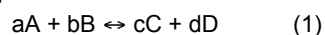


Chemical Equilibrium

Equilibrium Constants

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

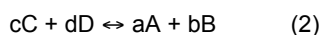


$$K_{\text{eq1}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- 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

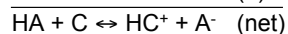
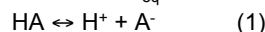


the equilibrium constant is the inverse of the forward reaction:

$$K_{\text{eq2}} = \frac{1}{K_{\text{eq1}}} = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

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:

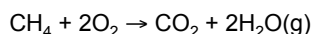


$$K_1 = \frac{[H^+][A^-]}{[HA]} \quad K_2 = \frac{[HC^+]}{[H^+][C]}$$

$$K_{\text{net}} = K_1 K_2 = \frac{[HC^+][A^-]}{[HA][C]}$$

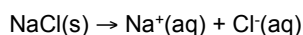
Thermodynamics

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



$$\Delta H_{\text{rxn}}^{\circ} = -802.34 \text{ kJ}$$

- Methane releases heat to the surrounding when combusted

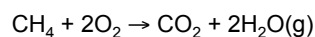


$$\Delta H_{\text{rxn}}^{\circ} = 3.87 \text{ kJ}$$

- Sodium chloride takes heat from the surroundings when dissolved

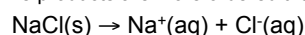
Thermodynamics

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



$$\Delta S_{\text{rxn}}^{\circ} = -5.14 \text{ J/K}$$

- The products are more ordered than the reactants



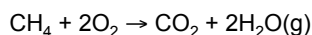
$$\Delta S_{\text{rxn}}^{\circ} = 43.4 \text{ J/K}$$

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

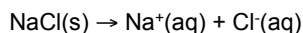
Thermodynamics

- Gibb's Free Energy, ΔG , is a measure of the energy available to do work following reaction

- Definition: $\Delta G = \Delta H - T\Delta S$



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



$$\Delta G^\circ_{\text{rxn}} = -9.00 \text{ kJ}$$

Thermodynamics

- ΔG 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:

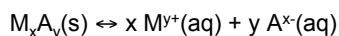
$$K_{\text{eq}} = \exp\{-\Delta G^\circ_{\text{rxn}}/RT\}$$

$$R = \text{gas constant} = 8.314 \text{ J/mol}\cdot\text{K}$$

$$T = \text{temperature (in K)}$$

Solubility Products

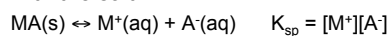
- The solubility product, K_{sp} , for a salt is a specific type of equilibrium constant
- Given an excess of salt, K_{sp} for the salt will determine how much of the salt will dissolve in water:



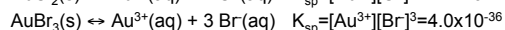
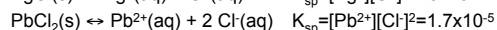
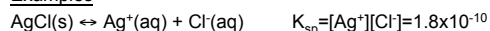
$$K_{\text{sp}} = [\text{M}^{y+}]^x [\text{A}^{x-}]^y$$

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



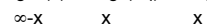
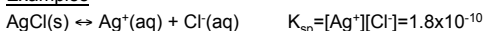
Examples



Solubility Products

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

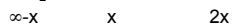
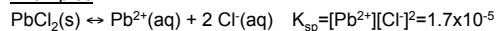
Examples



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

Solubility Products

Examples



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

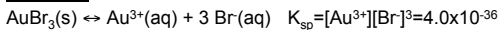
$$4x^3 = 1.7 \times 10^{-5} \Rightarrow x = 1.6 \times 10^{-2} \text{ M}$$

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

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

Solubility Products

Examples



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

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

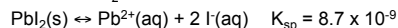
$$[\text{Au}^{3+}] = 6.2 \times 10^{-10} \text{ M}$$

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

Solubility Products

Examples—Common ion effect

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



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

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

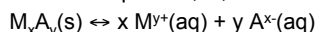
$$4x^3 + .0400x^2 + 1.0 \times 10^{-4}x - 8.7 \times 10^{-9} = 0$$

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

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

Precipitation

- Define ion quotient, Q, as:



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

Q looks just like K_{eq} , but the system is not in equilibrium

- A precipitate will form only when Q exceeds K_{sp}
 - $Q < K_{\text{sp}}$: solution is unsaturated—no precipitate
 - $Q > K_{\text{sp}}$: solution is saturated—precipitate forms
 - $Q = K_{\text{sp}}$: 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?

