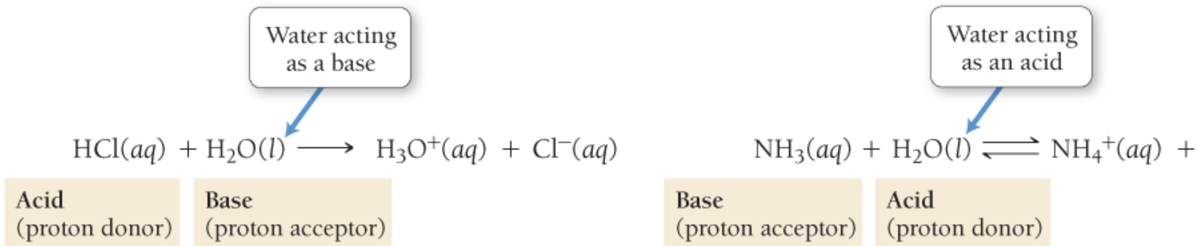
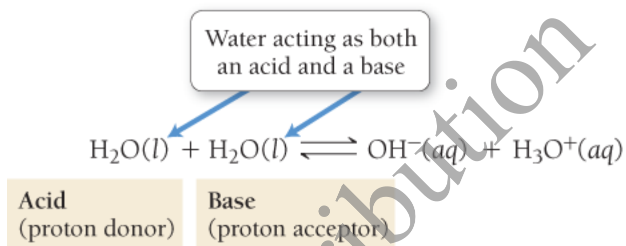
Pearson

16.6: Autoionization of Water and pH

We saw previously that water acts as a base when it reacts with HCl and as an acid when it reacts with NH_3:



Water is *amphoteric*; it can act as either an acid or a base. Even when pure, water acts as an acid and a base with itself, a process called **autoionization**:



We can also write the autoionization reaction as:

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

The equilibrium constant expression for this reaction is the product of the concentration of the two ions:

$$K_w = \left[H_3O^+\right]\left[OH^-\right] = \left[H^+\right]\left[OH^-\right]$$

This equilibrium constant is the **ion product constant for water (K_w)** (sometimes called the *dissociation constant for water*). At 25°C, $K_w = 1.0 \times 10^{-14}$. In pure water, since H_2O is the only source of these ions, the concentrations of H_3O^+ and OH^- are equal, and the solution is **neutral**. Since the concentrations of the two ions are equal, we can easily calculate them from K_w:

$$\left[H_3O^+\right] = \left[OH^-\right] = \sqrt{K_w} = 1.0 \times 10^{-7} (\text{in pure water at } 25\ °C)$$

As you can see, in pure water, the concentrations of H_3O^+ and OH^- are *very small* $\left(1.0 \times 10^{-7} M\right)$ at room temperature.

An **acidic solution** contains an acid that creates additional H_3O^+ ions, causing $\left[H_3O^+\right]$ to increase. However, the *ion product constant still applies*:

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

The concentration of H_3O^+ *times the concentration of* OH^- *is always* 1.0×10^{-14} *at* 25 °C If $\left[H_3O^+\right]$ increases, then

$[OH^-]$ must decrease for the ion product constant to remain 1.0×10^{-14}. For example, if $[H_3O^+] = 1.0 \times 10^{-3}$, we can find $[OH^-]$ by solving the ion product constant expression for $[OH^-]$:

$$(1.0 \times 10^{-3})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\text{ M}$$

In an acidic solution, $[H_3O^+] > [OH^-]$.

A **basic solution** contains a base that creates additional OH^- ions, causing $[OH^-]$ to increase and $[H_3O^+]$ to decrease, but again the *ion product constant still applies*. Suppose $[OH^-] = 1.0 \times 10^{-2}$ we can find $[H_3O^+]$ by solving the ion product constant expression for $[H_3O^+]$:

$$[H_3O^+](1.0 \times 10^{-2}) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\text{ M}$$

In a basic solution, $[OH^-] > [H_3O^+]$.

Notice that changing $[H_3O^+]$ in an aqueous solution produces an inverse change in $[OH^-]$ and vice versa.

