Acid-Base Titration and pH

The pH of solutions is important to the chemistry of life.
Aqueous Solutions and the Concept of pH

Hydronium Ions and Hydroxide Ions

You have already seen that acids and bases form hydronium ions and hydroxide ions, respectively, in aqueous solutions. However, these ions formed from the solute are not the only such ions present in an aqueous solution. Hydronium ions and hydroxide ions are also provided by the solvent, water.

Self-Ionization of Water

Careful electrical-conductivity experiments have shown that pure water is an extremely weak electrolyte. Water undergoes self-ionization, as shown in the model in Figure 16-1. In the self-ionization of water, two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton. The following equilibrium takes place.

\[ \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

Conductivity measurements show that concentrations of H$_3$O$^+$ and OH$^-$ in pure water are each only $1.0 \times 10^{-7}$ mol/L of water at 25°C.

There is a standard notation to represent concentration in moles per liter. The formula of the particular ion or molecule is enclosed in brackets, [ ]. For example, the symbol [H$_3$O$^+$] means “hydronium ion concentration in moles per liter,” or “molar hydronium ion concentration.” In water at 25°C, [H$_3$O$^+$] $= 1.0 \times 10^{-7}$ M and [OH$^-$] $= 1.0 \times 10^{-7}$ M.

The mathematical product of [H$_3$O$^+$] and [OH$^-$] remains constant in water and dilute aqueous solutions at constant temperature. This

FIGURE 16-1  Water undergoes self-ionization to a slight extent. A proton is transferred from one water molecule to another. A hydronium ion, H$_3$O$^+$, and a hydroxide ion, OH$^-$, are produced.
constant mathematical product is called the ionization constant of water, \( K_w \), and is expressed by the following equation.

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

For example, in water and dilute aqueous solutions at 25°C, the following relationship is valid.

\[
K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (1.0 \times 10^{-7} \text{ M})(1.0 \times 10^{-7} \text{ M}) = 1.0 \times 10^{-14} \text{ M}^2
\]

The ionization of water increases as temperature increases. Therefore, the ion product, \( K_w \), also increases as temperature increases, as shown in Table 16-1. However, at any given temperature \( K_w \) is always a constant value. The value \( 1.0 \times 10^{-14} \text{ M}^2 \) is assumed to be constant within the ordinary range of room temperatures. In this chapter, you can assume that these conditions are present unless otherwise stated.

### Neutral, Acidic, and Basic Solutions

Because the hydronium ion and hydroxide ion concentrations are the same in pure water, it is neutral. Any solution in which \([\text{H}_3\text{O}^+] = [\text{OH}^-]\) is also neutral. Recall from Chapter 15 that acids increase the concentration of \( \text{H}_3\text{O}^+ \) in aqueous solutions, as shown in Figure 16-2(a). Solutions in which the \( [\text{H}_3\text{O}^+] \) is greater than the \( [\text{OH}^-] \) are acidic. Bases increase the concentration of \( \text{OH}^- \) in aqueous solutions, as shown in Figure 16-2(b). In basic solutions, the \( [\text{OH}^-] \) is greater than the \( [\text{H}_3\text{O}^+] \).

As stated earlier, the \( [\text{H}_3\text{O}^+] \) and the \( [\text{OH}^-] \) of a neutral solution at 25°C both equal \( 1.0 \times 10^{-7} \text{ M} \). Therefore, if the \( [\text{H}_3\text{O}^+] \) is increased to greater than \( 1.0 \times 10^{-7} \text{ M} \), the solution is acidic. A solution containing \( 1.0 \times 10^{-5} \text{ mol H}_3\text{O}^+ \text{ ion/L at 25°C} \) is acidic because \( 1.0 \times 10^{-5} \) is greater than \( 1.0 \times 10^{-7} \). If the \( [\text{OH}^-] \) is increased to greater than \( 1.0 \times 10^{-7} \text{ M} \), the solution is basic. A solution containing \( 1.0 \times 10^{-4} \text{ mol OH}^- \text{ ions/L at 25°C} \) is basic because \( 1.0 \times 10^{-4} \) is greater than \( 1.0 \times 10^{-7} \).

### Table 16-1  \( K_w \) at Selected Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( K_w ) (M²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 1.2 \times 10^{-15} )</td>
</tr>
<tr>
<td>10</td>
<td>( 3.0 \times 10^{-15} )</td>
</tr>
<tr>
<td>25</td>
<td>( 1.0 \times 10^{-14} )</td>
</tr>
<tr>
<td>50</td>
<td>( 5.3 \times 10^{-14} )</td>
</tr>
</tbody>
</table>

### Figure 16-2

(a) Addition of dry ice, carbon dioxide, to water increases the \([\text{H}_3\text{O}^+]\), which is shown by the color change of the indicator bromthymol blue to yellow. The white mist is formed by condensation of water droplets because the dry ice is cold. (b) Addition of sodium peroxide to water increases the \([\text{OH}^-]\), which is shown by the color change of the indicator phenolphthalein to pink.
Calculating $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

Recall that strong acids and bases are considered completely ionized or dissociated in weak aqueous solutions. A review of strong acids and bases is given in Table 16-2. Notice that 1 mol of NaOH will yield 1 mol of OH$^-$ in an aqueous solution. Therefore, a $1.0 \times 10^{-2}$ M NaOH solution has an $[\text{OH}^-]$ of $1.0 \times 10^{-2}$ M, as shown by the following.

$$\text{NaOH} (s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(aq) + \text{OH}^-(aq)$$

1 mol 1 mol 1 mol

$$\frac{1.0 \times 10^{-2} \text{ mol NaOH}}{\text{L solution}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = \frac{1.0 \times 10^{-2} \text{ mol OH}^-}{\text{L solution}} = 1.0 \times 10^{-2} \text{ M OH}^-$$

Notice that the $[\text{OH}^-]$ is greater than $1.0 \times 10^{-7}$ M. This solution is basic.

Because the $K_w$ of an aqueous solution is a relatively constant $1.0 \times 10^{-14}$ M$^2$ at ordinary room temperatures, the concentration of either ion can be determined if the concentration of the other ion is known. The $[\text{H}_3\text{O}^+]$ of this solution is calculated as follows.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-2} \text{ M}} = 1.0 \times 10^{-12} \text{ M}$$

The $[\text{OH}^-]$, $1.0 \times 10^{-2}$ M, is greater than the $[\text{H}_3\text{O}^+]$, $1.0 \times 10^{-12}$ M, as is true for all basic solutions.

Now consider a $1.0 \times 10^{-4}$ M H$_2$SO$_4$ solution. Because H$_2$SO$_4$ is a diprotic acid, the $[\text{H}_3\text{O}^+]$ is $2.0 \times 10^{-4}$ M, as shown by the following.

$$\text{H}_2\text{SO}_4(l) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$$

1 mol 2 mol 2 mol 1 mol

$$\frac{1.0 \times 10^{-4} \text{ mol H}_2\text{SO}_4}{\text{L solution}} \times \frac{2 \text{ mol H}_3\text{O}^+}{1 \text{ mol H}_2\text{SO}_4} = \frac{2.0 \times 10^{-4} \text{ mol H}_3\text{O}^+}{\text{L solution}} = 2.0 \times 10^{-4} \text{ M H}_3\text{O}^+$$

Notice that the $[\text{H}_3\text{O}^+]$ is greater than $1.0 \times 10^{-7}$ M. This solution is acidic. The $[\text{OH}^-]$ of this solution is calculated as follows.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{2.0 \times 10^{-4} \text{ M}} = 5.0 \times 10^{-10} \text{ M}$$

As is true for all acidic solutions, the $[\text{H}_3\text{O}^+]$ is greater than the $[\text{OH}^-]$. You may have realized that in order for $K_w$ to remain constant, an increase in either the $[\text{H}_3\text{O}^+]$ or the $[\text{OH}^-]$ in an aqueous solution causes a decrease in the concentration of the other ion. Another example of the calculation of the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ of an acidic solution is shown in Sample Problem 16-1.
A 1.0 \times 10^{-4} \text{ M solution of HNO}_3 \text{ has been prepared for a laboratory experiment.}

a. Calculate the [H_3O^+] of this solution.

b. Calculate the [OH^-].

