Chemical Equilibrium

Equilibrium Constants

- For a generic chemical reaction, the equilibrium constant is defined as:
  \[ aA + bB \rightleftharpoons cC + dD \]  
  \[ K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

- The “equilibrium constant”, \( K_{eq} \), for a chemical reaction indicates whether the reactants or the products will be favored in an equilibrium process.

Equilibrium Constants

- For the reverse reaction
  \[ cC + dD \rightleftharpoons aA + bB \]
  the equilibrium constant is the inverse of the forward reaction:
  \[ K_{eq2} = \frac{1}{K_{eq1}} = \frac{[A]^a[B]^b}{[C]^c[D]^d} \]

Equilibrium Constants

- When reactions are added to produce a net reaction, the net equilibrium constant is the product of the \( K_{eq} \)s for each reaction:
  \[ HA \rightleftharpoons H^+ + A^- \]  
  \[ H^+ + C \rightleftharpoons HC^+ \]  
  \[ HA + C \rightleftharpoons HC^+ + A^- \]  
  \[ K_1 = \frac{[H^+][A^-]}{[HA]} \]
  \[ K_2 = \frac{[HC^+]}{[H^+][C]} \]
  \[ K_{net} = K_1K_2 = \frac{[HC^+][A^-]}{[HA][C]} \]

Thermodynamics

- Enthalpy, \( \Delta H \), is a measure of the change in heat content between reactants and products
  \[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g) \]
  \[ \Delta H_{rxn} = -802.34 \text{ kJ} \]
  - Methane releases heat to surrounding when combusted
  - NaCl(s) → Na^+(aq) + Cl^-(aq)
  \[ \Delta H_{rxn} = 3.87 \text{ kJ} \]
  - Sodium chloride takes heat from surroundings when dissolved

Thermodynamics

- Entropy, \( \Delta S \), is a measure of the change of disorder when going from reactants to products
  \[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g) \]
  \[ \Delta S_{rxn} = -5.14 \text{ J/K} \]
  - The products are more ordered than the reactants
  - NaCl(s) → Na^+(aq) + Cl^-(aq)
  \[ \Delta S_{rxn} = 43.4 \text{ J/K} \]
  - The products are more disordered than the reactants—more space between ions in solution
Thermodynamics

- Gibb’s Free Energy, $\Delta G$, is a measure of the energy available to do work following reaction.
- Definition: $\Delta G = \Delta H - T \Delta S$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$$
$$\Delta G^0_{\text{rxn}} = -800.78 \text{ kJ}$$

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$\Delta S^0_{\text{rxn}} = -9.00 \text{ kJ}$$

- $\Delta G$ is also a measure of where the equilibrium for a reaction will lie:
  - If $\Delta G_{\text{rxn}} < 0$, the reaction is product favored
  - If $\Delta G_{\text{rxn}} > 0$, the reaction is reactant favored
  - If $\Delta G_{\text{rxn}} = 0$, the reaction is in equilibrium

- The equilibrium constant is related to the Gibb’s Free Energy:
  $$K_{eq} = \exp\{-\Delta G^0_{\text{rxn}}/RT\}$$
  $$R = \text{gas constant} = 8.314 \text{ J/mol} \cdot \text{K}$$
  $$T = \text{temperature (in K)}$$

Solubility Products

- The solubility product, $K_{sp}$, for a salt is a specific type of equilibrium constant
- Given an excess of salt, $K_{sp}$ for the salt will determine how much of the salt will dissolve in water:

$$M_xA_y(s) \leftrightarrow x M^{y+}(aq) + y A^{-}(aq)$$

$$K_{sp} = [M^{y+}]^x[A^{-}]^y$$

- Many salts are only slightly soluble
- The solubility product is a measure of the concentration of ions in a solution saturated with the salt

$$MA(s) \leftrightarrow M^+(aq) + A^-(aq) \quad K_{sp} = [M^+][A^-]$$

Examples

- $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq) \quad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$
- $PbCl_2(s) \leftrightarrow Pb^{2+}(aq) + 2 Cl^-(aq) \quad K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.7 \times 10^{-5}$
- $AuBr_3(s) \leftrightarrow Au^{3+}(aq) + 3 Br^-(aq) \quad K_{sp} = [Au^{3+}][Br^-]^3 = 4.0 \times 10^{-36}$

