OFB Chapter 7
Chemical Equilibrium

7-1 Chemical Reactions in Equilibrium
7-2 Calculating Equilibrium Constants
7-3 The Reaction Quotient
7-4 Calculation of Gas-Phase Equilibrium
7-5 The effect of External Stresses on Equilibria:
    Le Châtelier’s Principle
7-6 Heterogeneous Equilibrium
7-7 Extraction and Separation Processes
Last Day to Drop
• Oct. 8

Mid-Term Grades
• Due Sept. 24
• Satisfactory
• Unsatisfactory

All exercises
Homework:
Chapter 7:
-8, 14, 24, 42, 54

Note: this is all that’s on WebCT… Be familiar with equilibrium problems – these are very important
$aA + bB \xrightarrow{\text{forward}} cC + dD$

$\xleftarrow{\text{reverse}}$

(b) Carbon dioxide

Room temperature

~220 K (-53°C)
7-1 Chemical Reactions and Equilibrium

The equilibrium condition for *every* reaction can be summed up in a single equation in which a number, the **equilibrium constant (K)** of the reaction, equals an **equilibrium expression**, a function of properties of the reactants and products.

\[ \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g) \ @ \ 25^\circ\text{C} \]

\[ K = 0.03126 \]

\[ \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g) \ @ \ 30^\circ\text{C} \]

\[ K = 0.04187 \]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>0.01683</td>
</tr>
<tr>
<td>17.0</td>
<td>0.01912</td>
</tr>
<tr>
<td>19.0</td>
<td>0.02168</td>
</tr>
<tr>
<td>21.0</td>
<td>0.02454</td>
</tr>
<tr>
<td>23.0</td>
<td>0.02772</td>
</tr>
<tr>
<td>25.0</td>
<td>0.03126</td>
</tr>
<tr>
<td>30.0</td>
<td>0.04187</td>
</tr>
<tr>
<td>50.0</td>
<td>0.1217</td>
</tr>
</tbody>
</table>

9/22/2004
Chemical Reactions and Equilibrium

\[ \text{H}_2\text{O} (l) \leftrightarrow \text{H}_2\text{O} (g) \]

\[ \frac{P_{\text{H}_2\text{O}}}{P_{\text{ref}}} = K \quad P_{\text{ref}} \text{ is numerically equal to 1} \]

The convention in the book is to express all pressures in atmospheres and to omit factors of \( P_{\text{ref}} \) because their value is unity. An equilibrium constant \( K \) is a pure number.
Chemical Reactions and Equilibrium

An equilibrium reaction

\[ 2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \]
\[ \text{N}_2\text{O}_4(g) \rightarrow 2 \text{NO}_2(g) \]
Chemical Reactions and Equilibrium

\[
\begin{align*}
2 \text{NO}_2(g) & \rightarrow \text{N}_2\text{O}_4(g) & \downarrow T & \uparrow P \\
\text{N}_2\text{O}_4(g) & \rightarrow 2 \text{NO}_2(g) & \uparrow T & \downarrow P
\end{align*}
\]

\[
2 \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g); \quad K = 8.8 \ @ \ 25^\circ\text{C}
\]
Chemical Reactions and Equilibrium

As the equilibrium state is approached, the forward and backward rates of reaction approach equality. At equilibrium the rates are equal, and no further net change occurs in the partial pressures of reactants or products.

Four fundamental characteristics of equilibrium states in isolated systems:

1. They display no macroscopic evidence of change.
2. They are reached through spontaneous processes.
3. They show a dynamic balance of forward and backward processes.
4. They are the same regardless of the direction from which they are approached.
The Form of Equilibrium Expressions

In a chemical reaction in which $a$ moles of species A and $b$ moles of species B react to form $c$ moles of species C and $d$ moles of species D, the partial pressures at equilibrium are related through

\[ 	ext{forward} \quad aA + bB \quad \text{reverse} \quad cC + dD \]

provided that all species are present as low-pressure gases.
Exercise 7-1

Write equilibrium expressions for the reactions defined by the following equations:

\[ 3 \, H_2(g) + \text{SO}_2(g) \Leftrightarrow \text{H}_2\text{S}(g) + 2 \, \text{H}_2\text{O}(g) \]

\[ 2 \, \text{C}_2\text{F}_5\text{Cl}(g) + 4 \, \text{O}_2(g) \Leftrightarrow \text{Cl}_2(g) + 4 \, \text{CO}_2(g) + 5 \, \text{F}_2(g) \]
Example 7-2

