Chapter 12: Chemical Equilibrium

- Chemical Equilibrium
- Equilibrium Constants
- Equilibrium Concentrations
- Le Châtelier’s Principle
- Solubility Equilibrium
- Acid and Bases
- Free Energy and Chemical Equilibrium

Forward and Reverse Reactions

- Water in an open system, such as a glass, will slowly evaporate, decreasing the amount of liquid water over time.
- Water in a closed system, such as a covered glass, will establish a dynamic equilibrium, where the amount of liquid water present does not decrease over time.

- This photo sequence shows the water level in two glasses over the course of 17 days. The glass on the left is covered.
Forward and Reverse Reactions

• The equilibrium between liquid and vapor in a closed container is governed by the kinetics of evaporation and condensation.
  – In (c), the two rates are equal.

![Diagram of Forward and Reverse Reactions](image)

Forward and Reverse Reactions

• At the start of a chemical reaction, the reactant concentrations decrease over time, with a corresponding decrease in rate of the forward reaction.

• As the reactants are being consumed, the product concentration increases, with a corresponding increase in the rate of the reverse reaction.

• When the rate of the forward reaction equals the rate of the reverse reaction, the reaction has reached equilibrium.
  – Reactants form products at the same rate the products reform the reactants.
  – The concentrations of reactants and products do not change over time at equilibrium.
**Forward and Reverse Reactions**

A chemical system reaches equilibrium when the rate of the forward reaction equals the rate of the reverse reaction. The concentration of products and reactants does not change at equilibrium.

**Chemical Equilibrium**

- The state where the concentrations of all the reactants and products remain *constant* with time.

- On the *molecular level*, there is frantic activity. Equilibrium is not static, but is a *highly dynamic* situation.
Molecular Representation of Equilibrium

A molecular representation of the reaction $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ over time in a closed vessel.

a) Initially all NO$_2$

b) Some NO$_2$ has been converted to N$_2$O$_4$

c) Equilibrium has been reached

d) Concentrations are remaining constant

Mathematical Relationships

• For any reaction involving reactants, R, and products, P, the chemical reaction is written at equilibrium with a double arrow.

\[ R \rightleftharpoons P \]

• Rate laws for the forward and reverse reaction can be written.

\[ \text{Rate}_{\text{for}} = k_{\text{for}}[R] \]
\[ \text{Rate}_{\text{rev}} = k_{\text{rev}}[P] \]
Mathematical Relationships

- At equilibrium \( \text{Rate}_{for} = \text{Rate}_{rev} \).
  - Therefore \( k_{for}[R] = k_{rev}[P] \)
  - or \( \frac{k_{for}}{k_{rev}} = \frac{[P]_{eq}}{[R]_{eq}} = K \)
  - Since both \( k_{for} \) and \( k_{rev} \) are constants, and as long as temperature does not change, the left hand side of the equation is a constant.
  - This means at a given temperature, the ratio \( [P]_{eq}/[R]_{eq} \) is also a constant, \( K \).

Equilibrium Constants

- The amounts of reactants and products are determined using a mathematical model to describe equilibrium.
  - A relationship exists between reactant and product concentrations at equilibrium (the ratio of products to reactants is constant at a given temperature).
- This relationship is often called the law of mass action.
The Equilibrium (Mass Action) Expression

- For the general chemical equation
  \[ a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D} \]

- A ratio of concentrations, whether or not at equilibrium, can be defined, where \( Q \) is the reaction quotient.
  \[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

- At equilibrium, \( Q = K \), the equilibrium constant, and this ratio becomes the equilibrium expression.
  \[ K = \frac{[C]^c_{\text{eq}}[D]^d_{\text{eq}}}{[A]^a_{\text{eq}}[B]^b_{\text{eq}}} \]

General Expressions of Equilibrium Constant

\[ a \text{ A} + b \text{ B} \rightleftharpoons g \text{ G} + h \text{ H} \]

Equilibrium constant = \( K = \frac{[G]^g[H]^h}{[A]^a[B]^b} \)

Thermodynamic

Equilibrium constant = \( K_{\text{eq}} = \frac{(a_G)^g(a_H)^h}{(a_A)^a(a_B)^b} \)

\[ a_B = \frac{[B]}{c_B^0} = \gamma_B[B] \quad c_B^0 \text{ is a standard reference state} \]

\[ = 1 \text{ mol L}^{-1} \text{ (ideal conditions)} \]
Units and the Equilibrium Constant

• The equilibrium constant $K$ is dimensionless.
  
