Chemical Equilibrium

Equilibrium Constants

- For a generic chemical reaction, the equilibrium constant is defined as:

  $$aA + bB \leftrightarrow cC + dD \qquad (1)$$

  $$K_{eq1} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

- 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

  $cC + dD \leftrightarrow aA + bB$ (2)

  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:

  $HA \leftrightarrow H^+ + A^-$ (1)

  $H^+ + C \leftrightarrow HC^+$ (2)

  $HA + C \leftrightarrow HC^+ + A^-$ (net)

$$K_1 = \frac{[H^+]\,[A^-]}{[HA]} \qquad K_2 = \frac{[HC^+]}{[H^+][C]}$$

$$K_{net} = K_1K_2 = \frac{[HC^+][A^-]}{[HA][C]}$$

Thermodynamics

- Enthalpy, ΔH, is a measure of the change in heat content between reactants and products

  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$

  $\Delta H^o_{rxn} = -802.34$ kJ

  - Methane releases heat to surrounding when combusted

  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

  $\Delta H^o_{rxn} = 3.87$ kJ

  - Sodium chloride takes heat from surroundings when dissolved

Thermodynamics

- Entropy, ΔS, is a measure of the change of disorder when going from reactants to products

  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$

  $\Delta S^o_{rxn} = -5.14$ J/K

  - The products are more ordered than the reactants

  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

  $\Delta S^o_{rxn} = 43.4$ J/K

  - The products are more disordered than the reactants—more space between ions in solution

Thermodynamics

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

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$

$\Delta G^o_{rxn} = -800.78$ kJ

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

$\Delta S^o_{rxn} = -9.00$ kJ

Thermodynamics

- ΔG is also a measure of where the equilibrium for a reaction will lie:
  - If $\Delta G_{rxn} < 0$, the reaction is product favored
  - If $\Delta G_{rxn} > 0$, the reaction is reactant favored
  - If $\Delta G_{rxn} = 0$, the reaction is in equilibrium
- The equilibrium constant is related to the Gibb's Free Energy:

$K_{eq} = \exp\{-\Delta G^o_{rxn}/RT\}$

R = gas constant = 8.314 J/mol·K

T = 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:

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

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

Solubility Products

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

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

<u>Examples</u>

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

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

$AuBr_3(s) \leftrightarrow Au^{3+}(aq) + 3\, Br^-(aq)$ $\quad$ $K_{sp}=[Au^{3+}][Br^-]^3=4.0\text{x}10^{-36}$

Solubility Products

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

Examples

$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$ $K_{sp}=[Ag^+][Cl^-]=1.8x10^{-10}$

∞-x x x

$x^2 = 1.8 \times 10^{-10}$ $\Rightarrow$ $x = 1.3 \times 10^{-5}$ M = $[Ag^+] = [Cl^-]$

Solubility Products

Examples

$PbCl_2(s) \leftrightarrow Pb^{2+}(aq) + 2\ Cl^-(aq)$ $K_{sp}=[Pb^{2+}][Cl^-]^2=1.7x10^{-5}$

∞-x x 2x

$x(2x)^2 = 1.7 \times 10^{-5}$

$4x^3 = 1.7 \times 10^{-5}$ $\Rightarrow$ $x = 1.6 \times 10^{-2}$ M

$[Pb^{2+}] = 1.6 \times 10^{-2}$ M

$[Cl^-] = 3.2 \times 10^{-2}$ M

Solubility Products

Examples

$AuBr_3(s) \leftrightarrow Au^{3+}(aq) + 3\,Br^-(aq)$ $K_{sp}=[Au^{3+}][Br^-]^3=4.0\times10^{-36}$

∞-x x 3x

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

$27x^4 = 4.0 \times 10^{-36} \Rightarrow x = 6.2 \times 10^{-10}$ M

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

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

Solubility Products

Examples—Common ion effect

How much PbI_2 will dissolve in a 0.0100 M solution of NaI?

$PbI_2(s) \leftrightarrow Pb^{2+}(aq) + 2\,I^-(aq)$ $K_{sp} = 8.7 \times 10^{-9}$

∞-x x 2x + .0100

$x(2x+.0100)^2 = 8.7 \times 10^{-9}$

$x(4x^2 + 0.0400x + 1.0\times10^{-4}) = 8.7 \times 10^{-9}$

$4x^3 + .0400x^2 + 1.0\times10^{-4}x - 8.7\times10^{-9} = 0$

$x = 8.4 \times 10^{-5}$ M

vs 1.3×10^{-3} M if no $I^-(aq)$ were present initially

Precipitation

- Define ion quotient, Q, as:

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

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

  Q looks just like K_{eq}, 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

Precipitation

Example: a solution contain 0.0200 M Pb^{2+} and 0.0500M Ag^+. You want to remove one of the ions from solution by adding Cl^- without precipitating the other ion.