Consider the equilibrium

\[ 4 \text{NO}_2(g) \leftrightarrow 2 \text{N}_2\text{O}(g) + 3 \text{O}_2(g) \]

The three gases are introduced into a container at partial pressures of 3.6 atm (for \( \text{NO}_2 \)), 5.1 atm (for \( \text{N}_2\text{O} \)), and 8.0 atm (for \( \text{O}_2 \)) and react to reach equilibrium at a fixed temperature. The equilibrium partial pressure of the \( \text{NO}_2 \) is measured to be 2.4 atm. Calculate the equilibrium constant of the reaction at this temperature, assuming that no competing reactions occur.

\[
\begin{array}{ccc}
\text{initial partial pressure (atm)} & \text{change in partial pressure (atm)} & \text{equilibrium partial pressure (atm)} \\
\hline
\end{array}
\]
\[ 4 \text{NO}_2(g) \leftrightarrow 2 \text{N}_2\text{O}(g) + 3 \text{O}_2(g) \]

<table>
<thead>
<tr>
<th>initial partial pressure (atm)</th>
<th>change in partial pressure (atm)</th>
<th>equilibrium partial pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.6 - 4x) = 2.4 atm NO(_2);</td>
<td>(5.1 + 2(0.3 \text{ atm})) = 5.7 atm N(_2)O</td>
<td>(x = 0.3 \text{ atm}) (8.0 + 3(0.3 \text{ atm})) = 8.9 atm O(_2)</td>
</tr>
</tbody>
</table>

\[ K = \frac{(P_{\text{N}_2\text{O}})^2(P_{\text{O}_2})^3}{(P_{\text{NO}_2})^4} = \frac{(5.7)^2(8.9)^3}{(2.4)^4} = \]
Exercise 7-2

The compound GeWO$_4$(g) forms at high temperature in the reaction

\[ 2 \text{GeO} (g) + \text{W}_2\text{O}_6(g) \rightleftharpoons 2 \text{GeWO}_4(g) \]

Some GeO (g) and W$_2$O$_6$ (g) are mixed. Before they start to react, their partial pressures both equal 1.000 atm. After their reaction at constant temperature and volume, the equilibrium partial pressure of GeWO$_4$(g) is 0.980 atm. Assuming that this is the only reaction that takes place, (a) determine the equilibrium partial pressures of GeO and W$_2$O$_6$, and (b) determine the equilibrium constant for the reaction.

<table>
<thead>
<tr>
<th>initial partial pressure (atm)</th>
<th>change in partial pressure (atm)</th>
<th>equilibrium partial pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 GeO (g) + W$_2$O$_6$ (g) ⇌ 2 GeWO$_4$(g)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ \text{2 GeO}(g) + \text{W}_2\text{O}_6(g) \rightleftharpoons \text{2 GeWO}_4(g) \]

**initial partial pressure (atm)**

**change in partial pressure (atm)**

**equilibrium partial pressure (atm)**

\[
0 + 2x = 0.980 \text{ atm GeWO}_4; \quad 1.000 - 2(0.490) = 0.020 \text{ atm GeO} \\
x = 0.490 \text{ atm} \quad 1.000 - 0.490 = 0.510 \text{ atm W}_2\text{O}_6
\]

\[
K = \frac{(P_{\text{GeWO}_2})^2}{(P_{\text{GeO}})^2(P_{\text{W}_2\text{O}_6})} = \frac{(0.980)^2}{(0.020)^2(0.510)}
\]
Relationships Among the K’s of Related Reactions

Rule 1: The equilibrium constant for a reverse reaction is always the reciprocal of the equilibrium constant for the corresponding forward reaction.

\[
\begin{align*}
#1 & \quad 2 \text{H}_2(g) + \text{O}_2(g) \leftrightarrow 2 \text{H}_2\text{O}(g) & \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2})^2(P_{\text{O}_2})} = K_1 \\
#2 & \quad 2 \text{H}_2\text{O}(g) \leftrightarrow 2 \text{H}_2(g) + \text{O}_2(g) & \frac{(P_{\text{H}_2})^2(P_{\text{O}_2})}{(P_{\text{H}_2\text{O}})^2} = K_2 \\
\end{align*}
\]

K_1 = 1/K_2
Relationships Among the K’s of Related Reactions

Rule 2: When the coefficients in a balanced chemical equation are all multiplied by a constant factor, the corresponding equilibrium constant is raised to a power equal to that factor.