  – The concentrations used to calculate the equilibrium constant are divided by the standard concentration of 1 M, which has no numerical consequence.
  
  – A dimensionless $K$ is required when $K$ is used as the argument in a natural log function.

Pure Liquids and Solids

• Equilibrium constant expressions do not contain concentration terms for solid or liquid phases of a single component (that is, pure solids or liquids).
  – Pure solids and liquids have an activity of one

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

\[
K = [\text{CO}_2]
\]
Pure Solids and Liquids

• For the decomposition reaction of $\text{CaCO}_3(s)$ forming $\text{CaO}(s)$ and $\text{CO}_2(g)$, the equilibrium constant only depends on the $\text{CO}_2$ concentration because $\text{CaCO}_3$ and $\text{CaO}$ are solids.

Homogeneous and Heterogeneous Equilibria

• *Homogeneous equilibria* - the reactants and products are in the same phase, either gaseous or aqueous.

• *Heterogeneous equilibria* - the reactants and products are in different phases.
  
  – Heterogeneous equilibrium expressions *do not contain terms for solids and liquids.*
**Gas Phase Equilibria: $K_p$ vs. $K_C$**

- Equilibrium expressions can be written for gas phase reactions using partial pressures.
  - $K_p$ is the equilibrium constant in terms of partial pressures.

$$a \text{ A(g)} + b \text{ B(g)} \rightleftharpoons c \text{ C(g)} + d \text{ D(g)}$$

$$K_p = \frac{(P_c)^{eq} (P_d)^{eq}}{(P_a)^{eq} (P_b)^{eq}}$$

**Gas Phase Equilibria: $K_p$ vs. $K_C$**

- The values of $K_c$ and $K_p$ are not necessarily equal.

The relationship between $K_c$ and $K_p$ is:

$$K_p = K_c \left( RT \right)^{\Delta n_{\text{gas}}}$$

- $\Delta n_{\text{gas}}$ is moles of product gas minus the moles of reactant gas.
- Only when $\Delta n_{\text{gas}} = 0$ does $K_p = K_c$.
- Often the subscript “c” is omitted:
  $$K_c = K$$
**Equilibrium Constant Expression Example #1**

Write the proper expression for $K$ for each of the following equilibria.

(a) $4 \text{NH}_3(g) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{N}_2(g) + 6 \text{H}_2\text{O}(g)$

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

(c) $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$

(d) $\text{Co(OH)}_2(s) + \text{H}_2(g) \rightleftharpoons \text{Co}(s) + 2 \text{H}_2\text{O}(g)$

**The Significance of the Magnitude of the Equilibrium Constant.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant, $K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(l)$</td>
<td>$1.4 \times 10^{83}$ at 298 K</td>
</tr>
<tr>
<td>$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$</td>
<td>$1.9 \times 10^{-23}$ at 298 K</td>
</tr>
<tr>
<td>$2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$</td>
<td>1.0 at about 1200 K</td>
</tr>
<tr>
<td>$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$</td>
<td>3.4 at 1000 K</td>
</tr>
<tr>
<td>$1.6 \times 10^{-21}$ at 298 K</td>
<td>10.0 at about 1100 K</td>
</tr>
</tbody>
</table>

$K >> 1 \rightarrow$ [products]$\gg$[reactants] $\rightarrow$ Reaction is product-favored

$K << 1 \rightarrow$ [products]$\ll$[reactants] $\rightarrow$ Reaction is reactant-favored
Equilibrium Concentrations

• The equilibrium concentrations of reactants and products for a chemical reaction can be predicted using the balanced chemical equation and known equilibrium constants.
  
  – There are three basic features for the strategy used in any equilibrium calculation.
    • Write a balanced chemical equation for the relevant equilibrium or equilibria.
    • Write the corresponding equilibrium expression or expressions.
    • Create a table of concentrations for all reacting species.
      – Often call an ICE table (Initial conc., Change in conc. and Equilibrium Conc.)

