

# ACIDS AND BASES

**TABLE 18-1** Common Strong Acids and Strong Bases

Strong Acids	
HCl	HNO <sub>3</sub>
HBr	HClO <sub>4</sub>
HI	HClO <sub>3</sub>
	H <sub>2</sub> SO <sub>4</sub>
Strong Bases	
LiOH	
NaOH	
KOH	Ca(OH) <sub>2</sub>
RbOH	Sr(OH) <sub>2</sub>
CsOH	Ba(OH) <sub>2</sub>

water-soluble compounds may be classified as either electrolytes or nonelectrolytes. **Electrolytes** are compounds that ionize (or dissociate into their constituent ions) to produce aqueous solutions that conduct an electric current. **Nonelectrolytes** exist as molecules in aqueous solution, and such solutions do not conduct an electric current.

**Strong electrolytes** are ionized or dissociated completely, or very nearly completely, in dilute aqueous solutions. Strong electrolytes include strong acids, strong bases, and most soluble salts.

Concentrations of ions in aqueous solutions of strong electrolytes can be calculated directly from the molarity of the strong electrolyte, as the following example illustrates.

## EXAMPLE 18-1 Calculation of Concentrations of Ions

Calculate the molar concentrations of Ba<sup>2+</sup> and OH<sup>-</sup> ions in 0.030 M barium hydroxide.

### Plan

Write the equation for the dissociation of Ba(OH)<sub>2</sub>, and construct the reaction summary. Ba(OH)<sub>2</sub> is a strong base that is completely dissociated.

### Solution

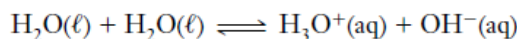
From the equation for the dissociation of barium hydroxide, we see that *one* mole of Ba(OH)<sub>2</sub> produces *one* mole of Ba<sup>2+</sup> ions and *two* moles of OH<sup>-</sup> ions.

(strong base)	Ba(OH) <sub>2</sub> (s)	→	Ba <sup>2+</sup> (aq)	+ 2OH <sup>-</sup> (aq)
initial	0.030 M			
change due to rxn	-0.030 M		+0.030 M	+2(0.030 M)
final	0 M		0.030 M	0.060 M

$$[\text{Ba}^{2+}] = 0.030 \text{ M} \quad \text{and} \quad [\text{OH}^-] = 0.060 \text{ M}$$

## 18-2 THE AUTOIONIZATION OF WATER

Careful experiments on its electrical conductivity have shown that pure water ionizes to a very slight extent.



Because the H<sub>2</sub>O is pure, its activity is 1, so we do not include its concentration in the equilibrium constant expression. This equilibrium constant is known as the **ion product for water** and is usually represented as  $K_w$ .

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

The formation of an  $\text{H}_3\text{O}^+$  ion by the ionization of water is always accompanied by the formation of an  $\text{OH}^-$  ion. Thus, in *pure* water the concentration of  $\text{H}_3\text{O}^+$  is *always* equal to the concentration of  $\text{OH}^-$ . Careful measurements show that, in pure water at  $25^\circ\text{C}$ ,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol/L}$$

Substituting these concentrations into the  $K_w$  expression gives

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \end{aligned}$$

Temperature (°C)	$K_w$
0	$1.1 \times 10^{-15}$
10	$2.9 \times 10^{-15}$
25	$1.0 \times 10^{-14}$
37*	$2.4 \times 10^{-14}$
45	$4.0 \times 10^{-14}$
60	$9.6 \times 10^{-14}$

\*Normal human body temperature.

Although the expression  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  was obtained for pure water, it is also valid for dilute aqueous solutions at  $25^\circ\text{C}$ . This is one of the most useful relationships chemists have discovered. It gives a simple relationship between  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentrations in *all* dilute aqueous solutions.

The *value* of  $K_w$  is different at different temperatures (Table 18-2), but the *relationship*  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$  is still valid.

### EXAMPLE 18-2 Calculation of Ion Concentrations

Calculate the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions in a  $0.050 \text{ M}$   $\text{HNO}_3$  solution.