Given: Concentration of the solution = 1.0 \times 10^{-4} \text{ M HNO}_3

Unknown: a. [H_3O^+] \quad b. [OH^-]

HNO_3 is a strong acid, which means that it is essentially 100% ionized in dilute solutions. One molecule of acid produces one hydronium ion. The concentration of the hydronium ions thus equals the concentration of the acid. Because the ion product, [H_3O^+] [OH^-], is a constant, [OH^-] can easily be determined by using the value for [H_3O^+].

a. HNO_3(l) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(assuming 100\% ionization)}

molarity of HNO_3 = \frac{\text{mol HNO}_3}{\text{L solution}}

\frac{\text{mol HNO}_3}{\text{L solution}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HNO}_3} = \frac{\text{mol H}_3\text{O}^+}{\text{L solution}} = \text{molarity of H}_3\text{O}^+

b. [H_3O^+] [OH^-] = 1.0 \times 10^{-14} \text{ M}^2

[OH^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[H_3O^+]}$

\textbf{3. COMPUTE}

a. \frac{1.0 \times 10^{-4} \text{ mol HNO}_3}{\text{L solution}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HNO}_3} = \frac{1.0 \times 10^{-4} \text{ mol H}_3\text{O}^+}{\text{L solution}} = 1.0 \times 10^{-4} \text{ M H}_3\text{O}^+

b. [OH^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[H_3O^+]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-4} \text{ M}} = 1.0 \times 10^{-10} \text{ M}$

\textbf{4. EVALUATE}

Because the [H_3O^+], 1.0 \times 10^{-4}, is greater than 1.0 \times 10^{-7}, the [OH^-] must be less than 1.0 \times 10^{-7}. The answers are correctly expressed to two significant digits.

\textbf{PRACTICE}

1. Determine the hydronium and hydroxide ion concentrations in a solution that is 1 \times 10^{-4} \text{ M HCl.} \quad \textbf{Answer} \quad [H_3O^+] = 1 \times 10^{-4} \text{ M; [OH^-] = 1 \times 10^{-10} M}

2. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0 \times 10^{-3} \text{ M HNO}_3. \quad \textbf{Answer} \quad [H_3O^+] = 1.0 \times 10^{-3} \text{ M; [OH^-] = 1.0 \times 10^{-11} M}

3. Determine the hydronium and hydroxide ion concentrations in a solution that is 3.0 \times 10^{-2} \text{ M NaOH.} \quad \textbf{Answer} \quad [H_3O^+] = 3.3 \times 10^{-13} \text{ M; [OH^-] = 3.0 \times 10^{-2} M}

4. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0 \times 10^{-4} \text{ M Ca(OH)}_2. \quad \textbf{Answer} \quad [H_3O^+] = 5.0 \times 10^{-11} \text{ M; [OH^-] = 2.0 \times 10^{-4} M}
The pH Scale

Expressing acidity or basicity in terms of the concentration of $\text{H}_3\text{O}^+$ or $\text{OH}^-$ can be cumbersome because the values tend to be very small. A more convenient quantity, called pH, also indicates the hydronium ion concentration of a solution. The letters pH stand for the French words pouvoir hydrogène, meaning “hydrogen power.” The pH of a solution is defined as the negative of the common logarithm of the hydronium ion concentration, $[\text{H}_3\text{O}^+]$. The pH is expressed by the following equation.

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

The common logarithm of a number is the power to which 10 must be raised to equal the number. A neutral solution at 25°C has a $[\text{H}_3\text{O}^+]$ of $1 \times 10^{-7}$ M. The logarithm of $1 \times 10^{-7}$ is $-7.0$. The pH is determined as follows.

$$
\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1 \times 10^{-7}) = -(7.0) = 7.0
$$

The relationship between the pH and $[\text{H}_3\text{O}^+]$ is shown on the scale in Figure 16-3.

Likewise, the pOH of a solution is defined as the negative of the common logarithm of the hydroxide ion concentration, $[\text{OH}^-]$.

$$
\text{pOH} = -\log [\text{OH}^-]
$$

A neutral solution at 25°C has a $[\text{OH}^-]$ of $1 \times 10^{-7}$ M. Therefore, the pH is 7.0.

Remember that the values of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are related by $K_w$. The negative logarithm of $K_w$ at 25°C, $1 \times 10^{-14}$, is 14.0. You may have noticed that the sum of the pH and the pOH of a neutral solution at 25°C is also equal to 14.0. The following relationship is true at 25°C.

$$
\text{pH} + \text{pOH} = 14.0
$$

At 25°C the range of pH values of aqueous solutions generally falls between 0 and 14, as shown in Table 16-3.
Suppose the \([\text{H}_3\text{O}^+]\) in a solution is greater than the \([\text{OH}^-]\), as is true for acidic solutions. For example, the pH of an acidic solution at 25°C with a \([\text{H}_3\text{O}^+]\) of \(1 \times 10^{-6}\) M is 6.0.

\[
pH = -\log [\text{H}_3\text{O}^+] = -\log (1 \times 10^{-6}) = -(6.0) = 6.0
\]

The pH of this solution is less than 7. This is the case for all acidic solutions at 25°C. The following calculation shows that the pOH is greater than 7.0, as is true for all acidic solutions at 25°C.

\[
pOH = 14.0 - pH = 14.0 - 6.0 = 8.0
\]

Similar calculations show that the pH of a basic solution at 25°C is more than 7.0 and the pOH is less than 7.0. These and other relationships are listed in Table 16-4. Remember that as the temperature changes, the exact values will change because the value of \(K_w\) changes. However, the relationships between the values will remain the same.

### Table 16-3 Approximate pH Range of Some Common Materials (at 25°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>Material</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric juice</td>
<td>1.0–3.0</td>
<td>Bread</td>
<td>5.0–6.0</td>
</tr>
<tr>
<td>Lemons</td>
<td>2.2–2.4</td>
<td>Rainwater</td>
<td>5.4–5.8</td>
</tr>
<tr>
<td>Vinegar</td>
<td>2.4–3.4</td>
<td>Potatoes</td>
<td>5.6–6.0</td>
</tr>
<tr>
<td>Soft drinks</td>
<td>2.0–4.0</td>
<td>Milk</td>
<td>6.3–6.6</td>
</tr>
<tr>
<td>Apples</td>
<td>2.9–3.3</td>
<td>Saliva</td>
<td>6.5–7.5</td>
</tr>
<tr>
<td>Grapefruit</td>
<td>3.0–3.3</td>
<td>Pure water</td>
<td>7.0</td>
</tr>
<tr>
<td>Oranges</td>
<td>3.0–4.0</td>
<td>Blood</td>
<td>7.3–7.5</td>
</tr>
<tr>
<td>Cherries</td>
<td>3.2–4.0</td>
<td>Eggs</td>
<td>7.6–8.0</td>
</tr>
<tr>
<td>Tomatoes</td>
<td>4.0–4.4</td>
<td>Sea water</td>
<td>8.0–8.5</td>
</tr>
<tr>
<td>Bananas</td>
<td>4.5–5.7</td>
<td>Milk of magnesia</td>
<td>10.5</td>
</tr>
</tbody>
</table>

