Chapter 17

Equilibrium
Chemists believe molecules react by colliding with each other.

If a collision is violent enough to break bonds, new bonds can form.

Consider the following reaction:

$$2\text{BrNO}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g)$$
(a) Two BrNO molecules approach each other at high speeds.
(b) The collision occurs.
(c) The energy of the collision causes Br-N bonds to break and Br-Br bonds to form.
(d) The products: one Br₂ and two NO molecules.
Some collisions are not strong enough to break bonds. There is a minimum amount of energy that is necessary.

**Activation Energy** \((E_a)\) – the minimum energy requirement that must be overcome to produce a chemical reaction.

In collisions with energy less than \(E_a\), molecules just bounce off each other.
Conditions That Affect Reaction Rates

- As the temperature is increased more molecules are colliding that have energy requirements exceeding $E_a$.
- It is possible to speed up a reaction without changing the temperature or reactant concentrations using a catalyst.

**Catalyst** – A substance that speeds up a reaction without being consumed.
Think of a catalyst as lowering the $E_a$; it gives the reaction a new pathway, kind of like driving around a mountain instead of over it.

The catalyst does NOT take part in the reaction, so never gets used up.
Figure 17.4: Comparison of the activation energies for an uncatalyzed reaction and for the same reaction with a catalyst present.
A Summary of the Main Factors That Affect Reaction Rates

- Nature of Reactants: bond strengths and structures vary among substances.
- Concentration (or Pressure): reaction rates increase as concentration, or pressure for gases, increases.
- Temperature: higher temperatures equate to increased rates.
- Surface Area: The greater the surface area, the greater the rates.
Section 17.4: The Equilibrium Condition

- **Equilibrium** – the exact balancing of two processes, one of which is the opposite of the other.
- Equilibrium can only be reached in closed systems.
- Equilibrium does not mean reactants and products are present in equal amounts; the balance is between forward and reverse reaction rates.
The Equilibrium Condition

- Ultimately this means there are reversible reactions: they can occur in either direction, forward or reverse, for example:
  \[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \text{ or } \text{N}_2\text{O}_4(g) \rightarrow \text{NO}_2(g) + \text{NO}_2(g) \]
- It is easier to write with a double arrow.
  \[ \text{NO}_2(g) + \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g) \]
The Equilibrium Constant: An Introduction

- In 1864, Guldberg & Waage proposed the “law of chemical equilibrium.”
- They postulated that for a reaction of the type: \( aA + bB \rightleftharpoons cC + dD \) (where A, B, C, & D are the chemicals and \( a, b, c, \) & \( d \) are their coefficients in the balanced equation), the law of chemical equilibrium can be represented by an equilibrium expression.
For the reaction \( aA + bB \rightleftharpoons cC + dD \)

- The square brackets indicate the concentrations \( \textit{at equilibrium} \) (in \( \text{mol/L} \)).
- \( K \) is a constant called the \( \textit{equilibrium constant} \).
The Equilibrium Constant: An Introduction

Consider the following reaction:

$$2 \ O_3(g) \rightleftharpoons 3 \ O_2(g)$$

The equilibrium expression would be:

$$K = \frac{[O_2]^3}{[O_3]^2}$$
Practice

1) Write the equilibrium expression for each of the following reactions:

a) $\text{CH}_3\text{OH}(g) \rightleftharpoons \text{CH}_2\text{O}(g) + \text{H}_2(g)$

b) $4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$
So what does the equilibrium constant really tell us? What's the point?

It tells us, at any given temperature, where a chemical reaction will reach equilibrium; given concentrations of reactants, how much product will ultimately form once equilibrium is reached.

It allows us to fairly accurately predict final product concentrations.
Examine the following data for the reaction (at 500 °C):

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

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Initial Concentrations</th>
<th>Equilib. Concentrations</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{N}_2]_0) 1.00 M, ([\text{H}_2]_0) 1.00M, ([\text{NH}_3]_0) 0</td>
<td>([\text{N}_2]) 0.921 M, ([\text{H}_2]) 0.763 M, ([\text{NH}_3]) 0.157 M</td>
<td>0.0602</td>
</tr>
<tr>
<td>2</td>
<td>([\text{N}_2]_0) 0, ([\text{H}_2]_0) 0, ([\text{NH}_3]_0) 1.00M</td>
<td>([\text{N}_2]) 0.399 M, ([\text{H}_2]) 1.197 M, ([\text{NH}_3]) 0.203 M</td>
<td>0.0602</td>
</tr>
<tr>
<td>3</td>
<td>([\text{N}_2]_0) 2.00 M, ([\text{H}_2]_0) 1.00M, ([\text{NH}_3]_0) 3.00M</td>
<td>([\text{N}_2]) 2.59M, ([\text{H}_2]) 2.77M, ([\text{NH}_3]) 1.82M</td>
<td>0.0602</td>
</tr>
</tbody>
</table>
Note that for the previous data $K=0.0602$ regardless of the amounts of reactants or products used initially.

All $K$ values were based on concentrations at equilibrium.

