Ch 6 Chemical Equilibrium

Nitrogen dioxide shown immediately after expanding into the vessel (L) & after reaching a state of equilibrium (R)

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

(reddish brown) (colorless)
When NO\textsubscript{2} is placed in an evacuated, sealed glass vessel at 25°C, \textit{the initial dark brown color decreases in intensity as the NO\textsubscript{2} is converted to colorless N\textsubscript{2}O\textsubscript{4}}.
However, the contents of the reaction vessel do not become colorless finally. Instead, the intensity of the brown color eventually become constant, which means that the concentration of NO₂ is no longer changing.
Figure 6.1: reaction of $2\text{NO}_2(g)$ and $\text{N}_2\text{O}_4(g)$ over time in a closed vessel
**Chemical equilibrium**: the state in which the concs of all reactants & products remain constant with time.

*Far to the right*: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \)
(almost completion)

*Far to the left*: \( \text{CaO} \rightarrow \text{Ca} + \frac{1}{2} \text{O}_2 \)
(almost an undetectable reaction)
In this chapter we will discuss how & why a chemical system comes to equilibrium & the characteristics of a system at equilibrium. In particular, we will discuss how to calculate the concs of the reactants & products present for a given system at equilibrium.
6-1 The equilibrium condition

The equilibrium condition is a highly *dynamic situation.*

\[\text{H}_2\text{O}(g) + \text{CO}(g) \iff \text{H}_2(g) + \text{CO}_2(g)\]

Assume that the same number of moles of gaseous CO & H\textsubscript{2}O are placed in a closed vessel & allowed to react.
Figure 6.2: Changes in concentration with time for the reaction
Figure 6.3: H$_2$O and CO are mixed in equal numbers
Why does equilibrium occur?

Collisions - break bonds / form bonds & then rearrange to form the products.

The collision rate of the molecules depends on the concs of molecules & the rate of a reaction depends on the concs of the reactants. Thus, the reactants collide & react to form products.
As the concs of the reactants decrease, this causes the rate of this reaction (the forward reaction) to decrease - that is, the reaction slows down (the rate of the reverse reaction increases). At equilibrium, both rates are equal.
**Forward reaction**: \( \text{H}_2\text{O} (g) + \text{CO} (g) \rightarrow \text{H}_2 (g) + \text{CO}_2 (g) \)

The rate of the forward reaction proceeds, & then the rate starts to decrease.

**Reverse reaction**: \( \text{H}_2 (g) + \text{CO}_2 (g) \rightarrow \text{H}_2\text{O} (g) + \text{CO} (g) \)

Initially the reverse reaction cannot occur, & then the rate of the reverse reaction starts to increase when the products are building up.
Figure 6.4: Changes with time in the rates of forward and reverse reactions
What would happen to the gaseous equilibrium mixture of reactants & products represented in Fig. 6.3, part (c) & (d), if we injected some $\text{H}_2\text{O}_\text{(g)}$ into the box?

*It will speed up (accelerate) the forward reaction first, & then this will also cause the reverse reaction to speed up.* Thus, the system will change until the forward & reverse reaction rate again become equal. $K$?
The **equilibrium position** of a reaction is determined by many factors: **the initial conc., the relative energies of the reactants & products, & the relative “degree of organization” of the reactants & products. Energy & organization** come into play because nature tries to achieve **minimum energy** ($\Delta H$) & **maximum disorder** ($\Delta S$).
The characteristics of chemical equilibrium

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

Discovered in Germany [Fritz Haber (1868-1934)] just before World War I in a search for ways to produce nitrogen-based explosives.
There are two possible reasons why the concs of the reactants & products of a given chemical reaction remains unchanged when mixed:

1. The system is at chemical equilibrium.
2. The forward & reverse reactions are so slow that the system moves toward equilibrium at an undetectable rate.
The second reason applies to the N\textsubscript{2}, H\textsubscript{2}, & NH\textsubscript{3} mixture at 25°C. *Because the molecules involved have strong chemical bonds,* mixtures of N\textsubscript{2}, H\textsubscript{2}, & NH\textsubscript{3} at 25°C can exist with no apparent change over long period of time, *unless the condition can reach 400 °C & 200 atm (15 % yield).*
Bacteria, however, manage to fix $N_2$ (convert it to $NH_3$ & then to $NO_2^-$ & $NO_3^-$) at 0.8 atm & RT in Nodules (根瘤) of the root of legumes (豆科植物). The nitrogenase enzyme that catalyzes this reaction is a complex iron-molybdenum-sulfur protein. The structure of the active sites have been determined by X-ray crystallography (*Science*, 1993, 260, 792).
Figure 6.5: Concentration profile for the reaction

\[ \text{Equilibrium} \]

\[ \begin{align*}
\text{Time} & \quad \text{Concentration} \\
1 & \quad \text{N}_2 \\
2 & \quad \text{NH}_3 \\
3 & \quad \text{H}_2
\end{align*} \]
6.2 The equilibrium constant

Science is fundamentally empirical - it is based on experiment. *Law of mass action* can be used as a general description of the equilibrium condition (proposed by Cato Maximilian Guldberg & Peter Waage in 1864).
For a reaction of the type,

\[ jA + kB \rightleftharpoons lC + mD \]

where A, B, C, & D represent chemical species & j, k, l, & m are the coefficients in the balanced equation, the law of mass action is represented by the following equilibrium expression:

\[ K = \frac{[C]^l[D]^m}{[A]^j[B]^k} \]

\( K \) : equilibrium constant
Thus, the value of *equilibrium constant* for a given reaction system can be calculated from the measured *equilibrium concs of reactants / products* present at equilibrium, *the result is a constant at a given temperature & assuming ideal behavior.*
Example 6.1

The following equilibrium concentrations were observed for the Haber process at 127°C:

\[
\begin{align*}
[NH_3] &= 3.1 \times 10^{-2} \text{ mol/L} \\
[N_2] &= 8.5 \times 10^{-1} \text{ mol/L} \\
[H_2] &= 3.1 \times 10^{-3} \text{ mol/L}
\end{align*}
\]

a. Calculate the value of \( K \) at 127°C for this reaction.

b. Calculate the value of the equilibrium constant at 127°C for the reaction

\[
2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)
\]

c. Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation

\[
\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)
\]
Solution

a. The balanced equation for the Haber process is

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

Thus, using the law of mass action to construct the expression for \( K \), we have

\[
K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2} \text{ mol/L})^2}{(8.5 \times 10^{-1} \text{ mol/L})(3.1 \times 10^{-3} \text{ mol/L})^3} = 3.8 \times 10^4 \text{ L}^2/\text{mol}^2
\]

b. This reaction is written in the reverse order of the equation given in part a. This leads to the equilibrium expression

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

which is the reciprocal of the expression used in part a. So

\[
K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4 \text{ L}^2/\text{mol}^2} = 2.6 \times 10^{-5} \text{ mol}^2/\text{L}^2
\]
c. We use the law of mass action: 
\[ K'' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} \]

If we compare this expression with the one obtained in part a, we see that since 
\[ \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \left( \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2} \]

then 
\[ K'' = K^{1/2} \]

Thus 
\[ K'' = K^{1/2} = (3.8 \times 10^4 \text{ L}^2/\text{mol}^2)^{1/2} = 1.9 \times 10^2 \text{ L/mol} \]
We can draw some important conclusions from the results of Example 6.1. For a reaction of the form

\[ jA + kB \rightleftharpoons lC + mD \]

the equilibrium expression is

\[ K = \frac{[C]^l[D]^m}{[A]^j[B]^k} \]

If this reaction is reversed, the new equilibrium expression is

\[ K' = \frac{[A]^j[B]^k}{[C]^l[D]^m} = \frac{1}{K} \]

If the original reaction is multiplied by some factor \( n \) to give

\[ njA + nkB \rightleftharpoons nlC + nmD \]

the equilibrium expression becomes

\[ K'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = K^n \]
Some characteristics of the equilibrium expression:

