Chapter 15
Chemical Equilibrium

Learning goals and key skills:
- Understand what is meant by chemical equilibrium and how it relates to reaction rates
- Write the equilibrium-constant expression for any reaction
- Relate \( K_c \) and \( K_p \)
- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture.
- Manipulate the equilibrium constant to reflect changes in the chemical equation
- Write the equilibrium-constant expression for a heterogeneous reaction
- Calculate an equilibrium constant from concentration measurements
- Predict the direction of a reaction given the equilibrium constant and concentrations of reactants and products
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration
- Calculate equilibrium concentrations given the equilibrium constant and the starting concentrations
- Understand how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

The Concept of Equilibrium

Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

The Concept of Equilibrium

- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.
- Once equilibrium is achieved, the amount of each reactant and product remains constant.
Chemical equilibrium occurs when opposing reactions are proceeding at equal rates.

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

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow.

Forward reaction: \[ \mathrm{N}_2\mathrm{O}_4 (g) \rightarrow 2 \mathrm{NO}_2 (g) \]
Reverse reaction: \[ 2 \mathrm{NO}_2 (g) \rightarrow \mathrm{N}_2\mathrm{O}_4 (g) \]

Rate Law:
Rate = \( k_f [\mathrm{N}_2\mathrm{O}_4] \)
Rate = \( k_r [\mathrm{NO}_2]^2 \)

Equilibrium Constant

- Therefore, at equilibrium
  \[ \frac{k_f}{k_r} [\mathrm{NO}_2]^2 = \frac{k_r}{k_f} [\mathrm{N}_2\mathrm{O}_4] \]
  \[ K_{eq} = \frac{k_f}{k_r} = \frac{[\mathrm{NO}_2]^2}{[\mathrm{N}_2\mathrm{O}_4]} \]

The Equilibrium Constant

- Consider the generalized reaction
  \[ a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \]
  The equilibrium expression for this reaction would be
  \[ K_c = \frac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b} \]
  Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written
  \[ K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \]
Relationship Between $K_c$ and $K_p$

From the Ideal Gas Law we know that:

\[ PV = nRT \quad \text{and} \quad P = (n/V)RT = [A]RT \]

Plugging this into the expression for $K_p$ for each substance, the relationship between $K_c$ and $K_p$ becomes

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

where

$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$

Equilibrium Can Be Reached from Either Direction

The ratio of $[\text{NO}_2]^2$ to $[\text{N}_2\text{O}_4]$ remains constant at this temperature no matter what the initial concentrations of NO$_2$ and N$_2$O$_4$ are.

Equilibrium Can Be Reached from Either Direction

It doesn’t matter whether we start with N$_2$ and H$_2$ or whether we start with NH$_3$: we will have the same proportions of all three substances at equilibrium.
What Does the Value of $K$ Mean?

• If $K >> 1$, the reaction is **product-favored**; product predominates at equilibrium.

• If $K << 1$, the reaction is **reactant-favored**; reactant predominates at equilibrium.

*When $10^{-3} < K < 10^3$, the reaction is considered to contain a significant amount of both reactants and products at equilibrium.*

Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.

\[
\begin{align*}
\text{N}_2\text{O}_4 (g) & \rightleftharpoons 2 \text{ NO}_2 (g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \text{ at } 100 ^\circ \text{C} \\
2 \text{ NO}_2 (g) & \rightleftharpoons \text{N}_2\text{O}_4 (g) \quad K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = 4.72 \text{ at } 100 ^\circ \text{C}
\end{align*}
\]

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

Manipulating $K_c$'s

• Reverse directions. 
  \[K_{c,\text{new}} = \text{inverse of } K_{c,\text{old}}\]

• Multiply a reaction by a number, $n$. 
  \[K_{c,\text{new}} = (K_{c,\text{old}})^n\]

• Add chemical equations, multiply the $K$'s.
The Concentrations of Solids and Liquids Are Essentially Constant

Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

\[ \text{PbCl}_2 (s) \rightleftharpoons \text{Pb}^{2+} (aq) + 2 \text{Cl}^- (aq) \]

\[ K_c = [\text{Pb}^{2+}] [\text{Cl}^-]^2 \]

As long as some \( \text{CaCO}_3 \) or \( \text{CaO} \) remain in the system, the amount of \( \text{CO}_2 \) above the solid will remain the same.

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

Equilibrium constant, \( K_c \) (\( K_{eq} \) or \( K \))

- Always products divided by reactants. (Although sometimes products are equal to 1 and reactants are equal to 1.)
- All concentrations are equilibrium values.
- Each concentration is raised to its stoichiometric coefficient.
- \( K_c \) depends on the rate constants which in turn depend on the reaction (\( E_a \)) and temperature.
- No units on \( K_c \).
- Pure solids and pure liquids are excluded from \( K_c \).
- A catalyst does not change the equilibrium concentrations, so it does not change \( K_c \).
An Equilibrium Problem

A closed system initially containing $1.000 \times 10^{-3} \text{ M} \text{H}_2$ and $2.000 \times 10^{-3} \text{ M} \text{I}_2$ at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is $1.87 \times 10^{-3} \text{ M}$. Calculate $K_c$ at 448 °C for the reaction taking place, which is

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

What Do We Know?

