Chapter 15
Chemical Equilibrium
The Concept of Equilibrium

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

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.
A System at Equilibrium

Once equilibrium is achieved, the amount of each reactant and product remains constant.
In a system at equilibrium, both the forward and reverse reactions are being carried out; as a result, we write its equation with a double arrow

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

- Remember both forward and reverse reactions are *elementary reactions*
The Equilibrium Constant

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

- Rate law:
  \[ \text{Rate} = k_f [\text{N}_2\text{O}_4] \]
The Equilibrium Constant

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

- Rate law:
  \[ \text{Rate} = k_r [\text{NO}_2]^2 \]
The Equilibrium Constant

- Therefore, at equilibrium

\[ \text{Rate}_f = \text{Rate}_r \]

\[ k_f [\text{N}_2\text{O}_4] = k_r [\text{NO}_2]^2 \]

- Rewriting this, it becomes

\[ \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]
The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$
We learn following things from these reactions about equilibrium:

1. When a mixture of reactants and products is formed in which the concentration no longer change with time, it indicates that an equilibrium is reached.

2. For an equilibrium to occur neither reactant or product can escape.

3. At equilibrium the ratio of concentrations remains constant.
The **Equilibrium Constant**

- To generalize this expression, consider the elementary reaction
  \[ aA + bB \rightleftharpoons cC + dD \]
- The **law of mass action** states that if the system is at equilibrium at a given temperature, then the following ratio is a constant
  \[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

The **equilibrium constant** for this reaction would be $K_c$ i.e. the constant when molarity of the solution is considered. This relationship is called equilibrium-constant expression.
• The Law of Mass Action expresses the relationship between the concentrations of the reactants and products present at equilibrium.

\[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
The equilibrium constant expression depends only on the stoichiometry of the reaction, not on its mechanism.

• And remember that the reactants go into the denominator.

• $K_c$ is independent of the initial concentration of the reactants and products, but on the concentrations at the equilibrium.
• The equilibrium constant is written without a unit.
What Are the Equilibrium Expressions for These Equilibria?

\[ \text{SnO}_2(s) + 2\text{CO}(g) \rightleftharpoons \text{Sn}(s) + 2\text{CO}_2(g) \]

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

\[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}(aq) \]
**K\textsubscript{c}** is independent of the initial concentration of the reactants:

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

As you can see, 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 \(\text{NO}_2\) and \(\text{N}_2\text{O}_4\) are.

Calculate the \(K\text{c}\) for yourself.
The Equilibrium Constant

Because pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

\[ K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \]
• The numerical value of $K_c$ is different than the numerical value of $K_p$. We must indicate the subscript $c$ or $p$. 
Relationship between $K_c$ and $K_p$

- From the ideal gas law we know that

\[ PV = nRT \]

- Rearranging it, we get

\[ P = \frac{n}{V} \cdot RT \]
\[ \frac{n}{V} \] is nothing but molarity (moles/liter).

So for substance A we can write

\[ P = \frac{n_A}{V} \cdot RT \]

\[ P = [A] \cdot RT \]

or \[ [A] = \frac{P}{RT} \]
Equilibrium

Relationship between $K_c$ and $K_p$

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

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

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

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$\Delta n = c + d - (a + b)$$
Relationship between $K_c$ and $K_p$

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

$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$
\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \]

\[ \Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \]
\[ = 2 - 1 \]
\[ = 1 \]
\[ K_p = K_c (RT)^{\Delta n} \]

So \[ K_p = K_c (RT) \]

If \( \Delta n = 0 \) i.e. same number of moles of gas appear in the reactant and the product then
\[ K_p = K_c \]
As anything raised to 0 is 1
In the synthesis of ammonia from nitrogen and hydrogen,

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

\( K_c = 9.60 \text{ at } 300^\circ C \). Calculate \( K_p \)

\( \Delta n = 2-4=-2 \)