Knowing the $K_{sp}$, we can calculate the concentration of ions in solution

Examples

- $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq) \quad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

$$\begin{align*}
-x &\quad x &\quad x \\
\Rightarrow x^2 &\quad = 1.8 \times 10^{-10} \Rightarrow x = 1.3 \times 10^{-5} \text{ M} \quad [Ag^+] = [Cl^-]
\end{align*}$$

- $PbCl_2(s) \leftrightarrow Pb^{2+}(aq) + 2 Cl^-(aq) \quad K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.7 \times 10^{-5}$

$$\begin{align*}
-x &\quad x &\quad 2x \\
\Rightarrow x(2x)^2 &\quad = 1.7 \times 10^{-5} \Rightarrow x = 1.6 \times 10^{-2} \text{ M} \\
[\text{Pb}^{2+}] &\quad = 1.6 \times 10^{-2} \text{ M} \\
[\text{Cl}^-] &\quad = 3.2 \times 10^{-2} \text{ M}
\end{align*}$$
Solubility Products

**Examples**

**AuBr₃(s)**

\[ Au^{3+}(aq) + 3 Br^{-}(aq) \rightleftharpoons AuBr₃(s) \]

\[ K_{sp} = \left[ Au^{3+} \right] \left[ Br^{-} \right]^3 = 4.0 \times 10^{-36} \]

\[ x(3x)^3 = 4.0 \times 10^{-36} \]

\[ 27x^4 = 4.0 \times 10^{-36} \]

\[ x = 6.2 \times 10^{-10} \text{ M} \]

\[ [Au^{3+}] = 6.2 \times 10^{-10} \text{ M} \]

\[ [Br^{-}] = 1.9 \times 10^{-9} \text{ M} \]

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**Precipitation**

- Define ion quotient, Q, as:

  \[ M_x A_y(s) \rightarrow x M^{x+} + y A^{-} \]

  \[ Q = \left[ M^{x+} \right]^x \left[ A^{-} \right]^y \]

  Q looks just like \( K_{sp} \), but the system is not in equilibrium.

- A precipitate will form only when Q exceeds \( K_{sp} \):
  - \( Q < K_{sp} \): solution is unsaturated—no precipitate
  - \( Q > K_{sp} \): solution is saturated—precipitate forms
  - \( Q = K_{sp} \): solution at saturation point

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**Precipitation**

**Example:**

A solution contains 0.0200 M Pb²⁺ and 0.0500 M Ag⁺. You want to remove one of the ions from solution by adding Cl⁻ without precipitating the other ion.

- Which metal will precipitate first?

  \[ K_{sp}(AgCl) = [Ag^{+}][Cl^{-}] = 1.8 \times 10^{-10} \]
  \[ K_{sp}(PbCl₂) = [Pb^{2+}][Cl^{-}]^2 = 1.7 \times 10^{-5} \]

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**Precipitation**

**Example:**

How much Cl⁻ must be added before each metal begins to precipitate?

- **Silver:**

  \[ [Cl^{-}] = K_{sp}/[Ag^{+}] = 1.8 \times 10^{-10}/0.0500 = 3.6 \times 10^{-8} \text{ M} \]

- **Lead:**

  \[ [Cl^{-}] = (K_{sp}/[Pb^{2+}])^{1/2} = (1.7 \times 10^{-5}/0.0200) = 0.029 \text{ M} \]

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**Precipitation**

**Example:**

How much Ag⁺ will remain in solution when lead begins to precipitate?

