Acids and Bases

References : 1. General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette)
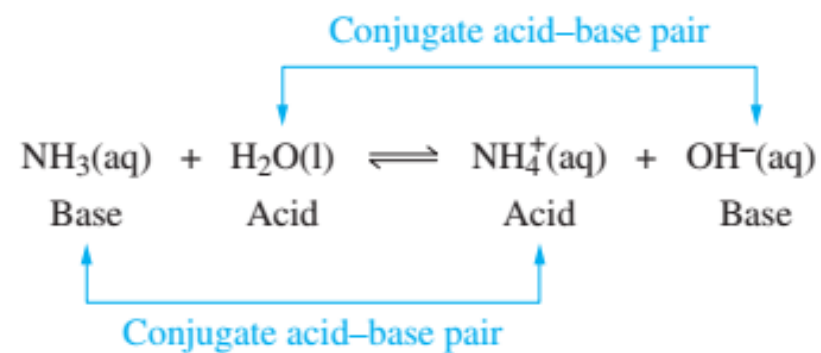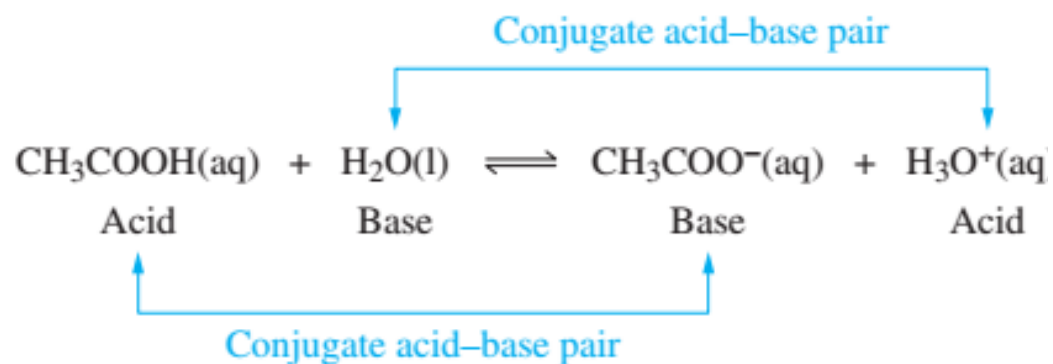
2. Chemistry-10th Edition (Raymond Chang)

Acids, Bases, and Conjugate Acid–Base Pairs

One of the most useful theories of acids and bases, particularly for describing the reactions of acids and bases in aqueous solutions, is the Brønsted–Lowry theory. In 1923, J. N. Brønsted and T. M. Lowry in Great Britain independently proposed that an acid is a proton donor and a base is a proton acceptor. Let's use the Brønsted–Lowry theory to describe the ionization of CH_3COOH in aqueous solution.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad (16.1)$$

In reaction, CH_3COOH acts as an acid. It gives up a proton, H^+, which is taken up by H_2O. Thus, H_2O acts as a base. In the reverse reaction, the hydronium ion, H_3O^+ acts as an acid and CH_3COO^- acts as a base.

When CH_3COOH loses a proton, it is converted into CH_3COO^- . Notice that the formulas of these two species differ by a single proton, H^+ . Species that differ by a single proton (H^+) constitute a conjugate acid–base pair. Within this pair, the species with the added H^+ is the acid, and the species without the H^+ is the base. Thus, for reaction (16.1), we can identify two conjugate acid–base pairs.

Conjugate acid–base pair

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

Acid   Base   Base   Acid

Conjugate acid–base pair

Conjugate acid–base pair

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

Base   Acid   Acid   Base

Conjugate acid–base pair

An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.

It will be helpful to summarize some key aspects of the Brønsted–Lowry theory.

1. <u>**An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.**</u> For this reason, an acid may be represented in the Brønsted–Lowry theory by the general formula HA, H_2A, H_3A, etc., depending on the number of ionizable H atoms, and a base is represented by :B. There are substances that contain both an ionizable H atom and an atom with a lone pair of electrons. Such substances may behave as either an acid or a base, depending on the situation, and are said to be amphiprotic.