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

\[ = 9.60 \left( 0.0821 \times 573 \right)^{-2} \]

\[ = \frac{9.60}{\left( 0.0821 \times 573 \right)^2} = 4.34 \times 10^{-3} \]
For the equilibrium
\[ 2\text{SO}_3 (g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g) \]
\( K_c = 4.08 \times 10^{-3} \) at 1000K. Calculate \( K_p \)

\[
K_p = K_c \ (RT)^{\Delta n}
\]
\( \Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \)
\[ = 3 - 2 = 1 \]

\[
K_p = 4.08 \times 10^{-3} \times (0.0821 \times 1000)
\]
\[ = 0.33496 = 0.3 \]
Equilibrium Can Be Reached from Either Direction

It does not 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 $K \gg 1$, the reaction is *product-favored*; product predominates 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.
SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The reaction of \( \text{N}_2 \) with \( \text{O}_2 \) to form NO might be considered a means of “fixing” nitrogen:

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

The value for the equilibrium constant for this reaction at 25°C is \( K_c = 1 \times 10^{-30} \). Describe the feasibility of fixing nitrogen by forming NO at 25°C.
SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The reaction of N\textsubscript{2} with O\textsubscript{2} to form NO might be considered a means of “fixing” nitrogen:

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

The value for the equilibrium constant for this reaction at 25°C is \( K_c = 1 \times 10^{-30} \). Describe the feasibility of fixing nitrogen by forming NO at 25°C.

Because \( K_c \) is so small, very little NO will form at 25°C. The equilibrium lies to the left, favoring the reactants. Consequently, this reaction is an extremely poor choice for nitrogen fixation, at least at 25°C.
PRACTICE EXERCISE
For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?
PRACTICE EXERCISE

For the reaction \[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g), \quad K_p = 794 \text{ at } 298 \text{ K and } K_p = 54 \text{ at } 700 \text{ K.} \] Is the formation of HI favored more at the higher or lower temperature?

**Answer:** The formation of product, HI, is favored at the lower temperature because \( K_p \) is larger at the lower temperature.
Manipulating Equilibrium Constants

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

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

\[ 2 \text{NO}_2 (g) \rightleftharpoons \text{N}_2\text{O}_4 (g) \quad K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \text{ at } 100^\circ\text{C} \]
• With this information the direction of the reaction needs to be specified when the equilibrium constant is given.
• Also the temperature too needs to be given as the constant depends at the temperature.
SAMPLE EXERCISE 15.4 Evaluating an Equilibrium Constant When an Equation Is Reversed

(a) Write the equilibrium-constant expression for $K_c$ for the following reaction: $2 \text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$

(b) Using information in exercise 15.3, determine the value of this equilibrium constant at 25°C.
SAMPLE EXERCISE 15.4 Evaluating an Equilibrium Constant When an Equation Is Reversed

(a) Write the equilibrium-constant expression for \( K_c \) for the following reaction: \( 2 \text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \)

(b) With the information given in sample exercise 15.3, determine the value of this equilibrium constant at 25°C.

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The reaction of \( \text{N}_2 \) with \( \text{O}_2 \) to form \( \text{NO} \) might be considered a means of “fixing” nitrogen:

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

The value for the equilibrium constant for this reaction at 25°C is \( K_c = 1 \times 10^{-30} \). Describe the feasibility of fixing nitrogen by forming NO at 25°C.

a. Writing products over reactants, we have

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

b.

\[
K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}
\]
PRACTICE EXERCISE
For the formation of NH$_3$ from N$_2$ and H$_2$, N$_2$(g) + 3 H$_2$(g) $\rightleftharpoons$ 2 NH$_3$(g), $K_p = 4.34 \times 10^{-3}$ at 300°C. What is the value of $K_p$ for the reverse reaction?