1. The *equilibrium expression* for a reaction written in reverse is the reciprocal of that for the original reaction.

2. When the balanced equation for a reaction is multiplied by a factor $n$, the *equilibrium expression* for the new reaction is the original expression raised to the $n$th power. Thus, $K_{\text{new}} = (K_{\text{original}})^n$. 
3. The *apparent units* for K are determined by the powers of the various conc. terms. The (apparent) units for K therefore depend on the reaction being considered.
### TABLE 6.1  Results of Three Experiments for the Reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Concentrations</th>
<th>Equilibrium Concentrations</th>
<th>( K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>([\text{N}_2]_0 = 1.000 \ M)</td>
<td>([\text{N}_2] = 0.921 \ M)</td>
<td>( K = 6.02 \times 10^{-2} \ \text{L}^2/\text{mol}^2 )</td>
</tr>
<tr>
<td></td>
<td>([\text{H}_2]_0 = 1.000 \ M)</td>
<td>([\text{H}_2] = 0.763 \ M)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>([\text{NH}_3]_0 = 0 )</td>
<td>([\text{NH}_3] = 0.157 \ M)</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>([\text{N}_2]_0 = 0 )</td>
<td>([\text{N}_2] = 0.399 \ M)</td>
<td>( K = 6.02 \times 10^{-2} \ \text{L}^2/\text{mol}^2 )</td>
</tr>
<tr>
<td></td>
<td>([\text{H}_2]_0 = 0 )</td>
<td>([\text{H}_2] = 1.197 \ M)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>([\text{NH}_3]_0 = 1.000 \ M)</td>
<td>([\text{NH}_3] = 0.203 \ M)</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>([\text{N}_2]_0 = 2.00 \ M)</td>
<td>([\text{N}_2] = 2.59 \ M)</td>
<td>( K = 6.02 \times 10^{-2} \ \text{L}^2/\text{mol}^2 )</td>
</tr>
<tr>
<td></td>
<td>([\text{H}_2]_0 = 1.00 \ M)</td>
<td>([\text{H}_2] = 2.77 \ M)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>([\text{NH}_3]_0 = 3.00 \ M)</td>
<td>([\text{NH}_3] = 1.82 \ M)</td>
<td></td>
</tr>
</tbody>
</table>
Although the special ratio of products to reactants defined by the equilibrium expression is constant for a given reaction system at a given temperature, the equilibrium concs will not always be the same. Three sets of data in Table 6.1, the equilibrium concs are quite different, the equilibrium constant, which depends on the ratio of the concs, remains the same.
Each set of equilibrium concs is called an equilibrium position. The specific equilibrium position adopted by a system depends on the initial concs (an infinite number of equilibrium positions), but the equilibrium constant does not.
6.3 Equilibrium expressions involving pressures

PV = nRT or P = (n/V)RT = CRT
C represents the molar conc. of the gas.

For the ammonia synthesis reaction, the equilibrium expression can be written in terms of concentrations,

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

or in terms of the equilibrium partial pressures of the gases,

\[ K_p = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \]

In this book, \( K \) denotes an equilibrium constant in terms of concentrations, and \( K_p \) represents an equilibrium constant in terms of partial pressures.
For the ammonia synthesis reaction:

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

\[
= \frac{\left( \frac{P_{\text{NH}_3}}{RT} \right)^2}{\left( \frac{P_{\text{N}_2}}{RT} \right)\left( \frac{P_{\text{H}_2}}{RT} \right)^3} = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \times \left( \frac{1}{RT} \right)^2
\]

\[
= \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} (RT)^2 = K_p (RT)^2
\]
However, for the synthesis of hydrogen fluoride from its elements,

$$\text{H}_2(g) + \text{F}_2(g) \rightleftharpoons 2\text{HF}(g)$$

the relationship between $K$ and $K_p$ is

$$K = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{C_{\text{HF}}^2}{(C_{\text{H}_2})(C_{\text{F}_2})} = \left(\frac{P_{\text{HF}}}{RT}\right)^2 = \frac{P_{\text{HF}}^2}{(P_{\text{H}_2})(P_{\text{F}_2})} = K_p$$
For the general reaction

\[ jA + kB \rightleftharpoons lC + mD \]

the relationship between \( K \) and \( K_p \) is

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

where \( \Delta n \) is the sum of the coefficients of the *gaseous* products minus the sum of the coefficients of the *gaseous* reactants.

