Chapter 14: Chemical Equilibrium

Characteristics of Chemical Equilibrium

- Species do not stop forming OR being destroyed
- Rate of formation = rate of removal
- Concentrations are constant.

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

**Equilibrium** occurs when [A], [B], [C] and [D] stop changing - a *dynamic* equilibrium:
- Species do not stop forming OR being destroyed
- Rate of formation = rate of removal
- Concentrations are constant.

Equilibrium is Dynamic

For the 2-butene isomerization:
\[ \text{C=CCH}_3 \rightleftharpoons \text{C=CHCH}_3 \]

Equilibrium is Independent of Direction of Approach

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

Equilibrium and Catalysts

**Catalysts** do not affect equilibrium concentrations.

A catalyst
- speeds up a forward reaction...
- ...but also speeds up the reverse reaction.
- decreases the time needed to reach equilibrium.

The Equilibrium Constant

For the 2-butene isomerization:
\[ \text{H}_3\text{C} \text{C=CH}_3 \rightleftharpoons \text{H}_3\text{C} \text{C=CH}_3 \]

At equilibrium:
rate forward = rate in reverse

An elementary reaction, so:
\[ k_{\text{forward}}[\text{cis}] = k_{\text{reverse}}[\text{trans}] \]
At equilibrium the concentrations become constant. The equilibrium constant, $K_c$, is defined as:

$$K_c = \frac{[C][D]}{[A][B]}$$

For a general reaction:

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

$$K_c = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibria involving pure liquids and solids:

- Pure solids are omitted because their concentrations remain constant throughout the reaction.
- Pure liquids are omitted for the same reason.

Equilibria in dilute solutions:

- Water is omitted from $K_c$ in dilute solution reactions.
- For example:

$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$

$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^5 \text{ (at 25°C)}$$

$K_c$ is the equilibrium constant.
The Equilibrium Constant

What is the equilibrium constant for:

\[ \text{SiH}_4(g) + 2 \text{O}_2(g) \rightleftharpoons \text{SiO}_2(s) + 2 \text{H}_2\text{O}(g) \] ?

Omit SiO\(_2\) (a solid)
Include H\(_2\)O (a gas)

Write down \( K_c \) for:

\[ 2 \text{NaOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightleftharpoons \text{Na}_2\text{SO}_4(aq) + 2 \text{H}_2\text{O}(l) \]

Omit H\(_2\)O (aq. solution)
Include H\(_2\)O (a gas)

\[ \text{K}_c = \left( \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2\text{O}]} \right)^{\frac{1}{2}} \]

\[ \text{K}_c \text{ for Related Reactions} \]

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

\[ \text{K}_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \]

Reverse a reaction… … Invert \( K_c \):

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

\[ \text{K}_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} \]

\[ \text{K}_c \text{ for a Reaction that Combines Reactions} \]

If a reaction can be written as a series of steps:

**step 1**

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

\[ \text{K}_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \]

**step 2**

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

\[ \text{K}_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \]

**overall**

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

\[ \text{K}_c = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} \]

The overall \( K_c \) is the product of the steps:

\[ \text{K}_c(\text{step1}) \times \text{K}_c(\text{step2}) = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} \]

**Equilibrium Constants in Terms of Pressure**

In a constant-\( V \) reaction, partial pressures change as concentrations change.

At constant \( T \), \( P \) is proportional to molar conc.:

Ideal gas:

\[ PV = nRT \]

and for gas \( A \):

\[ P_A = \frac{n_A RT}{V} = [A]RT \]

\( P \) is easily measured, so another \( K \) is used…

**Equilibrium Constants in Terms of Pressure**

For a gas-phase reaction:

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

\[ K_p = \frac{P_c^c P_d^d}{P_a^a P_b^b} \]

In general, \( K_p \neq K_c \). Your text shows:

\[ \text{K}_p = \text{K}_c(\text{RT})^{\Delta n_{\text{gas}}} \]

\( \Delta n_{\text{gas}} = (c + d) - (a + b) \)

\( = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants}) \)
Calculate $K_p$ from $K_c$ for the reaction:

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

$K_c = 5.8 \times 10^5$ at 25°C.