### Table 16-4 \([\text{H}_3\text{O}^+], [\text{OH}^-], \text{pH, and pOH of Solutions}\)

<table>
<thead>
<tr>
<th>Solution</th>
<th>General condition</th>
<th>At 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>([\text{H}_3\text{O}^+] = [\text{OH}^-]) pH = pOH</td>
<td>([\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7}) M pH = pOH = 7.0</td>
</tr>
<tr>
<td>Acidic</td>
<td>([\text{H}_3\text{O}^+] &gt; [\text{OH}^-]) pH &lt; pOH</td>
<td>([\text{H}_3\text{O}^+] &gt; 1 \times 10^{-7}) M ([\text{OH}^-] &lt; 1 \times 10^{-7}) M pH &lt; 7.0 pOH &gt; 7.0</td>
</tr>
<tr>
<td>Basic</td>
<td>([\text{H}_3\text{O}^+] &lt; [\text{OH}^-]) pH &gt; pOH</td>
<td>([\text{H}_3\text{O}^+] &lt; 1 \times 10^{-7}) M ([\text{OH}^-] &gt; 1 \times 10^{-7}) M pH &gt; 7.0 pOH &lt; 7.0</td>
</tr>
</tbody>
</table>
Calculations Involving pH

If either the $[\text{H}_3\text{O}^+]$ or pH of a solution is known, the other can be calculated. Significant figures involving pH must be handled carefully. Because pH represents a logarithm, the number to the left of the decimal only locates the decimal point. It is not included when counting significant figures. So there must be as many significant figures to the right of the decimal as there are in the number whose logarithm was found. For example, a $[\text{H}_3\text{O}^+]$ value of $1 \times 10^{-7}$ has one significant figure. Therefore, the pH, or $-\log$, of this value must have one digit to the right of the decimal. Thus, $\text{pH} = 7.0$ has the correct number of significant figures.

Calculating pH from $[\text{H}_3\text{O}^+]$

You have already seen the simplest pH problems. In these problems, the $[\text{H}_3\text{O}^+]$ of the solution is an integral power of 10, such as 1 M or 0.01 M. The pH of this type of solution is the exponent of the hydronium ion concentration with the sign changed. For example, the pH of a solution in which $[\text{H}_3\text{O}^+]$ is $1 \times 10^{-5}$ M is 5.0.

**SAMPLE PROBLEM 16-2**

What is the pH of a $1.0 \times 10^{-3}$ M NaOH solution?

**SOLUTION**

1. **ANALYZE**
   - Given: Identity and concentration of solution = $1.0 \times 10^{-3}$ M NaOH
   - Unknown: pH of solution

2. **PLAN**
   - concentration of base $\rightarrow$ concentration of $\text{OH}^-$ $\rightarrow$ concentration of $\text{H}_3\text{O}^+$$\rightarrow$ pH

   NaOH is completely dissociated when it is dissolved in water. A $1.0 \times 10^{-3}$ M NaOH solution therefore produces a $[\text{OH}^-]$ equal to $1.0 \times 10^{-3}$ M. The ion product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is a constant, $1.0 \times 10^{-14}$ M$^2$. By substitution, the $[\text{H}_3\text{O}^+]$ can be determined. The pH can then be calculated.

3. **COMPUTE**

   \[
   [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2 \\
   [\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-3} \text{ M}} = 1.0 \times 10^{-11} \text{ M} \\
   \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.0 \times 10^{-11}) = 11.00
   \]

4. **EVALUATE**

   The answer correctly indicates that NaOH forms a solution with pH > 7, which is basic.

**PRACTICE**

1. Determine the pH of the following solutions:
   a. $1 \times 10^{-3}$ M HCl
   b. $1 \times 10^{-5}$ M HNO$_3$
   c. $1 \times 10^{-4}$ M NaNO$_3$
   d. $1.0 \times 10^{-2}$ M KOH

   **Answer**
   a. pH = 3.0
   b. pH = 5.0
   c. pH = 10.0
   d. pH = 12.00
Using a Calculator to Calculate pH from $[\text{H}_3\text{O}^+]$

Some problems involve hydronium ion concentrations that are not equal to integral powers of 10. These problems require a calculator. Most scientific calculators have a “log” key. Consult the instructions for your particular calculator.

An estimate of pH can be used to check your calculations. For example, suppose the $[\text{H}_3\text{O}^+]$ of a solution is $3.4 \times 10^{-5}$ M. Because $3.4 \times 10^{-5}$ lies between $10^{-4}$ and $10^{-5}$, the pH of the solution must be between 4 and 5. Sample Problem 16-3 continues the actual calculation of the pH value for a solution with $[\text{H}_3\text{O}^+] = 3.4 \times 10^{-5}$ M.

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**SAMPLE PROBLEM 16-3**

**What is the pH of a solution if the $[\text{H}_3\text{O}^+]$ is $3.4 \times 10^{-5}$ M?**

**SOLUTION**

1. **ANALYZE**
   - Given: $[\text{H}_3\text{O}^+] = 3.4 \times 10^{-5}$ M
   - Unknown: pH of solution

2. **PLAN**
   
   $[\text{H}_3\text{O}^+] \rightarrow \text{pH}$

   The only difference between this problem and previous pH problems is that you will determine the logarithm of $3.4 \times 10^{-5}$ using your calculator. You can convert numbers to logarithms on most calculators by using the “log” key.

3. **COMPUTE**

   \[
   \text{pH} = -\log [\text{H}_3\text{O}^+] \\
   = -\log (3.4 \times 10^{-5}) \\
   = 4.47
   \]

   On most calculators, this problem is entered in the following steps.

   ![Calculator steps]

4. **EVALUATE**

   The pH of a $1 \times 10^{-5}$ M H$_3$O$^+$ solution is 5.0. Therefore, it follows that a solution with a greater concentration of hydronium ions would be more acidic and have a pH less than 5.

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**PRACTICE**

1. What is the pH of a solution if the $[\text{H}_3\text{O}^+]$ is $6.7 \times 10^{-4}$ M?  
   - Answer  
   - pH = 3.17

2. What is the pH of a solution with a hydronium ion concentration of $2.5 \times 10^{-2}$ M?  
   - Answer  
   - pH = 1.60

3. Determine the pH of a $2.5 \times 10^{-6}$ M HNO$_3$ solution.  
   - Answer  
   - pH = 5.60

4. Determine the pH of a $2.0 \times 10^{-2}$ M Sr(OH)$_2$ solution.  
   - Answer  
   - pH = 12.60
Calculating [H₃O⁺] and [OH⁻] from pH

You have now learned to calculate the pH of a solution, given its [H₃O⁺]. Suppose that you are given the pH of a solution instead. How can you determine its hydronium ion concentration?

You already know the following equation.

\[ \text{pH} = -\log \left[ \text{H}_3\text{O}^+ \right] \]

Remember that the base of common logarithms is 10. Therefore, the antilog of a common logarithm is 10 raised to that number.

\[ \log \left[ \text{H}_3\text{O}^+ \right] = -\text{pH} \]
\[ \left[ \text{H}_3\text{O}^+ \right] = \text{antilog} \left( -\text{pH} \right) \]
\[ \left[ \text{H}_3\text{O}^+ \right] = 10^{-\text{pH}} \]

The simplest cases are those in which pH values are integers. The exponent of 10 that gives the [H₃O⁺] is the negative of the pH. For an aqueous solution that has a pH of 2, for example, the [H₃O⁺] is equal to 10⁻² M. Likewise, when the pH is 0, the [H₃O⁺] is 1 M because 10⁰ = 1. Sample Problem 16-4 shows how to convert a pH value that is an integer. Sample Problem 16-5 shows how to use a calculator to convert a pH that is not an integer number.

**SAMPLE PROBLEM 16-4**

Determine the hydronium ion concentration of an aqueous solution that has a pH of 4.0.