- Which metal will precipitate first?

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

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

Precipitation

Example:

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

  Silver: $[Cl^-] = K_{sp}/[Ag^+] = 1.8 \times 10^{-10}/0.0500$

  $= 3.6 \times 10^{-9}$ M

  Lead: $[Cl^-] = \{K_{sp}/[Pb^{2+}]\}^{1/2}$

  $= \{1.7 \times 10^{-5}/0.0200\}$

  $= 0.029$ M

Precipitation

Example:

- How much Ag^+ will remain in solution when lead begins to precipitate?
  - $[Cl^-] = 0.029$ M when lead begins to precipitate

  $[Ag^+] = K_{sp}/[Cl^-] = 1.8 \times 10^{-10}/0.029$

  $= 6.2 \times 10^{-9}$ M

  %Ag remaining $= 6.2 \times 10^{-9}/0.0500 \times 100\%$

  $= .0000124\%$

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:

  $Cu^{2+} + 4NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq)$

  $K_{eq} = 2.3 \times 10^{12}$

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

Complex Formation

Cu^{2+} electron configuration: [Ar] $4s^2\ 3d^6$

Cu^{2+} hybridizes to sp^3d^2 which leaves unoccupied hybrid orbitals

Each NH_3 has an electron lone pair on the nitrogen atom which fills the hybrid orbitals to make a complex ion:

$$\begin{matrix} & :NH_3 & \\ H_3N: & Cu^{2+} & :NH_3 \\ & :NH_3 & \end{matrix} \Rightarrow \left[\begin{matrix} & NH_3 & \\ & | & \\ H_3N- & Cu & -NH_3 \\ & | & \\ & NH_3 & \end{matrix}\right]^{2+}$$

Complex Formation

<u>Example:</u> Determine the concentration of Cu^{2+} in a 0.50 M $NH_3(aq)$ solution

$Cu^{2+} + 4NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq)$

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

$\therefore$ let reaction go completely to right, and then allow some dissociation back to reactants

$Cu^{2+} + 4NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq)$

x 4x 0.125 - x

Complex Formation

<u>Example:</u> Determine the concentration of Cu^{2+} in a 0.50 M $NH_3(aq)$ solution

$$K_{eq} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.3 \times 10^{12}$$

$$= \frac{(0.125 - x)}{x\,(4x)^4} = 2.3 \times 10^{12} \qquad \text{assume x is negligible}$$

$$\text{rearranging gives}: 256\,x^5 = \frac{0.125}{2.3\text{x}10^{12}}$$

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

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

<u>Examples</u>

$$HCl(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + Cl^-(aq)$$

acid base conjugate acid conjugate base

Conjugate Acids & Bases

<u>Examples</u>

NaOH(aq) + $H_2O(\ell)$ ↔ OH^-(aq) + $H_2O(\ell)$ + Na^+(aq)

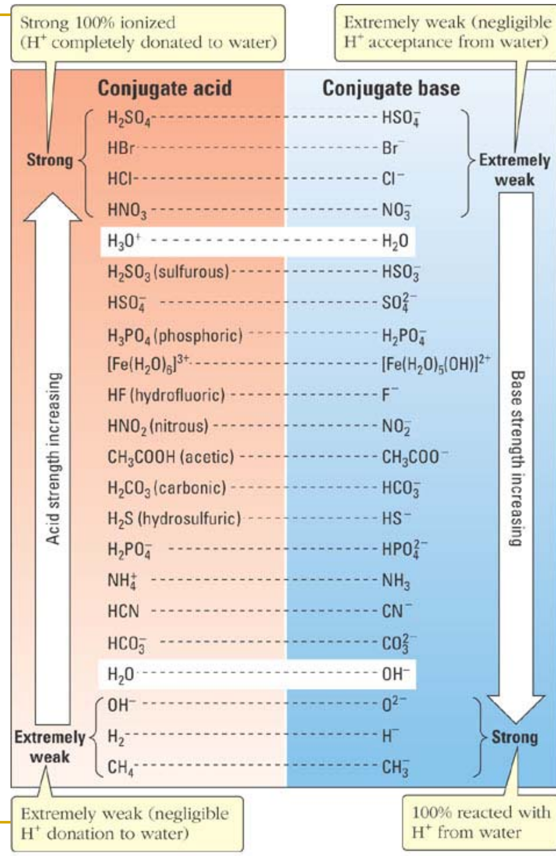
base acid conjugate base conjugate acid

CH_3COOH(aq) + $H_2O(\ell)$ ↔ CH_3COO^-(aq) + H_3O^+(aq)

acid base conjugate base conjugate acid

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



The pH Scale

- pH is a measure of the hydronium ion content of a solution
- pH is defined as:

