrium:

\[
\frac{[\text{Cl}_2]}{[\text{CO}][\text{COCl}_2]} = K_c
\]

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

\[
Q = \frac{[\text{Cl}_2]}{[\text{CO}][\text{COCl}_2]} = 2C_1 \cdot \frac{[\text{Cl}_2]}{[\text{CO}][\text{COCl}_2]} = 2K_c
\]

### Sample Problem
Will the ratio of concentrations \([\text{CO}]/[\text{COCl}_2]\) in reaction

\[ \text{Cl}_2(g) + \text{CO}(g) \rightleftharpoons \text{COCl}_2(g) \]

increase, decrease or stay constant if we:

1. Add \( \text{Cl}_2 \) at constant volume
2. Add \( \text{Ar} \) at constant volume
3. Compress the container
4. Decompress the container

\[
\begin{align*}
\text{Cl}_2 & \quad \text{CO} \\
\text{COCl}_2 & \quad \text{Cl}_2
\end{align*}
\]

Sample Problem

1. Add \( \text{Cl}_2 \) at constant volume: \([\text{CO}]/[\text{COCl}_2]\) decreases
2. Add \( \text{Ar} \) at constant volume: No change
3. Compress the container: \([\text{CO}]/[\text{COCl}_2]\) decreases
4. Decompress the container: \([\text{CO}]/[\text{COCl}_2]\) increases
**Temperature Effects**

Treat the heat of reaction as a reactant: $$\text{A} \rightleftharpoons \text{B} + \text{“heat”}$$

- **Exothermic**
  - Increase temperature ➔ Increase [“heat”]
  - Decrease temperature ➔ Decrease [“heat”]
  - $K$ decreases

- **Endothermic**
  - Increase temperature ➔ Decrease [“heat”]
  - Decrease temperature ➔ Increase [“heat”]
  - $K$ increases

2NO₂ (brown) $\rightleftharpoons$ N₂O₄ (colorless) + heat

---

**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:

- **Reaction**
  - H₂O(s) $\rightleftharpoons$ H₂O(l)
  - NO₂(g) + NO₃(g) $\rightleftharpoons$ N₂O₅(g)
  - Hem-O₂ $\rightleftharpoons$ Hemoglobin + O₂

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):

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = (\Delta G^\circ_{\text{products}}) - (\Delta G^\circ_{\text{reactants}})$$

$$K = e^{-\frac{\Delta G^\circ_{\text{rxn}}}{RT}}$$

Reaction is thermodynamically:

- **Favored** if $\Delta G^\circ < 0$
- **Unfavored** if $\Delta G^\circ > 0$

- Increase T $K$ decreases
- Decrease T $K$ increases

---

**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.

---

**The Haber-Bosch Process**

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

---

**Le Châtelier’s Principle Summary**

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<tr>
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**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:

- **Reaction**
  - H₂O(s) $\rightleftharpoons$ H₂O(l)
  - NO₂(g) + NO₃(g) $\rightleftharpoons$ N₂O₅(g)
  - Hem-O₂ $\rightleftharpoons$ Hemoglobin + O₂

Breaking bonds consumes heat, and making them releases it.

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**Equilibrium Thermodynamics**

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

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = (\Delta G^\circ_{\text{products}}) - (\Delta G^\circ_{\text{reactants}})$$

$$K = e^{-\frac{\Delta G^\circ_{\text{rxn}}}{RT}}$$

Reaction is thermodynamically:

- **Favored** if $\Delta G^\circ < 0$
- **Unfavored** if $\Delta G^\circ > 0$

- Increase T $K$ decreases
- Decrease T $K$ increases

---

**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.

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