**SOLUTION**

1. **ANALYZE**
   
   Given: \( \text{pH} = 4.0 \)
   
   Unknown: \( \left[ \text{H}_3\text{O}^+ \right] \)

2. **PLAN**
   
   \( \text{pH} \rightarrow \left[ \text{H}_3\text{O}^+ \right] \)
   
   This problem requires that you rearrange the pH equation and solve for the [H₃O⁺]. Because 4.0 has one digit to the right of the decimal, the answer must have one significant figure.

   \[ \text{pH} = -\log \left[ \text{H}_3\text{O}^+ \right] \]
   
   \[ \log \left[ \text{H}_3\text{O}^+ \right] = -\text{pH} \]
   
   \[ \left[ \text{H}_3\text{O}^+ \right] = \text{antilog} \left( -\text{pH} \right) \]
   
   \[ \left[ \text{H}_3\text{O}^+ \right] = 1 \times 10^{-\text{pH}} \]

3. **COMPUTE**
   
   \[ \left[ \text{H}_3\text{O}^+ \right] = 1 \times 10^{-4} \text{ M} \]

4. **EVALUATE**
   
   A solution with a pH of 4.0 is acidic. The answer, 1 \( \times \) 10⁻⁴ M, is greater than 1.0 \( \times \) 10⁻⁷ M, which is correct for an acidic solution.
The pH of a solution is determined to be 7.52.

1. **What is the hydronium ion concentration?**
2. **What is the hydroxide ion concentration?**
3. **Is the solution acidic or basic?**

**Given:** pH of the solution = 7.52

**Unknown:** a. \([H_3O^+]\)  b. \([OH^-]\)  c. Is the solution acidic or basic?

**Solution**

1. **Analyze**
   
   **Given:** pH of the solution = 7.52
   
   **Unknown:** a. \([H_3O^+]\)  b. \([OH^-]\)  c. Is the solution acidic or basic?

2. **Plan**
   
   This problem is very similar to previous pH problems. You will need to substitute values into the pH = \(-\log [H_3O^+]\) equation and use a calculator. Once the \([H_3O^+]\) is determined, the ion-product constant \([H_3O^+] [OH^-] = 1.0 \times 10^{-14}\) may be used to calculate \([OH^-]\).

3. **Compute**
   
   a. \[\text{pH} = -\log [H_3O^+]\]
      
      \[\log [H_3O^+] = -\text{pH}\]
      
      \[ [H_3O^+] = \text{antilog} (-\text{pH}) = \text{antilog} (-7.52) = 1.0 \times 10^{-7.52} = 3.0 \times 10^{-8} \text{ M} \]

      On most calculators, this is entered in one of the following two ways.

      \[ 7 \ 8 \ 9 \ 6 \ 5 \ 4 \ +/- \ \times/y \ 10^x \ or \ 7 \ 8 \ 9 \ 6 \ 5 \ 4 \ +/- \ \times/y \ 10^x \]

   b. \([H_3O^+] [OH^-] = 1.0 \times 10^{-14} \text{ M}^2\]
      
      \[ [OH^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[H_3O^+]} \]
      
      \[ = \frac{1.0 \times 10^{-14} \text{ M}^2}{3.0 \times 10^{-8} \text{ M}} = 3.3 \times 10^{-7} \text{ M} \]

   c. A pH of 7.52 is slightly greater than a pH of 7. This means that the solution is slightly basic.

4. **Evaluate**
   
   Because the solution is slightly basic, a hydroxide ion concentration slightly larger than 10^{-7} M is predicted. A hydronium ion concentration slightly less than 10^{-7} M is also predicted. The answers agree with these predictions.

**Practice**

1. The pH of a solution is determined to be 5.0. What is the hydronium ion concentration of this solution?  
   
   **Answer**  
   
   \([H_3O^+] = 1 \times 10^{-5} \text{ M}\)

2. The pH of a solution is determined to be 12.0. What is the hydronium ion concentration of this solution?  
   
   **Answer**  
   
   \([H_3O^+] = 1 \times 10^{-12} \text{ M}\)

3. The pH of an aqueous solution is measured as 1.50. Calculate the \([H_3O^+]\) and the \([OH^-]\).  
   
   **Answer**  
   
   \([H_3O^+] = 3.2 \times 10^{-2} \text{ M}; \]
   \([OH^-] = 3.2 \times 10^{-13} \text{ M}\)

4. The pH of an aqueous solution is 3.67. Determine \([H_3O^+]\).  
   
   **Answer**  
   
   \([H_3O^+] = 2.1 \times 10^{-4} \text{ M}\)
### SECTION REVIEW

1. What is the concentration of hydronium and hydroxide ions in pure water at 25°C?
2. Why does the pH scale generally range from 0 to 14 in aqueous solutions?
3. Why does a pH of 7 represent a neutral solution at 25°C?
4. Identify each of the following as being true of acidic or basic solutions at 25°C:
   - a. \([H_3O^+] = 1 \times 10^{-3} \text{ M}\)  
   - b. \([OH^-] = 1 \times 10^{-4} \text{ M}\)  
   - c. pH = 5.0  
   - d. pH = 8.0
5. A solution contains \(4.5 \times 10^{-3}\) HCl. Determine the following for the solution:
   - a. \([H_3O^+]\)  
   - b. \([OH^-]\)  
   - c. pH
6. A Ca(OH)\(_2\) solution has a pH of 8.0. Determine the following for the solution:
   - a. \([H_3O^+]\)  
   - b. \([OH^-]\)  
   - c. [Ca(OH)\(_2\)]

---

### pH Calculations and the Strength of Acids and Bases

So far, we have discussed the pH of solutions that contain only strong acids or strong bases. We must also consider weak acids and weak bases. Table 16-5 lists the \([H_3O^+]\), the \([OH^-]\), and the pH for several solutions.

KOH, the solute in the first solution listed, is a soluble ionic compound and a strong base. The molarity of a KOH solution directly indicates the \([OH^-]\), and the \([H_3O^+]\) can be calculated. Once the \([H_3O^+]\) is known, the pH can be calculated as in Sample Problem 16-3. If the pH of this solution is measured experimentally, it will be the same as this calculated value. Methods for experimentally determining the pH of solutions will be presented in Section 16-2. Hydrochloric acid, HCl, is a strong acid, and similar calculations can be made for solutions that contain HCl.

Solutions of weak acids, such as acetic acid, CH\(_3\)COOH, present a different problem. The \([H_3O^+]\) cannot be calculated directly from the molar concentration because not all of the acetic acid molecules are ionized. The same problem occurs for weak bases such as ammonia, NH\(_3\). The pH of these solutions must be measured experimentally. The \([H_3O^+]\) and \([OH^-]\) can then be calculated from the measured pH values.

### Table 16-5 Relationship of \([H_3O^+]\) to \([OH^-]\) and pH (at 25°C)

<table>
<thead>
<tr>
<th>Solution</th>
<th>([H_3O^+])</th>
<th>([OH^-])</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 × 10(^{-2}) M KOH</td>
<td>1.0 × 10(^{-12})</td>
<td>1.0 × 10(^{-2})</td>
<td>12.00</td>
</tr>
<tr>
<td>1.0 × 10(^{-2}) M NH(_3)</td>
<td>2.4 × 10(^{-11})</td>
<td>4.2 × 10(^{-4})</td>
<td>10.62</td>
</tr>
<tr>
<td>Pure H(_2)O</td>
<td>1.0 × 10(^{-7})</td>
<td>1.0 × 10(^{-7})</td>
<td>7.00</td>
</tr>
<tr>
<td>1.0 × 10(^{-3}) M HCl</td>
<td>1.0 × 10(^{-3})</td>
<td>1.0 × 10(^{-11})</td>
<td>3.00</td>
</tr>
<tr>
<td>1.0 × 10(^{-1}) M CH(_3)COOH</td>
<td>1.3 × 10(^{-3})</td>
<td>7.7 × 10(^{-12})</td>
<td>2.88</td>
</tr>
</tbody>
</table>
In 1987, Dr. Ken Simmons tested some rainbow trout in the waters of north-central Massachusetts’ Whetstone Brook. He placed the trout in cages in the brook so that their behavior and survival could be monitored. Three days later, they were all dead. Acid rain had lowered the pH level of the water to a point at which the trout simply could not survive.