Summarizing K_w:

- A *neutral solution* contains $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\text{M}$ (at 25 °C).
- An *acidic solution* contains $[H_3O^+] > [OH^-]$.
- A *basic solution* contains $[OH^-] > [H_3O^+]$.
- In *all aqueous solutions*, both H_3O^+ and OH^- are present and $[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$ (at 25 °C).

Example 16.2 Using K_w in Calculations

Calculate $[OH^-]$ at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

a. $[H_3O^+] = 7.5 \times 10^{-5}\text{M}$

b. $[H_3O^+] = 1.5 \times 10^{-9}\text{M}$

c. $[H_3O^+] = 1.0 \times 10^{-7}\text{M}$

SOLUTION

a. To find $[OH^-]$ use the ion product constant. Substitute the given value for $[H_3O^+]$ and solve the equation for $[OH^-]$.

Since $[H_3O^+] > [OH^-]$, the solution is acidic.

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

$$(7.5 \times 10^{-5})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-5}} = 1.3 \times 10^{-10}\text{M}$$

Acidic solution

b. Substitute the given value for $[H_3O^+]$ and solve the acid ionization equation for $[OH^-]$.

b. Substitute the given value for $\left[H_3O^+\right]$ and solve the acid ionization equation for $\left[OH^-\right]$

Since $\left[H_3O^+\right] < \left[OH^-\right]$, the solution is basic.

$$\left(1.5 \times 10^{-9}\right)\left[OH^-\right] = 1.0 \times 10^{-14}$$
$$\left[OH^-\right] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6} M$$

Basic solution

c. Substitute the given value for $\left[H_3O^+\right]$ and solve the acid ionization equation for $\left[OH^-\right]$.

Since $\left[H_3O^+\right] = 1.0 \times 10^{-7}$ and $\left[OH^-\right] = 1.0 \times 10^{-7}$, the solution is neutral.

$$\left(1.0 \times 10^{-7}\right)\left[OH^-\right] = 1.0 \times 10^{-14}$$
$$\left[OH^-\right] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} M$$

Neutral solution

FOR PRACTICE 16.2 Calculate $\left[H_3O^+\right]$ at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

a. $\left[OH^-\right] = 1.5 \times 10^{-2} M$

b. $\left[OH^-\right] = 1.0 \times 10^{-7} M$

c. $\left[OH^-\right] = 8.2 \times 10^{-10} M$

Specifying the Acidity or Basicity of a Solution: The pH Scale

The pH scale is a compact way to specify the acidity of a solution. We define **pH** as the negative of the log of the hydronium ion concentration:

$$pH = -\log\left[H_3O^+\right]$$

A solution with $\left[H_3O^+\right] = 1.0 \times 10^{-3} M$ (acidic) has a pH of:

$$\begin{aligned} pH &= -\log\left[H_3O^+\right] \\ &= -\log\left(1.0 \times 10^{-3}\right) \\ &= -(-3.00) \\ &= 3.00 \end{aligned}$$

The log of a number is the exponent to which 10 must be raised to obtain that number. Thus, $\log 10^1 = 1$; $\log 10^2 = 2$; $\log 10^{-1} = -1$; $\log 10^{-2} = -2$, and so on (see Appendix I).

Notice that we report the pH to two *decimal places* here. This is because only the numbers to the right of the decimal point are significant in a logarithm. Because our original value for the concentration had two significant figures, the log of that number has two decimal places:

$$-\log \underbrace{1.0}_{\text{2 significant digits}} \times 10^{-3} = 3.\underbrace{00}_{\text{2 decimal places}}$$

If the original number had three significant digits, we would report the log to three decimal places:

3 significant digits 3 decimal places

$$-\log 1.00 \times 10^{-3} = 3.000$$

A solution with $[H_3O^+] = 1.0 \times 10^{-7} M$ (neutral) has a pH of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log\left(1.0 \times 10^{-7}\right) \\ &= -(-7.00) \\ &= 7.00 \end{aligned}$$

In general, at 25 °C

- pH < 7 The solution is *acidic*.
- pH > 7 The solution is *basic*.
- pH = 7 The solution is *neutral*.