#### Plan

Write the equation for the ionization of  $\text{HNO}_3$ , a strong acid, and construct the reaction summary, which gives the concentrations of  $\text{H}_3\text{O}^+$  (and  $\text{NO}_3^-$ ) ions directly. Then use the relationship  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  to find the concentration of  $\text{OH}^-$  ions.

#### Solution

The reaction summary for the ionization of  $\text{HNO}_3$ , a strong acid, is

(strong acid)	$\text{HNO}_3$	+	$\text{H}_2\text{O}$	$\longrightarrow$	$\text{H}_3\text{O}^+$	+	$\text{NO}_3^-$
initial	$0.050 \text{ M}$				$\approx 0 \text{ M}$		$0 \text{ M}$
change due to rxn	$-0.050 \text{ M}$				$+0.050 \text{ M}$		$+0.050 \text{ M}$
at equil	$0 \text{ M}$				$0.050 \text{ M}$		$0.050 \text{ M}$

$$[\text{H}_3\text{O}^+] = [\text{NO}_3^-] = 0.050 \text{ M}$$

The  $[\text{OH}^-]$  is determined from the equation for the autoionization of water and its  $K_w$ .

	$2\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{OH}^-$
initial			$0.050 \text{ M}$		
change due to rxn	$-2x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
at equil			$(0.050 + x) \text{ M}$		$x \text{ M}$

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

$$1.0 \times 10^{-14} = (0.050 + x)(x)$$

Because the product  $(0.050 + x)(x)$  is a very small number, we know that  $x$  must be very small. Thus, it will not matter whether we add  $x$  to  $0.050$ ; we can assume that  $(0.050 + x) \approx 0.050$ . We substitute this approximation into the equation and solve.

$$1.0 \times 10^{-14} = (0.050)(x) \quad \text{or} \quad x = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13} \text{ M} = [\text{OH}^-]$$

We see that the assumption that  $x$  is much smaller than  $0.050$  was a good one.

In solving Example 18-2 we assumed that *all* of the  $\text{H}_3\text{O}^+$  ( $0.050\text{ M}$ ) came from the ionization of  $\text{HNO}_3$ , and neglected the  $\text{H}_3\text{O}^+$  formed by the ionization of  $\text{H}_2\text{O}$ . The ionization of  $\text{H}_2\text{O}$  produces only  $2.0 \times 10^{-13}\text{ M H}_3\text{O}^+$  and  $2.0 \times 10^{-13}\text{ M OH}^-$  in this solution. Thus, we were justified in assuming that the  $[\text{H}_3\text{O}^+]$  is derived solely from the strong acid. A more concise way to carry out the calculation to find the  $[\text{OH}^-]$  concentration is to write directly

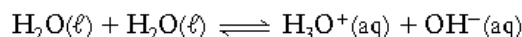
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{or} \quad [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

Then we substitute to obtain

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13}\text{ M}$$

From now on, we shall use this more direct approach for such calculations.

When nitric acid is added to water, large numbers of  $\text{H}_3\text{O}^+$  ions are produced. The large increase in  $[\text{H}_3\text{O}^+]$  shifts the water equilibrium far to the left (LeChatelier's Principle), and the  $[\text{OH}^-]$  decreases.



In acidic solutions the  $\text{H}_3\text{O}^+$  concentration is always greater than the  $\text{OH}^-$  concentration. We should not conclude that acidic solutions contain no  $\text{OH}^-$  ions. Rather, the  $[\text{OH}^-]$  is always less than  $1.0 \times 10^{-7}\text{ M}$  in such solutions. The reverse is true for basic solutions, in which the  $[\text{OH}^-]$  is always greater than  $1.0 \times 10^{-7}\text{ M}$ . By definition, "neutral" aqueous solutions at  $25^\circ\text{C}$  are solutions in which  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}\text{ M}$ .