Acid rain begins with the fossil fuels we burn to power our cars and factories. The fumes released by those fuels contain sulfur dioxides and nitrous oxides that combine with the water vapor in the atmosphere and turn it acidic. While normal rainwater has a pH level around 5.7, acid rain’s pH can be less than 4.2.

The rain lowers the pH level of the brook and significantly affects most of the organisms living in it. Some fish, like the rainbow trout, simply die. Other species refuse to spawn in acidic waters, as the Whetstone’s brown trout did in 1987.

The year that the brown trout refused to spawn, the pH level of Whetstone Brook averaged 5.97. The population of all the trout dropped dangerously low, and in 1989, Dr. Simmons and other researchers instituted an experiment to decrease the acidity of the stream. They created a system to constantly add calcium carbonate, or limestone, in measured amounts to part of the brook. The limestone, ground into a powder, dissolved instantly and acted as a buffer against the acid, raising the pH level of the water.

The experiment lasted three years and managed to raise the average pH level of the stream from 5.97 to 6.54, meeting the scientists’ goal. At the same time, the amount of toxic aluminum in the limed area decreased, while it increased in untreated parts of the brook.

The success of the project was most convincingly demonstrated by the stream’s residents. The population of brook trout increased, the mortality rate of brown trout decreased, and for the first time in years, fish actually began to move into the stream from its source, the Millers River. In 1991, Dr. Simmons again tested rainbow trout in the waters of the Whetstone. This time, they all survived.

“We clearly don’t view it as a solution,” says Dr. Simmons. “It’s a band-aid approach, but we need data to make intelligent management decisions as to how useful or harmful liming could be. And I think that is the key thing this study has shown. It has provided us with information that we can use.”

Describe two possible benefits of adding measured amounts of \( \text{CaCO}_3 \), a base, to an acidified stream.
**Indicators and pH Meters**

An approximate value for the pH of a solution can be obtained using acid-base indicators. **Acid-base indicators are compounds whose colors are sensitive to pH.** In other words, the color of an indicator changes as the pH of a solution changes.

Indicators change colors because they are either weak acids or weak bases. In solution, the equilibrium of an indicator that is a weak acid can be represented by the equation below, which is modeled in Figure 16-4.

$$\text{H} \text{In} \rightleftharpoons \text{H}^+ + \text{In}^-$$

($\text{In}^-$ is the symbol of the anion part of the indicator.) The colors that an indicator displays result from the fact that $\text{H} \text{In}$ and $\text{In}^-$ are different colors.

In acidic solutions, any $\text{In}^-$ ions that are present act as Brønsted bases and accept protons from the acid. The indicator is then present in largely nonionized form, $\text{H} \text{In}$. The indicator has its acid-indicating color, as shown for litmus in Figure 16-4.

In basic solutions, the $\text{OH}^-$ ions from the base combine with the $\text{H}^+$ ions produced by the indicator. The indicator molecules further ionize to offset the loss of $\text{H}^+$ ions. The indicator is thus present largely in the form of its anion, $\text{In}^-$. The solution now displays the base-indicating color, which for litmus is blue.

**FIGURE 16-4** Basic solutions shift the equilibrium of litmus to the right. The ionized form, $\text{In}^-$, then predominates, and the litmus turns blue. Acidic solutions shift the equilibrium of the indicator litmus to the left. The nonionized form, $\text{H} \text{In}$, predominates, and the litmus turns red.
Indicators come in many different colors. The exact pH range over which an indicator changes color also varies. The pH range over which an indicator changes color is called its transition interval. Table 16-6 gives the color changes and transition intervals for a number of common acid-base indicators.

Indicators that change color at pH lower than 7, such as methyl orange, are simply stronger acids than the other types of indicators. They tend to ionize more completely than the others. The $\text{In}^-$ anions that these indicators produce are weaker Brønsted bases and have less tendency to accept protons from any acid being tested. These indicators therefore do not shift to their nonionized ($\text{HIn}$) form unless the concentration of $\text{H}^+$ is fairly high. The color transition of these indicators occurs at rather low pH. In contrast, indicators that undergo transition in the higher pH range, such as phenolphthalein, are weaker acids.

Universal indicators are made by mixing several different indicators. Paper soaked in universal indicator solution is called pH paper. This paper can turn almost any color of the rainbow and provides a fairly accurate way of distinguishing the pH of solutions, as shown in Figure 16-5.

If an exact value for the pH of a solution is needed, a pH meter, shown in Figure 16-6, should be used. A pH meter determines the pH of a solution by measuring the voltage between the two electrodes that are placed in the solution. The voltage changes as the hydronium ion concentration in the solution changes.
### TABLE 16-6 Color Ranges of Various Indicators Used in Titrations

<table>
<thead>
<tr>
<th>Titration type</th>
<th>Indicator</th>
<th>Acid color</th>
<th>Transition color</th>
<th>Base color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong-acid/strong-base</td>
<td>methyl red (4.4–6.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bromthymol blue (6.2–7.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong-acid/weak-base</td>
<td>methyl orange (3.1–4.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bromphenol blue (3.0–4.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weak-acid/strong-base</td>
<td>phenolphthalein (8.0–10.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>phenol red (6.4–8.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Testing the pH of Rainwater

Question

Do you have acid precipitation in your area?

Materials

- rainwater
- distilled water
- 500 mL jars
- thin, transparent metric ruler (± 0.1 cm)
- pH test paper: narrow range, ± 0.2–0.3, or pH meter

Procedure

Record all your results in a data table.

1. Each time it rains, set out five clean jars to collect the rainwater. If the rain continues for more than 24 hours, put out new containers at the end of each 24-hour period until the rain stops. (The same procedure can be used with snow if the snow is allowed to melt before measurements are taken. You may need to use larger containers if a heavy snowfall is expected.)

2. After the rain stops or at the end of each 24-hour period, measure the depth of the water to the nearest 0.1 cm with a thin plastic ruler. Test the water with the pH paper to determine its pH to the nearest 0.2–0.3.

3. Record the following information:
   a. the date and time the collection was started
   b. the date and time the collection was ended
   c. the location where the collection was made (town and state)
   d. the amount of rainfall in centimeters
   e. the pH of the rainwater

4. Find the average pH of each collection that you have made for each rainfall, and record it in the data table.

5. Collect samples on at least five different days. The more samples you collect, the more reliable your data will be.

6. For comparison, determine the pH of pure water by testing five samples of distilled water with pH paper. Record your results in a separate data table, and then calculate an average pH for distilled water.

Discussion

1. What is the pH of distilled water?

2. What is the pH of normal rainwater? How do you explain any differences between the pH readings?

3. What are the drawbacks of using a ruler to measure the depth of collected water? How could you increase the precision of your measurement?

4. Does the amount of rainfall or the time of day the sample is taken have an effect on its pH? Explain any variability among samples.

5. What conclusion can you draw from this investigation? Explain how your data support your conclusion.
As you know, neutralization reactions occur between acids and bases. The \( \text{OH}^- \) ion acquires a proton from the \( \text{H}_3\text{O}^+ \) ion, forming two molecules of water. The following equation summarizes this reaction.

\[
\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l)
\]

This equation shows that one mol of hydronium ions, 19.0 g, and one mol of hydroxide ions, 17.0 g, are chemically equivalent masses. They combine in a one-to-one ratio. Neutralization occurs when hydronium ions and hydroxide ions are supplied in equal numbers by reactants, as shown in Figure 16-7.