Equilibrium Concentrations

• Equilibrium concentrations can be determined from initial concentrations by realizing:
  
  – The first row contains the Initial concentrations.
  – The second row contains the Changes in the initial concentrations as the system come to equilibrium.
  – The third row contains the final Equilibrium concentrations.
  – ICE Table

• Equilibrium concentrations can be determined from initial concentrations by realizing which direction the reaction will shift to achieve equilibrium, express the concentration change in terms of a single variable, and solve for the equilibrium concentrations using the equilibrium expression.
Equilibrium Calculations #1

Equilibrium is established for the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$ at 25°C. The quantities of the two gases present in a 3.00 liter vessel are 7.64 g $\text{N}_2\text{O}_4$ and 1.56 g $\text{NO}_2$. What is the value of $K$ for this reaction?

Equilibrium Calculations #2

Equilibrium is established for the reaction $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$ at 900K. When a 0.0200 mol sample of $\text{SO}_3(g)$ is introduced into a 1.52 liter vessel, 0.0142 mol of $\text{SO}_3(g)$ is found to be present at equilibrium. What is the value of $K$ for this reaction?

Equilibrium Calculations #3

A 0.0240 mol sample of $\text{N}_2\text{O}_4(g)$ is allowed to dissociate and come to equilibrium with $\text{NO}_2(g)$ in an 0.372 liter flask at 25°C. What is the percent dissociation of the $\text{N}_2\text{O}_4$?

\[
\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2(g) \quad K = 4.61 \times 10^{-3}
\]

Equilibrium Calculations #4

A solution is prepared having these initial concentrations: $[\text{Fe}^{3+}] = [\text{Hg}_2^{2+}] = 0.5000$ M; $[\text{Fe}^{2+}] = [\text{Hg}^{2+}] = 0.03000$ M. The following reaction occurs among these ions at 25°C.

\[
2 \text{Fe}^{3+} + \text{Hg}_2^{2+} \rightleftharpoons 2 \text{Fe}^{2+} + 2 \text{Hg}^{2+} \quad K = 9.14 \times 10^{-6}
\]

What will be the ionic concentrations when equilibrium is reached?
The Reaction Quotient, $Q$: Predicting the Direction of Net Change.

$$\text{CO(g)} + 2 \text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$$

- Equilibrium can be approached various ways.
- Qualitative determination of change of initial conditions as equilibrium is approached is needed.

$$Q = \frac{[G]^c[B]^h}{[A]^a[B]^b}$$

At equilibrium $Q = K$

**Reaction Quotient**

Initial condition: (a) Pure reactants, (b) “Left” of equilibrium, (c) Equilibrium, (d) “Right” of equilibrium, (e) Pure products.

Reaction proceeds: $Q_c = 0 < K_c = K_c > K_c = \infty$

- to the right
- to the left
**Predicting the Direction of Net Change Example**

Consider the equilibrium among $N_2(g)$, $H_2(g)$ and $NH_3(g)$ in 1 liter flask.

\[ N_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad K = 9.5 \text{ at } 300^\circ\text{C} \]

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

<table>
<thead>
<tr>
<th>$n_{N_2}$</th>
<th>$n_{H_2}$</th>
<th>$n_{NH_3}$</th>
<th>Q</th>
<th>Direction of change</th>
<th>$[\text{NH}_3]$ ↑ or ↓</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td>0.3</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1.7</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Place the last mixture in a 10 liter flask (conc. ↓ by a factor of 10)

| 0.3 | 1.7 | 1 |

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**Le Châtelier’s Principle**

- *Le Châtelier’s principle* - When a system at equilibrium is stressed, it responds by reestablishing equilibrium to reduce the stress.

- There are three common means to introduce a stress to an equilibrium.
  - Changes in concentration
  - Changes in pressure (or volume)
  - Changes in temperature
Effect of a Change in Concentration

• For a reaction at equilibrium, a change in concentration for one or more of the reactants and/or products will disturb the equilibrium.
  − The system will react to re-establish equilibrium.

