ACIDS AND BASES

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.

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

Strong Acids	
HCl	HNO_3
HBr	$HClO_4$
HI	$HClO_3$
	H_2SO_4
Strong Bases	
LiOH	
NaOH	
KOH	$Ca(OH)_2$
RbOH	$Sr(OH)_2$
CsOH	$Ba(OH)_2$

EXAMPLE 18-1 *Calculation of Concentrations of Ions*

Calculate the molar concentrations of Ba^{2+} and OH^- ions in 0.030 *M* barium hydroxide.

Plan

Write the equation for the dissociation of $Ba(OH)_2$, and construct the reaction summary. $Ba(OH)_2$ is a strong base that is completely dissociated.

Solution

From the equation for the dissociation of barium hydroxide, we see that *one* mole of $Ba(OH)_2$ produces *one* mole of Ba^{2+} ions and *two* moles of OH^- ions.

(strong base)	$Ba(OH)_2(s)$ $\longrightarrow$	Ba^{2+} (aq) +	$2OH^-$ (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*

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

18-2 THE AUTOIONIZATION OF WATER

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

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Because the H_2O 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.

$$K_w = [H_3O^+][OH^-]$$

The formation of an H_3O^+ ion by the ionization of water is always accompanied by the formation of an OH^- ion. Thus, in *pure* water the concentration of H_3O^+ is *always* equal to the concentration of OH^-. Careful measurements show that, in pure water at 25°C,

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol/L}$$

Substituting these concentrations into the K_w expression gives

$$K_w = [H_3O^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7})$$
$$= 1.0 \times 10^{-14} \qquad \text{(at 25°C)}$$

TABLE 18-2 *K_w at Some Temperatures*

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

**Normal human body temperature.*

Although the expression $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ was obtained for pure water, *it is also valid for dilute aqueous solutions at 25°C*. This is one of the most useful relationships chemists have discovered. It gives a simple relationship between H_3O^+ and OH^- concentrations in *all* dilute aqueous solutions.

The *value* of K_w is different at different temperatures (Table 18-2), but the *relationship* $K_w = [H_3O^+][OH^-]$ is still valid.

EXAMPLE 18-2 *Calculation of Ion Concentrations*

Calculate the concentrations of H_3O^+ and OH^- ions in a 0.050 *M* HNO_3 solution.

Plan

Write the equation for the ionization of HNO_3, a strong acid, and construct the reaction summary, which gives the concentrations of H_3O^+ (and NO_3^-) ions directly. Then use the relationship $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ to find the concentration of OH^- ions.

Solution

The reaction summary for the ionization of HNO_3, a strong acid, is

(strong acid)	HNO_3	$+ H_2O \longrightarrow$	H_3O^+	$+$	NO_3^-
initial	0.050 *M*		≈0 *M*		0 *M*
change due to rxn	−0.050 *M*		+0.050 *M*		+0.050 *M*
at equil	0 *M*		0.050 *M*		0.050 *M*

$$[H_3O^+] = [NO_3^-] = 0.050\ M$$

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

	$2H_2O$	$\rightleftharpoons$	$H_3O^+(aq)$	$+$	OH^-
initial			0.050 *M*		
change due to rxn	$-2x$ *M*		$+x$ *M*		$+x$ *M*
at equil			$(0.050 + x)$ *M*		x *M*

$$K_w = [H_3O^+][OH^-]$$
$$1.0 \times 10^{-14} = (0.050 + x)(x)$$

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.

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

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 H_3O^+ (0.050 M) came from the ionization of HNO_3 and neglected the H_3O^+ formed by the ionization of H_2O. The ionization of H_2O produces only 2.0×10^{-13} M H_3O^+ and 2.0×10^{-13} M OH^- *in this solution*. Thus, we were justified in assuming that the $[H_3O^+]$ is derived solely from the strong acid. A more concise way to carry out the calculation to find the $[OH^-]$ concentration is to write directly

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad \text{or} \qquad [OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$

Then we substitute to obtain

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

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

When nitric acid is added to water, large numbers of H_3O^+ ions are produced. The large increase in $[H_3O^+]$ shifts the water equilibrium far to the left (LeChatelier's Principle), and the $[OH^-]$ decreases.