• Answer: $2.30 \times 10^2$
Manipulating Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

\[ \text{N}_2\text{O}_4 (g) \longrightarrow 2 \text{NO}_2 (g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \text{ at } 100^\circ\text{C} \]

\[ 2 \text{N}_2\text{O}_4 (g) \longrightarrow 4 \text{NO}_2 (g) K_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2} = (0.212)^2 \text{ at } 100^\circ\text{C} \]
Manipulating Equilibrium Constants

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.
\[
\begin{align*}
2\text{NOBr}(g) & \rightleftharpoons 2\text{NO} + \text{Br}_2 (g) \quad \text{K}_c = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2} = 0.014 \\
\text{Br}_2 (g) + \text{Cl}_2 (g) & \rightleftharpoons 2\text{BrCl} (g) \quad \text{K}_c = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = 7.2
\end{align*}
\]

The net sum of these two reactions is

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

\[
\text{K}_c = \frac{[\text{NO}]^2 [\text{BrCl}]^2}{[\text{NOBr}]^2 [\text{Cl}_2]} = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2} \times \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = 0.014 \times 7.2 = 0.10
\]
• What is the difference between this and what happens to $\Delta H$?
• For $\Delta H$ the values are added, here they are multiplied.
SAMPLE EXERCISE 15.5 Combining Equilibrium Expressions

Given the following information,

\[
\begin{align*}
\text{HF}(aq) & \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq) \\
K_c &= 6.8 \times 10^{-4} \\
\text{H}_2\text{C}_2\text{O}_4(aq) & \rightleftharpoons 2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) \\
K_c &= 3.8 \times 10^{-6}
\end{align*}
\]

determine the value of \( K_c \) for the reaction

\[
2 \text{HF}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightleftharpoons 2 \text{F}^-(aq) + \text{H}_2\text{C}_2\text{O}_4(aq)
\]

Now we have two equations that sum to give the net equation, and we can multiply the individual \( K_c \) values to get the desired equilibrium constant.

\[
\begin{align*}
2 \text{HF}(aq) & \rightleftharpoons 2 \text{H}^+(aq) + 2 \text{F}^-(aq) \\
K_c &= 4.6 \times 10^{-7} \\
2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4(aq) \\
K_c &= 2.5 \times 10^5 \\
2 \text{HF}(aq) + \text{C}_2\text{O}_4^{2-}(aq) & \rightleftharpoons 2 \text{F}^-(aq) + \text{H}_2\text{C}_2\text{O}_4(aq) \\
K_c &= (4.6 \times 10^{-7})(2.5 \times 10^5) = 0.12
\end{align*}
\]
SAMPLE EXERCISE 15.5 continued

PRACTICE EXERCISE

Given that, at 700 K, $K_p = 54.0$ for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, determine the value of $K_p$ for the reaction $2 \text{NH}_3(\text{g}) + 3 \text{I}_2(\text{g}) \rightleftharpoons 6 \text{HI}(\text{g}) + \text{N}_2(\text{g})$ at 700 K.

Answer: $\frac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9$
Heterogeneous Equilibrium
• The example of N\textsubscript{2} and H\textsubscript{2} to give NH\textsubscript{3} is a homogeneous equilibria.

• There can also be heterogeneous equilibria when the substances in the equilibrium are in different phases. An example is the equilibrium that gets established when a substance is dissolved in water to give a saturated solution.

Example:

\[ \text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^- \]
When a solid or liquids is encountered in a reaction its concentration is not mentioned as the concentrations of solids and liquids are essentially constant.

Can you understand why?

The concentration of a solid and liquids can be derived in terms of moles per unit volume but it is not required in equilibrium constant expressions.

Remember we are referring to liquids not dissolved substances.
The Concentrations of Solids and Liquids Are Essentially Constant

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

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

\[ K_c = [\text{Pb}^{2+}] [\text{Cl}^-]^2 \]
\[
\text{CaCO}_3 (s) \rightleftharpoons \text{CO}_2 (g) + \text{CaO} (s)
\]

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.

The equilibrium expression for the reaction is

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

and

\[
K_c = [\text{CO}_2]
\]
• When a solvent is involved in an equilibrium as a reactant or a product its concentration is also excluded from the equilibrium constant expression.