• For a reaction at equilibrium, increasing the concentration of one of the reactants will shift the equilibrium toward the products.
  − After addition $Q < K$, so the equilibrium shifts to the right
  − The reactant concentration will decrease as reactant is converted to product, and the product concentration will increase. So $Q$ increases until $Q = K$.

Effect of a Change in Concentration

Placed in an empty flask, $\text{NO}_2$ achieves equilibrium by reacting to form $\text{N}_2\text{O}_4$.

Once at equilibrium, additional $\text{NO}_2$ is added. The system responds to this stress by shifting the equilibrium toward $\text{N}_2\text{O}_4$. 
Effect of a Change in Concentration

Table 12.2

The effects of concentration changes on equilibrium can be rationalized by considering the reaction quotient, \( Q \), and comparing it to the equilibrium constant, \( K \).

<table>
<thead>
<tr>
<th>Type of Concentration Change</th>
<th>Resulting Change in ( Q )</th>
<th>Response of System</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Products] increased</td>
<td>( Q &gt; K )</td>
<td>More reactants formed</td>
</tr>
<tr>
<td>[Products] decreased</td>
<td>( Q &lt; K )</td>
<td>More products formed</td>
</tr>
<tr>
<td>[Reactants] increased</td>
<td>( Q &lt; K )</td>
<td>More products formed</td>
</tr>
<tr>
<td>[Reactants] decreased</td>
<td>( Q &gt; K )</td>
<td>More reactants formed</td>
</tr>
</tbody>
</table>

Effect of a Change in Pressure

• For reactions involving gases, if the number of moles of gas differs between reactants and products, a shift in pressure (due to a volume change) will result in a change in equilibrium position.
  
  – For an increase in pressure, the equilibrium will shift toward the side of the equation with fewer moles of gas.
  
  – For a decrease in pressure, the equilibrium will shift toward the side of the equation with more moles of gas.

• Adding an inert gas at a constant volume has no impact on the equilibrium position.
  
  – Total pressure increases but the partial pressure of the reactants remains the same.
Effect of a Change in Pressure

- For the equilibrium between \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \), the increase in pressure is offset by reducing the moles of gas present by forming \( \text{N}_2\text{O}_4 \).
- Decreasing the volume from 10 L to 2 L initially increases the pressure from 1.0 atm to 5.0 atm.
  - Equilibrium is re-established when the pressure is reduced to 4.6 atm by reacting 2 \( \text{NO}_2 \) to form \( \text{N}_2\text{O}_4 \).

Effect of a Change in Temperature on Equilibrium

- During a temperature change, heat flows in or out of the reacting system.
  - Heat is treated as a product for an exothermic reaction.
    \[
    \text{Reactants} \rightleftharpoons \text{Products} + \text{Heat}
    \]
  - Heat is treated as a reactant for an endothermic reaction.
    \[
    \text{Reactants} + \text{Heat} \rightleftharpoons \text{Products}
    \]
- Increase the temperature, equilibrium shifts away from the side with the heat.
- Decrease the temperature, equilibrium shifts toward the side with the heat.
- Note: temperature changes affect the value of the K.
Effect of a Change in Temperature on Equilibrium

- Temperature effect on the equilibrium between NO₂ and N₂O₄, an exothermic reaction.
  - As temperature increases, the amount of NO₂ increases, as indicated by the deepening color of the NO₂ gas in the 50°C water bath (right) compared to the ice bath (left).

<table>
<thead>
<tr>
<th>Type of Reaction</th>
<th>Type of Temperature Change</th>
<th>Response of System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic</td>
<td>$T$ increase</td>
<td>More reactants formed</td>
</tr>
<tr>
<td>Exothermic</td>
<td>$T$ decrease</td>
<td>More products formed</td>
</tr>
<tr>
<td>Endothermic</td>
<td>$T$ increase</td>
<td>More products formed</td>
</tr>
<tr>
<td>Endothermic</td>
<td>$T$ decrease</td>
<td>More reactants formed</td>
</tr>
</tbody>
</table>
Effect of a Catalyst on Equilibrium

- When a catalyst is added to a system at equilibrium, there is no impact on the equilibrium position.
  - *Catalysts* speed up the rate of the forward and reverse reactions **to the same extent**.
  - The equilibrium concentrations of products and reactants do not change.
  - But a catalyst does affect the *rate* at which equilibrium is attained.