\[
K_p = \frac{(P_C)^l(P_D)^m}{(P_A)^j(P_B)^k} = \frac{(C_C \times RT)^l(C_D \times RT)^m}{(C_A \times RT)^j(C_B \times RT)^k}
\]

\[ = \frac{(C_C)^i(C_D)^m}{(C_A)^j(C_B)^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)} = K(RT)^\Delta n \]

where \( \Delta n = (l + m) - (j + k) \), the difference in the sums of the coefficients for the gaseous products and reactants.
For the reaction:

\[ \text{H}_2(g) + \text{F}_2(g) \leftrightarrow 2\text{HF}(g) \]

\[ K = \frac{\text{[HF]}^2}{\text{[H}_2\text{]}\text{[F}_2\text{]}} = \frac{(\text{mol/L})^2}{\text{mol/L}\text{mol/L}} \]

⇒ No units

\[ K_p = \frac{P_{\text{HF}}^2}{P_{\text{H}_2}\text{P}_{\text{F}_2}} = \frac{(\text{atm})^2}{\text{atm}\text{atm}} \]

⇒ No units
6.4 The concept of activity

Activity (i\textsuperscript{th} component) = a\textsubscript{i} = P\textsubscript{i} / P\textsubscript{reference}

P\textsubscript{i} = partial pressure of the i\textsuperscript{th} gaseous component
P\textsubscript{reference} = 1 atm (exactly) & where ideal gas behavior is assumed.
Using the concept of activities, the equilibrium expression for the reaction

\[ jA(g) + kB(g) \rightleftharpoons lC(g) + mD(g) \]

is written as

\[
K = \frac{(a_C)^l(a_D)^m}{(a_A)^j(a_B)^k} = \frac{\left( \frac{P_C}{P_{\text{ref}}} \right)^l \left( \frac{P_D}{P_{\text{ref}}} \right)^m}{\left( \frac{P_A}{P_{\text{ref}}} \right)^j \left( \frac{P_B}{P_{\text{ref}}} \right)^k}
\]

With all the pressures expressed in atmospheres, we have

\[
K_p = \frac{\left( \frac{P_C \text{ (atm)}}{1 \text{ atm}} \right)^l \left( \frac{P_D \text{ (atm)}}{1 \text{ atm}} \right)^m}{\left( \frac{P_A \text{ (atm)}}{1 \text{ atm}} \right)^j \left( \frac{P_B \text{ (atm)}}{1 \text{ atm}} \right)^k} = \frac{P_C^l P_D^m}{P_A^j P_B^k}
\]

(no units)

where \( K_p \) is unitless as shown.
When the equilibrium composition of a system is expressed in units of moles per liter, the reference state is (exactly 1 mol/L = M).

Because of the difference in reference states, in general,

\[ K_{(C)} \text{ (conc. units)} \neq K_p \text{ (pressure units)} \]

If \( \Delta n = 0 \), \( K = K_p \)
6.5 Heterogeneous equilibria

Homogeneous equilibria
Heterogeneous equilibria

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

\[ K' = [\text{CO}_2][\text{CaO}]/[\text{CaCO}_3] \]

Experimental results show that the position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.
\[ a_{\text{CaCO}_3} = \frac{[\text{CaCO}_3]}{[\text{CaCO}_3]} = 1 \]
(pure solid) (pure solid / reference state)

\[ a_{\text{CaO}} = \frac{[\text{CaO}]}{[\text{CaO}]} = 1 \]

\[ K = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]} = \frac{[\text{CO}_2](1)/(1)}{[\text{CO}_2]} = [\text{CO}_2] \]

