Chemical Equilibrium

GENERAL CONCEPTS OF CHEMICAL EQUILIBRIUM

This Lecture introduces equilibria for the solubility of ionic compounds, complex formation, and acid-base reactions.

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Chemical Equilibrium

The state where the concentrations of all reactants and products remain constant with time. Equilibrium is not static, but is a highly dynamic situation

Chemical equilibrium provides a foundation not only for chemical analysis, but also for other subjects such as biochemistry, geology, and oceanography.

2-Chemical Reactions: The Rate Concept

A + B $\longrightarrow$ C + D (forward Reaction)

C + D $\longrightarrow$ A + B (reverse Reaction)

The Equilibrium Constant

For the reaction $aA + bB \rightleftharpoons cC + dD$

we write the **equilibrium constant,** K, in the form

Equilibrium constant:

$$\text{Rate}_{fwd} = k_{fwd}[A]^a[B]^b$$

where rate_{fwd} is the rate of the forward reaction

k_{fwd} is the **rate constant**

[A] and [B] represent the molar concentrations of A and B.

$$\text{Rate}_{rev} = k_{rev}[C]^c[D]^d$$

At equilibrium, the rate of the reverse reaction equals the rate of the forward reaction.

$k_{fwd}[A]^a[B]^b = k_{rev}[C]^c[D]^d$

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_{fwd}}{k_{rev}} = K$$

Law of Mass Action

Which states that the rate of a chemical reaction is proportional to the "active masses" of the reacting substances present at any time. The active masses may be concentrations or pressures

- The law of mass action applies to solution and gaseous equilibria

1. Concentrations of solutes should be expressed as moles per liter.
2. Concentrations of gases should be expressed in bars.
3. Concentrations of pure solids, pure liquids, and solvents are omitted because they are unity.

1) Homogeneous Equilibria

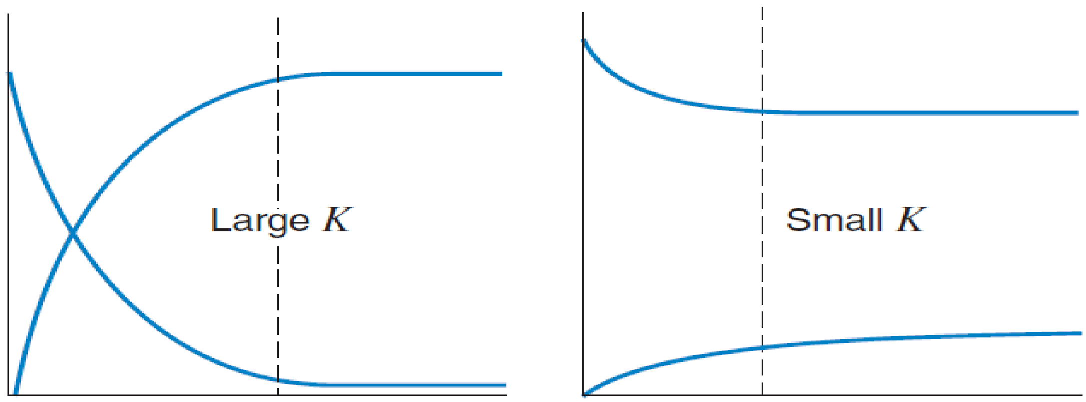
All reactants and products are in one phase.
gases for example K can be used in terms of either concentration or pressure

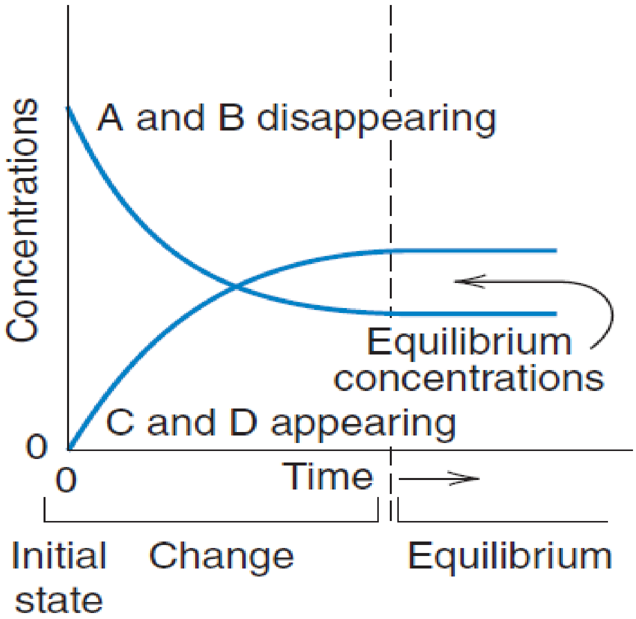
2) Heterogeneous Equilibria

If the reaction involves pure solids or pure liquids as well as gases, the concentration of the solid or the liquid does not change.

Progress of a Chemical Reaction:

The larger the equilibrium constant, the farther to the right is the reaction at equilibrium.





Types of Equilibria

Equilibrium constants may be written for dissociations, associations, reactions, or distributions.

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acid dissociation constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

Equilibrium Constants for Dissociating or Combining Species Weak Electrolytes and Precipitates:

- When a substance dissolves in water, it will often partially or completely dissociate or ionize.
- Electrolytes that tend to dissociate only partially are called weak electrolytes, and those that tend to dissociate completely are strong electrolytes.
- For example, acetic acid only partially ionizes in water and is therefore a weak electrolyte.

- But hydrochloric acid is completely ionized and is therefore a strong electrolyte.

Equilibrium Constants for Acid – Base **equilibrium system**

$$HA \rightleftharpoons H^+ + A^- \qquad K_1 = \frac{[H^+][A^-]}{[HA]}$$

$$H^+ + A^- \rightleftharpoons HA \qquad K_1' = \frac{[HA]}{[H^+][A^-]} = 1/K_1$$

$$
\begin{array}{lcl}
\text{HA} & \rightleftharpoons & \cancel{[\text{H}^+]} + \text{A}^- \qquad K_1 \\
\cancel{[\text{H}^+]} + \text{C} & \rightleftharpoons & \text{CH}^+ \qquad K_2 \\
\hline
\text{HA} + \text{C} & \rightleftharpoons & \text{A}^- + \text{CH}^+ \qquad K_3
\end{array}
$$

$$K_3 = K_1K_2 = \frac{\cancel{[\text{H}^+]}[\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{CH}^+]}{\cancel{[\text{H}^+]}[\text{C}]} = \frac{[\text{A}^-][\text{CH}^+]}{[\text{HA}][\text{C}]}$$

Some species dissociate stepwise. A compound A_2B, for example, may dissociate as follows:

$$\text{A}_2\text{B} \rightleftharpoons \text{A} + \text{AB} \quad K_1 = \frac{[\text{A}][\text{AB}]}{[\text{A}_2\text{B}]}$$

$$\text{AB} \rightleftharpoons \text{A} + \text{B} \quad K_2 = \frac{[\text{A}][\text{B}]}{[\text{AB}]}$$

$$\text{A}_2\text{B} \rightleftharpoons 2\text{A} + \text{B} \qquad K_{\text{eq}} = \frac{[\text{A}]^2[\text{B}]}{[\text{A}_2\text{B}]}$$

$$K_{\text{eq}} = K_1K_2 = \frac{[\text{A}][\text{AB}]}{[\text{A}_2\text{B}]} \cdot \frac{[\text{A}][\text{B}]}{[\text{AB}]}$$

$$= \frac{[\text{A}]^2[\text{B}]}{[\text{A}_2\text{B}]}$$

$$K_{\text{forward}} = 1/K_{\text{backward}}$$