Le Châtelier’s Principle Example

Consider the following equilibrium processes:

\[ 2\text{N}_2(g) + 6\text{H}_2\text{O}(g) \rightleftharpoons 4\text{NH}_3(g) + 3\text{O}_2(g) \ \Delta H = 1486.4 \text{ kJ/mol} \]

\[ 2\text{N}_2(g) + 6\text{H}_2\text{O}(l) \rightleftharpoons 4\text{NH}_3(g) + 3\text{O}_2(g) \ \Delta H = 1530.4 \text{ kJ/mol} \]

Indicate the effect on the mass of NH₃ and the value of K by:

<table>
<thead>
<tr>
<th>Action taken</th>
<th>$\text{H}_2\text{O}(g)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Some N₂ removed</td>
<td>$m_{\text{NH}_3}$</td>
<td>K</td>
</tr>
<tr>
<td>Some H₂O added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume increased</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature decreased</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A catalyst is added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon gas is added</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Effects of Changes on the System

1. Concentration:
   a. The system will shift away from an added component.
   b. The system will shift toward from removed component.

2. Pressure:
   a. Addition of inert gas at constant volume does not affect the equilibrium position.
   b. Decreasing the volume shifts the equilibrium toward the side with fewer moles of gas.
   c. Increasing the volume shifts the equilibrium toward the side with more moles of gas.

3. Temperature: $K$ will change depending upon the temperature (treat the energy change as a reactant).

Acids and Bases

- *Strong acids* and *strong bases* completely dissociate in solution.

- *Weak acids* and *weak bases* only partially dissociate in solution.
  
  - Partial dissociation is due to an equilibrium for the weak acid or base.

- A *Brønsted-Lowry acid* is a proton donor.

- A *Brønsted-Lowry base* is a proton acceptor.
The Role of Water in the Brønsted-Lowry Theory

- When an acid ionizes in water, the acid transfers a proton to water, creating hydronium, H₃O⁺.
  \[ \text{HA(aq)} + \text{H}_2\text{O(ℓ)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

- When a base ionizes in water, water transfers a proton to the base, creating hydroxide, OH⁻.
  \[ \text{B(aq)} + \text{H}_2\text{O(ℓ)} \rightarrow \text{OH}^-(aq) + \text{HB}^+(aq) \]

- A substance, such as water, that can be either an acid or a base is referred to as amphoteric.
  \[ \text{H}_2\text{O(ℓ)} + \text{H}_2\text{O(ℓ)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

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The Role of Water in the Brønsted-Lowry Theory

- The reaction between a weak acid or base and water is a dynamic equilibrium.
  - The equilibrium is composed of two conjugate acid-base pairs.
    - The conjugate acid of a base is the acid formed when the base accepted a proton.
    - The conjugate base of an acid is the base formed when the acid donated a proton.
The Role of Water in the Bronsted-Lowry Theory

- For the equilibrium between ammonia and water,

\[
\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

- \(\text{NH}_3\) is the base and \(\text{NH}_4^+\) is the conjugate acid.

- \(\text{H}_2\text{O}\) is the acid and \(\text{OH}^-\) is the conjugate base.

<table>
<thead>
<tr>
<th>Acid Ionization Constant</th>
<th>Base Ionization Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}][\text{H}_2\text{O}]})</td>
<td>(K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]})</td>
</tr>
<tr>
<td>(K_a = K_{[\text{H}_2\text{O}]} = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]})</td>
<td>(K_b = K_{[\text{H}_2\text{O}]} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]})</td>
</tr>
</tbody>
</table>
Relative Strengths of Some Acids and Bases

