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
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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.

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

$$ K = 0.03126 $$

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

$$ K = 0.04187 $$

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<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (atm)</th>
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<tr>
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</tr>
<tr>
<td>50.0</td>
<td>0.1217</td>
</tr>
</tbody>
</table>
Chemical Reactions and Equilibrium

\[ H_2O (l) \leftrightarrow H_2O (g) \]

\[
\frac{P_{H_2O}}{P_{ref}} = K
\]

Pref is numerically equal to 1

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

Chemical Reactions and Equilibrium

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

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

An equilibrium reaction

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.

\[ aA + bB \xrightleftharpoons{\text{forward}}{\text{reverse}} cC + dD \]
The Form of Equilibrium Expressions

**Exercise 7-1**
Write equilibrium expressions for the reactions defined by the following equations:

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

\[2 \text{C}_2\text{F}_5\text{Cl}(\text{g}) + 4 \text{O}_2(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + 4 \text{CO}_2(\text{g}) + 5 \text{F}_2(\text{g})\]

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7-2 Calculating Equilibrium Constants

**Example 7-2**
Consider the equilibrium

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

The three gases are introduced into a container at partial pressures of 3.6 atm (for NO\(_2\)), 5.1 atm (for N\(_2\)O), and 8.0 atm (for O\(_2\)) and react to reach equilibrium at a fixed temperature. The equilibrium partial pressure of the 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.

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

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

The compound GeWO₄(g) forms at high temperature in the reaction

\[ 2 \text{ GeO (g)} + \text{ W₂O₆(g)} \rightleftharpoons 2 \text{ GeWO₄(g)} \]

Some GeO (g) and W₂O₆(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 GeWO₄(g) is 0.980 atm. Assuming that this is the only reaction that takes place, (a) determine the equilibrium partial pressures of GeO and W₂O₆, and (b) determine the equilibrium constant for the reaction.

\[
\begin{align*}
\text{initial partial pressure (atm)} & \\
\text{change in partial pressure (atm)} & \\
\text{equilibrium partial pressure (atm)} & \\
\end{align*}
\]

\[
K = \frac{(P_{\text{GeWO}_4})^2}{(P_{\text{GeO}})^2(P_{\text{W}_2\text{O}_6})} = \]

---

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.

\[
\begin{align*}
2 \text{ H}_2(g) + \frac{1}{2} \text{ O}_2(g) \leftrightarrow \text{ H}_2\text{O}(g) & \quad \text{Rxn 3} \\
2 \text{ H}_2(g) + \text{ O}_2(g) \leftrightarrow 2 \text{ H}_2\text{O}(g) & \quad \text{Rxn 1} \\
\end{align*}
\]

\[
\frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2})^2(P_{\text{O}_2})} = K_1 \quad K_1 = 1/K_2
\]

\[
\frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2})^2} = K_2
\]

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.

\[
\begin{align*}
2 \text{ H}_2(g) + \text{ O}_2(g) \leftrightarrow 2 \text{ H}_2\text{O}(g) & \quad \text{Rxn 1} \\
\text{H}_2(g) + \frac{1}{2} \text{ O}_2(g) \leftrightarrow \text{ H}_2\text{O}(g) & \quad \text{Rxn 3} \\
\end{align*}
\]

\[
\frac{(P_{\text{H}_2\text{O}})}{(P_{\text{H}_2})(P_{\text{O}_2})^{1/2}} = K_3 \quad K_3 = K_1^{1/2} = \sqrt{K_1}
\]
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.

\[ 2 \text{ BrCl}(g) \leftrightarrow \text{ Br}_2(g) + \text{ Cl}_2(g) \quad \frac{(P_{\text{BrCl}})(P_{\text{Cl}_2})}{(P_{\text{BrCl}})^2} = K_1 = 0.45 \quad @ \quad 25^\circ C \]

\[ \text{ Br}_2(g) + \text{ I}_2(g) \leftrightarrow 2 \text{ IBr}(g) \quad \frac{(P_{\text{Br}})^2}{(P_{\text{Br}_2})(P_{\text{I}_2})} = K_2 = 0.051 \quad @ \quad 25^\circ C \]

\[ = K_1 K_2 \]

\[ = (0.45)(0.051) \]

7-3 The Reaction Quotient

\[ \text{ aA + bB } \xrightarrow{\text{ forward}} \xleftarrow{\text{ reverse}} \text{ cC + dD} \]

Note that \( K \) (the Equilibrium Constant) uses \textit{equilibrium partial pressures}.