#1 \[ 2 \text{H}_2(g) + \text{O}_2(g) \leftrightarrow 2 \text{H}_2\text{O}(g) \quad \text{Rxn 1} \]

#3 \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \leftrightarrow \text{H}_2\text{O}(g) \quad \text{Rxn 3} \]

\[
\frac{(P_{\text{H}_2\text{O}})}{(P_{\text{H}_2})(P_{\text{O}_2})^{1/2}} = K_3
\]

\[ K_3 = K_1^{1/2} = \sqrt{K_1} \]
Relationships Among the K’s of Related Reactions

Rule 3: when chemical equations are added to give a new equation, their equilibrium constants are multiplied to give the equilibrium constant associated with the new equation.

\[
\begin{align*}
2 \text{BrCl}(g) & \leftrightarrow \text{Br}_2(g) + \text{Cl}_2(g) & \quad \frac{(P_{\text{Br}_2})(P_{\text{Cl}_2})}{(P_{\text{BrCl}})^2} = K_1 = 0.45 \quad @ \ 25^\circ C \\
\text{Br}_2(g) + \text{I}_2(g) & \leftrightarrow 2 \text{IBr}(g) & \quad \frac{(P_{\text{IBr}})^2}{(P_{\text{Br}_2})(P_{\text{I}_2})} = K_2 = 0.051 \quad @ \ 25^\circ C \\
& & = K_1 K_2 \\
& & = (0.45)(0.051) \\
& & = 0.023 \quad @ \ 25^\circ C
\end{align*}
\]
7-3 The Reaction Quotient

\[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = K \]

\[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = Q \]

Note that **K (the Equilibrium Constant)** uses *equilibrium partial pressures*

Note that **Q (the reaction quotient)** uses *prevailing partial pressures*, not necessarily at equilibrium
The Reaction Quotient

\[ \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = Q \]

If \( Q < K \), reaction proceeds in a forward direction (toward products);

If \( Q > K \), reaction proceeds in a backward direction (toward reactants);

If \( Q = K \), the reaction stops because the reaction is in equilibrium.
Exercise 7-4

The equilibrium constant for the reaction \( P_4(g) \leftrightarrow 2 \ P_2(g) \) is 1.39 at 400\(^\circ\)C. Suppose that 2.75 mol of \( P_4(g) \) and 1.08 mol of \( P_2(g) \) are mixed in a closed 25.0 L container at 400\(^\circ\)C. Compute \( Q_{\text{init}} \) (the Q at the moment of mixing) and state the direction in which the reaction proceeds.

\[
\frac{(P_{P_2})^2}{(P_{P_4})^1} = K = 1.39
\]

\[
P_{P_4(\text{init})} = n_{P_4(\text{init})} \frac{RT}{V}
\]

\[
P_{P_2(\text{init})} = n_{P_2(\text{init})} \frac{RT}{V}
\]

\[
Q = \frac{(2.39)^2}{(6.08)} = 0.939
\]

\[
0.939 < 1.39; \ Q < K
\]
7-4 Calculations of Gas-Phase Equilibria

Exercise 7-5

Carbon monoxide reacts with water to give hydrogen:

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

At 900 K, the equilibrium constant for this reaction, the so-called shift reaction, equals 0.64. Suppose the partial pressures of three gases at equilibrium at 900 K are

\[ P_{\text{CO}} = 2.00 \text{ atm}, \ P_{\text{CO}_2} = 0.80 \text{ atm}, \text{ and } P_{\text{H}_2} = 0.48 \text{ atm} \]

Calculate the partial pressure of water under these conditions.
Exercise 7-5
Carbon monoxide reacts with water to give hydrogen:

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

At 900 K, the equilibrium constant for this reaction, the so-called shift reaction, equals 0.64. Suppose the partial pressures of three gases at equilibrium at 900 K are

\[ P_{\text{CO}} = 2.00 \text{ atm}, \quad P_{\text{CO}_2} = 0.80 \text{ atm}, \quad \text{and} \quad P_{\text{H}_2} = 0.48 \text{ atm} \]

Calculate the partial pressure of water under these conditions.
• Solving quadratic equations
7-5 Effects of External Stresses on Equilibria: Le Châtelier’s Principle

A system in equilibrium that is subjected to a stress reacts in a way that counteracts the stress.