One liter of a 0.10 M HCl solution contains 0.10 mol of hydronium ions. Now suppose that 0.10 mol of solid NaOH is added to 1 L of 0.10 M HCl solution. The NaOH dissolves and supplies 0.10 mol of hydroxide ions to the solution. HCl and NaOH are present in chemically equivalent amounts. Hydronium and hydroxide ions, which are present in equal numbers, combine until the product \([\text{H}_3\text{O}^+] [\text{OH}^-]\) returns to the value of \(1 \times 10^{-14} \text{ M}^2\). NaCl, the salt produced in the reaction, is the product of the neutralization of a strong acid and a strong base. The resulting solution is neutral.

Because acids and bases react, the progressive addition of an acid to a base (or a base to an acid) can be used to compare the concentrations of the acid and the base. **Titration** is the controlled addition and measurement of the amount of a solution of known concentration required to react completely with a measured amount of a solution of unknown concentration. Titration provides a sensitive means of determining the chemically equivalent volumes of acidic and basic solutions.

**FIGURE 16-7** The solution on the left turns pH paper red because it is acidic. The solution on the right turns pH paper blue because it is basic. When equal numbers of \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) from the acidic and basic solutions react, the resulting solution is neutral. The neutral solution turns pH paper green.
Equivalence Point

The point at which the two solutions used in a titration are present in chemically equivalent amounts is the **equivalence point**. Indicators and pH meters can be used to determine the equivalence point. A pH meter will show a large voltage change occurring at the equivalence point. If an indicator is used, it must change color over a range that includes the pH of the equivalence point, as shown in Figure 16-8. **The point in a titration at which an indicator changes color is called the end point of the indicator.**

Some indicators, such as litmus, change color at about pH 7. However, the color-change interval for litmus is broad, pH 5.5–8.0. This broad range makes it difficult to determine an accurate pH. Bromthymol blue is better because it has a limited transition interval, pH 6.0–7.6 (see Table 16-6). Indicators that undergo transition at about pH 7 are used to determine the equivalence point of strong-acid/strong-base titrations because the neutralization of strong acids with strong bases produces a salt solution with a pH of approximately 7.

Indicators that change color at pH lower than 7 are useful in determining the equivalence point of strong-acid/weak-base titrations. Methyl orange is an example of this type. The equivalence point of a strong-acid/weak-base titration is acidic because the salt formed is itself a weak acid. Thus the salt solution has a pH lower than 7.

Indicators that change color at pH higher than 7 are useful in determining the equivalence point of weak-acid/strong-base titrations. Phenolphthalein is an example. These reactions produce salt solutions whose pH is greater than 7. This occurs because the salt formed is a weak base.

You may be wondering what type of indicator is used to determine the equivalence point of weak-acid/weak-base titrations. The surprising answer is “none at all.” The pH of the equivalence point of weak acids and weak bases may be almost any value, depending on the relative strengths of the reactants. The color transition of an indicator helps

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**FIGURE 16-8** Indicators change color at the end point of a titration. Phenolphthalein (a) turns pink and methyl red (b) turns red at the end point of these titrations.
very little in determining whether reactions between such acids and bases are complete.

In a titration, successive additions of an aqueous base can be made to a measured volume of an aqueous acid. As base is added, the pH changes from a low numerical value to a high one. The change in pH occurs slowly at first, then rapidly through the equivalence point, then slowly again as the solution becomes more basic. Typical pH curves for strong-acid/strong-base and weak-acid/strong-base titrations are shown in Figure 16-9.

**Figure 16-9**  (a) When a strong acid, such as 50.0 mL of 1.00 M HCl, is titrated with a strong base, such as 1.00 M NaOH, the equivalence point occurs at about pH 7. (b) When a weak acid, such as 50 mL of 1.00 M CH₃COOH, is titrated with a strong base, such as 1.00 M NaOH, the equivalence point occurs at a pH above 7.

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**Molarity and Titration**

Figure 16-10 on pages 500–501 shows the proper method of carrying out a titration. If the concentration of one solution is known precisely, the concentration of the other solution in a titration can be calculated from the chemically equivalent volumes. *The solution that contains the precisely known concentration of a solute is known as a standard solution.* It is often called simply the “known” solution.

To be certain of the concentration of the known solution, that solution must first be compared with a solution of a primary standard. *A primary standard is a highly purified solid compound used to check the concentration of the known solution in a titration.* The known solution is prepared first, and its volume is adjusted to give roughly the desired concentration. The concentration is then determined more precisely by titrating the solution with a carefully measured quantity of a solution of the primary standard.
Following is the proper method for carrying out an acid-base titration. To be sure you have an accurate value, you should repeat the titration until you have three results that agree within 0.05 mL. This procedure would be used to determine the unknown concentration of an acid using a standardized base solution. First set up two clean burets as shown. Decide which of the burets will be used for the acid and which for the base. Rinse the acid buret three times with the acid to be used in the titration. Repeat this procedure for the base buret with the base solution to be used.

1. Fill the first buret to a point above the calibration mark with the acid of unknown concentration.
2. Release some acid from the buret to remove any air bubbles and to lower the volume to the calibrated portion of the buret.
3. Record the reading at the top of the acid in the buret to the nearest 0.01 mL as your starting point.
4. Subtract the current volume reading on the buret from the initial reading. This is the exact volume of the acid released into the flask. Record it to the nearest 0.01 mL.
5. Release a predetermined volume of the acid (determined by your teacher or lab procedure) into a clean, dry Erlenmeyer flask.
6. Add three drops of the appropriate indicator (in this case phenolphthalein) to the flask.
7. Subtract the current volume reading on the buret from the initial reading. This is the exact volume of the acid released into the flask. Record it to the nearest 0.01 mL.
Fill the other buret with the standard base solution to a point above the calibration mark. The concentration of the standard base is known to a certain degree of precision because it was previously titrated with an exact mass of solid acid.

Place the Erlenmeyer flask under the base buret as shown. Notice that the tip of the buret extends into the mouth of the flask.

Record the reading at the top of the base to the nearest 0.01 mL as your starting point.

Release some base from the buret to remove any air bubbles and to lower the volume to the calibrated portion of the buret.

Place the Erlenmeyer flask under the base buret as shown. Notice that the tip of the buret extends into the mouth of the flask.

Slowly release base from the buret into the flask while constantly swirling the contents of the flask. The pink color of the indicator should fade with swirling.

The titration is nearing the end point when the pink color stays for longer periods of time. At this point, add base drop by drop.

The equivalence point is reached when a very light pink color remains after 30 seconds of swirling.

Subtract the current volume reading on the buret from the initial reading. This is the exact volume of the base released into the flask. Record it to the nearest 0.01 mL.
The known solution can be used to determine the molarity of another solution by titration. Suppose 20.0 mL of $5.0 \times 10^{-3}$ M NaOH is required to reach the end point in the titration of 10.0 mL of HCl of unknown concentration. How can these titration data be used to determine the molarity of the acidic solution?