$K_p = K_c(RT)^{\Delta n_{gas}}$

$T = 25 + 273 = 298$ K

$\Delta n_{gas} = 2 - (3 + 1) = -2$

$K_p = 5.8 \times 10^5 \left(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}(298 \text{ K})\right)^2$

$= 9.7 \times 10^2$ atm$^{-2}$

mol and L units are assumed to cancel (units omitted from $K_c$).

$K_p = 9.7 \times 10^2$ atm$^{-2}$

If all the equilibrium concentrations are known it’s easy to calculate $K_c$ for a reaction:

For:

$a \ A + b \ B \rightleftharpoons c \ C + d \ D$

$K_c = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Example

Consider: $2 \ A(aq) \rightleftharpoons B(aq)$

At equilibrium $[A] = 2.0 \text{ M}$ & $[B] = 4.0 \text{ M}$. What is $K_c$?

$K_c = [B]/[A]^2 = 4.0/(2.0)^2 = 1.0$

In other cases stoichiometry is used to find some concentrations.

Example

$H_2(g)$ and $I_2(g)$ were added to a heated container. $[H_2]_{\text{initial}} = 0.0100 \text{ mol/L}$ and $[I_2]_{\text{initial}} = 0.00800 \text{ mol/L}$. At equilibrium $[I_2] = 0.00560 \text{ mol/L}$. Determine $K_c$.

$H_2(g) + I_2(g) \rightleftharpoons 2 \text{ HI(g)}$

Concentrations change – use stoichiometry:

$[H_2]_{\text{equil}} = 0.01000 - x$

$[I_2]_{\text{equil}} = 0.00800 - x$

$[\text{HI}]_{\text{equil}} = 2x$

$1H_2 \equiv 2\text{HI}$

$1I_2 \equiv 2\text{HI}$

Let $HI$ made $= 2x$

$[\text{HI}]_{\text{equil}} = 2x$

$[H_2]_{\text{equil}} = 0.01000$ M at equilibrium

$[I_2]_{\text{equil}} = 0.00800 - x$

$x = 0.00240$ M

$[\text{HI}]_{\text{equil}} = 2(0.00240) = 0.00480$ M

$K_c = \frac{[\text{HI}]^2}{[H_2][I_2]} = \frac{(0.00480)^2}{(0.01000)(0.00800)} = 0.541$
Meaning of the Equilibrium Constant

When:

- $K_c >> 1$ Reaction is strongly product favored.
  - Very little reactant remains
  - Often written as a forward reaction only.
  - Assume reaction goes to completion.
- $K_c << 1$ Reaction is strongly reactant favored.
  - Very little product forms
  - Usually written as “no reaction” or NR
- $K_c = 1$ Reactants & products present at equilibrium.
  - Use equilibrium methods discussed here.

Predicting the Direction of a Reaction

The reaction quotient, $Q$, can be used to predict the direction of a reaction:

For the reaction: $aA + bB \rightleftharpoons cC + dD$

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

$Q$ looks identical to $K_c$, BUT… the concentrations are not equilibrium values.

($K_c = Q$ whenever a system is at equilibrium)

Predicting the Direction of a Reaction

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

$K_c = \frac{[\text{Products}]_{\text{equilib}}}{[\text{Reactants}]_{\text{equilib}}}$

$K_c$ is a constant (only changes if $T$ changes). So:
If $Q < K_c$, $Q$ must increase to reach equilibrium.
  - Make more product (and less reactant).
  - Move forward
If $Q > K_c$, $Q$ must decrease to reach equilibrium.
  - Make less product (and more reactant).
  - Move back

Predicting the Direction of a Reaction

$2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$

$K_c = 245$ at 1000 K

Predict the direction of the reaction if $\text{SO}_2$ (0.085 M), $\text{O}_2$ (0.100 M) and $\text{SO}_3$ (0.250 M) are mixed in a reactor at 1000 K.