<table>
<thead>
<tr>
<th></th>
<th>[H₂], M</th>
<th>[I₂], M</th>
<th>[HI], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>$1.000 \times 10^{-3}$</td>
<td>$2.000 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td>$1.87 \times 10^{-3}$</td>
</tr>
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[HI] Increases by $1.87 \times 10^{-3} \text{ M}$

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<td></td>
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Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

<table>
<thead>
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<tr>
<td>Change</td>
<td>$-9.35 \times 10^{-4}$</td>
<td>$-9.35 \times 10^{-4}$</td>
<td>$+1.87 \times 10^{-3}$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
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We can now calculate the equilibrium concentrations of all three compounds...

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</tr>
<tr>
<td>Equilibrium</td>
<td>$6.5 \times 10^{-5}$</td>
<td>$1.065 \times 10^{-3}$</td>
<td>$1.87 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

...and, therefore, the equilibrium constant.

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

\[
= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}
\]

\[
= 51
\]
Example

Phosphorus pentachloride gas partially decomposes to phosphorus trichloride gas and chlorine gas. 1.20 mol PCl₅ is placed in a 1.00 L container at 200 °C. At equilibrium 1.00 mol PCl₅ remains. Calculate K_c and K_p at 200 °C.

The Reaction Quotient (Q)

- Q gives the same ratio the equilibrium expression gives, but for a system that is not at equilibrium.
- To calculate Q, substitute the (initial) concentrations of reactants and products into the equilibrium expression.

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

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

Comparing K and Q

If Q < K
- There’s too much reactant
- Need to increase the amount of products and decrease the amount of reactants

If Q > K
- There’s too much product
- Need to decrease the amount of products and increase the amount of reactants
Example

In the steam-reforming reaction, methane reacts with water vapor to form carbon monoxide and hydrogen gas. At 900 K, $K_c = 2.4 \times 10^{-4}$.

If 0.012 mol of methane, 0.0080 mol of water vapor, 0.016 mol of carbon monoxide and 0.0060 mol of hydrogen gas are placed in a 2.0-L steel reactor and heated to 900 K, which way will the reaction proceed: to the right (products) or left (reactants)?

Example

Problem: Finding equilibrium concentrations from initial concentrations and the equilibrium constant.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_c = 0.10$ at 2000 °C

A reaction mixture at 2000 °C initially contains $[N_2] = 0.200$ M and $[O_2] = 0.200$ M.

Find the equilibrium concentrations of the reactants and products at this temperature.

• Represent the change in concentration of one of the reactants (or products) with the variable $x$.

• Define the changes in concentration of the other reactants and/or products in terms of $x$.

• Tip: Usually convenient to let $x$ represent the change in concentration of the reactant (or product) with the smallest stoichiometric coefficient.

Example

Problem: Finding equilibrium concentrations from initial concentrations and the equilibrium constant.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 0.36$ at 2000 °C

A reaction mixture at 2000 °C initially contains $[NO_2] = 0.100$ M. Find the equilibrium concentrations of the reactants and products at this temperature.
If a system at equilibrium is disturbed by a change in temperature, pressure or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

Changing concentration
Temperature
Changing volume/pressure

Example: Le Châtelier’s Principle

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

\[ K_p = 0.0214 \text{ at } 540 \text{ K} \]

Example: at equilibrium

\[ P_{\text{H}_2} = 2.319 \text{ atm} \]
\[ P_{\text{NH}_3} = 0.454 \text{ atm} \]
\[ P_{\text{N}_2} = 0.773 \text{ atm} \]

What happens upon addition of 1 atm of \text{H}_2?
The Haber Process

If $\text{H}_2$ is added to the system, $\text{N}_2$ will be consumed and the two reagents will form more $\text{NH}_3$.

The Haber Process

This apparatus helps push the equilibrium to the right by removing the ammonia ($\text{NH}_3$) from the system as a liquid.
Le Châtelier’s Principle: pressure

\[ CO(g) + 3H_2(g) = CH_4(g) + H_2O(g) \]

Boyle’s law: at a fixed temperature, \( PV = k \)

\[ K = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \]

Double the pressure (concentration)

\[ Q = \frac{2[CH_4][2H_2O]}{(3[CO])(2[H_2])^3} = \frac{K_p}{4} \quad Q < K_p, \text{ reaction forms products} \]

In summary, if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.
Le Châtelier’s Principle: temperature

endothermic  $\Delta H > 0$
heat can be thought of as a reactant
increasing $T$ results in an increase in $K$

exothermic  $\Delta H < 0$
heat can be thought of as a product
increasing $T$ results in a decrease in $K$

The Effect of Changes in Temperature
$\text{Co(H}_2\text{O)}_{6}^{2+}(\text{aq}) + 4 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6 \text{H}_2\text{O (l)}$

Example: Le Châtelier’s Principle
$\text{N}_2\text{O}_4 (g) \leftrightharpoons 2 \text{NO}_2 (g)$ is endothermic.
What occurs with increasing temperature?
Catalysts

Catalysts increase the rate of both the forward and reverse reactions.

When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.