Begin with the balanced neutralization reaction equation. From the equation, determine the chemically equivalent amounts of HCl and NaOH.

$$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

1 mol 1 mol 1 mol 1 mol

Calculate the number of moles of NaOH used in the titration.

$$\frac{5.0 \times 10^{-3} \text{ mol NaOH}}{1000 \text{ mL}} \times 20.0 \text{ mL} = 1.0 \times 10^{-4} \text{ mol NaOH used}$$

Because 1 mol of NaOH is needed to neutralize 1 mol of HCl, the amount of HCl in the titration must be $1.0 \times 10^{-4}$ mol. This is confirmed by the following equation.

$$1.0 \times 10^{-4} \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 1.0 \times 10^{-4} \text{ mol HCl}$$

This amount of acid must be in the 10.0 mL of the HCl solution used for the titration. The molarity of the HCl solution can now be calculated.

$$\frac{1 \times 10^{-4} \text{ mol HCl}}{10.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{1.0 \times 10^{-2} \text{ mol HCl}}{\text{L}}$$

$$= 1.0 \times 10^{-2} \text{ M HCl}$$

Sample Problem 16-6 illustrates the following four steps.

1. Start with the balanced equation for the neutralization reaction, and determine the chemically equivalent amounts of the acid and base.
2. Determine the moles of acid (or base) from the known solution used during the titration.
3. Determine the moles of solute of the unknown solution used during the titration.
4. Determine the molarity of the unknown solution.

**SAMPLE PROBLEM 16-6**

In a titration, 27.4 mL of 0.0154 M Ba(OH)$_2$ is added to a 20.0 mL sample of HCl solution of unknown concentration. What is the molarity of the acid solution?

**SOLUTION**

1. **ANALYZE**

   **Given:** volume and concentration of known solution = 27.4 mL of 0.0154 M Ba(OH)$_2$

   **Unknown:** volume of unknown HCl solution = 20.0 mL
2 PLAN

1. balanced neutralization equation $\rightarrow$ chemically equivalent amounts

$$\text{Ba(OH)}_2 + 2\text{HCl} \rightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$$

$$1 \text{ mol} \quad 2 \text{ mol} \quad 1 \text{ mol} \quad 2 \text{ mol}$$

2. volume of known basic solution used (mL) $\rightarrow$ amount of base used (mol)

$$\frac{\text{mol Ba(OH)}_2}{\text{L}} \times \text{mL of Ba(OH)}_2 \text{ solution} \times \frac{1 \text{ L}}{1000 \text{ mL}} = \text{mol Ba(OH)}_2$$

3. mole ratio, moles of base used $\rightarrow$ moles of acid used from unknown solution

$$\frac{2 \text{ mol HCl}}{1 \text{ mol Ba(OH)}_2} \times \text{mol Ba(OH)}_2 \text{ in known solution} = \text{mol HCl in unknown solution}$$

4. volume of unknown, moles of solute in unknown $\rightarrow$ molarity of unknown

$$\frac{\text{amount of solute in unknown solution (mol)}}{\text{volume of unknown solution (mL)}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \text{molarity of unknown solution}$$

3 COMPUTE

1. The mole ratio from the equation is 1 mol Ba(OH)$_2$ for every 2 mol HCl.

2. $$\frac{0.0154 \text{ mol Ba(OH)}_2}{\text{L}} \times 27.4 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.22 \times 10^{-4} \text{ mol Ba(OH)}_2$$

3. $$\frac{2 \text{ mol HCl}}{1 \text{ mol Ba(OH)}_2} \times 4.22 \times 10^{-4} \text{ mol Ba(OH)}_2 = 8.44 \times 10^{-4} \text{ mol HCl}$$

4. $$\frac{8.44 \times 10^{-4} \text{ mol HCl}}{20.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 4.22 \times 10^{-2} \text{ mol HCl} \text{ L} = 4.22 \times 10^{-2} \text{ M HCl}$$

PRACTICE

1. A 15.5 mL sample of 0.215 M KOH solution required 21.2 mL of aqueous acetic acid solution in a titration experiment. Calculate the molarity of the acetic acid solution. **Answer** 0.157 M CH$_3$COOH

2. By titration, 17.6 mL of aqueous H$_2$SO$_4$ neutralized 27.4 mL of 0.0165 M LiOH solution. What was the molarity of the aqueous acid solution? **Answer** 0.0128 M H$_2$SO$_4$

SECTION REVIEW

1. Name an appropriate indicator for titrating the following:
   a. a strong acid and a weak base
   b. a strong base and a weak acid

2. Suppose you have an NaOH solution of unknown concentration. Name three possible substances that could be used in "known" solutions to titrate the NaOH solution.

3. If 20.0 mL of 0.0100 M aqueous HCl is required to neutralize 30.0 mL of an aqueous solution of NaOH, determine the molarity of the NaOH solution.

4. Suppose that 20.0 mL of 0.10 M Ca(OH)$_2$ is required to neutralize 12.0 mL of aqueous HCl solution. What is the molarity of the HCl solution?
CHAPTER 16 REVIEW

CHAPTER SUMMARY

16-1  • Pure water undergoes self-ionization to give
1.0 \times 10^{-7} \text{ M H}_2\text{O}^+ and 1.0 \times 10^{-7} \text{ M OH}^- at 25°C.
• pH = \text{−log[H}_2\text{O}^+]; pOH = \text{−log[OH}^−]
At 25°C, pH + pOH = 14.0.
• At 25°C, acids have a pH of less than 7, bases have a pH of greater than 7, and neutral solutions have a pH of 7.

Vocabulary
pH (485) pOH (485)

16-2  • If a solution contains a strong acid or a strong base, the [H_3O^+] and [OH^-] and pH can be calculated from the molarity of the solution. If a solution contains a weak acid or a weak base, the [H_3O^+] and the [OH^-] must be calculated from an experimentally measured pH.

Vocabulary
end point (498) acid-base indicators (493)
equivalence point (498) pH meter (494)
primary standard (499) titration (497)
standard solution (499) transition interval (494)

REVIEWING CONCEPTS

1. Why does pure water weakly conduct an electric current? (16-1)
2. What does it mean when the formula of a particular ion or molecule is enclosed in brackets? (16-1)
3. a. What is the [H_3O^+] of pure water at 25°C? b. Is this true at all temperatures? Why or why not? (16-1)
4. a. What is always true about the [H_3O^+] value of acidic solutions? b. What is true about the [H_3O^+] value of acidic solutions at 25°C? (16-1)
5. a. Describe what is meant by the pH of a solution. b. Write the equation for determining pH. c. Explain and illustrate what is meant by the common logarithm of a number. (16-1)
6. Identify each of the following as being true of acidic, basic, or neutral solutions at 25°C:
a. [H_3O^+] = 1.0 \times 10^{-7} \text{ M}
b. [H_3O^+] = 1.0 \times 10^{-10} \text{ M}
c. [OH^-] = 1.0 \times 10^{-7} \text{ M}
d. [OH^-] = 1.0 \times 10^{-11} \text{ M}
e. [H_3O^+] = [OH^-]
f. pH = 3.0
g. pH = 13.0
(16-1)
7. Arrange the following common substances in order of increasing pH:
a. eggs f. potatoes b. apples g. lemons c. tomatoes h. milk of magnesia d. milk i. sea water
e. bananas (16-1)
8. What is meant by the transition interval of an indicator? (16-2)
9. Explain how an indicator’s equilibrium determines the color the indicator displays at a given pH. (16-2)
10. a. Other than through indicators, how can the equivalence point of a titration experiment or the pH of a solution be determined?
   b. What can be observed about the rate of change in the pH of a solution near the end point of a titration? (16-2)

11. a. What is meant by the end point of a titration?
   b. What is the role of an indicator in the titration process?
   c. On what basis is an indicator selected for a particular titration experiment? (16-2)

12. For each of the four possible types of acid-base titration combinations, indicate the approximate pH at the end point. Also name a suitable indicator for detecting that end point. (16-2)

13. Based on Figures 14-9(a) and 14-9(b), draw a pH curve for a strong-acid/weak-base titration. (16-2)

14. An unknown solution is colorless when tested with phenolphthalein but causes the indicator phenol red to turn red. Based on this information, what is the approximate pH of this solution? (16-2)