$Q = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.250)^2}{(0.085)^2(0.100)} = 86.5$

$s < K_c$, $Q$ must increase to reach equilibrium.
  - Need more product (less reactant).
  - Forward direction

Calculating Equilibrium Concentrations

If $K_c$ is known, $[\text{ }]_{\text{equilib}}$ can be calculated.

Problem

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

0.0500 mol of HI is placed in an empty 1.00 L flask at 600 K. What will be $[\text{HI}]$, $[\text{H}_2]$ and $[\text{I}_2]$ at equilibrium?

$K_c = 76$ at 600 K.
Calculating Equilibrium Concentrations

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

<table>
<thead>
<tr>
<th>[ \text{Initial} ]</th>
<th>[ \text{Change} ]</th>
<th>[ \text{Equilib} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.0500 - 2x</td>
<td>0.0500 - 2x</td>
</tr>
</tbody>
</table>

Amount lost

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

\[ K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.0500 - 2x)^2}{x(x)} \]

Since \( K_c = 76 \)

\[ 76x^2 = (0.0500 - 2x)^2 \]

Take the square root of both sides:

\[ 8.718 x = \pm (0.0500 - 2x) \]

\[ x = 4.67 \times 10^{-3} \quad \text{or} \quad x = -7.44 \times 10^{-3} \]

Ignore the negative root (x cannot be negative).

Calculating Equilibrium Concentrations

So:

\[ [\text{H}_2]_{\text{equilib}} = x = 0.00467 \text{ M} \]

\[ [\text{I}_2]_{\text{equilib}} = x = 0.00467 \text{ M} \]

\[ [\text{HI}]_{\text{equilib}} = 0.0500 - 2x = 0.0407 \text{ M} \]

It’s a good idea to check your work:

\[ K_c = \frac{[\text{HI}]_2}{[\text{H}_2][\text{I}_2]} = \frac{(0.0407 \text{ M})^2}{(0.00467 \text{ M})(0.00467 \text{ M})} = 76. \]

Calculating Equilibrium Concentrations

Consider:

\[ \text{A}(g) \rightleftharpoons \text{B}(g) + \text{C}(g) \quad K_c = 2.500 \]

A is added to an empty container. \([A]_{\text{initial}} = 0.1000 \text{ M}\). What are \([A], [B]\) and \([C]\) at equilibrium?

\[ K_c = \frac{[\text{B}][\text{C}]}{[\text{A}]} = \frac{(x)(x)}{(0.1000 - x)} \]

\[ 2.500 = \frac{x^2}{(0.1000 - x)} \]

\[ x^2 + 2.500x - 0.2500 = 0 \]

A quadratic equation

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

Here:

\[ a = 1, b = 2.500, c = -0.2500 \]

\[ x = \frac{-2.500 \pm \sqrt{(2.500)^2 - 4(1)(-0.250)}}{2(1)} \]

\[ x = +0.0963 \text{ M} \quad \text{or} \quad -2.596 \text{ M} \]
Calculating Equilibrium Concentrations

Ignore the negative root (negative concentration!)
Then \( x = 0.0963 \) M, and:

\[
\begin{align*}
[A] &= 0.1000 - x = 0.0037 \text{ M} \\
[B] &= x = 0.0963 \text{ M} \\
[C] &= x = 0.0963 \text{ M}
\end{align*}
\]

Most of the A is converted to products.
Check: \((0.0963)(0.0963)/0.0037 = 2.5\).