- **Silver:**

  \[ [Cl^{-}] = 0.029 \text{ M when lead begins to precipitate} \]

  \[ [Ag^{+}] = K_{sp}/[Cl^{-}] = 1.8 \times 10^{-10}/0.029 = 6.2 \times 10^{-9} \text{ M} \]

  \[ \%Ag remaining = 6.2 \times 10^{-9}/0.0500 \times 100\% = 0.0000124\% \]
Complex Formation

- Frequently, a metal may combine with one or more simple anions or neutral species to form an ion soluble in water. The resulting ion is called a complex ion:

\[ \text{Cu}^{2+} + 4\text{NH}_3(aq) \rightarrow \text{Cu(NH}_3)_4^{2+}(aq) \]

\[ K_{eq} = 2.3 \times 10^{12} \]

Copper acts as a Lewis Acid (accepts pair of electrons) and ammonia acts as a Lewis Base (donates pair of electrons).

Example: Determine the concentration of Cu\(^{2+}\) in a 0.50 M NH\(_3\)(aq) solution

\[ \text{Cu}^{2+} + 4\text{NH}_3(aq) \rightarrow \text{Cu(NH}_3)_4^{2+}(aq) \]

because the equilibrium constant is large, the reaction will strongly favor the product.

.: let reaction go completely to right, and then allow some dissociation back to reactants

\[ \text{Cu}^{2+} + 4\text{NH}_3(aq) \rightarrow \text{Cu(NH}_3)_4^{2+}(aq) \]

\[ x \quad 4x \quad 0.125 - x \]

\[ K_{eq} = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4] = 2.3 \times 10^{12} \]

\[ \frac{(0.125 - x)}{x(4x)^4} = 2.3 \times 10^{12} \]

rearranging gives: \(256x^5 = \frac{0.125}{2.3 \times 10^{12}}\)

\[ x = 7.3 \times 10^{-4} \text{ M} = [\text{Cu}^{2+}] \]

Acids and Bases

- Brønsted-Lowry acids and base
  - Acid: H\(^+\) ion donor
  - Base: H\(^+\) ion acceptor
- A Brønsted-Lowry acids are also called protic acids because they donate protons (H\(^+\))

Conjugate Acids & Bases

- Acids react with bases and vice versa
- All acids and bases come with a conjugate pair—a base or acid, respectively, that is formed in conjunction with the original species.

Examples:

\[ \text{HCl(aq)} + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}^+(aq) + \text{Cl}^-(aq) \]

Conjugate acid

Conjugate base
Conjugate Acids & Bases

Examples

\[ \text{NaOH}(aq) + H_2O(\ell) \leftrightarrow \text{OH}^-(aq) + H_2O(\ell) + \text{Na}^+(aq) \]

Base          Acid    Conjugate  Conjugate

\[ \text{CH}_3\text{COOH}(aq) + H_2O(\ell) \leftrightarrow \text{CH}_3\text{COO}^-(aq) + H_3O^+(aq) \]

Acid          Base    Conjugate       Conjugate

Strengths of Acids and Bases

- Strong acids donate H\(^+\) ions more easily
  - The stronger the acid, the weaker the conjugate base associated with that acid
- Strong bases accept H\(^+\) ions more easily
  - The stronger the base, the weaker the conjugate acid associated with that base

\[ \text{pH} \]

- pH is a measure of the hydronium ion content of a solution
- pH is defined as:
  \[ \text{pH} = -\log[H_3O^+] \]
  - log is log base 10, not ln (natural log)
  - \[H_3O^+\] is given in molar units (M)
- pH of pure water (\([H_3O^+] = 1.0 \times 10^{-7} \text{ M}\)):
  \[ \text{pH} = -\log(1.0 \times 10^{-7}) = 7.0 \]