2. <u>**For a conjugate acid–base pair, the molecular formulas for the acid and base differ by a single proton (H^+).**</u> Therefore, to identify the species in a solution that constitute a conjugate acid–base pair, we need only identify those species that have molecular formulas that differ by one H^+ ion. Once such a pair has been identified, the species with the added H is the acid, and the species without the H^+ is the base. For example, H_2O and OH^- are a conjugate acid–base pair because their formulas differ by one H . In this pair, H_2O is the acid and OH is the base. Similarly, because the formulas of NH_4^+ and NH_3 differ by one H^+ , these two species constitute a conjugate acid–base pair, with NH_4^+ as the acid and NH_3 as the base.

3**. When added to water, acids protonate water molecules to form hydronium (H_3O^+) ions and bases deprotonate water molecules to form hydroxide (OH⁻) ions.** The ability of the Brønsted–Lowry theory to account for the presence these ions in solution arises from its recognition of the role played by the solvent and makes it a more general and useful theory than the Arrhenius theory.

Self-Ionization of Water and the pH Scale

H_2O molecule can act as either an acid or a base it is amphiprotic. It should come as no surprise that amongst themselves water molecules can produce H_3O^+ and OH^- ions via the following self-ionization reaction or autoionization reaction:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$\text{acid}_1 \quad \text{base}_2 \quad\quad \text{acid}_2 \quad\quad \text{base}_1$$
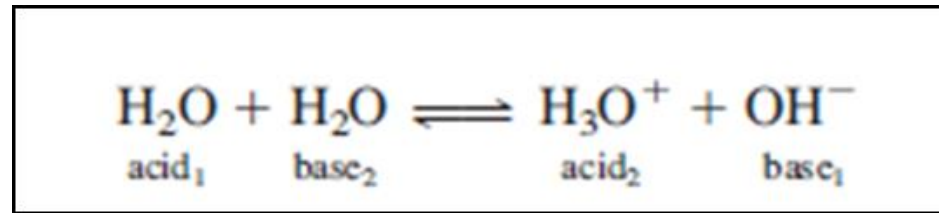
The Ion Product of Water

In the study of acid-base reactions, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. Because only a very small fraction of water molecules are ionized, the concentration of water remains virtually unchanged. Therefore, the equilibrium constant for the autoionization of water, is

$$K_c = [H_3O^+][OH^-]$$
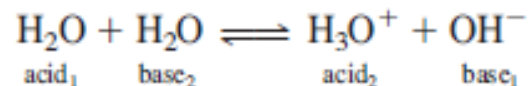
$$\underset{acid_1}{H_2O} + \underset{base_2}{H_2O} \rightleftharpoons \underset{acid_2}{H_3O^+} + \underset{base_1}{OH^-}$$

Because we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$K_c = [H^+][OH^-]$$

To indicate that the equilibrium constant refers to the autoionization of water, we replace K_c by K_w

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] \qquad (15.2)$$

where K_w is called the **ion-product constant,** which is *the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.*

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M. Thus, from Equation (15.2), at 25°C

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether we have pure water or an aqueous solution of dissolved species, the following relation *always* holds at 25°C:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \qquad (15.3)$$

The self-ionization of water is an important reaction, from a conceptual point of view, because it reveals an important relationship between $[H_3O]$ and $[OH^-]$ that applies to all aqueous solutions. From a practical standpoint, the reaction is not of much concern to us except when dealing with extremely dilute solutions.

In fact, the self-ionization of water is partially suppressed by the addition of acid or base to water.

This statement is easily justified by applying Le Châtelier's principle to reaction (16.3). When an acid is added to water, H_2O molecules are protonated and $[H_3O^+]$ increases. The increase in $[H_3O^+]$ causes net change to the left in reaction (16.3), and, thus, the self-ionization of water is partially suppressed. Similarly, the addition of a base to water increases $[OH^-]$, causes net change to the left, and partially suppresses the self-ionization of water.