<table>
<thead>
<tr>
<th>Increasing acid strength</th>
<th>Conjugate pairs</th>
<th>Increasing base strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perochloric acid</td>
<td>HClO₄⁻</td>
<td>Perchlorate ion</td>
</tr>
<tr>
<td>Hydroiodic acid</td>
<td>HI</td>
<td>I⁻</td>
</tr>
<tr>
<td>Hydrobromic acid</td>
<td>HBr</td>
<td>Bromide ion</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>Chloride ion</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>Hydrogen sulfate ion</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>Nitrate ion</td>
</tr>
<tr>
<td>Hydronium ion</td>
<td>H₃O⁺</td>
<td>Water</td>
</tr>
<tr>
<td>Hydrogen sulfate ion</td>
<td>HSO₄⁻</td>
<td>Sulfate ion</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂</td>
<td>Nitrite ion</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>HC₂H₃O₂</td>
<td>Acetate ion</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H₂CO₃</td>
<td>Hydrogen carbonate ion</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH₄⁺</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Hydrogen carbonate ion</td>
<td>H₂CO₃⁻</td>
<td>Carbonate ion</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>Hydroxide ion</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>Methoxide ion</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>Amide ion</td>
</tr>
</tbody>
</table>

HCl + OH⁻ ⇌ Cl⁻ + H₂O  \[ \text{NH}_4^+ + \text{CO}_3^{2-} \not\Rightarrow \text{NH}_3 + \text{HCO}_3^- \]

HClO₄ + H₂O ⇌ ClO₄⁻ + H₃O⁺  \[ H_2O + I^- \not\Rightarrow OH^- + HI \]

An acid base reaction always proceeds to form the weaker acid and base. H₃O⁺ and OH⁻ are the strongest acid and base that can be present in an aqueous solution.

**Leveling Effect**

- In aqueous solutions, H₃O⁺ (aq) & OH⁻ (aq) are the strongest acids & bases that exist.

Stronger bases react with water to form OH⁻ (aq).
\[ \text{O}_2^- (aq) + \text{H}_2\text{O} (\ell) \rightarrow \text{OH}^- (aq) + \text{OH}^- (aq) \]

Stronger acids react with water to form H₃O⁺ (aq).
\[ \text{HCl} (aq) + \text{H}_2\text{O} (\ell) \rightarrow \text{H}_3\text{O}^+ (aq) + \text{Cl}^- (aq) \]

This is known as the **Leveling Effect**
The Self-Ionization of Water

Ion Product of Water

\[ K_w = K[H_2O][H_2O] = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at 25°C} \]

Consider

- \( HA + H_2O \leftrightarrow A^- + H_3O^+ \) \( K_a \)
- \( A^- + H_2O \leftrightarrow HA + OH^- \) \( K_b \)

\[ K_a \cdot K_b = \left( \frac{[A^-]}{[HA]} \right) \left( \frac{[HA]}{[A^-]} \right) = [H_3O^+][OH^-] = K_w \]

\[ K_b = \frac{K_w}{K_a} \text{ so } K_b \propto \frac{1}{K_a} \]
The pH Scale and pH Values of some Common Substances

- The pH scale provides an easy way to measure the relative acidity or basicity of aqueous solutions.
Strong Acids and Bases

In calculating $[\text{H}_3\text{O}^+]$ in an aqueous solution of a strong acid, the strong acid is the only significant source of $\text{H}_3\text{O}^+$. 

$$[\text{H}_3\text{O}^+] = [\text{HA}]$$

In calculating $[\text{OH}^-]$ in an aqueous solution of a strong base, the strong base is the only significant source of $\text{OH}^-$. 

$$[\text{OH}^-] = [\text{B}]$$

### The Common Strong Acids and Strong Bases

<table>
<thead>
<tr>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>LiOH</td>
</tr>
<tr>
<td>HBr</td>
<td>NaOH</td>
</tr>
<tr>
<td>HI</td>
<td>KOH</td>
</tr>
<tr>
<td>HClO₄</td>
<td>RbOH</td>
</tr>
<tr>
<td>HNO₃</td>
<td>CsOH</td>
</tr>
<tr>
<td>H₂SO₄⁺</td>
<td>Mg(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Sr(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Ba(OH)₂</td>
</tr>
</tbody>
</table>

*H₂SO₄ ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 687).*

### Strong Acid and Bases Examples

1. Calculate the pH of a solution of 0.400 g of HI in 500. ml of solution.

2. Calculate the mass of Sr(OH)₂ which must be dissolved in 600. ml of solution to make a pH of 12.00 at 25°C.
**Weak Acids**

- Weak acids react with water to produce a conjugate acid-base system in which the acid and base in the products are stronger than their conjugate acid and base in the reactants.
  - Weak acid equilibria favor reactants.
  - Only a small percentage of acid molecules ionize.

\[ \text{HA(aq)} + \text{H}_2\text{O(ℓ)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

- The $K$ for the dissociation of a weak acid is called the *acid ionization constant*, $K_a$.

