

## 16.1: The Autoionization of Water

### Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and  $pK_w$ .

As you learned in [Chapter 8](#) and [Chapter 4](#), acids and bases can be defined in several different ways ([Table 16.1.1](#)). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce  $H^+$  ions (protons), and an Arrhenius base is a substance that dissociates in water to produce  $OH^-$  (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that *donate* a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can *accept* a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton, as we demonstrated in [Chapter 8](#). Consequently, all Brønsted–Lowry acid–base reactions actually involve *two* conjugate acid–base pairs and the transfer of a *proton* from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, discussed in [Chapter 8](#), focuses on accepting or donating *pairs of electrons* rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

**Table 16.1.1 Definitions of Acids and Bases**

|                | Acids                  | Bases               |
|----------------|------------------------|---------------------|
| Arrhenius      | $H^+$ donor            | $OH^-$ donor        |
| Brønsted–Lowry | $H^+$ donor            | $H^+$ acceptor      |
| Lewis          | electron-pair acceptor | electron-pair donor |

Because this chapter deals with acid–base equilibria in *aqueous solution*, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

In [Chapter 8](#), we also introduced the acid–base properties of water, its *autoionization reaction*, and the definition of pH. The purpose of this section is to review those concepts and describe them using the concepts of chemical equilibrium developed in [Chapter 15](#).

### Acid–Base Properties of Water

The structure of the water molecule, with its polar O–H bonds and two lone pairs of electrons on the oxygen atom, was described in [Chapter 8](#) and [Chapter 4](#), and the structure of liquid water was discussed in [Chapter 13](#). Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions ( $Cl^-$ ) and protons ( $H^+$ ). As you learned in [Chapter 8](#), the proton, in turn, reacts with a water molecule to form the *hydronium ion* ( $H_3O^+$ ):

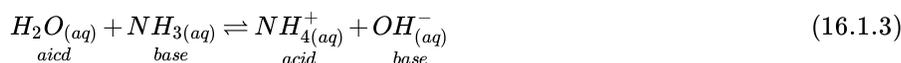


In this reaction, HCl is the acid, and water acts as a base by accepting an  $H^+$  ion. The reaction in [Equation 16.1.1](#) is often written in a simpler form by removing  $H_2O$  from each side:



In [Equation 16.1.2](#), the hydronium ion is represented by  $H^+$ , although free  $H^+$  ions do not exist in liquid water.

Water can also act as an acid, as shown in [Equation 16.1.3](#). In this equilibrium reaction,  $H_2O$  donates a proton to  $NH_3$ , which acts as a base:



Thus water is amphiprotic. Substances that can behave as either an acid or a base in a chemical reaction, depending on the nature of the other reactant(s), meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that [Equation 16.3](#) is an equilibrium reaction as indicated by the double arrow.

### The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an  $OH^-$  ion and an  $H_3O^+$  ion in an autoionization process:



The equilibrium constant  $K$  for this reaction can be written as follows:

$$K = \frac{[H_3O^+_{(aq)}][OH^-_{(aq)}]}{[H_2O(l)]^2} \quad (16.1.5)$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at  $25^\circ C$ , the concentrations of the hydronium ion and the hydroxide ion are equal:  $[H_3O^+] = [OH^-] = 1.003 \times 10^{-7} M$ . Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate  $[H_2O]$  at  $25^\circ C$  from the density of water at this temperature (0.997 g/mL):

$$[H_2O(l)] = mol/L = (0.997 \text{ g/mL}) \left( \frac{1 \text{ mol}}{18.02 \text{ g}} \right) \left( \frac{1000 \text{ mL}}{L} \right) = 55.3 M \quad (16.1.6)$$

With so few water molecules dissociated, the equilibrium of the autoionization reaction ([Equation 16.4](#)) lies far to the left. Consequently,  $[H_2O]$  is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange [Equation 16.1.5](#) to define a new equilibrium constant, the ion-product constant of liquid water ( $K_w$ )

$$K = \frac{K_w}{[H_2O(l)]^2} \quad (16.1.7a)$$

with

$$K_w = [H_3O^+_{(aq)}][OH^-_{(aq)}] = [H_3O^+_{(aq)}][OH^-_{(aq)}] \quad (16.1.7b)$$

Substituting the values for  $[H_3O^+]$  and  $[OH^-]$  at  $25^\circ C$  into this expression,

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \quad (16.1.8)$$

Thus, to three significant figures,  $K_w = 1.01 \times 10^{-14} M$ . Like any other equilibrium constant,  $K_w$  varies with temperature, ranging from  $1.15 \times 10^{-15}$  at  $0^\circ C$  to  $4.99 \times 10^{-13}$  at  $100^\circ C$ .

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If  $[H_3O^+] > [OH^-]$ , however, the solution is acidic, whereas if  $[H_3O^+] < [OH^-]$ , the solution is basic. For an aqueous solution, the  $H_3O^+$  concentration is a quantitative measure of acidity: the higher the  $H_3O^+$  concentration, the more acidic the solution. Conversely, the higher the  $OH^-$  concentration, the more basic the solution. In most situations that you will encounter, the  $H_3O^+$  and  $OH^-$  concentrations from the dissociation of water are so small ( $1.003 \times 10^{-7} M$ ) that they can be ignored in calculating the  $H_3O^+$  or  $OH^-$  concentrations of solutions of acids and bases, but this is not always the case.