& \[ K_P = P_{\text{CO}_2}(1)/(1) = P_{\text{CO}_2} \]

In summary : *the activity of a pure solid or liquid is always 1.*
Figure 6.6: Position of the equilibrium
6.6 Applications of the equilibrium constant

Knowing the \textit{equilibrium constant} for a reaction allow us to predict several important features:

1. \textit{the tendency of the reaction to occur},
2. \textit{whether a given set of conc represents an equilibrium condition},
3. \textit{the equilibrium position that will be achieved from a given set of initial conc.}
The extent of reaction

\[ K \gg 1, \] at equilibrium the reaction system will consist of mostly products – the equilibrium lies to the right.

\[ K \ll 1, \] at equilibrium the reaction system will consist of mostly reactants – the equilibrium far to the left.
It is important to understand that the size of $K$ & the time required to reach equilibrium (equilibrium constant: thermodynamic aspect) are not directly related. Actually, the time required to achieve equilibrium depends on the reaction rate, $k$ (rate constant: kinetic aspect).
Reaction quotient (商)

The reaction quotient is obtained by applying the law of mass action, but using **initial concs** ($Q$) instead of **equilibrium concs** ($K$).

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

$$Q = \frac{[NH_3]_o^2}{[N_2]_o[H_2]_o^3}$$

$$K = \frac{[NH_3]_{equil}^2}{[N_2]_{equil}[H_2]_{equil}^3}$$
To determine in which direction a system will shift to reach equilibrium, we compare the values of $Q$ & $K$. There are three possible situations:

1. $Q = K$: the system is at equilibrium.
2. $Q > K$: shift to the left.
3. $Q < K$: shift to the right.
Calculating equilibrium pressures & concs

A typical equilibrium problem involves finding the equilibrium concs (or pressures) of reactants & products, given the value of the equilibrium constant & the initial concs (or pressures).
Ex. 6.3 Assume that the reaction for the formation of gaseous HF from H₂ & F₂ has an equilibrium constant of $1.15 \times 10^2$ at a certain temperature. In a particular experiment at this temperature 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concs of all species.
Solution

The balanced equation for the reaction is

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

We first calculate the initial concentrations:

$$[HF]_0 = [H_2]_0 = [F_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000 \text{ M}$$

From the value of $Q$,

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$
\[
\begin{align*}
\text{H}_2(g) & + \text{F}_2(g) \rightarrow 2\text{HF}(g) \\
x \text{ mol/L} + x \text{ mol/L} & \rightarrow 2x \text{ mol/L}
\end{align*}
\]

Now the equilibrium concentrations can be expressed in terms of \(x\):

<table>
<thead>
<tr>
<th>Initial Concentration (mol/L)</th>
<th>Change (mol/L)</th>
<th>Equilibrium Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{H}_2]_0 = 2.000)</td>
<td>(-x)</td>
<td>([\text{H}_2] = 2.000 - x)</td>
</tr>
<tr>
<td>([\text{F}_2]_0 = 2.000)</td>
<td>(-x)</td>
<td>([\text{F}_2] = 2.000 - x)</td>
</tr>
<tr>
<td>([\text{HF}]_0 = 2.000)</td>
<td>(+2x)</td>
<td>([\text{HF}] = 2.000 + 2x)</td>
</tr>
</tbody>
</table>

These concentrations can be represented in a shorthand table as follows:

\[
\begin{align*}
\text{H}_2(g) & + \text{F}_2(g) \rightleftharpoons 2\text{HF}(g) \\
\text{Initial:} & \hspace{1cm} 2.000 \hspace{1cm} 2.000 \hspace{1cm} 2.000 \\
\text{Change:} & \hspace{1cm} -x \hspace{1cm} -x \hspace{1cm} +2x \\
\text{Equilibrium:} & \hspace{1cm} 2.000 - x \hspace{1cm} 2.000 - x \hspace{1cm} 2.000 + 2x
\end{align*}
\]