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad\qquad (16.3)$$
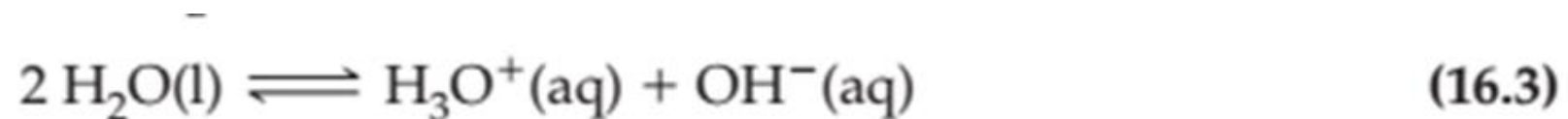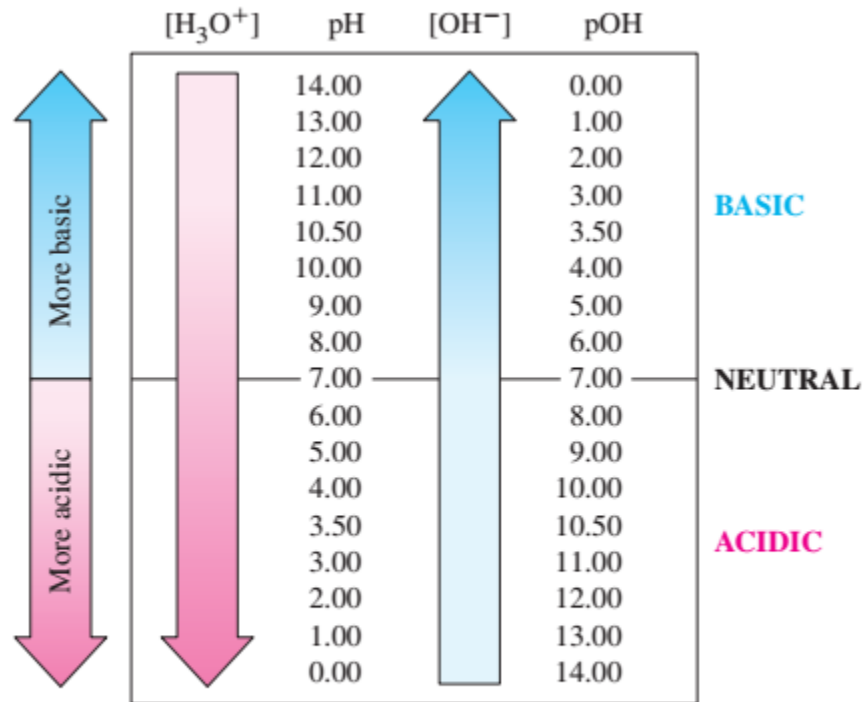
pH and pOH

Because the concentrations of H and OH ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, Soren Sorensen† in 1909 proposed a more practical measure called pH. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L).

Acidic, Basic, and Neutral Solutions

In pure water, the concentrations of H_3O^+ and OH^- are equal. However, when an acid or a base is added to water, the H_3O^+ and OH^- ions are no longer present in equal amounts. By comparing the values of $[H_3O^+]$ and $[OH^-]$, we can classify a solution as acidic, basic, or neutral (Table 16.1).

TABLE 16.1 Acidic, Basic, and Neutral Solutions			
	Neutral Solution	Acidic Solution	Basic Solution
Relationship between $[H_3O^+]$ and $[OH^-]$	$[H_3O^+] = [OH^-]$	$[H_3O^+] > [OH^-]$	$[H_3O^+] < [OH^-]$
$[H_3O^+]$ at 25 °C	$[H_3O^+] = 1.0 \times 10^{-7}$ M	$[H_3O^+] > 1.0 \times 10^{-7}$ M	$[H_3O^+] < 1.0 \times 10^{-7}$ M
pH at 25 °C	pH = 7	pH < 7	pH > 7

The classification can also be made, at , by focusing on either $[H_3O^+]$ or the pH. The relationships between $[H_3O]$, $[OH]$, pH, and pOH, for acidic, basic, and neutral solutions, are illustrated in Figure 16-4. The pH values of a number of materials—some acidic and others basic—are depicted in Figure 16-5.

▲ FIGURE 16-4
Relating $[H_3O^+]$, pH, $[OH^-]$, and pOH
In aqueous solutions at 25 °C, the sum of the pH and pOH values is always equal to 14.