### 18-3 THE pH AND pOH SCALES

The pH and pOH scales provide a convenient way to express the acidity and basicity of dilute aqueous solutions. The pH and pOH of a solution are defined as

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] & \text{or} & & [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\log [\text{OH}^-] & \text{or} & & [\text{OH}^-] &= 10^{-\text{pOH}} \end{aligned}$$

Note that we use pH rather than  $\text{pH}_3\text{O}$ . At the time the pH concept was developed,  $\text{H}_3\text{O}^+$  was represented as  $\text{H}^+$ . Various "p" terms are used. In general a lowercase "p" before a symbol means "negative logarithm of the symbol." Thus, pH is the negative logarithm of the  $\text{H}_3\text{O}^+$  concentration, pOH is the negative logarithm of the  $\text{OH}^-$  concentration, and  $\text{p}K$  refers to the negative logarithm of an equilibrium constant. It is convenient to describe the autoionization of water in terms of  $\text{p}K_w$ .

$$\text{p}K_w = -\log K_w$$

#### EXAMPLE 18-4 Calculation of $\text{H}_3\text{O}^+$ Concentration from pH

The pH of a solution is 3.301. What is the concentration of  $\text{H}_3\text{O}^+$  in this solution?

##### Plan

By definition,  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ . We are given the pH, so we solve for  $[\text{H}_3\text{O}^+]$ .

**Solution**

From the definition of pH, we write

$$-\log [\text{H}_3\text{O}^+] = 3.301$$

Multiplying through by  $-1$  gives

$$\log [\text{H}_3\text{O}^+] = -3.301$$

Taking the inverse logarithm (antilog) of both sides of the equation gives

$$[\text{H}_3\text{O}^+] = 10^{-3.301} \quad \text{so} \quad [\text{H}_3\text{O}^+] = 5.00 \times 10^{-4} \text{ M}$$

A convenient relationship between pH and pOH in *all dilute solutions at 25°C* can be easily derived. We start with the  $K_w$  expression.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking the logarithm of both sides of this equation gives

$$\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = \log (1.0 \times 10^{-14})$$

Multiplying both sides of this equation by  $-1$  gives

$$(-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) = -\log (1.0 \times 10^{-14})$$

or

$$\text{pH} + \text{pOH} = 14.00$$

We can now relate  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  as well as pH and pOH.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{and} \quad \text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25^\circ\text{C})$$

**EXAMPLE 18-5** *Calculations Involving pH and pOH*

Calculate  $[\text{H}_3\text{O}^+]$ , pH,  $[\text{OH}^-]$ , and pOH for a  $0.015 \text{ M}$   $\text{HNO}_3$  solution.

**Plan**

We write the equation for the ionization of the strong acid  $\text{HNO}_3$ , which gives us  $[\text{H}_3\text{O}^+]$ . Then we calculate pH. We use the relationships  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  and  $\text{pH} + \text{pOH} = 14.00$  to find pOH and  $[\text{OH}^-]$ .

**Solution**

Because nitric acid is a strong acid (it ionizes completely), we know that

$$[\text{H}_3\text{O}^+] = 0.015 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.015) = -(-1.82) = 1.82$$

We also know that  $\text{pH} + \text{pOH} = 14.00$ . Therefore,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 1.82 = 12.18$$

Because  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ ,  $[\text{OH}^-]$  is easily calculated.

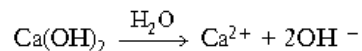
$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13} \text{ M}$$

**EXAMPLE 18-6** *Calculations Involving pH and pOH*

Calculate  $[\text{H}_3\text{O}^+]$ , pH,  $[\text{OH}^-]$ , and pOH for a 0.015 M  $\text{Ca}(\text{OH})_2$  solution.

**Plan**

We write the equation for the ionization of the strong base  $\text{Ca}(\text{OH})_2$ , which gives us  $[\text{OH}^-]$ . Then we calculate pOH. We use the relationships  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  and  $\text{pH} + \text{pOH} = 14.00$  to find pH and  $[\text{H}_3\text{O}^+]$ .

**Solution**

Because calcium hydroxide is a strong base (it dissociates completely), we know that

$$[\text{OH}^-] = 2 \times 0.015 \text{ M} = 0.030 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.030) = -(-1.52) = 1.52$$

We also know that  $\text{pH} + \text{pOH} = 14.00$ . Therefore,

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.52 = 12.48$$

Because  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ ,  $[\text{H}_3\text{O}^+]$  is easily calculated.

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.030} = 3.3 \times 10^{-13} \text{ M}$$