• But the concentration of the reactant and product has to be very low.

\[ \text{H}_2\text{O(l)} + \text{CO}_3^{2-} \rightleftharpoons \text{OH}^- (\text{aq}) + \text{HCO}_3^- (\text{aq}) \]

• The equilibrium expression will be:

\[ K_c = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} \]
• When added to Fe₃O₄(s) in a closed container, which one of the following substances—H₂(g), H₂O(g), O₂(g)—will allow equilibrium to be established in the reaction

\[3\text{Fe}(s) + 4\text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\]
SAMPLE EXERCISE 15.6 Writing Equilibrium-Constant Expressions

(a) \( \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(l) \)
(b) \( \text{SnO}_2(s) + 2 \text{CO}(g) \rightleftharpoons \text{Sn}(s) + 2 \text{CO}_2(g) \)

- Write the equilibrium-constant expression for \( K_c \) for each of the above
PRACTICE EXERCISE

Write the following equilibrium-constant expressions:

(a) $K_c$ for $\text{Cr}(s) + 3 \text{Ag}^+(aq) \rightleftharpoons \text{Cr}^{3+}(aq) + 3 \text{Ag}(s)$
(b) $K_p$ for $3 \text{Fe}(s) + 4 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4 \text{H}_2(g)$

Remember only solids and liquids are not considered. The gases are taken into account.

Answers: (a) $K_c = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3}$, (b) $K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$
Equilibrium Calculations
SAMPLE EXERCISE 15.8 Calculating $K$ When All Equilibrium Concentrations Are Known

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472°C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm $\text{H}_2$, 2.46 atm $\text{N}_2$, and 0.166 atm $\text{NH}_3$. From these data, calculate the equilibrium constant $K_p$ for the reaction

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

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$
When the equilibrium concentrations are not known:

- We do not need to know the equilibrium concentration of all the species.
- We can use the stoichiometry of the reaction to deduce the equilibrium concentrations of the unknown ones.
1. Tabulate all the known initial and equilibriums of all the species.

2. Calculate the change of concentrations for the species for which the initial and equilibrium concentrations are known.

3. Use the stoichiometry of the reaction to calculate the changes in concentration for all other species.

4. Calculate the $K_c$. 

Equilibrium
Equilibrium Calculations

Here is an example

A closed system initially containing
1.000 x 10^{-3} \text{ M H}_2 \text{ and } 2.000 x 10^{-3} \text{ M I}_2
At 448°C is allowed to reach equilibrium.

Analysis of the equilibrium mixture shows that the
concentration of HI is 1.87 x 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 x 10⁻³</td>
<td>2.000 x 10⁻³</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td></td>
<td>1.87 x 10⁻³</td>
</tr>
</tbody>
</table>

\[ \text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g) \]
[HI] Increases by $1.87 \times 10^{-3}$ M

<table>
<thead>
<tr>
<th></th>
<th>[H$_2$], M</th>
<th>[I$_2$], M</th>
<th>[HI], M</th>
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<tr>
<td>Initially</td>
<td>$1.000 \times 10^{-3}$</td>
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<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td>$+1.87 \times 10^{-3}$</td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td></td>
<td>$1.87 \times 10^{-3}$</td>
</tr>
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</table>

$$
\text{H}_2\,(g) + \text{I}_2\,(g) \rightleftharpoons 2\text{HI}\,(g)
$$
Stoichiometry tells us $[\text{H}_2]$ and $[\text{I}_2]$ decrease by half as much.

<table>
<thead>
<tr>
<th></th>
<th>$[\text{H}_2], \text{M}$</th>
<th>$[\text{I}_2], \text{M}$</th>
<th>$[\text{HI}], \text{M}$</th>
</tr>
</thead>
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<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>$-9.35 \times 10^{-4}$</td>
<td>$-9.35 \times 10^{-4}$</td>
<td>$+1.87 \times 10^{-3}$</td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td></td>
<td>$1.87 \times 10^{-3}$</td>
</tr>
</tbody>
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$$\text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g)$$
We can now calculate the equilibrium concentrations of all three compounds...