To solve for \(x\), we substitute the equilibrium concentrations into the equilibrium expression:

\[
K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}
\]
The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

which yields $x = 1.528$. The equilibrium concentrations can now be calculated:

$$[H_2] = [F_2] = 2.000 \ M - x = 0.472 \ M$$

$$[HF] = 2.000 \ M + 2x = 5.056 \ M$$

**Check:** Checking these values by substituting them into the equilibrium expression gives

$$\frac{[HF]^2}{[H_2][F_2]} = \frac{(5.056)^2}{(0.472)^2} = 1.15 \times 10^2$$

which agrees with the given value of $K$. 

Copyright © 2000 by Houghton Mifflin Company. All rights reserved.
6.7 Solving equilibrium problem

The typical procedure can be summarized as below:

1. Write the *balanced equation* for the reaction.
2. Write the *equilibrium expression* using the law of mass action.
3. Calculate $Q$ & determine the direction of the shift to equilibrium.
4. Define **the change** needed to reach equilibrium, & define the equilibrium concs by applying the change to the initial concs.

5. Substitute the equilibrium concs into the **equilibrium expression**, & solve for the unknown.

6. Check your **calculated equilibrium concs** by making sure that they give the correct K.
6.8 Le Châtelier’s principle

It is important to understand the factors that control the position of a chemical equilibrium. Note that the amount of NH$_3$ at equilibrium increases with an increase in pressure but decreases with an increase in temperature.
Thus, the amount of $NH_3$ present at equilibrium is favored by conditions of low temperature & high pressure.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>300 atm</th>
<th>400 atm</th>
<th>500 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>48% NH₃</td>
<td>55% NH₃</td>
<td>61% NH₃</td>
</tr>
<tr>
<td>500</td>
<td>26% NH₃</td>
<td>32% NH₃</td>
<td>38% NH₃</td>
</tr>
<tr>
<td>600</td>
<td>13% NH₃</td>
<td>17% NH₃</td>
<td>21% NH₃</td>
</tr>
</tbody>
</table>

*Each experiment was begun with a 3:1 mixture of H₂ and N₂.
Le Châtelier’s principle (1884) states that if a change in conditions (a “stress”) is imposed on a system at equilibrium, the equilibrium position will shift in a direction that tends to reduce that change in conditions.
I. The effect of a change in conc

To see how we can predict the effect of a change in conc on a system at equilibrium, we may consider the ammonia synthesis reaction.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
Suppose there is an equilibrium position described by the following concentrations:

\[ [N_2] = 0.399 \text{ M}, \ [H_2] = 1.197 \text{ M}, \ & \ [NH_3] = 0.202 \text{ M} \]

What will happen if 1.000 M of \( N_2 \) is suddenly injected into the system at constant volume?
\[
[N_2]_0 = 0.399 \text{ M} + 1.000 \text{ M} = 1.399 \text{ M} \\
\uparrow \\
\text{Added N}_2
\]

\[
[H_2]_0 = 1.197 \text{ M}
\]

\[
[NH_3]_0 = 0.202 \text{ M}
\]

Note that we label these as "initial concentrations" because the system is no longer at equilibrium. Then

\[
Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}
\]

Since we are not given the value of \( K \), we must calculate it from the first of equilibrium concentrations:

\[
K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}
\]
As we might have expected, because the concentration of N₂ was increased, Q is less than K. The system will shift to the right to arrive at the new equilibrium position. Rather than do the calculations, we simply summarize the results:

<table>
<thead>
<tr>
<th>Equilibrium Position I</th>
<th>Equilibrium Position II</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N₂] = 0.399 M</td>
<td>[N₂] = 1.348 M</td>
</tr>
<tr>
<td>[H₂] = 1.197 M</td>
<td>[H₂] = 1.044 M</td>
</tr>
<tr>
<td>[NH₃] = 0.202 M</td>
<td>[NH₃] = 0.304 M</td>
</tr>
</tbody>
</table>

\[
K = \frac{(0.202+2x)^2}{[(0.399-x)(1.197-3x)^3]}
\]
Figure 6.7: The initial equilibrium mixture of $N_2$, $H_2$, and $H_2$
If a gaseous reactant or product is added to a system at equilibrium, the system will shift away from the added component. If a gaseous reactant or product is removed to a system at equilibrium, the system will shift toward the removed component.
Example 6.4

