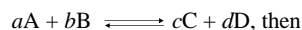


Chapters 6 and 8 Chemical Equilibrium & Activity

Equilibrium Constant

Most chemical systems are governed by equilibria such that if:



$$K = \frac{(ac)^c (ad)^d}{(aa)^a (ab)^b} \text{ where } ax = \gamma[X], \gamma \text{ is the activity coefficient}$$

In dilute solutions, $\gamma \rightarrow 1$, if we assume $\gamma = 1$,

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

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

Table 6.1

Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid-base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a , acidity constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{m-}$	K_{sp} , solubility product
Complex formation	$M^{n+} + aL^{z-} \rightleftharpoons ML_n^{(n-az)+}$	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

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Equilibrium Constant



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

- If K is very large, that the equilibrium lies far to the right (or towards products). If K is small, the reaction lies towards reactants.
- Knowledge of reaction stoichiometry and the equilibrium constant allows us to make some predictions about the system.

Important items to regarding K expressions

1. All solute concentrations should be in mol/L (M).
2. All gas concentrations should be in atmospheres.
3. By convention, all K's are calculated relative to 1 M solutions or 1 atm gas, so the resulting constants are dimensionless.
4. Concentrations of pure solids, pure liquids and solvents are omitted from the equilibrium constant expression.

Equilibrium constant expressions are thermodynamic relations.

Equilibrium and Thermodynamics

- Gibbs free energy:

$$\Delta G^\circ = -RT \ln K$$

$$K = e^{-\Delta G^\circ / RT}$$

- If $K > 1 \rightarrow \Delta G^\circ < 0 \rightarrow$ Spontaneous
- If $K < 1 \rightarrow \Delta G^\circ > 0 \rightarrow$ NOT Spontaneous

Reaction Quotient (Q)

The equilibrium constant expression with non-equilibrium concentrations plugged in.

- If $Q > K$, the reaction must proceed to the left
- If $Q < K$, the reaction must proceed to the right
- If $Q = K$ the reaction is at equilibrium

Using equilibria to characterize systems

Solubility: solubility product (K_{sp})

Complexation: formation constants (K_f), cumulative formation constants (β_n) (Ch.12)

Acids and Bases: acid dissociation constant (K_a), base hydrolysis constant (K_b)

Solubility

The solubility product (K_{sp}) describes the concentrations of species present when ions are in equilibrium with undissolved salt.

Example: $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$
 $K = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/[\text{CaCO}_3] = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{sp} = 6.0 \times 10^{-9}$

What is the concentration of calcium in a saturated solution of calcium carbonate?

This presence of carbonate results in a *common ion effect*. What should happen?

Solubility - Separation by precipitation

It is possible to quantitatively separate two or more species based on their solubility.

Ability to do so is related to the magnitudes of the K_{sp} for each ion.

Example:

Is it possible to precipitate 99% of 0.010M Ce^{3+} by adding oxalate ($\text{C}_2\text{O}_4^{2-}$) without precipitate 0.010M Ca^{2+} ?

CaC_2O_4 $K_{sp} = 1.3 \times 10^{-8}$

$\text{Ce}_2(\text{C}_2\text{O}_4)_3$ $K_{sp} = 3.0 \times 10^{-29}$

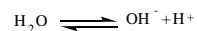
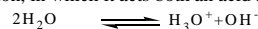
Solubility – Common Ion Effects

A salt will be less soluble if one of its constituent ions is already present in the solution.

Example: What is the solubility of ferric hydroxide in pH 8.0 buffered aqueous solution

Acids and Bases

- Definitions: Lewis – Electrons (acid: electron pair acceptor); Brønsted-Lowry (acid: proton donor)
- Conjugate Acid-Base Pairs: related by the gain or loss of one proton (ex. Acetic acid & acetate ion).
- Neutralization Reactions: reactions of acid and base to form salts and water
- Solvent Autoprotolysis or self-ionization: water is the most common, in which it acts both an acid and a base:



Autoprotolysis constant (equilibrium constants)

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

pH



P-function: $\text{pX} = -\log[\text{X}]$

$$\text{pH} = -\log[\text{H}^+]$$

$\text{pH} > 7$ is basic, $\text{pH} < 7$ is acidic

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00 \text{ at } 25^\circ\text{C}$$

Ex. Concentration of H^+ and OH^- in pure water at 25°C

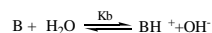
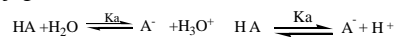
ANS: $1.0 \times 10^{-7} \text{ M}$

Acid and Base Strength

Based on percent dissociation in solution

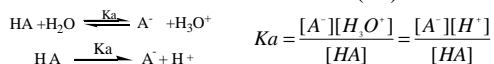
- *Strong* acids/bases dissociate essentially completely in water (Table 6-2, p.108)

- *Weak* acids/bases only partially dissociate, results in equilibrium concentrations of both the acid and its conjugate base



Weak Acid/Base Equilibria

- Weak Acid: acid dissociation constant (K_a)