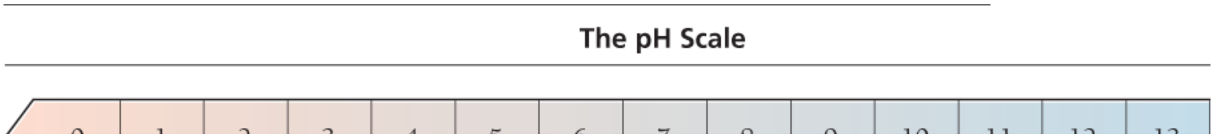
> Concentrated acid solutions can have a negative pH. For example, if $[H_3O^+] = 2.0$ M the pH is −0.30.

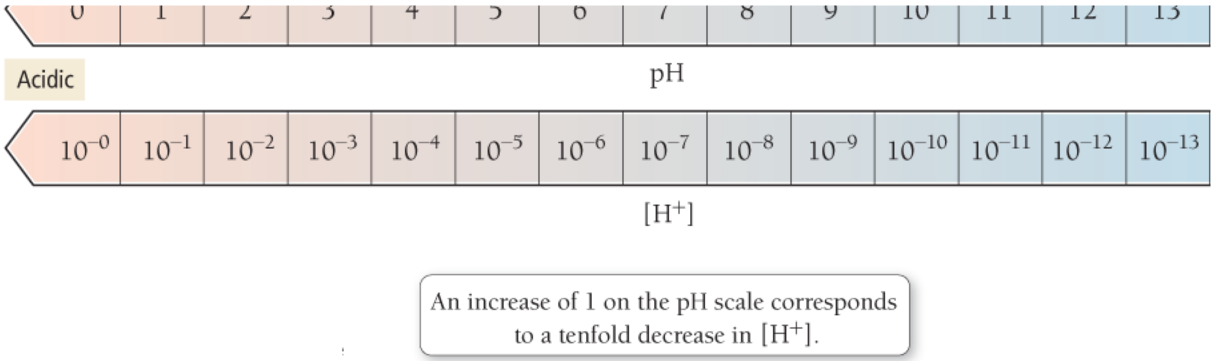
Table 16.6 lists the pH of some common substances. As we discussed in Section 16.2, many foods, especially fruits, are acidic and have low pH values. Relatively few foods are basic. The foods with the lowest pH values are limes and lemons, and they are among the sourest. Because the pH scale is a *logarithmic scale*, a change of 1 pH unit corresponds to a tenfold change in H_3O^+ concentration (Figure 16.7). For example, a lime with a pH of 2.0 is 10 times more acidic than a plum with a pH of 3.0 and 100 times more acidic than a cherry with a pH of 4.0.

Table 16.6 The pH of Some Common Substances

Substance	pH
Gastric juice (human stomach)	1.0–3.0
Limes	1.8–2.0
Lemons	2.2–2.4
Soft drinks	2.0–4.0
Plums	2.8–3.0
Wines	2.8–3.8
Apples	2.9–3.3
Peaches	3.4–3.6
Cherries	3.2–4.0
Beers	4.0–5.0
Rainwater (unpolluted)	5.6
Human blood	7.3–7.4
Egg whites	7.6–8.0
Milk of Magnesia	10.5
Household ammonia	10.5–11.5
4% NaOH solution	14

Figure 16.7 The pH Scale





Example 16.3 Calculating pH from $[H_3O^+]$ or $[OH^-]$

Calculate the pH of each solution at 25 °C and indicate whether the solution is acidic or basic.

a. $[H_3O^+] = 1.8 \times 10^{-4} M$

b. $[OH^-] = 1.3 \times 10^{-2} M$

SOLUTION

a. To calculate pH, substitute the given $[H_3O^+]$ into the pH equation.

Since pH < 7, this solution is acidic.

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.8 \times 10^{-4}) \\ &= -(-3.74) \\ &= 3.74 (\text{acidic}) \end{aligned}$$

b. First use K_w to find $[H_3O^+]$ from $[OH^-]$.

Then substitute $[H_3O^+]$ into the pH expression to find pH.

Since pH > 7, this solution is basic.

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

$$[H_3O^+](1.3 \times 10^{-2}) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13} M$$

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(7.7 \times 10^{-13}) \\ &= -(-12.11) \\ &= 12.11 (\text{basic}) \end{aligned}$$

FOR PRACTICE 16.3 Calculate the pH of each solution and indicate whether the solution is acidic or basic.

a. $[H_3O^+] = 9.5 \times 10^{-9} M$

b. $[OH^-] = 7.1 \times 10^{-3} M$

Interactive Worked Example 16.3 **Calculating pH from $[H_3O^+]$ or $[OH^-]$**

Example 16.4 Calculating $[H_3O^+]$ from pH

Calculate $[H_3O^+]$ for a solution with a pH of 4.80.