Arsenic can be extracted from its ores by first reacting the ore with ox (a process called roasting) to form solid \( \text{As}_4\text{O}_6 \), which is then reduced with carbon:

\[
\text{As}_4\text{O}_6(s) + 6\text{C}(s) \rightleftharpoons \text{As}_4(g) + 6\text{CO}(g)
\]

Predict the direction of the shift of the equilibrium position for this reaction in response to each of the following changes in conditions.

a. addition of CO
b. addition or removal of C or \( \text{As}_4\text{O}_6 \)
c. removal of \( \text{As}_4 \)
Solution

a. Le Châtelier’s principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when CO is added.

b. Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of C or As$_4$O$_6$ will have no effect.

c. If gaseous As$_4$ is removed, the equilibrium position will shift to the right to form more products. In industrial processes the desired product is continuously removed from the reaction system to increase the yield.
II. The effect of a change in pressure

Basically, there are three ways to change the pressure of a reaction system involving gaseous components at a given temperature:
1. *Add or remove a gaseous reactant or product at constant volume.*

2. *Add an inert gas (one not involved in the reaction) at constant volume.*

3. *Change the volume of the container.*
When an inert gas is added at constant volume, there is no effect on the equilibrium position. The addition of an inert gas increases the total pressure but has no effect on the concs or partial pressures of the reactants or products (assuming ideal gas behavior). Thus the system remains at the original equilibrium position.
When the volume of the container is changed, the concs / the partial pressures of both reactants or products are changed. *We could calculate Q & predict the direction of the shift.* However, for systems involving gaseous components there is an easier way: *We focus on the volume.*
The central idea is that \textit{when the volume of the container holding a gas system is reduced, the system responds by reducing its own volume.}

\textit{This is done by decreasing the total number of gaseous molecules in the system} (\(N/V\)).
Suppose we have a mixture of gaseous $\text{N}_2$, $\text{H}_2$, & $\text{NH}_3$ at equilibrium. If we suddenly reduce the volume, what will happen to the equilibrium position?
The reaction system can reduce its volume by reducing the number of molecules present. Consequently, the reaction will shift to the right – reducing the total number of gaseous molecules present (→).

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
Figure 6.8: A mixture of \( \text{NH}_3(g) \), \( \text{N}_2(g) \), and \( \text{H}_2(g) \) at equilibrium
Figure 6.9: Brown NO$_2$(g) and colorless N$_2$O$_4$(g) at equilibrium in a syringe
(2NO$_2$(g) $\rightleftharpoons$ N$_2$O$_4$(g))

Source: Ken O'Donoghue
When the container volume is increased, the system will shift in the direction that increases its volume. An increase in volume in the ammonia synthesis system will produce a shift to the left to increase the number of gaseous molecules present (←).
Example 6.5

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

a. the preparation of liquid phosphorus trichloride:
   \[ \text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_3(\text{l}) \]

b. the preparation of gaseous phosphorus pentachloride:
   \[ \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g}) \]

c. the reaction of phosphorus trichloride with ammonia:
   \[ \text{PCl}_3(\text{g}) + 3\text{NH}_3(\text{g}) \rightleftharpoons \text{P}(\text{NH}_2)_3(\text{g}) + 3\text{HCl}(\text{g}) \]
Solution

a. Since P₄ and PCl₃ are a pure solid and a pure liquid, respectively, we need to consider only the effect of the decrease in volume on Cl₂. The position of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.

b. Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule and the reactant side has two.

c. Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.
III. The effect of a change in temperature