  $pH = -\log[H_3O^+]$

  log is log base 10, not ln (natural log)

  $[H_3O^+]$ is given in molar units (M)
- pH of pure water ($[H_3O^+] = 1.0 \times 10^{-7}$ M):

  $pH = -\log(1.0 \times 10^{-7}) = 7.0$

The pH Scale

- Neutral is defined as the pH of pure water:

  $pH = 7$
- Acidic solutions have pH lower than 7:

  $pH < 7 \Rightarrow$ acidic
- Basic solutions have pH larger than 7:

  $pH > 7 \Rightarrow$ basic

The pH Scale

- We can also use pOH to describe a solution
- pOH is defined as:

  $pOH = -\log[OH^-]$
- The sum of pH and pOH must equal 14

  $pH + pOH = 14$

  assuming room temperature (25 ^oC)

The pH Scale

<u>Example</u>

Find $[H_3O^+]$ of a solution that has pOH = 9.37

Method 1: Calculate pH, then $[H_3O^+]$

Step 1: Determine pH

$pH = 14 - pOH = 14.00 - 9.37 = 4.63$

Step 2: Determine $[H_3O^+]$

$[H_3O^+] = 10^{-pH} = 10^{-4.63} = 2.34 \times 10^{-5}$ M

The pH Scale

<u>Example (con't.)</u>

Find $[H_3O^+]$ of a solution that has pOH = 9.37

Method 2: Calculate $[OH^-]$, then $[H_3O^+]$ using K_w

Step 1: Determine $[OH^-]$

$[OH^-] = 10^{-pOH} = 10^{-9.37} = 4.27 \times 10^{-10}$ M

Step 2: Determine $[H_3O^+]$ using K_w

$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(4.27 \times 10^{-10})$

$= 2.34 \times 10^{-5}$ M

Ionization Constants

- The extent of dissociation of an acid or base in H_2O can be quantified using its *ionization constant*—K_a is a specific type of equilibrium constant

$$HA(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

acid base c. acid c. base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][\text{conjugate base}]}{[\text{acid}]}$$

[HA] = undissociated acid in solution

Ionization Constants

Example:

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

Determine the pH of a 0.2 M acetic acid solution

$$CH_3COOH(aq) + H_2O(\ell) \leftrightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

	CH_3COOH	CH_3COO^-	H_3O^+
initial	0.2	0	0
Δ	-x	x	x
equil	.2 – x	x	x

Ionization Constants

Example (con't.): Determine the pH of a 0.2 M acetic acid solution

$$K_a = 1.8 \times 10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{.2 - x} \quad \Rightarrow \quad x = 0.0019\,M$$

$$pH = -\log[H_3O^+] = -\log(.0019) = 2.7$$

Ionization Constants

- K_b is a specific equilibrium constant for bases

$$B(aq) + H_2O(l) \leftrightarrow HB^+(aq) + OH^-(aq)$$

base acid c. acid c. base

$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{[OH^-][\text{conjugate acid}]}{[\text{base}]}$$

[B] = undissociated base in solution

Ionization Constants

Example:

Determine [B] in a 1.82×10^{-3} M solution of NH_3

$NH_3(aq) + H_2O(\ell) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

	NH_3	NH_4^+	OH^-
initial	1.82×10^{-3}	0	0
Δ	-x	x	x
equil	$1.82 \times 10^{-3} - x$	x	x

Ionization Constants

Example:

$NH_3(aq) + H_2O(\ell) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

$$K_b = 1.8\times10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{1.82\times10^{-3} - x}$$

$x = 1.72 \times 10^{-4}$ M $= [NH_4^+] = [OH^-]$

$[NH_3] = 1.82 \times 10^{-3}$ M $- 1.72 \times 10^{-4}$ M

$= 1.65 \times 10^{-3}$ M

Ionization Constants

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

  $K_a \cdot K_b = K_w$

  $K_a = K_w/K_b$

  $K_b = K_w/K_a$

- Example: Acetic acid has $K_a = 1.8 \times 10^{-5}$. what is K_b for acetate ion (CH_3COO^-)?

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