<table>
<thead>
<tr>
<th></th>
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<th>[I₂], M</th>
<th>[HI], M</th>
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<td>0</td>
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<tr>
<td>Change</td>
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<td>+1.87 x 10⁻³</td>
</tr>
<tr>
<td>At equilibrium</td>
<td>6.5 x 10⁻⁵</td>
<td>1.065 x 10⁻³</td>
<td>1.87 x 10⁻³</td>
</tr>
</tbody>
</table>

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

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

\[ = 51 \]
Applications for Equilibrium Constants

a. Predict the direction of the reaction
b. To calculate equilibrium concentrations.
Suppose we take a mixture of 2.00 mol of H₂, 1.00 mol of N₂ and 2.00 mole of NH₃ in a 1 L container at 472°C. 

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

The concentration ratio at start of the reaction

\[
\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2.00M)^2}{(1.00M)(2.00M)^3} = 0.500
\]

This ratio is called the reaction quotient Q

when \( K_c \) is 0.105

To reach the equilibrium Q, 0.500 will have to decrease to 0.105.

This can happen only if the concentration of NH₃ decreases and the concentration of H₂ and N₂ increases.

So the reaction is going to proceed from right to left.
The Reaction Quotient (Q)

- To calculate $Q$, one substitutes the initial concentrations on reactants and products into the equilibrium expression.
- $Q$ gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
If $Q = K$, the system is at equilibrium.
If $Q > K$, there is too much product and the equilibrium shifts to the left.
If $Q < K$, there is too much reactant, and the equilibrium shifts to the right.
SAMPLE EXERCISE 15.10 Predicting the Direction of Approach to Equilibrium

At 448°C the equilibrium constant $K_c$ for the reaction

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

is 50.5. Predict in which direction 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 H$_2$, and $3.0 \times 10^{-2}$ mol of I$_2$ in a 2.00-L container.

First calculate the concentration or Molarity as the moles are given and the volume is given. Then calculate the reaction quotient.
PRACTICE EXERCISE
At 1000 K the value of $K_p$ for the reaction $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$ is 0.338. Calculate the value for $Q_p$, and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are $P_{\text{SO}_3} = 0.16 \text{ atm}$; $P_{\text{SO}_2} = 0.41 \text{ atm}$; $P_{\text{O}_2} = 2.5 \text{ atm}$.

Answer: $Q_p = 16; Q_p > K_p$, and so the reaction will proceed from right to left, forming more $\text{SO}_3$. 
Calculating equilibrium concentrations

We earlier learnt to calculate the equilibrium constant when the initial concentrations of the reactants as given.

Now we will learn to calculate the equilibrium concentrations of the various components.
Calculating equilibrium concentrations.

For the Haber process, \( \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \), \( K_p = 1.45 \times 10^{-5} \) at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of \( \text{H}_2 \) is 0.928 atm and that of \( \text{N}_2 \) is 0.432 atm. What is the partial pressure of \( \text{NH}_3 \) in this equilibrium mixture?
Calculating equilibrium concentrations.

For the Haber process, \( N_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \), \( K_p = 1.45 \times 10^{-5} \) at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of \( \text{H}_2 \) is 0.928 atm and that of \( \text{N}_2 \) is 0.432 atm. What is the partial pressure of \( \text{NH}_3 \) in this equilibrium mixture?

Equilibrium pressure (atm) 

\[
\begin{array}{ccc}
\text{N}_2(g) & \text{H}_2(g) & \text{NH}_3(g) \\
0.432 & 0.928 & x \\
\end{array}
\]

\[
K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}
\]

We now rearrange the equation to solve for \( x \):

\[
x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}
\]

\[
x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3} \text{ atm} = P_{\text{NH}_3}
\]

**Comment:** We can always check our answer by using it to recalculate the value of the equilibrium constant:

\[
K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}
\]
SAMPLE EXERCISE 15.12 Calculating Equilibrium Concentrations

A 1.000-L flask is filled with 1.000 mol of H\textsubscript{2} and 2.000 mol of I\textsubscript{2} at 448°C. The value of the equilibrium constant $K_c$ for the reaction

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

at 448°C is 50.5. What are the equilibrium concentrations of H\textsubscript{2}, I\textsubscript{2}, and HI in moles per liter?