Please keep in mind that both conc & pressure can shift the equilibrium position, but not change the equilibrium constant. However, the effect of temperature on equilibrium is different, because the value of $K$ changes with temperature.
(1) \( \text{N}_2(g) + 3\text{H}_2(g) \Leftrightarrow 2\text{NH}_3(g) + \text{energy} \) (exothermic)

If energy in the form of heat is added to this system at equilibrium, *Le Châtelier’s principle* predicts the shift will be in the direction that consumes energy, in this case to the left. *Note that this shift decreases the conc of NH}_3 & increases the concs of N}_2 & H}_2, thus decreasing the value of K.*
For a reaction that consumes energy (an *endothermic* reaction), such as the decomposition of calcium carbonate. In this case, an increase in temperature will cause the equilibrium to shift to the right and the value of $K$ to increase.
TABLE 6.3  Observed Value of $K$ for the Ammonia Synthesis Reaction as a Function of Temperature*

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K$ (L$^2$/mol$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>90</td>
</tr>
<tr>
<td>600</td>
<td>3</td>
</tr>
<tr>
<td>700</td>
<td>0.3</td>
</tr>
<tr>
<td>800</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*For this exothermic reaction the value of $K$ decreases as the temperature increases, as predicted by Le Châtelier’s principle.
Shifting the $\text{N}_2\text{O}_4(g)$ and $2\text{NO}_2(g)$ equilibrium by changing the temperature (a) left : 100°C & (b) right : 0°C ($\text{N}_2\text{O}_4(g) \Leftrightarrow 2\text{NO}_2(g)$).

100 °C

2$\text{NO}_2(g)$ (reddish brown) → $\text{N}_2\text{O}_4(g)$ (colorless)

0 °C
### TABLE 6.4  Shifts in the Equilibrium Position for the Reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

<table>
<thead>
<tr>
<th>Change</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of $\text{N}_2\text{O}_4(g)$</td>
<td>Right</td>
</tr>
<tr>
<td>Addition of $\text{NO}_2(g)$</td>
<td>Left</td>
</tr>
<tr>
<td>Removal of $\text{N}_2\text{O}_4(g)$</td>
<td>Left</td>
</tr>
<tr>
<td>Removal of $\text{NO}_2(g)$</td>
<td>Right</td>
</tr>
<tr>
<td>Addition of $\text{He}(g)$</td>
<td>None</td>
</tr>
<tr>
<td>Decrease in container volume</td>
<td>Left</td>
</tr>
<tr>
<td>Increase in container volume</td>
<td>Right</td>
</tr>
<tr>
<td>Increase in temperature</td>
<td>Right</td>
</tr>
<tr>
<td>Decrease in temperature</td>
<td>Left</td>
</tr>
</tbody>
</table>

endothermic
In summary, *to use Le Châtelier’s principle* to describe the effect of a temperature change on a system at equilibrium, *treat energy as a reactant (in an endothermic process) or as a product (in an exothermic process)*, & predict the direction of the shift as if an actual reactant or product is added or removed.
Although *Le Châtelier’s principle* cannot predict the size of the change in $K$, it can correctly predict the direction of the change.

$$\Delta G = \Delta H - T\Delta S = -RT\ln K$$

$$K = e^{(T\Delta S - \Delta H) / RT}$$
6.9 Equilibria involving real gases

\[ N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \]

\[ K_{P}^{\text{obs}} = \left( \frac{P_{NH_3}^{\text{obs}}}{} \right)^2 / \left( P_{N_2}^{\text{obs}}(P_{H_2}^{\text{obs}})^3 \right) \]

\( P^{\text{obs}} < P^{\text{ideal}} \) for a real gas at pressure above 1 atm
<table>
<thead>
<tr>
<th>Total Pressure (atm)</th>
<th>$K_P^{obs}$ (atm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$4.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>50</td>
<td>$4.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>100</td>
<td>$5.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>300</td>
<td>$7.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>600</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>1000</td>
<td>$5.3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
In general, for equilibrium pressures of 1 atm or less, the value of $K_P$ calculated from the observed equilibrium pressures is expected to be within about 1% of the true value. However, at high pressures the deviations can be quite severe.