Le Châtelier’s Principle provides a way to predict the response of an equilibrium system to an external perturbation, such as…

Effects of Adding or Removing Reactants or Products

Effects of Changing the Volume of the System

Effects of Changing the Temperature
Effects of Adding or Removing Reactants or Products

\[ \text{PCl}_5(g) \leftrightarrow \text{PCl}_3(g) + \text{Cl}_2(g) \]

add extra PCl\(_5\)(g)
add extra PCl\(_3\)(g)
remove some PCl\(_5\)(g)
remove some PCl\(_3\)(g)

\[
\left( \frac{P_{PCl_3}}{P_{PCl_5}} \right) \left( \frac{P_{Cl_2}}{P_{PCl_5}} \right) = Q
\]
Effects of Changing the Volume of the System

\[ \text{PCl}_5(g) \leftrightarrow \text{PCl}_3(g) + \text{Cl}_2(g) \]

Let’s decrease the volume of the reaction container

Let’s increase the volume of the reaction container
### Equilibrium Shifts

<table>
<thead>
<tr>
<th>Volume Decreased (Pressure Increased)</th>
<th>Volume Increased (Pressure Decreased)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$V_{reactants} &gt; V_{products}$</strong></td>
<td><strong>Equilibrium shift right (toward products)</strong></td>
</tr>
<tr>
<td><strong>$V_{reactants} &lt; V_{products}$</strong></td>
<td><strong>Equilibrium Shifts left (toward reactants)</strong></td>
</tr>
<tr>
<td><strong>$V_{reactants} = V_{products}$</strong></td>
<td><strong>Equilibrium not affected</strong></td>
</tr>
</tbody>
</table>

### Chemical Equations

- $2 \text{P}_2(g) \leftrightarrow \text{P}_4(g)$
- $\text{PCl}_5(g) \leftrightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$
- $\text{CO}(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g)$

---

© 2003 Thomson-Brooks/Cole
Effects of Changing the Temperature

$$\text{PCl}_5(g) \Leftrightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$$

Let’s increase the temperature of the reaction

Let’s decrease the temperature of the reaction
If a forward reaction is **exothermic**,  
Then the reverse reaction must be **endothermic**

<table>
<thead>
<tr>
<th></th>
<th>Temperature Raised</th>
<th>Temperature Lowered</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Endothermic Reaction</strong></td>
<td>Equilibrium shift right (toward products)</td>
<td>Equilibrium Shifts left (toward reactants)</td>
</tr>
<tr>
<td>(absorb heat)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Exothermic Reaction</strong></td>
<td>Equilibrium Shifts left (toward reactants)</td>
<td>Equilibrium shift right (toward products)</td>
</tr>
<tr>
<td>(liberate heat)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Effects of Changing the Temperature

\[ \text{PCl}_5(g) \leftrightharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \quad K = 11.5 \ @ \ 300^\circ\text{C} = Q \]

Let’s increase the temperature of the reaction

Let’s decrease the temperature of the reaction
Driving Reactions to Completion

Industrial Synthesis of Ammonia

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

Forward reaction exothermic

<table>
<thead>
<tr>
<th>Volume Decreased (Pressure Increased)</th>
<th>Volume Increased (Pressure Decreased)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V reactants &gt; V products</td>
<td>Equilibrium shift right (toward products)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature Raised</th>
<th>Temperature Lowered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic Reaction (liberate heat)</td>
<td>Equilibrium Shifts left (toward reactants)</td>
</tr>
</tbody>
</table>
Review: Chemical Equilibrium

\[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = K \]

\[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = Q \]

\[ Q = K \]