Le Chatelier's Principle

“If a system is at equilibrium and the conditions are changed so that it is no longer at equilibrium, the system will react to reach a new equilibrium in a way that partially counteracts the change”

- A system at equilibrium resists change.
- If “pushed”, it “pushes back”

Changing Concentrations

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

Add A (or B) and the system adjusts to remove it.
- more product is created.
- the reaction shifts forward.

Remove A (or B) the system adjusts to add more.
- more reactant is created.
- the reaction shifts backward.

Changing V or P in Gaseous Equilibria

\( K \) does not change if \( P \) or \( V \) change.
Equilibrium position may change.

Consider: \( N_2O_4(g) \rightleftharpoons 2 \text{NO}_2(g) \)

If \( V \) doubles, all concentrations divide by 2
- 5 moles of \( \text{NO}_2 \) in 1 L, goes to 5 moles in 2 L.
- \([\text{NO}_2]\) = 5 M becomes \([\text{NO}_2]\) = 2.5 M.

\[
K_c \rightarrow Q = \frac{[\text{NO}_2]^2}{[N_2O_4]^2}
\]

At equilibrium:

\[
Q = \frac{[\text{NO}_2]^2}{[N_2O_4]^2} = \frac{\frac{1}{4} [\text{NO}_2]^2}{\frac{1}{4} [N_2O_4]^2} = \frac{1}{4} \frac{[\text{NO}_2]^2}{[N_2O_4]^2} = \frac{1}{4} K_c
\]

After \( V \) change, \( Q < K_c \), equilibrium shifts to products.

Changing V or P in Gaseous Equilibria

Consistent with Le Chatelier

\( N_2O_4(g) \rightleftharpoons 2 \text{NO}_2(g) \)

\( V \) doubled = lower concentration. Minimize change by:
- Making more molecules (increase concentration).
- Shifting toward products - convert 1 molecule into 2.

\( P \) doubled. Minimize the change by:
- Removing molecules (decrease \( P \)).
- Shift toward reactants - convert 2 molecules into 1.
Changing $V$ or $P$ in Gaseous Equilibria

$P$ and $V$ changes have no effect if $\Delta n_{\text{gas}} = 0$:

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)$$

If $V$ is doubled, the system cannot adjust – 2 gas molecules each side.

 Changing $V$ or $P$ in Gaseous Equilibria

Adding an inert gas to change $P$ has no effect.

- Total $P$ increases
- $V$ does not change, nor do $n_{\text{reactants}}$ or $n_{\text{products}}$
- $\ldots$ [reactant] and [product] do not change.

$$P_A = \frac{n_A}{V} RT = [A]RT$$

Changing Temperature

A change in $T$ changes $K_c$.

- $K_c$ may increase or decrease if $T$ is increased.

$$N_2(g) + O_2(g) \rightleftharpoons 2 \text{NO}(g) \quad \Delta H^\circ = 180.5 \text{ kJ}$$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$4.5 \times 10^{-31}$</td>
</tr>
<tr>
<td>900</td>
<td>$6.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>2300</td>
<td>$8.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$K_c$ increases as $T$ increases. Explaned by LeChatelier…

Changing Temperature

**Exothermic** reactions:
- $K_c$ decreases as $T$ increases.
- Are less product favored at higher $T$.

**Endothermic** reactions:
- $K_c$ increases as $T$ increases.
- Are more product favored at higher $T$.

The Haber-Bosch Process

Production of NH$_3$ for fertilizer from atmospheric N$_2$

$$N_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$$

Process developed by Fritz Haber (chemist) and Carl Bosch (engineer). Perfected in 1914.

Germany could not import guano from S. America and needed to make explosives…
The Haber-Bosch Process

\[ \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) \quad \Delta H^\circ = -92.2 \text{ kJ} \]

It is:
- Exothermic – product favored at low-\(T\), but…
- … very slow at room-\(T\), and must be heated.
- Carried out at high-\(P\) (200 atm), to favor product.
- Uses a catalyst to speed the reaction.

Run at 450°C; \(\text{NH}_3\) is continually liquefied and removed.