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

In acidic solutions the H_3O^+ concentration is always greater than the OH^- concentration. We should not conclude that acidic solutions contain no OH^- ions. Rather, the $[OH^-]$ is always less than 1.0×10^{-7} M in such solutions. The reverse is true for basic solutions, in which the $[OH^-]$ is always greater than 1.0×10^{-7} M. By definition, "neutral" aqueous solutions at 25°C are solutions in which $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ 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

$$\mathrm{pH} = -\log\,[H_3O^+] \qquad \text{or} \qquad [H_3O^+] = 10^{-\mathrm{pH}}$$
$$\mathrm{pOH} = -\log\,[OH^-] \qquad \text{or} \qquad [OH^-] = 10^{-\mathrm{pOH}}$$

Note that we use pH rather than pH_3O. At the time the pH concept was developed, H_3O^+ was represented as 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 H_3O^+ concentration, **pOH** is the negative logarithm of the OH^- concentration, and **p*K*** refers to the negative logarithm of an equilibrium constant. It is convenient to describe the autoionization of water in terms of **pK_w**.

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

EXAMPLE 18-4 *Calculation of H_3O^+ Concentration from pH*

The pH of a solution is 3.301. What is the concentration of H_3O^+ in this solution?

Plan

By definition, $\mathrm{pH} = -\log\,[H_3O^+]$. We are given the pH, so we solve for $[H_3O^+]$.

Solution

From the definition of pH, we write

$$-\log [H_3O^+] = 3.301$$

Multiplying through by -1 gives

$$\log [H_3O^+] = -3.301$$

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

$$[H_3O^+] = 10^{-3.301} \qquad \text{so} \qquad [H_3O^+] = 5.00 \times 10^{-4}\,M$$

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.

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Taking the logarithm of both sides of this equation gives

$$\log [H_3O^+] + \log [OH^-] = \log (1.0 \times 10^{-14})$$

Multiplying both sides of this equation by -1 gives

$$(-\log [H_3O^+]) + (-\log [OH^-]) = -\log (1.0 \times 10^{-14})$$

or

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

We can now relate $[H_3O^+]$ and $[OH^-]$ as well as pH and pOH.

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad \text{and} \qquad \text{pH} + \text{pOH} = 14.00 \qquad (\text{at } 25°\text{C})$$

EXAMPLE 18-5 *Calculations Involving pH and pOH*

Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH for a 0.015 M HNO_3 solution.

Plan

We write the equation for the ionization of the strong acid HNO_3, which gives us $[H_3O^+]$. Then we calculate pH. We use the relationships $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pOH and $[OH^-]$.

Solution

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

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

$$[H_3O^+] = 0.015\,M$$

$$\text{pH} = -\log [H_3O^+] = -\log (0.015) = -(-1.82) = 1.82$$

We also know that pH + pOH = 14.00. Therefore,

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

Because $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$, $[OH^-]$ is easily calculated.

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13}\,M$$

EXAMPLE 18-6 *Calculations Involving pH and pOH*

Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH for a 0.015 *M* $Ca(OH)_2$ solution.

Plan

We write the equation for the ionization of the strong base $Ca(OH)_2$, which gives us $[OH^-]$. Then we calculate pOH. We use the relationships $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$ and $pH + pOH = 14.00$ to find pH and $[H_3O^+]$.

Solution

$$Ca(OH)_2 \xrightarrow{H_2O} Ca^{2+} + 2OH^-$$

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

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

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

We also know that $pH + pOH = 14.00$. Therefore,

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

Because $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$, $[H_3O^+]$ is easily calculated.

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.030} = \boxed{3.3 \times 10^{-13}\ M}$$