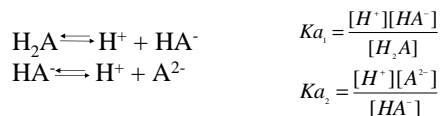
- Weak Base, hydrolysis reaction: base hydrolysis constant (K_b)



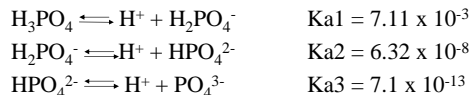
- Relationship between K_a and K_b for conjugate acid/base pairs:

$$K_w = K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Diprotic acids/Dibasic bases Polyprotic acids/Polybasic bases

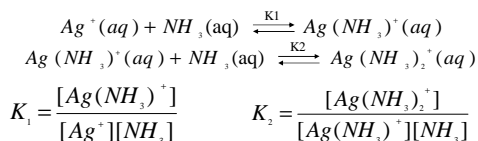


$K_{a1}, K_{a2} \dots$

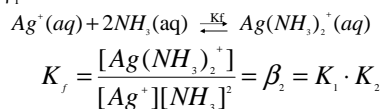


Complex Formation

Formation of coordinate bonds between Lewis Acids/Bases



Formation constants (K_f) are the equilibrium constants for complex ion formation. The overall, or cumulative, formation constants are denoted β_1



Activity

If $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, then

$$K = \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b} = \frac{(\gamma_c[\text{C}])^c (\gamma_d[\text{D}])^d}{(\gamma_a[\text{A}])^a (\gamma_b[\text{B}])^b}$$

where a_x is the activity of x

$a_x = \gamma_x[\text{X}]$, γ_x is the activity coefficient

$$K = \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b} = \frac{(\gamma_c[\text{C}])^c (\gamma_d[\text{D}])^d}{(\gamma_a[\text{A}])^a (\gamma_b[\text{B}])^b}$$

If $\gamma_x \rightarrow 1$, $a_x \rightarrow [\text{X}]$

Activity Coefficient

- Related to the size of the hydrated species
- Calculate γ using the extended Debye-Hückel equation, which relates activity coefficients to the ability of ions in solution to interact with one another.

$$\log r = -\frac{0.51z^2\sqrt{\mu}}{1 + \frac{\alpha\sqrt{\mu}}{305}}$$

z = charge of the ion
 α = effective diameter "hydrated" of the ion in nanometers
 μ = ionic strength of the solution

Ionic Strength

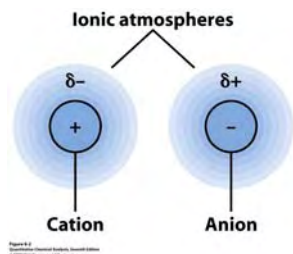
$$\mu = \frac{1}{2}(c_1z_1^2 + c_2z_2^2 + \dots) = \frac{1}{2}\sum_i c_i z_i^2$$

where c is concentration and z is charge of each ion

Ex. What is the ionic strength of a 0.010 M Na_2SO_4 ?
 $\frac{1}{2}\{(0.020*1)+(0.010*(-2)^2)\}=0.030 \text{ M}$

If add 0.020 M KBr ?
 $\frac{1}{2}\{(0.020*1) + (0.020*1) + (0.020*1) + (0.010*4)\}=0.050 \text{ M}$

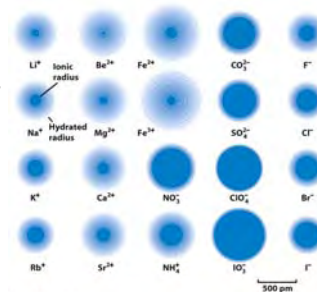
Ionic Strength and Ionic Atmospheres



The greater the ionic strength of a solution, the higher the charge in the ionic atmosphere. Each ion-plus-atmosphere contains less net charge and there is less attraction between any particular cation and anion.

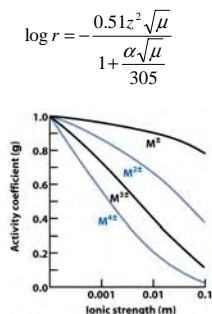
Hydrated Radius

- Ions with small ionic radii and large charge tend to more strongly bind to solvent molecules (Ion-dipole interactions).
- The result of this binding is a larger hydrated radius, causing diminished interaction with other ions.



Ionic Strength, Ion Charge, and Ion Size effect

- Increased ionic conc. \rightarrow decreased activity coefficient
- Increased ion charge (\pm) \rightarrow increased departure of activity coefficient from unity (Multiply charged ions are generally more likely to interact with other ions than singly charged.)
- Smaller hydrated radius \rightarrow increased importance of activity effects



pH Revisited

- Concentration is replaced with activity
 $\text{pH} = -\log a_{\text{H}^+} = -\log [\text{H}^+]\gamma_{\text{H}^+}$

Examples (P.147):

- Calculate the pH of pure water using activity coefficients correctly.
- Calculate the pH of water containing 0.10 M KCl at 25°C.