Chapter 6: Phenomena

Scientists studied the following reactions by putting different amounts of substances (reactants and products) into a sealed rigid vessel and measuring the concentration as a function of time. What patterns do you notice about the data?

<table>
<thead>
<tr>
<th>Reaction 1: A(aq) ⇌ B(aq)</th>
<th>Reaction 2: B(aq) ⇌ 2C(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trial</strong></td>
<td><strong>Initial</strong></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Phenomena: Scientists studied the following reactions by putting different amounts of substances (reactants and products) into a sealed rigid vessel and measuring the concentration as a function of time. What patterns do you notice about the data?

Big Idea: Reactions proceed to an equilibrium condition. When equilibrium is reached the rate of formation of products equals the rate of formations of reactants. When a system at equilibrium is disturbed the reaction responds by minimizing the disturbance.

Dynamic Equilibrium

Is the following statement true or false? At equilibrium the amount of products always equals the amount of reactants.

- a) True
- b) False
- c) Not Enough Information

Dynamic Equilibrium: The condition in which the rate of the forward reaction equals the rate of the reverse reaction.

<table>
<thead>
<tr>
<th>Full</th>
<th>Simplified</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = \frac{[B][C]}{[A]}$</td>
<td>$K = \frac{[B][C]}{[A]}$</td>
</tr>
</tbody>
</table>

Activity ($a_j$): The effective concentration or pressure of a species $j$ expressed as the partial pressure or concentration of the species relative to its standard value.
Chapter 6: Chemical Equilibrium

Liquids and Solids

- Solids and liquids only have one concentration, therefore, this is also the reference concentration. Any number divide by itself is 1 which results in solids and liquids not being included in the equilibrium constant.

Note: Since the equation for activity is concentration over concentration or pressure over pressure, many books do not put units on equilibrium expressions.

Equilibrium Constant

<table>
<thead>
<tr>
<th>Aqueous Solutions</th>
<th>Gas Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_j = \frac{[J]}{c^*} )</td>
<td>( a_j = \frac{P_j}{P^*} )</td>
</tr>
</tbody>
</table>
| \( c^* = \text{reference concentration (1 M)} \) | \( P^* = \text{reference pressure (1 atm)} \)

What does \( K_{eq} \) tell us?

- \( K_{eq} << 1 \)
  - lots of reactants, not many products at equilibrium
  - reverse reaction is favored/faster*

- \( K_{eq} \approx 1 \)
  - equal amounts of reactants and product at equilibrium
  - neither direction favored/faster

- \( K_{eq} >> 1 \)
  - lots of products, not many reactants at equilibrium
  - forward reaction is favored/faster*

*when equal amounts of products and reactants are present

Equilibrium Constant

\( a_j = \frac{[J]}{c^*} \)
\( a_j = \frac{P_j}{P^*} \)

Before Class Question

Student Question

How are \( K \) and \( K_P \) related for the following reaction?

\[ \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \]

- \( a) \ K_P = K \)
- \( b) \ K_P = \sqrt{RTK} \)
- \( c) \ K_P = \frac{1}{\sqrt{RTK}} \)
- \( d) \ K_P = RTK \)
- \( e) \ None \ of \ the \ above \)

Reaction Quotient

What does \( Q \) tell us?

- \( Q > K \)
  - There are more products present than there should be at equilibrium. Therefore, the reverse reaction is spontaneous and products tend to decompose into reactants.

- \( Q = K \)
  - The system is at equilibrium.

- \( Q < K \)
  - There are more reactants present than there should be at equilibrium. Therefore, the forward reaction is spontaneous and reactants tend to form into products.

Determine Equilibrium Concentration/Pressure

- **Step 1:** Write a balanced chemical reaction.
- **Step 2:** Write the expression for \( K \) or \( K_P \).
- **Step 3:** Make a chart.

<table>
<thead>
<tr>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species 1</td>
<td>Species 2</td>
<td></td>
</tr>
</tbody>
</table>

- **Step 4:** Plug in equilibrium values into equilibrium expression.
- **Step 5:** Use guess and check, quadratic formula, or an assumption to solve for \( x \).
- **Step 6:** Calculate equilibrium concentrations/pressures.
Chapter 6: Chemical Equilibrium

Determining Equilibrium Concentration/Pressure

Example 1:
- 3.4 mol of SO$_3$ is put in an otherwise empty 1.0 L container. What are the concentrations of the species at equilibrium if the following reaction occurs:
\[
2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})
\]
\[K = 3.43 \text{ (at 1000. K)}\]

Example 2:
- The following data was collected at equilibrium for the system:
\[
\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})
\]

\[P_{H_2} = 0.639 \text{ atm}\]
\[P_{I_2} = 0.0586 \text{ atm}\]
\[P_{HI} = 0.135 \text{ atm}\]
- If 0.300 atm of each gas was added to the container after the equilibrium was established. What are the new equilibrium pressures?

Example 3:
- The following equilibrium is known to occur:
\[
\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons 2\text{H}^+\text{(aq)} + \text{CO}_3^{2-}\text{(aq)}
\]
\[K = 2.4 \times 10^{-17}\]
- What are the concentrations at equilibrium if initially there is only 0.14 M H$_2$CO$_3$ present?

Checking Assumptions:
- Assumption are good when the amount subtracted off is less than 5% of the number it is being subtracted from. (5% Rule)

\[
\text{Calculating the Percentage Lost/Gained} = \frac{\text{amount lost/gained}}{\text{original concentration}} \times 100\%
\]

Note: This assumption is usually good when K or Kp is less than 10$^{-5}$.

