

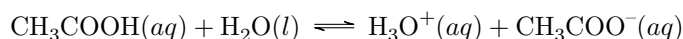
# Finding the Equilibrium Constant for a New Reaction

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***



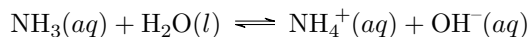
$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

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



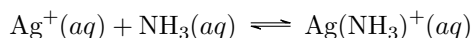
$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

where  $K_{\text{a}}$  is the acid dissociation constant; ***base dissociation reactions***

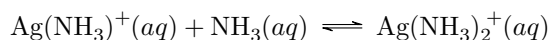


$$K_{\text{b}} = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

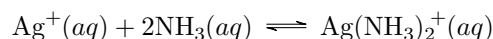
where  $K_{\text{b}}$  is the base dissociation constant; and ***complexation reactions***



$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = 2040$$



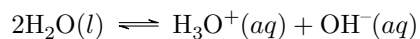
$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} = 8130$$



$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = K_1 \times K_2 = 2040 \times 8130 = 1.66 \times 10^7$$

where  $K_1$  and  $K_2$  are stepwise 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 reaction***

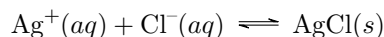


$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

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 we reverse the direction of an equilibrium reaction, its new equilibrium constant is the reciprocal of the original equilibrium constant
- if we add together two equilibrium reactions, the equilibrium constant for the new reaction is the product of the two original equilibrium constants

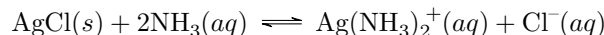
For example, consider the equilibrium constant for the precipitation of AgCl. The reaction



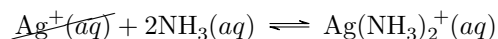
is the reverse of the solubility reaction for AgCl. The equilibrium constant, therefore, is the reciprocal of silver chloride's solubility product; thus

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

Or, consider the solubility of AgCl in a solution of  $\text{NH}_3$



This reaction is the sum of the solubility reaction for AgCl and the overall formation constant for  $\text{Ag}(\text{NH}_3)_2^+$



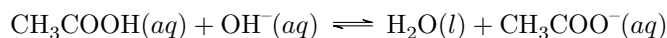
thus, the equilibrium constant is just the product of  $K_{\text{sp}}$  and  $\beta_2$

$$K = K_{\text{sp}} \times \beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = (1.8 \times 10^{-10}) \times (1.66 \times 10^7) = 3.0 \times 10^{-3}$$

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

## Reaction of a Weak Acid with a Strong Base

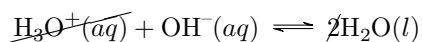
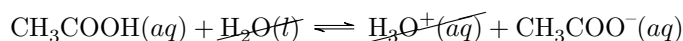
Consider the reaction of acetic acid,  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$



where we omit the sodium ion,  $\text{Na}^+$  because it is not involved in the reaction. 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 for which  $K_b$  is  $5.7 \times 10^{-10}$ . The equilibrium constant for this reaction, therefore, is

$$K = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{OH}^-]} = \frac{1}{K_b} = \frac{1}{5.7 \times 10^{-10}} = 1.75 \times 10^9$$

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

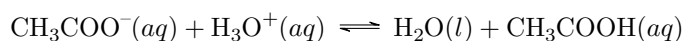


giving

$$K = \frac{K_a}{K_w} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{\text{CH}_3\text{COOH}} \times \frac{1}{[\text{H}_3\text{O}^+][\text{OH}^-]} = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{OH}^-]} = \frac{1.75 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.75 \times 10^9$$

## Reaction of a Weak Base With a Strong Acid

Consider the reaction of the acetate ion,  $\text{CH}_3\text{COO}^-$ , with  $\text{HCl}$ .

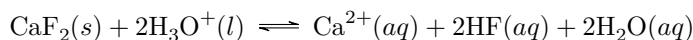


where the  $\text{HCl}$  is present as  $\text{H}_3\text{O}^+$ . If we look at this reaction in reverse we see that it is the reaction of a weak acid with water; that is, the reverse reaction is the acid dissociation reaction for acetic acid. The equilibrium constant for this reaction, therefore, is

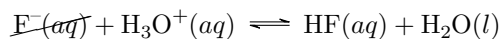
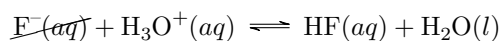
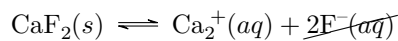
$$K = \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]} = \frac{1}{K_a} = \frac{1}{1.75 \times 10^{-5}} = 5.71 \times 10^4$$

## Solubility of a Salt Whose Anion is a Weak Base

Consider the solubility of  $\text{CaF}_2$  under conditions where its anion, which is a weak base, becomes protonated



If we look at this reaction we see that it is a summation of the solubility reaction for  $\text{CaF}_2$  and the reverse of the acid dissociation reaction for  $\text{HF}$  (taken twice); thus

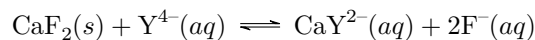


The equilibrium constant, therefore, is

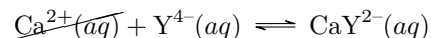
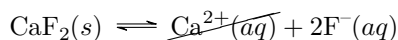
$$K = \frac{K_{\text{sp}}}{(K_a)^2} = \frac{[\text{Ca}^{2+}][\text{F}^-]^2}{[\text{CaF}_2(s)]} \times \left( \frac{[\text{HF}]}{[\text{H}_3\text{O}^+][\text{F}^-]} \right)^2 = \frac{[\text{Ca}^{2+}][\text{HF}]^2}{[\text{H}_3\text{O}^+]^2} = \frac{3.9 \times 10^{-11}}{(7.2 \times 10^{-4})^2} = 7.5 \times 10^{-5}$$

### Solubility of a Salt in the Presence of a Ligand

Consider the solubility of  $\text{CaF}_2$  in the presence of EDTA (which we abbreviate here as  $\text{Y}^{4-}$ ), a ligand that binds  $\text{Ca}^{2+}$  strongly.



This reaction is the summation of the solubility reaction for  $\text{CaF}_2$  and the metal-ligand complexation reaction between  $\text{Ca}^{2+}$  and EDTA; thus



The equilibrium constant, therefore, is

$$K = K_{\text{sp}} \times K_1 = \frac{[\text{Ca}^{2+}][\text{F}^-]^2}{[\text{CaF}_2(s)]} \times \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]} = \frac{[\text{CaY}^{2-}][\text{F}^-]^2}{[\text{Y}^{4-}]} = (3.9 \times 10^{-11}) \times (4.9 \times 10^{10}) = 1.9$$