1. Effects of Adding or Removing Reactants or Products

2. Effects of Changing the Volume (or Pressure) of the System

3. Effects of Changing the Temperature
Exercise 7-10

State the effect of an increase in temperature and also of a decrease in volume on the equilibrium yield of the products in each of the following reactions.

a) \( \text{CH}_3\text{OCH}_3 \text{ (g)} + \text{H}_2\text{O} \text{ (g)} \leftrightarrow 2 \text{CH}_4 \text{ (g)} + \text{O}_2 \text{ (g)} \)

Increase Temp?  
Decrease Volume?

b) \( \text{H}_2\text{O} \text{ (g)} + \text{CO} \text{ (g)} \leftrightarrow \text{HCOOH} \text{ (g)} \)

Increase Temp?  
Decrease Volume?
Heterogeneous Equilibrium

**Solids**

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

**Liquids**

\[
\text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g)
\]

**Dissolved species**

\[
\text{I}_2(s) \leftrightarrow \text{I}_2(aq)
\]
Law of Mass Action

1. Gases enter equilibrium expressions as partial pressures, in atmospheres. E.g., \( P_{CO_2} \)

2. Dissolved species enter as concentrations, in moles per liter. E.g., \([Na^+]\)

3. Pure solids and pure liquids are represented in equilibrium expressions by the number 1 (unity); a solvent taking part in a chemical reaction is represented by unity, provided that the solution is dilute. E.g.,

\[
I_2(s) \leftrightarrow I_2(aq)
\]

\[
K = \frac{[I_2(aq)]}{[I_2(s)]} = \frac{[I_2(aq)]}{1} = [I_2]
\]
Law of Mass Action

4. Partial pressures and concentrations of products appear in the numerator and those of the reactants in the denominator. Each is raised to a power equal to its coefficient in the balanced chemical equation.

\[ aA + bB \leftrightarrow cC + dD \]
Exercise 7-11

Write equilibrium-constant equations for the following Equilibria:

(a) \( \text{Si}_3\text{N}_4(s) + 4 \text{O}_2(g) \rightleftharpoons 3 \text{SiO}_2(s) + 2 \text{N}_2\text{O}(g) \)

(b) \( \text{O}_2(g) + 2 \text{H}_2\text{O}(l) \rightleftharpoons 2 \text{H}_2\text{O}_2(aq) \)

(c) \( \text{CaH}_2(s) + 2 \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{Ca(OC}_2\text{H}_5)_2(s) + 2 \text{H}_2(g) \)
Exercise 7-12

A vessel holds pure CO (g) at a pressure of 1.282 atm and a temperature of 354K. A quantity of nickel is added, and the partial pressure of CO (g) drops to an equilibrium value of 0.709 atm because of the reaction

\[ \text{Ni (s) + 4CO (g) } \rightleftharpoons \text{Ni(CO)}_4 \text{ (g)} \]

Compute the equilibrium constant for this reaction at 354K.
Exercise 7-12

A vessel holds pure CO (g) at a pressure of 1.282 atm and a temperature of 354K. A quantity of nickel is added, and the partial pressure of CO (g) drops to an equilibrium value of 0.709 atm because of the reaction

\[
\text{Ni (s) + 4CO (g) } \leftrightarrow \text{Ni(CO)}_4 (g)
\]

Compute the equilibrium constant for this reaction at 354K.

\[
K = \frac{P_{\text{Ni(CO)4}}}{(P_{\text{CO}})^4[Ni(s)]} = \frac{P_{\text{Ni(CO)4}}}{(P_{\text{CO}})^4(1)}
\]

<table>
<thead>
<tr>
<th>( P_{\text{CO}} ) (atm)</th>
<th>( P_{\text{Ni(CO)4}} ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial partial pressure (atm)</td>
<td></td>
</tr>
<tr>
<td>change in partial pressure (atm)</td>
<td></td>
</tr>
<tr>
<td>equilibrium partial pressure (atm)</td>
<td></td>
</tr>
</tbody>
</table>
7-7 Extraction and Separation Processes

• Extraction
  – Partitioning of a solute between two immiscible solvents

• Chromatography
  – Solute is partitioned between a mobile phase and a stationary phase
    • Column Chromatography
    • Gas-liquid Chromatography