Note: For test you must check your assumption to receive full credit.

Le Chatelier’s Principle
- Le Chatelier’s Principle: When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.
  - Concentration
    - If the concentration of a species is increased, to restore equilibrium, the reaction must proceed in the opposite direction of the added species.
    - If the concentration of a species is decreased, to restore equilibrium, the reaction must proceed towards the direction of the removed species.
  - Volume
    - If the volume is decreased, to restore equilibrium, the reaction must proceed towards the side of the equation with fewer moles of gas.
    - If the volume is increased, to restore equilibrium, the reaction must proceed towards the side of the equation with more moles of gas.

Endothermic Reaction: A reaction that absorbs heat (reactants + energy = products)

Exothermic Reaction: A reaction that releases heat (reactants = products + energy)
Le Chatelier’s Principle

**Temperature**
- Exothermic Reactions (R ⇌ P + heat)
  - If the temperature is raised, equilibrium shifts to the reactants.
  - If the temperature is lowered, equilibrium shifts to the products.
- Endothermic Reactions (R + heat ⇌ P)
  - If the temperature is raised, equilibrium shifts to the products.
  - If the temperature is lowered, equilibrium shifts to the reactants.

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**Student Question**
The following equilibrium is going on in the 3 tubes:
\[ 2\text{NO}_2(g \text{ brown}) \rightleftharpoons \text{N}_2\text{O}_4(g \text{ colorless}) + \text{heat} \]
What color is the gas in the hot water?
- a) Dark Brown (mainly reactant but some products)
- b) Light Brown (mainly products but some reactants)
- c) Not Enough Information

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Le Chatelier’s Principle

**Student Question**
The following \( K_p \) values were collected for a system:
\[ K_p = 6.8 \times 10^5 \quad 25^\circ C \]
\[ K_p = 1.9 \times 10^{-4} \quad 400^\circ C \]
What side of the equation is the heat on?
- a) Reactants
- b) Products
- c) Not enough information

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Determining Equilibrium Constants From Other Systems

If you knew the equilibrium constants of the first two reactions, could you determine the equilibrium constant for the third reaction?

Reaction 1
\[ 2\text{GeO}(g) + \text{W}_2\text{O}_6(g) \rightleftharpoons 2\text{GeWO}_4(g) \]
\[ K_1 = \frac{[\text{GeWO}_4]^2}{[\text{GeO}]^2[\text{W}_2\text{O}_6]} \]
Reaction 2
\[ \text{GeO}(g) + \text{W}_2\text{O}_6(g) \rightleftharpoons \text{GeW}_2\text{O}_7(g) \]
\[ K_2 = \frac{[\text{GeW}_2\text{O}_7]}{[\text{GeO}][\text{W}_2\text{O}_6]} \]
Reaction 3
\[ \text{GeO}(g) + \text{GeW}_2\text{O}_7(g) \rightleftharpoons 2\text{GeWO}_4(g) \]
\[ K_3 = \frac{[\text{GeWO}_4]^2}{[\text{GeO}][\text{GeW}_2\text{O}_7]} \]

**Student Question**
Given the following two reactions what is the equilibrium constant of \( 2\text{A(aq)} = \text{D(aq)} + \text{E(aq)} \)?
\[ \text{A(aq)} + \text{B(aq)} = \text{D(aq)} + \text{C(aq)} \quad K_1 = 5.0 \]
\[ 2\text{C(aq)} + \text{D(aq)} = 2\text{B(aq)} + \text{E(aq)} \quad K_2 = 2.0 \]
- a) 0.40
- b) 2.5
- c) 10.
- d) 20.
- e) None of the above

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Take Away From Chapter 6

**Big Idea:** Reactions proceed to an equilibrium condition. When equilibrium is reached the rate of formation of products equals the rate of formations of reactants. When a system at equilibrium is disturbed the reaction responds by minimizing the disturbance.

- **Dynamic Equilibrium**
  - Know what it means to be at dynamic equilibrium. (10)
- **Equilibrium Constant**
  - Be able to calculate the equilibrium expression for a reaction. (21,31,35)
  - Solids and liquids not included in equilibrium constant.
  - Be able to convert between the equilibrium expression in concentration and in pressure. (24,25,33)
**Take Away From Chapter 6**

- **Equilibrium Constant (Continued)**
  - Know what the value of the equilibrium constant represents.
  - $K=1$: Similar number of product and reactant at equilibrium.
  - $K>1$: More product than reactant at equilibrium.
  - $K<1$: More reactant than product at equilibrium.

- **Reaction Quotient**
  - Know what the value of $Q$ represents when compared to $K$:
    - $Q<K$: Too many products, reaction proceeds to reactant to reach equilibrium.
    - $Q=K$: At equilibrium.
    - $Q>K$: Too many reactants, reaction proceeds to products to reach equilibrium.

**Determining Equilibrium Concentration/Pressure**

- Be able to determine the equilibrium concentration or pressures, give initial concentration/pressure, and equilibrium constant.
  - Guess and check
  - Quadratic equation
  - Assumption (usually good when $K<10^{-5}$)

- **Le Chatelier’s Principle**
  - Be able to determine what a system will do if equilibrium is disturbed.
  - Determining Equilibrium Constants from Other Systems
  - (26, 72, 73)