# Finding the Equilibrium Constant for a New Reaction

Although every equilibrium reaction has an equilibrium constant, values for these constants are tabulated for only a few specific types of reactions; these are: **solubility** reactions

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10}$$

where $K_{sp}$ is the solubility product; **acid dissociation** reactions

$$CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8\times10^{-5}$$

where $K_a$ is the acid dissociation constant; **base dissociation** reactions

$$NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$$

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

where $K_b$ is the base dissociation constant; and **complexation** reactions

$$Ag^+(aq) + NH_3(aq) \leftrightarrows Ag(NH_3)^+(aq)$$

$$K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = 2040$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$$

$$K_2 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]} = 8130$$

$$Ag^+(aq) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$$

$$\beta_2 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = K_1\times K_2 = 1.66\times10^7$$

where $K_1$ and $K_2$ are step-wise formation constants and $\beta_2$ is an overall formation constant. In addition, a few special reactions have equilibrium constants whose values are readily available. The most important of these is that for **water's dissociation**

$$2H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.00\times10^{-14}$$

The equilibrium constant for any other reaction is determined by finding ways to combine the equilibrium constant expressions for reactions such as those outlined above. To do so we take advantage of two important observations

- if an equilibrium reaction is reversed its new equilibrium constant is the reciprocal of the original equilibrium constant

- if two equilibrium reactions are added together, the equilibrium constant for the new reaction is the product of the two original equilibrium constants

For example, consider the equilibrium constant for the precipitation of AgCl. The reaction

$$Ag^+(aq) + Cl^-(aq) \leftrightarrows AgCl(s)$$

is the reverse of the solubility reaction for AgCl. The equilibrium constant, therefore, is the reciprocal of silver chloride's solubility product; thus

$$K = \frac{1}{[Ag^+][Cl^-]} = \frac{1}{K_{sp}} = \frac{1}{1.8\times10^{-10}} = 5.6\times10^9$$

Or, consider the solubility of AgCl in a solution of $NH_3$

$$AgCl(s) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

This reaction is the sum of the solubility reaction for AgCl and the overall formation constant for $Ag(NH_3)_2^+$

$$AgCl(s) \leftrightarrows \cancel{Ag^+(aq)} + Cl^-(aq)$$

$$\cancel{Ag^+(aq)} + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$$

thus, the equilibrium constant is just the product of $K_{sp}$ and $\beta_2$

$$K = K_{sp}\times\beta_2 = [Ag^+][Cl^-]\times\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = 3.0\times10^{-3}$$

Recognizing how to combine standard equilibrium constant reactions to make a new equilibrium reaction takes some practice. Here are a few examples that you will encounter in this course:

- Reaction of a weak acid, such as acetic acid, with a strong base

$$CH_3COOH(aq) + OH^-(aq) \leftrightarrows H_2O(l) + CH_3COO^-(aq)$$

If we look at this reaction in reverse we see that it is the reaction of a weak base with water; that is, the reverse reaction is the base dissociation reaction for the acetate ion. The equilibrium constant for this reaction, therefore, is

$$K = \frac{[CH_3COO^-]}{[CH_3COOH][OH^-]} = \frac{1}{K_b} = \frac{1}{5.7\times10^{-10}} = 1.75\times10^9$$

Alternatively, we can see this reaction as the sum of the acid dissociation reaction for acetic acid and the inverse of water's dissociation reaction

$$CH_3COOH(aq) + \cancel{H_2O(l)} \leftrightarrows \cancel{H_3O^+(aq)} + CH_3COO^-(aq)$$

$$\cancel{H_3O^+(aq)} + OH^-(aq) \leftrightarrows \cancel{2}H_2O(l)$$

giving

$$K = \frac{K_a}{K_w} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}\times\frac{1}{[H_3O^+][OH^-]} = \frac{1.75\times10^{-5}}{1.00\times10^{-14}} = 1.75\times10^9$$

- Reaction of a weak base, such as the acetate ion, with a strong acid

$$CH_3COO^-(aq) + H_3O^+(aq) \leftrightarrows H_2O(l) + CH_3COOH(aq)$$

If we look at this reaction in reverse we see that it is the reaction of a weak acid with water; that is, the reverse reaction is the base dissociation reaction for the acetic acid. The equilibrium constant for this reaction, therefore, is

$$K = \frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]} = \frac{1}{K_a} = \frac{1}{1.75\times10^{-5}} = 5.71\times10^4$$

- Solubility of a salt whose anion is a weak base, such as $CaF_2$, under conditions where the weak base is protonated

$$CaF_2(s) + 2H_3O^+(l) \leftrightarrows Ca^{2+}(aq) + 2HF(aq) + 2H_2O\ (aq)$$

If we look at this reaction we see that it is a summation of the solubility reaction for $CaF_2$ and the reverse of the acid dissociation reaction for HF; thus

$$CaF_2(s) \leftrightarrows Ca^{2+}(aq) + \cancel{2F^-(aq)}$$

$$\cancel{F^-(aq)} + H_3O^+(l) \leftrightarrows HF(aq) + H_2O(aq)$$

$$\cancel{F^-(aq)} + H_3O^+(l) \leftrightarrows HF(aq) + H_2O(aq)$$

The equilibrium constant, therefore, is

$$K = \frac{[Ca^{2+}][HF]^2}{[H_3O^+]^2} = \frac{K_{sp}}{(K_a)^2} = \frac{3.9\times10^{-11}}{(7.2\times10^{-4})^2} = 7.5\times10^{-5}$$

- Solubility of a salt, such as $CaF_2$, in the presence of a ligand, such as EDTA (which is abbreviated as $Y^{4-}$)

$$CaF_2(s) + Y^{4-}(aq) \leftrightarrows CaY^{2-}(aq) + 2F^-(aq)$$

This reaction is the summation of the solubility reaction for $CaF_2$ and the metal-ligand complexation reaction between $Ca^{2+}$ and EDTA; thus

$$CaF_2(s) \leftrightarrows \cancel{Ca^{2+}(aq)} + 2F^-(aq)$$

$$\cancel{Ca^{2+}(aq)} + Y^{4-}(aq) \leftrightarrows CaY^{2-}(aq)$$

The equilibrium constant, therefore, is

$$K = \frac{[CaY^{2-}][F^-]^2}{[Y^{4-}]} = K_{sp}\times K_1 = (3.9\times10^{-11})\times(4.9\times10^{10}) = 1.9$$