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

$$K_{\text{sp}}(\text{PbCl}_2) = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = 1.7 \times 10^{-5}$$

Precipitation

Example:

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

$$\begin{aligned} \text{Silver: } [\text{Cl}^{-}] &= K_{\text{sp}}/[\text{Ag}^{+}] = 1.8 \times 10^{-10}/0.0500 \\ &= 3.6 \times 10^{-9} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{Lead: } [\text{Cl}^{-}] &= \{K_{\text{sp}}/[\text{Pb}^{2+}]\}^{1/2} \\ &= \{1.7 \times 10^{-5}/0.0200\}^{1/2} \\ &= 0.029 \text{ M} \end{aligned}$$

Precipitation

Example:

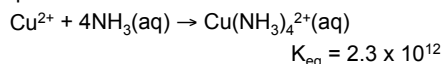
- How much Ag^{+} will remain in solution when lead begins to precipitate?

$$\begin{aligned} [\text{Cl}^{-}] &= 0.029 \text{ M when lead begins to precipitate} \\ [\text{Ag}^{+}] &= K_{\text{sp}}/[\text{Cl}^{-}] = 1.8 \times 10^{-10}/0.029 \\ &= 6.2 \times 10^{-9} \text{ M} \end{aligned}$$

$$\begin{aligned} \% \text{Ag remaining} &= 6.2 \times 10^{-9}/0.0500 \times 100\% \\ &= .0000124\% \end{aligned}$$

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:



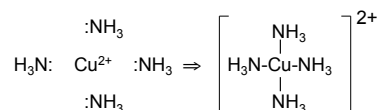
Copper acts as a Lewis Acid (accepts pair of electrons) and ammonia acts as a Lewis Base (donates pair of electrons)

Complex Formation

Cu^{2+} electron configuration: $[\text{Ar}] 4s^2 3d^7$

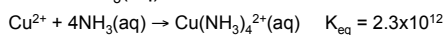
Cu^{2+} hybridizes to sp^3d^2 which leaves unoccupied hybrid orbitals

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



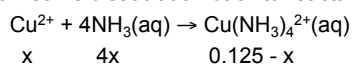
Complex Formation

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



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



Complex Formation

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

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

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

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

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

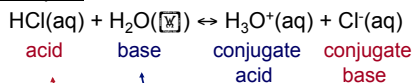
Acids and Bases

- Brønsted-Lowry acids and base
 - Acid: H^+ ion donor
 - Base: H^+ ion acceptor
- 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



acid base conjugate acid conjugate base



The pH Scale

Example

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

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

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

The pH Scale

Example (con't.)

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

Method 2: Calculate $[\text{OH}^-]$, then $[\text{H}_3\text{O}^+]$ using K_w

Step 1: Determine $[\text{OH}^-]$

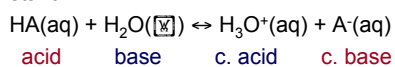
$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.37} = 4.27 \times 10^{-10} \text{ M}$$

Step 2: Determine $[\text{H}_3\text{O}^+]$ using K_w

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (4.27 \times 10^{-10}) \\ = 2.34 \times 10^{-5} \text{ M}$$

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



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

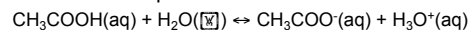
$[\text{HA}]$ = undissociated acid in solution

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	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

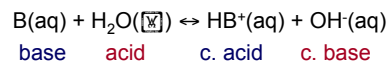
$$K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

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

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(.0019) = 2.7$$

Ionization Constants

- K_b is a specific equilibrium constant for bases



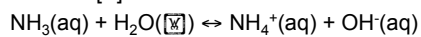
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} = \frac{[\text{OH}^-][\text{conjugate acid}]}{[\text{base}]}$$

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

Ionization Constants

Example:

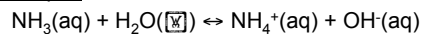
Determine [B] in a 1.82×10^{-3} M solution of NH_3



	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:



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.82 \times 10^{-3} - x}$$

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

$$\begin{aligned} [\text{NH}_3] &= 1.82 \times 10^{-3} \text{ M} - 1.72 \times 10^{-4} \text{ M} \\ &= 1.65 \times 10^{-3} \text{ M} \end{aligned}$$

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^-)?

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