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

**Weak Bases**

- For weak bases, an ionization equilibrium and equilibrium expression can be written.

\[ \text{B(aq)} + \text{H}_2\text{O(ℓ)} \rightleftharpoons \text{OH}^-(aq) + \text{HB}^+(aq) \]

- The $K$ for the reaction of a weak base with water is called the *base ionization constant*, $K_b$.

\[ K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \]

- $K_a K_b = K_w$
Illustration of Strong and Weak Acids

Graphic representation of the behavior of acids of different strengths in aqueous solution.
(a) A strong acid.
(b) A weak acid.

Illustration of Strong and Weak Acids

(a) A strong acid HA is completely ionized in water.
(b) A weak acid HB exists mostly as undisassociated HB molecules in water.

Note that the water molecules are not shown in this figure.
Direction of Reaction Example

Predict the direction favored in each of the following acid-base reactions. That is, does the reaction tend to go more in the forward or in the reverse direction?

1) \( \text{HOC}_6\text{H}_5 + \text{C}_2\text{H}_3\text{O}_2^- \rightleftharpoons \text{C}_6\text{H}_5\text{O}^- + \text{HC}_2\text{H}_3\text{O}_2 \)
2) \( \text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3 \)
3) \( \text{HSO}_4^- + \text{NO}_3^- \rightleftharpoons \text{HNO}_3 + \text{SO}_4^{2-} \)
4) \( \text{C}_2\text{H}_5\text{N} + \text{NH}_4^+ \rightleftharpoons \text{C}_2\text{H}_5\text{NH}^+ + \text{NH}_3 \)
5) \( \text{HClO}_2 + \text{OCl}^- \rightleftharpoons \text{ClO}_2^- + \text{HOCl} \)
6) \( \text{C}_2\text{H}_5\text{NH}^+ + \text{CN}^- \rightleftharpoons \text{C}_2\text{H}_5\text{N} + \text{HCN} \)
7) \( \text{HC}_2\text{H}_3\text{O}_2^- + \text{NH}_3 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{NH}_4^+ \)
Weak Acid/Base Examples

Determining a Value of $K_a$ from the pH of a Solution of a Weak Acid.

1. Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine $K_a$ for butyric acid.

2. Calculate the pH of a 0.20 M solution of KF at 25°C, $K_b$ for $\text{F}^-$ is $1.5 \times 10^{-11}$

Free Energy and Chemical Equilibrium

- Equilibrium is a state of minimum free energy.
  - $\Delta G = 0$ at equilibrium.

- A chemical system tends to move spontaneously toward equilibrium.
  - When equilibrium is reached, the change in free energy is zero.
Graphical Perspective

- Chemical reactions always proceed toward a minimum in free energy.

Free Energy and Nonstandard Conditions

- For reactions with negative free energy changes, the equilibrium is product-favored, or the value of $K$ is greater than 1.

- For reactions with positive free energy changes, the equilibrium is reactant-favored, or the value of $K$ is less than 1.

- The value of the equilibrium constant can be calculated from the Gibbs free energy change, or vice versa.

$$\Delta G^\circ = -RT \ln K$$
**ΔG° and K Examples**

1. What is the value of the equilibrium constant $K_p$ for the equilibrium at 25°C?

$$2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$$

Given

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta G_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(g)</td>
<td>86.57</td>
</tr>
<tr>
<td>NOCl(g)</td>
<td>66.07</td>
</tr>
</tbody>
</table>

2. At 25°C HBrO has a $K_a$ of $2.3 \times 10^{-9}$ what is $\Delta G°$ for the dissociation of HBrO at 25°C?

3. Does the decomposition of CaCO$_3$(s) occur to any significant extent at 25°C?

**Synthesis of Ammonia**

The optimum conditions are only for the equilibrium position and do not take into account the *rate* at which equilibrium is attained.