▲ FIGURE 16-5
The pH scale and pH values of some common materials
The scale shown here ranges from pH 0 to pH 14. Slightly negative pH values, perhaps to about −1 (corresponding to $[H_3O^+] \approx 10$ M), are possible. Also possible are pH values up to about 15 (corresponding to $[OH^-] \approx 10$ M). For practical purposes, however, the pH scale is useful only in the range $2 < pH < 12$, because the activities of H_3O^+ and OH^- in concentrated solutions may differ significantly from their molarities.
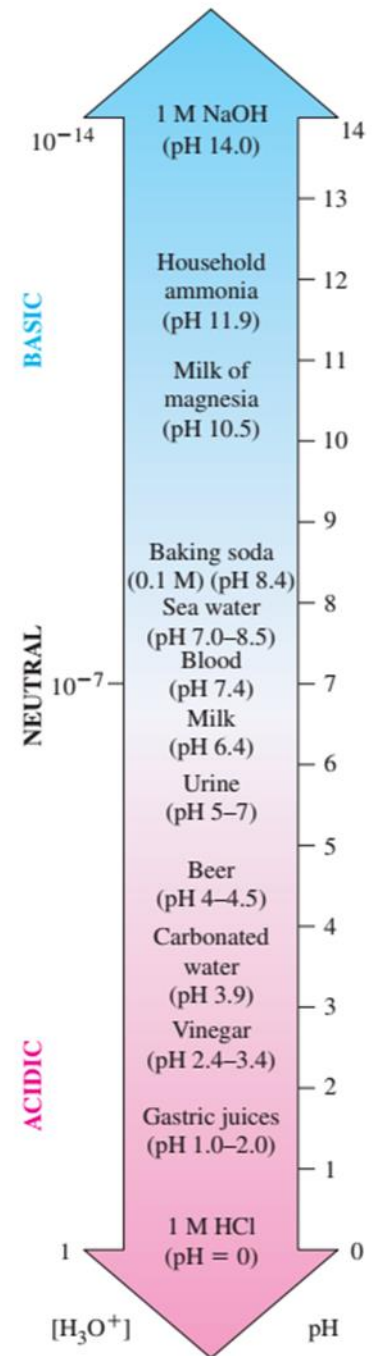
Ionization of Acids and Bases in Water

Figure 16-6 illustrates two ways of showing that ionization has occurred in a solution of acid. One is by the color of an acid–base indicator; the other, the response of a pH meter.

The pink color of the solution in Figure 16-7 tells us the pH of the HCl solution is less than 1.2. The pH meter registers a value of 1.20, indicating that $[H_3O] = 10^{-1.20}$ M=0.063 M in the HCl solution. The yellow color of the solution in Figure 16-7 indicates that the pH of 0.1 M CH_3COOH (acetic acid) is 2.8 or greater. The pH meter registers 2.80, and thus $[H_3O] = 10^{-2.80}$ M=0.0016 M.
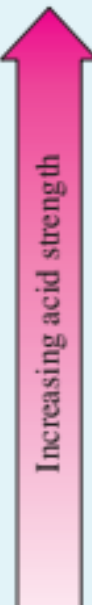

▲ FIGURE 16-6
Strong and weak acids compared
The color of thymol blue indicator, which is present in both solutions, depends on the pH of the solution.

pH < 1.2 < pH < 2.8 < pH
Red   Orange   Yellow

Notice that the ionization of HCl generates a higher $[H_3O^+]$ than does the ionization of CH_3COOH, even though the initial molarity of CH_3COOH (0.1 M) is greater than that of HCl (0.06 to 0.07 M). From this, we conclude that the ionization of HCl occurs to a greater extent than does the ionization of CH_3COOH, an indication that HCl is a much stronger acid than CH_3COOH. This conclusion is reflected in the placements of HCl and CH_3COOH in Table 16.2 which ranks a number of acids and bases in order of increasing acid or base strengths. This ordering is established by experiment.

TABLE 16.2 Relative Strengths of Some Common Brønsted–Lowry Acids and Bases

Acid		Conjugate Base	
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Hydroiodic acid	HI	Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
Hydrochloric acid	HCl	Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion[a]	H_3O^+	Water[a]	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	CH_3COOH	Acetate ion	CH_3COO^-
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
Water	H_2O	Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

Left axis: Increasing acid strength. Right axis: Increasing base strength.

[a]The hydronium ion–water combination refers to the ease with which a proton is passed from one water molecule to another; that is, $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$.

The strength of an acid or a base is quantified by the value of the equilibrium constant for the reaction describing its ionization in water. As discussed earlier, a monoprotic Brønsted–Lowry acid may be represented by the general formula HA. Therefore, the ionization of an acid may be represented generally by the following equation.