Note that \( Q \) (the reaction quotient) uses \textit{prevailing partial pressures}, not necessarily at equilibrium.

Exercise 7-4

The equilibrium constant for the reaction \( \text{ P}_4(g) \leftrightarrow 2 \text{ P}_2(g) \) is 1.39 at 400°C. Suppose that 2.75 mol of \( \text{ P}_4(g) \) and 1.08 mol of \( \text{ P}_2(g) \) are mixed in a closed 25.0 L container at 400°C. Compute \( Q_{(\text{init})} \) (the Q at the moment of mixing) and state the direction in which the reaction proceeds.
Carbon monoxide reacts with water to give hydrogen:

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

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

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

Calculate the partial pressure of water under these conditions.

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**Solving quadratic equations**

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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

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

\[ \frac{\left( P_{\text{PCl}_3} \right) \left( P_{\text{Cl}_2} \right)}{P_{\text{PCl}_5}} = Q \]

Effects of Changing the Volume of the System

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

- **Volume Decreased (Pressure Increased)**
  - V reactants > V products: Equilibrium shift right (toward products)
  - V reactants < V products: Equilibrium shifts left (toward reactants)
  - V reactants = V products: Equilibrium not affected

- **Volume Increased (Pressure Decreased)**
  - Equilibrium shifted left (toward reactants)
  - Equilibrium shift right (toward products)

Effects of Changing the Temperature

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

\[ 2 \text{P}_2(g) \leftrightarrow \text{P}_4(g) \]

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

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g) \]
If a forward reaction is **exothermic**, then the reverse reaction must be **endothermic**.
Heterogeneous Equilibrium

**Solids**  \( \text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g) \) \( P_{\text{CO}_2} = K \)

**Liquids**  \( \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g) \) \( P_{\text{H}_2\text{O}} = K \)

**Dissolved species**  \( \text{I}_2(s) \leftrightarrow \text{I}_2(aq) \) \( [\text{I}_2] \ (aq) = K \)

**Law of Mass Action**

1. Gases enter equilibrium expressions as partial pressures, in atmospheres. E.g., \( P_{\text{CO}_2} \)

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

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.,

\[
\text{I}_2(s) \leftrightarrow \text{I}_2(aq) \\
K = \frac{[\text{I}_2(aq)]}{[\text{I}_2(s)]} = \frac{[\text{I}_2(aq)]}{1} = [\text{I}_2]
\]

**Exercise 7-11**

Write equilibrium-constant equations for the following Equilibria:

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

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

(c) \( \text{CaH}_2(s) + 2 \text{C}_2\text{H}_5\text{OH}(l) \leftrightarrow \text{Ca(OC}_2\text{H}_5)_2(s) + 2 \text{H}_2(g) \)

\( a\text{A} + b\text{B} \leftrightarrow c\text{C} + d\text{D} \)
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

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

Compute the equilibrium constant for this reaction at 354K.

\[
K = \frac{P_{\text{Ni(CO)}_4}}{(P_{\text{CO}})^4[Ni(s)]} = \frac{P_{\text{Ni(CO)}_4}}{(P_{\text{CO}})^4(1)}
\]

\[
\begin{array}{c|c|c}
\text{initial partial pressure (atm)} & \text{change in partial pressure (atm)} & \text{equilibrium partial pressure (atm)} \\
\hline
P_{\text{CO}} \text{ (atm)} & P_{\text{Ni(CO)}_4} \text{ (atm)} & \\
\end{array}
\]

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

Chapter 7

Chemical Equilibrium

- Examples / Exercises
  - 7-1 to 7-5, 7-10, 7-11, 7-12
- Problems
  - 1, 2, 7, 9, 12, 15, 18, 24, 31, 42, 45