The pH Scale

- Neutral is defined as the pH of pure water:
  \[ \text{pH} = 7 \]
- Acidic solutions have pH lower than 7:
  \[ \text{pH} < 7 \Rightarrow \text{acidic} \]
- Basic solutions have pH larger than 7:
  \[ \text{pH} > 7 \Rightarrow \text{basic} \]

The pOH Scale

- We can also use pOH to describe a solution
- pOH is defined as:
  \[ \text{pOH} = -\log[OH^-] \]
- The sum of pH and pOH must equal 14
  \[ \text{pH} + \text{pOH} = 14 \]
  - assuming room temperature (25 °C)
The pH Scale

Example
Find $[\text{H}_3\text{O}^+]$ of a solution that has pH = 9.37

Method 1: Calculate pH, then $[\text{H}_3\text{O}^+]$

Step 1: Determine pH
\[ \text{pH} = 14 - \text{pOH} = 14.00 - 9.37 = 4.63 \]

Step 2: Determine $[\text{H}_3\text{O}^+]$
\[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.63} = 2.34 \times 10^{-5} \text{ M} \]

Ionization Constants

The extent of dissociation of an acid or base in H$_2$O can be quantified using its ionization constant—$K_a$ is a specific type of equilibrium constant

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

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

$[\text{HA}] = $ undissociated acid in solution

Example:
Acetic acid has a $K_a = 1.8 \times 10^{-5}$

Determine the pH of a 0.2 M acetic acid solution

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \]

\begin{align*}
\text{initial} & : 0.2 & 0 & 0 \\
\Delta & : -x & x & x \\
equilibrium & : 0.2-x & x & x
\end{align*}

\[ x = \sqrt{1.8 \times 10^{-7} \times 0.2} = 0.0019 \text{ M} \]

\[ \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0019) = 2.7 \]

Ionization Constants

Example (con’t):

Determine the pH of a 0.2 M acetic acid solution

\[ K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \]

\[ 1.8 \times 10^{-5} = \frac{x^2}{0.2-x} \Rightarrow x = 0.0019 \text{ M} \]

\[ \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0019) = 2.7 \]

Ionization Constants

$K_b$ is a specific equilibrium constant for bases

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

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

$[\text{B}] = $ undissociated base in solution

\begin{align*}
\text{example (continued)} & : \text{Find} [\text{H}_3\text{O}^+] \text{ of a solution that has pOH } = 9.37 \\
\text{Method 2: Calculate} [\text{OH}^-], \text{ then} [\text{H}_3\text{O}^+] \text{ using} K_w \\
\text{Step 1: Determine} [\text{OH}^-] \\
[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.37} = 4.27 \times 10^{-10} \text{ M} \\
\text{Step 2: Determine} [\text{H}_3\text{O}^+] \text{ using} K_w \\
[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{4.27 \times 10^{-10}} = 2.34 \times 10^{-5} \text{ M} \\
\end{align*}
Ionization Constants

Example:
Determine $[B]$ in a $1.82 \times 10^{-3}$ M solution of NH$_3$

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

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<th>NH$_3$</th>
<th>NH$_4^+$</th>
<th>OH$^-$</th>
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<td>$\Delta$</td>
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<td>equil</td>
<td>$1.82 \times 10^{-3} - x$</td>
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\[
K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}
\]

$x = 1.72 \times 10^{-4} \text{ M} = [\text{NH}_4^+] = [\text{OH}^-]$ \[\text{[NH}_3\text{]} = 1.82 \times 10^{-3} \text{ M} - 1.72 \times 10^{-4} \text{ M} = 1.65 \times 10^{-3} \text{ M}\]

Ionization Constants

$K_a$ and $K_b$ are related through $K_w$ (autoionization constant of water):

$K_w = K_a \cdot K_b$

$K_a = K_w/K_b$

$K_b = K_w/K_a$

Example: Acetic acid has $K_a = 1.8 \times 10^{-5}$. What is $K_b$ for acetate ion ($\text{CH}_3\text{COO}^-$)?

$K_b = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$