$[H_2] = 1.000 \text{ M}$ and $[I_2] = 2.000 \text{ M}$

**SAMPLE EXERCISE 15.12**

<table>
<thead>
<tr>
<th></th>
<th>$H_2(g)$</th>
<th>+</th>
<th>$I_2(g)$</th>
<th>$\rightleftharpoons$</th>
<th>2 HI(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.000 M</td>
<td></td>
<td>2.000 M</td>
<td>0 M</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For each $x$ mol of H\textsubscript{2} that reacts, $x$ mol of I\textsubscript{2} are consumed and 2$x$ mol of HI are produced:

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

<table>
<thead>
<tr>
<th></th>
<th>$H_2(g)$</th>
<th>+</th>
<th>$I_2(g)$</th>
<th>$\rightleftharpoons$</th>
<th>2 HI(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.000 M</td>
<td></td>
<td>2.000 M</td>
<td>0 M</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td></td>
<td>$-x$</td>
<td>+2$x$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{H}_2(g) & \quad + \quad \text{I}_2(g) & \quad \rightleftharpoons & \quad 2 \text{HI}(g) \\
\begin{array}{|c|c|c|}
\hline
\text{Initial} & 1.000\ M & 2.000\ M & 0\ M \\
\hline
\text{Change} & -x & -x & +2x \\
\hline
\text{Equilibrium} & (1.000 - x)\ M & (2.000 - x)\ M & 2x\ M \\
\hline
\end{array}
\end{align*}
\]

\[
K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5
\]

\[
(1.000 - x)(2.000 - x)
\]

\[
= 2.000 - 1.000x - 2.000x + x^2
\]

\[
= 2.000 - 3.000x + x^2
\]

\[
(2.000 - 3.000x + x^2)50.5
\]

\[
= 101 - 151.5x + 50.5x^2
\]

\[
4x^2 = 101 - 151.5x + 50.5x^2
\]

\[
0 = 101 - 151.5x + 50.5x^2 - 4x^2
\]

\[
0 = 101 - 151.5x + 46.5x^2
\]

\[
0 = 46.5x^2 - 151.5x + 101
\]
Equilibrium

\[ \begin{array}{|c|c|c|c|} 
\hline
 & H_2(g) & + & I_2(g) & \iff & 2 \text{ HI(g)} \\
\hline
\text{Initial} & 1.000 \text{ M} & & 2.000 \text{ M} & & 0 \text{ M} \\
\text{Change} & -x & & -x & & +2x \\
\text{Equilibrium} & (1.000 - x) \text{ M} & & (2.000 - x) \text{ M} & & 2x \text{ M} \\
\hline
\end{array} \]

\[ K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5 \]

\[ 4x^2 = 50.5(x^2 - 3.000x + 2.000) \]

\[ 46.5x^2 - 151.5x + 101.0 = 0 \]

Quadratic Equations:

\[ ax^2 + bx + c = 0 \]

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

\[ ax^2 + bx + c = 0 \]

\[ K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5 \]

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

\[ 4x^2 = 50.5(x^2 - 3.000x + 2.000) \]

\[ 46.5x^2 - 151.5x + 101.0 = 0 \]

Solving the quadratic equation (Appendix A.3) leads to two solutions for \( x \):

\[ x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935 \]

\([H_2] = 1.000 - x = 0.065 \text{ M}\]
\([I_2] = 2.000 - x = 1.065 \text{ M}\]
\([HI] = 2x = 1.870 \text{ M}\]