SOLUTION

To determine $[H_3O^+]$ from pH, start with the equation that defines pH. Substitute the given value of pH and then solve for $[H_3O^+]$. Because the given pH value was reported to two decimal places, the $[H_3O^+]$ is written to two significant figures. (Remember that $10^{\log x} = x$; see Appendix I. Some calculators use an inv log key to represent this function.)

$$\begin{aligned}
\text{pH} &= -\log[H_3O^+] \\
4.80 &= -\log[H_3O^+] \\
-4.80 &= \log[H_3O^+] \\
10^{-4.80} &= 10^{\log[H_3O^+]} \\
10^{-4.80} &= [H_3O^+] \\
[H_3O^+] &= 1.6 \times 10^{-5}\,\text{M}
\end{aligned}$$

FOR PRACTICE 16.4 Calculate $[H_3O^+]$ for a solution with a pH of 8.37.

pOH and Other p Scales

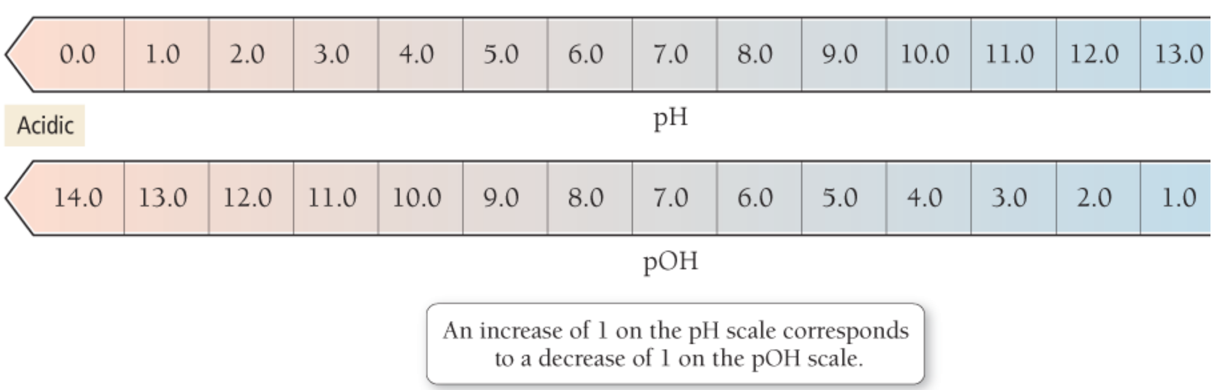
The pOH scale is analogous to the pH scale, but we define pOH with respect to $[OH^-]$ instead of $[H_3O^+]$.

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

A solution with an $[OH^-]$ of 1.0×10^{-3} M (basic) has a pOH of 3.00. On the pOH scale, a pOH less than 7 is basic and a pOH greater than 7 is acidic. A pOH of 7 is neutral (Figure 16.8). We can derive a relationship between pH and pOH at 25 °C from the expression for K_w:

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

Figure 16.8 pH and pOH



Taking the log of both sides, we get:

$$\log([H_3O^+][OH^-]) = \log(1.0 \times 10^{-14})$$
$$\log[H_3O^+] + \log[OH^-] = -14.00$$
$$-\log[H_3O^+] - \log[OH^-] = 14.00$$
$$\boxed{pH + pOH = 14.00}$$

The sum of pH and pOH is always equal to 14.00 at 25 °C. Therefore, a solution with a pH of 3 has a pOH of 11.

Another common p scale is the pK_a scale defined as:

$$pK_a = -\log K_a$$

> Notice that p is the mathematical operator $-\log$; thus, $pX = -\log X$.

The pK_a of a weak acid is another way to quantify strength. The smaller the pK_a, the stronger the acid. For example, chlorous acid, with a K_a of 1.1×10^{-2}, has a pK_a of 1.96 and formic acid, with a K_a of 1.8×10^{-4}, has a pK_a of 3.74.

Conceptual Connection 16.5 **pH and Acidity**

Interactive