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad (16.9)$$
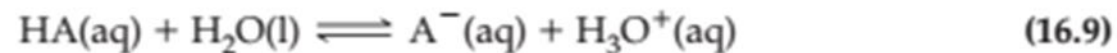
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad (16.10)$$

K_a values span an enormous range. For example, K_a is about 10^9 for HI and is less than 10^{-40} for CH_3CH_3. For this reason, we often use pK_a values instead. The pK_a value of an acid is defined as follows.

$$pK_a = -\log K_a \text{ or } K_a = 10^{-pK_a} \qquad (16.11)$$

The value of K_a or K_b gives an indication of the strength of an acid or a base. The following points are worth remembering

1. A strong acid or base has a large ionization constant: Ka or Kb is much greater than 1. Therefore, we expect that the corresponding ionization reaction goes almost to completion. In most situations, we can safely assume that a strong acid or strong base is completely ionized in solution. Fortunately, there are relatively few common strong acids and strong bases

TABLE 16.3
The Common Strong Acids and Strong Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HClO₄	RbOH
HNO₃	CsOH
H₂SO₄ᵃ	Mg(OH)₂
	Ca(OH)₂
	Sr(OH)₂
	Ba(OH)₂

ᵃH₂SO₄ ionizes in two distinct steps. It is a strong acid only in its first ionization

Notice that the listing in Table 16.3 does not include Ka or Kb values; these values are not needed. The main point is that the ionization constants are large enough to ensure that the acids and bases in Table 16.3 are almost completely ionized in aqueous solution.
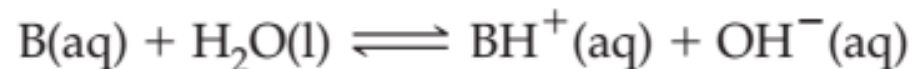
Memorizing the list in Table 16.3 can be extremely helpful. For example, if the situation we are dealing with involves a strong acid or base, we can safely assume the strong acid or base will react to completion. On the other hand, if the situation we are considering involves an acid and a base that are not listed in Table 16.3, we can safely assume that the acid and base are weak and react to a limited extent only.

The strong acids listed in Table 16.3 are molecular compounds whereas the strong bases are soluble ionic compounds called hydroxides. Molecular compounds ionize in water: Neutral HA molecules produce H_3O^+ and A^- ions by reacting with water (equation 16.9). On the other hand, soluble ionic hydroxides dissociate in water: Positive and negative ions (for example, Na and OH), which are already present in the solid structure, enter the solution as free ions.

TABLE 16.3 The Common Strong Acids and Strong Bases	
Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
$H_2SO_4{}^a$	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

$^a H_2SO_4$ ionizes in two distinct steps. It is a strong acid only in its first ionization

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad (16.9)$$

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

2. A weak acid or base has a small ionization constant: Ka or Kb is much less than 1. For a weak acid or base, the corresponding ionization reaction occurs to a limited extent, with a significant fraction of the acid or base not ionized. To determine the equilibrium composition of a solution of a weak acid or weak base, we need to solve an equilibrium problem, typically by using an ICE table and the value of the appropriate ionization constant, Ka or K b. Ionization constants of some weak acids and weak bases are provided in Table 16.4.

TABLE 16.4   Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		$K_a =$	p$K_a =$
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$ClCH_2COOH + H_2O \rightleftharpoons H_3O^+ + ClCH_2COO^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$	1.8×10^{-4}	3.74
Benzoic acid	$C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		$K_b =$	p$K_b =$
Diethylamine	$(CH_3CH_2)_2NH + H_2O \rightleftharpoons (CH_3CH_2)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

Percent Ionization

We have seen that the magnitude of K_a indicates the strength of an acid. Another measure of the strength of an acid is its *percent ionization,* which is defined as

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \quad (15.11)$$

The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H^+ ions or the concentration of the A^- ions at equilibrium. Therefore, we can write the percent ionization as

$$\text{percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\%$$

where $[H^+]$ is the concentration at equilibrium and $[HA]_0$ is the initial concentration.
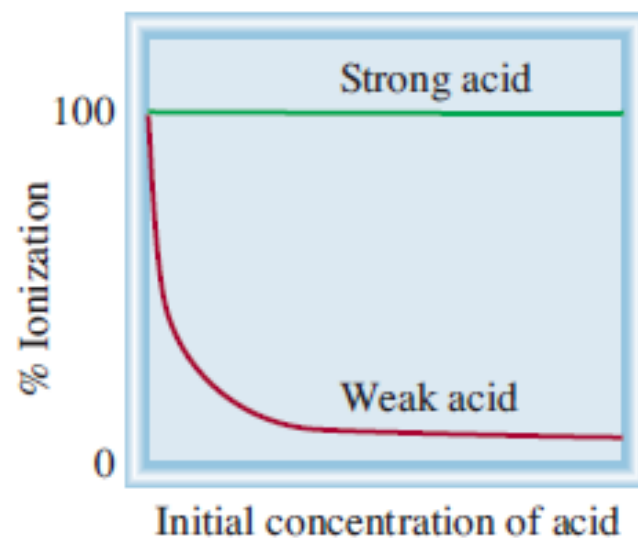
For a weak acid or a weak base, the degree of ionization increases with increasing dilution.