**Check:** We can check our solution by putting these numbers into the equilibrium-constant expression:

\[ K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.870)^2}{(0.065)(1.065)} = 51 \]
Le Châtelier’s Principle
Le Châtelier’s Principle

“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.”
Change in the Reactant or Product Concentration

- If a chemical system is in equilibrium and we add one of the substances, either a reactant or the product, the reaction will shift as to reestablish the equilibrium in a manner that the change is nullified.
The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH$_3$) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.
The Haber Process

If $H_2$ is added to the system, $N_2$ will be consumed and the two reagents will form more $NH_3$. 
The Haber Process

This apparatus helps push the equilibrium to the right by removing the ammonia (NH$_3$) from the system as a liquid.
Effect of Volume and Pressure on Equilibrium

- Reducing the volume of the reaction, hence increasing the pressure causes the equilibrium to move in a direction that reduces the number of moles of gas.

- More product will be formed
What will be effect of increasing the pressure on the following reaction;

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

The equilibrium will have more reactant.
LE CHÂTELIER’S PRINCIPLE
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.

An equilibrium mixture of brown NO$_2$(g) (red) and colorless N$_2$O$_4$(g) (gray) held in a gas-tight syringe.

The volume and hence the pressure are changed by moving the plunger. Compression of the mixture temporarily increases the concentration of NO$_2$.

When the mixture reestablishes equilibrium, the color is as light as that at the beginning because the formation of N$_2$O$_4$(g) is favored by the pressure increase.
• The volume and pressure do not change the value of K as long as the temperature remains constant.
The Effect of Changes in Temperature

\[
\text{Co(H}_2\text{O)}_{6}^{2+}(aq) + 4 \text{ Cl}^{(aq)} \rightarrow \text{CoCl}_4^{2-}(aq) + 6 \text{ H}_2\text{O (l)}
\]

- This is an endothermic reaction and heat is absorbed when the product is formed.
We can treat heat as one of the reactants

In an endothermic reaction
Reactant + heat → Product

In an Exothermic reaction
Reactant → Product + heat

When the temperature of a reaction is increased the reaction moves in the direction that consumes heat.
And vice versa
Equilibrium

**Endothermic reactions**

Reactants + heat $\rightleftharpoons$ Product

Increasing T $K = \frac{[\text{Products}]}{[\text{Reactants}]}$ increases K

Results in more product

**Exothermic reactions**

Reactant $\rightleftharpoons$ Product + heat

Increasing T $K = \frac{[\text{Products}]}{[\text{Reactants}]}$ reduces K

results in less product
**SAMPLE EXERCISE 15.13 Using Le Châtelier’s Principle to Predict Shifts in Equilibrium**

Consider the equilibrium

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad \Delta H^\circ = 58.0 \text{ kJ} \]

In which direction will the equilibrium shift when (a) \( \text{N}_2\text{O}_4 \) is added, (b) \( \text{NO}_2 \) is removed, (c) the total pressure is increased by addition of \( \text{N}_2(g) \), (d) the volume is increased, (e) the temperature is decreased?

(a) The system will adjust to decrease the concentration of the added \( \text{N}_2\text{O}_4 \), so the equilibrium shifts to the right, in the direction of products.

(b) The system will adjust to the removal of \( \text{NO}_2 \) by shifting to the side that produces more \( \text{NO}_2 \); thus, the equilibrium shifts to the right.

(c) Adding \( \text{N}_2 \) will increase the total pressure of the system, but \( \text{N}_2 \) is not involved in the reaction. The partial pressures of \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \) are therefore unchanged, and there is no shift in the position of the equilibrium.

(d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.

(e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more \( \text{N}_2\text{O}_4 \). Note that only this last change also affects the value of the equilibrium constant, \( K \).
Catalysts increase the rate of both the forward and reverse reactions as the activation energy of the forward and reverse reaction is lowered to the same extent.
Equilibrium is achieved faster, but the equilibrium composition remains unaltered.
Homework question:

- Sample integrative exercise page 657