**PROBLEMS**

### pH Calculations

15. Calculate the \([H_3O^+]\) and \([OH^-]\) for each of the following. (Hint: See Sample Problem 16-1.)
   a. 0.03 M HCl
   b. \(1 \times 10^{-4}\) M NaOH
   c. \(5 \times 10^{-3}\) M H\(_2\)SO\(_4\)
   d. 0.01 M Ca(OH)\(_2\)

16. Determine the pH of each of the following solutions. (Hint: See Sample Problem 16-2.)
   a. 1.0 \(\times 10^{-2}\) M HCl
   b. 1.0 \(\times 10^{-3}\) M HNO\(_3\)
   c. 1.0 \(\times 10^{-5}\) M HI
   d. 1.0 \(\times 10^{-4}\) M HBr

17. Given the following \([OH^-]\) values, determine the pH of each solution.
   a. 1.0 \(\times 10^{-6}\) M
   b. 1.0 \(\times 10^{-7}\) M
   c. 1.0 \(\times 10^{-2}\) M
   d. 1.0 \(\times 10^{-3}\) M

18. Determine the pH of each solution.
   a. 1.0 \(\times 10^{-2}\) M NaOH
   b. 1.0 \(\times 10^{-3}\) M KOH
   c. 1.0 \(\times 10^{-4}\) M LiOH

19. Determine the pH of solutions with each of the following \([H_3O^+]\). (Hint: See Sample Problem 16-3.)
   a. \(2.0 \times 10^{-5}\) M
   b. \(4.7 \times 10^{-7}\) M
   c. \(3.8 \times 10^{-3}\) M

20. Given the following pH values, determine the \([H_3O^+]\) for each solution. (Hint: See Sample Problem 16-4.)
   a. 3.0
   b. 7.00
   c. 11.0
   d. 5.0

21. Given the following pH values, determine the \([OH^-]\) for each solution.
   a. 7.00
   b. 11.00
   c. 4.00
   d. 6.00

22. Determine \([H_3O^+]\) for solutions with the following pH values. (Hint: See Sample Problem 16-5.)
   a. 4.23
   b. 7.65
   c. 9.48
   d. 5.0

23. A nitric acid solution is found to have a pH of 2.70. Determine each of the following:
   a. \([H_3O^+]\)
   b. \([OH^-]\)
   c. the number of moles of HNO\(_3\) required to prepare 5.50 L of this solution
   d. the mass of the moles of HNO\(_3\) in the solution in part (c)
   e. the milliliters of concentrated acid needed to prepare the solution in part (c) (Concentrated nitric acid is 69.5% HNO\(_3\) by mass and has a density of 1.42 g/mL.)

### Titrations

24. For each of the following acid-base titration combinations, determine the number of moles of the first substance listed that would be the chemically equivalent amount of the second substance.
   a. NaOH with 1.0 mol HCl
   b. HNO\(_3\) with 0.75 mol KOH
   c. Ba(OH)\(_2\) with 0.20 mol HF
   d. H\(_2\)SO\(_4\) with 0.60 mol Al(OH)\(_3\)

25. Suppose that 15.0 mL of 2.50 \(\times 10^{-2}\) M aqueous H\(_2\)SO\(_4\) is required to neutralize 10.0 mL of an aqueous solution of KOH. What is the molarity of the KOH solution? (Hint: See Sample Problem 16-6.)
26. In a titration experiment, a 12.5 mL sample of $1.75 \times 10^{-2}$ M Ba(OH)$_2$ just neutralized 14.5 mL of HNO$_3$ solution. Calculate the molarity of the HNO$_3$ solution.

**MIXED REVIEW**

27. a. What is the [OH$^-$] of a $4.0 \times 10^{-4}$ M solution of Ca(OH)$_2$?  
b. What is the [H$_3$O$^+$] of the solution?

28. Given the following [H$_3$O$^+$] values, determine the pH of each solution.  
a. $1.0 \times 10^{-7}$ M  
b. $1.0 \times 10^{-3}$ M  
c. $1.0 \times 10^{-12}$ M  
d. $1.0 \times 10^{-5}$ M

29. What is the [H$_3$O$^+$] for a solution that has a pH of 6.0?

30. Suppose that a $5.0 \times 10^{-5}$ M solution of Ba(OH)$_2$ is prepared. What is the pH of the solution?

31. a. Calculate the pH of a solution that has an [H$_3$O$^+$] of $8.4 \times 10^{-11}$ M.  
b. Calculate the [H$_3$O$^+$] of a solution that has a pH of 2.50.

32. a. What is the concentration of OH$^-$ in a $5.4 \times 10^{-5}$ M solution of magnesium hydroxide, Mg(OH)$_2$?  
b. Calculate the concentration of H$_3$O$^+$ for this solution.

33. a. Calculate the molarity of H$_3$O$^+$ in a solution that has a pH of 8.90.  
b. Calculate the concentration of OH$^-$ in the solution.

34. What is the pH of a solution for which [OH$^-$] equals $6.9 \times 10^{-10}$ M?

35. In a titration, 25.9 mL of $3.4 \times 10^{-3}$ M Ba(OH)$_2$ neutralized 16.6 mL of HCl solution. What is the molarity of the HCl solution?

36. Find the molarity of a Ca(OH)$_2$ solution, given that 428 mL of it is neutralized in a titration by 115 mL of $6.7 \times 10^{-3}$ M HNO$_3$.

37. Suppose that 10.1 mL of HNO$_3$ is neutralized by 71.4 mL of a $4.2 \times 10^{-3}$ M solution of KOH in a titration. Calculate the concentration of the HNO$_3$ solution.

**CRITICAL THINKING**

38. Interpreting Graphics  The following titration curve resulted from the titration of an unknown acid with 0.10 M NaOH. Analyze the curve. Make inferences related to the type of acidic solution titrated.

**TECHNOLOGY & LEARNING**

39. Graphing Calculator  Graphing Titration Data  
The graphing calculator can run a program that graphs data such as pH versus volume of base. Graphing the titration data will allow you to determine which combination of acid and base is represented by the shape of the graph. Begin by creating a table of data. Then program the calculator to plot the data.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating your lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.
42. Water quality depends on the ability of treatment facilities to reprocess waste water. Most waste-water treatment facilities use living organisms to break down wastes. Because of acid rain, the acidic nature of waste water can pose problems for a waste-treatment plant. Conduct library research on this topic and write a brief report. Include a description of how the low pH of acidic waste water can affect the ecology of a waste-water treatment plant.

**HANDBOOK SEARCH**

40. The normal pH of blood is about 7.4. When the pH shifts above or below that level, the results are acidosis or alkalosis. Review the section on blood pH in Group 14 of the *Elements Handbook*, then answer the following.
   a. What chemical species keep H$_3$O$^+$ in blood at the appropriate pH?
   b. What condition results when there is an excess of CO$_2$ in the blood?
   c. What is hyperventilation and how does it affect blood pH?

**ALTERNATIVE ASSESSMENT**

43. **Performance** Use pH paper to determine the approximate pH of various brands of orange juice, which contains citric acid.

44. **Performance** Design and conduct an experiment to extract possible acid-base indicators from sources such as red cabbage, berries, and flower petals. Use known acidic, basic, and neutral solutions to test the action of each indicator that you are able to isolate.

45. **Performance** Design and conduct an experiment to study the pH of rain for an extended period of time. Coordinate your data-collection activities with those of your classmates so that the pH readings are made in a variety of locations. Try to determine whether any patterns emerge in terms of location, season, time of day, degree of industrialization in the area, and so on.

**RESEARCH & WRITING**

41. Examine the labels of at least five brands of shampoo. Note what is written there, if anything, regarding the pH of the shampoo. Do library research to find out why such pH ranges are chosen and why other ranges might be harmful to hair or eyes.