The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percentage ionization (Figure 15.4). In qualitative terms, when an acid is diluted, the concentration of the "particles" in the solution is reduced. According to Le Châtelier's principle (see Section 14.5), this reduction in particle concentration (the stress) is counteracted by shifting the reaction to the side with more particles; that is, the equilibrium shifts from the nonionized acid side (one particle) to the side containing H^+ ions and the conjugate base (two particles): $HA \rightleftharpoons H^+ + A^-$. Consequently, the concentration of "particles" increases in the solution.

Strong Acids and Strong Bases

A strong acid, such as HCl, is essentially completely ionized in aqueous solution.* Consequently, in the equation for the ionization of HCl, we use a right arrow ($\longrightarrow$) instead of a double arrow ($\rightleftharpoons$):

$$HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$

In a solution of HCl, there are two sources of H_3O^+: the ionization of HCl and the self-ionization of water. However, adding HCl to water suppresses the self-ionization of water (see page 740), so the ionization of HCl is the only significant source of H_3O^+. The contribution from the self-ionization of water can generally be ignored *unless the solution is extremely dilute*. Even for 1.0×10^{-6} M HCl(aq), the self-ionization of water contributes less than 1% to the total concentration of H_3O^+ (see Exercise 102). For more concentrated solutions, the self-ionization of water contributes much less than 1%, a fact we verify in Example 16-5.

Polyprotic Acids

All the acids listed in Table 16.4 are weak monoprotic acids, meaning that their molecules have only one ionizable H atom, even though several of these acids contain more than one H atom. But some acids have more than one ionizable H atom per molecule. These are polyprotic acids.

The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases

An important relationship between the acid ionization constant and the ionization constant of its conjugate base can be derived as follows, using acetic acid as an example:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
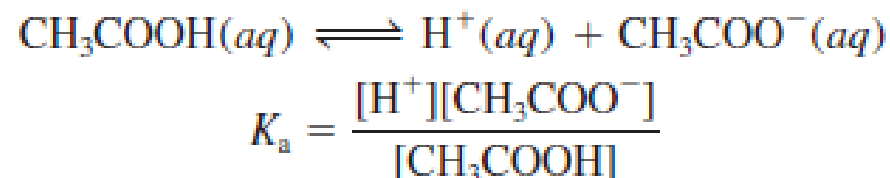
$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The conjugate base, CH_3COO^-, supplied by a sodium acetate (CH_3COONa) solution, reacts with water according to the equation
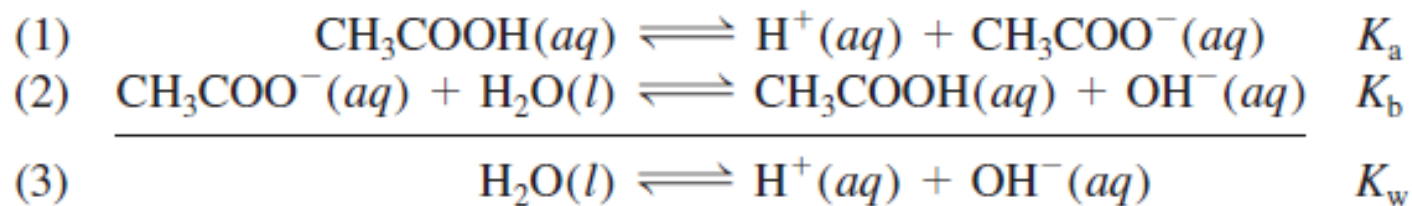
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

and we can write the base ionization constant as

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

The product of these two ionization constants is given by

$$K_a K_b = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
$$= [H^+][OH^-]$$
$$= K_w$$

This result may seem strange at first, but if we add the two equations we see that the sum is simply the autoionization of water.

(1) $\qquad$ $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ $\qquad$ K_a

(2) $\quad CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ $\quad K_b$

(3) $\qquad\qquad\qquad H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\qquad\qquad K_w$

This example illustrates one of the rules for chemical equilibria: When two reactions are added to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions (see Section 14.2). Thus, for any conjugate acid-base pair it is always true that

$$K_a K_b = K_w \qquad\qquad (15.12)$$

Expressing Equation (15.12) as

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$