From trial to trial, equilibrium concentrations will not necessarily be equal (but $K$ will be); they depend on initial concentrations.
1) Calculate $K$ for the reaction

$$2\text{NBr}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{Br}_2(g)$$

the system at equilibrium at a particular temperature is analyzed and the following concentrations are found:

$$[\text{NBr}_3] = 2.07 \times 10^{-3} \text{ M}$$
$$[\text{N}_2] = 4.11 \times 10^{-2} \text{ M}$$
$$[\text{Br}_2] = 1.06 \times 10^{-3} \text{ M}$$
Consider the following reaction:

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

Initially one would attempt to calculate $K$ by putting the concentrations of the products over the reactants.

But, the concentrations of pure liquids and solids cannot change, so they remain constant: $K = [\text{CO}_2]$
Heterogeneous Equilibria

Examine the following reactions:

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$K = [H_2]^2[O_2]$$

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$[H_2]^2[O_2]$$

$$K = \frac{[H_2O]^2}{[H_2O]^2}$$
Heterogeneous Equilibria

Examine the following reactions:

$$2H_2O(l) \Leftrightarrow 2H_2(g) + O_2(g)$$

$$K = [H_2]^2[O_2]$$

$$2H_2O(g) \Leftrightarrow 2H_2(g) + O_2(g)$$

$$\frac{[H_2]^2[O_2]}{[H_2O]^2}$$

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$
Section 17.8: Le Châtelier’s Principle

Le Châtelier’s Principle states that when a change is imposed on a system at equilibrium, the position of the equilibrium shifts in a direction that tends to reduce the effect of that change.
Le Châtelier’s Principle

- When a reactant or product is added to a system at equilibrium, the system shifts away from the added component.
- If something is removed, the system shifts toward that side.
Suppose the reaction system

$$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$$

has reached equilibrium. Predict the effect of each of the following changes on the position of equilibrium.

1) \(\text{SO}_2(g)\) is added to the system.
2) The \(\text{SO}_3(g)\) present is liquefied and removed from the system.
3) Some of the \(\text{O}_2(g)\) is removed from the system.
Le Châtelier’s Principle

- If the volume of a gas is decreased, the pressure is increased (a la Boyle’s Law).
- This increase in pressure causes a system shift to reduce the pressure.
- This will be the side with fewer moles of gas present.
- A decrease in pressure will have the opposite effect.
Le Châtelier’s Principle

Consider the homogeneous reaction:

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

If the volume is decreased, the pressure increases. To offset the pressure increase, the system shifts to the right, toward the side with the smaller number of gas particles.

There are 4 moles of gas reactants and only 2 moles of gas products.

The opposite is also true.
Practice

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

1) $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$

2) $\text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$
Le Châtelier’s Principle

- It should be noted all of these stresses we have placed on systems to this point have only changed the equilibrium position, not $K$.
- If we change the temperature of the system, we WILL change $K$.
- We can predict the direction of change in $K$.
- To do so, we need to classify the reactions as exo- or endothermic.
Le Châtelier’s Principle

- In **endothermic** reactions we consider heat to be a **reactant**.
- In **exothermic** reactions we consider heat to be a **product**.
- Consider the exothermic reaction:
  \[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons \text{2 NH}_3(g) + 92\text{kJ} \]
- Energy is considered a product, so adding heat would be the same as adding \( \text{NH}_3(g) \): a shift to the left.
Practice

1) The reaction

\[ \text{C}_2\text{H}_2(\text{g}) + 2\text{Br}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_2\text{Br}_4(\text{g}) \]

is exothermic as written. Will an increase in temperature shift the position of equilibrium left or right?

2) The reaction

\[ \text{ZrI}_4(\text{s}) \rightleftharpoons \text{Zr}(\text{s}) + 2\text{I}_2(\text{g}) \]

is endothermic as written. Will an increase in temperature shift the position of equilibrium left or right?
Le Châtelier’s Principle: Summary

Using the following reaction, predict what will happen in each situation:

\[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \]

<table>
<thead>
<tr>
<th>Change</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add ( \text{N}_2\text{O}_4(g) )</td>
<td>Left</td>
</tr>
<tr>
<td>Add ( \text{NO}_2(g) )</td>
<td>Right</td>
</tr>
<tr>
<td>Remove ( \text{N}_2\text{O}_4(g) )</td>
<td>Right</td>
</tr>
<tr>
<td>Remove ( \text{NO}_2(g) )</td>
<td>Left</td>
</tr>
<tr>
<td>Decrease Vol.</td>
<td>Right</td>
</tr>
<tr>
<td>Increase Vol.</td>
<td>Left</td>
</tr>
</tbody>
</table>
Applications Involving the Equilibrium Constant

- If we know the value of $K$ and all concentrations involved but one, we can use the knowns to find the unknown, for example the reaction:
  \[ \text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g}) \]

- If the concentrations of both $\text{F}_2(\text{g})$ and $\text{H}_2(\text{g}) = 0.0021 \text{ M}$ at equilibrium and $K = 2.1 \times 10^3$, what is $[\text{HF}]$?
1) Assume the equilibrium constant for the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

has a K value of $2.4 \times 10^{-3}$ at a particular temperature. When the system is analyzed at equilibrium at this temperature, it is found that $[H_2O(g)] = 1.1 \times 10^{-1} \text{ M}$ and $[H_2(g)] = 1.9 \times 10^{-2} \text{ M}$. What is the concentration of $O_2(g)$?