### The Relationship among pH, pOH, and $pK_w$

The *pH scale* is a concise way of describing the  $H_3O^+$  concentration and hence the acidity or basicity of a solution. Recall from [Chapter 8](#) that pH and the  $H^+$  ( $H_3O^+$ ) concentration are related as follows:

$$pH = -\log_{10}[H^+(aq)] \quad (16.1.9)$$

$$[H^+(aq)] = 10^{-pH} \quad (16.1.10)$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. (Refer to Essential Skills 3 in [Section 8.11](#), if you need to refresh your memory about how to use logarithms.) Recall also that the pH of a neutral solution is 7.00 ( $[H_3O^+] = 1.0 \times 10^{-7} \text{ M}$ ), whereas acidic solutions have  $\text{pH} < 7.00$  (corresponding to  $[H_3O^+] > 1.0 \times 10^{-7}$ ) and basic solutions have  $\text{pH} > 7.00$  (corresponding to  $[H_3O^+] < 1.0 \times 10^{-7}$ ).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous *pOH scale* to describe the hydroxide ion concentration of a solution. The pOH and  $[OH^-]$  are related as follows:

$$pOH = -\log_{10}[OH^-(aq)] \quad (16.1.11)$$

$$[OH^-(aq)] = 10^{-pOH} \quad (16.1.12)$$

The constant  $K_w$  can also be expressed using this notation, where  $pK_w = -\log K_w$ .

Because a neutral solution has  $[OH^-] = 1.0 \times 10^{-7}$ , the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is  $7.00 + 7.00 = 14.00$ . We can show that the sum of pH and pOH is equal to 14.00 for *any* aqueous solution at 25°C by taking the negative logarithm of both sides of [Equation 16.7](#):

$$-\log K_w = -\log([H_3O^+(aq)][OH^-(aq)]) = (-\log[H_3O^+(aq)]) + (-\log[OH^-(aq)]) = pH + pOH \quad (16.1.13)$$

Thus at any temperature,  $pH + pOH = pK_w$ , so at 25°C, where  $K_w = 1.0 \times 10^{-14}$ ,  $pH + pOH = 14.00$ . More generally, the pH of any neutral solution is half of the  $pK_w$  at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in [Figure 16.1.1](#) over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

### Note the Pattern

For any neutral solution,  $pH + pOH = 14.00$  (at 25°C) and  $pH = 14 - pOH$ .

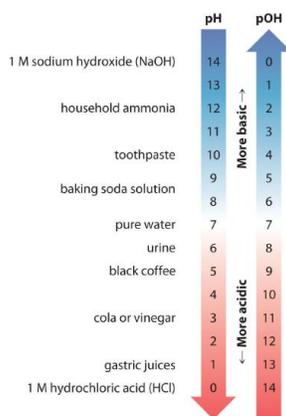


Figure 16.1.1 The Inverse Relationship between the pH and pOH Scales As pH decreases,  $[H^+]$  and the acidity increase. As pOH increases,  $[OH^-]$  and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

### Example 16.1.1

The  $K_w$  for water at 100°C is  $4.99 \times 10^{-13}$ . Calculate  $pK_w$  for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C. Report pH and pOH values to two decimal places.

**Given:**  $K_w$

**Asked for:**  $pK_w$ , pH, and pOH

**Strategy:**

**A** Calculate  $pK_w$  by taking the negative logarithm of  $K_w$ .

**B** For a neutral aqueous solution,  $[H_3O^+] = [OH^-]$ . Use this relationship and [Equation 16.7](#) to calculate  $[H_3O^+]$  and  $[OH^-]$ . Then determine the pH and the pOH for the solution.

**Solution:**

A Because  $pK_w$  is the negative logarithm of  $K_w$ , we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable:  $K_w$  is between  $10^{-13}$  and  $10^{-12}$ , so  $pK_w$  must be between 12 and 13.

B Equation 16.1.7 shows that  $K_w = [H_3O^+][OH^-]$ . Because  $[H_3O^+] = [OH^-]$  in a neutral solution, we can let  $x = [H_3O^+] = [OH^-]$ :

$$K_w = [H_3O^+][OH^-] = (x)(x) = x^2$$

$$x = \sqrt{K_w} = \sqrt{4.99 \times 10^{-13}} = 7.06 \times 10^{-7} \text{ M}$$

Because  $x$  is equal to both  $[H_3O^+]$  and  $[OH^-]$ ,

$$pH = pOH = -\log(7.06 \times 10^{-7}) = 6.15 \text{ (to two decimal places)}$$

We could obtain the same answer more easily (without using logarithms) by using the  $pK_w$ . In this case, we know that  $pK_w = 12.302$ , and from Equation 16.13, we know that  $pK_w = pH + pOH$ . Because  $pH = pOH$  in a neutral solution, we can use Equation 16.13 directly, setting  $pH = pOH = y$ . Solving to two decimal places we obtain the following:

$$pK_w = pH + pOH = y + y = 2y$$

$$y = \frac{pK_w}{2} = \frac{12.302}{2} = 6.15 = pH = pOH$$

Exercise

Humans maintain an internal temperature of about 37°C. At this temperature,  $K_w = 3.55 \times 10^{-14}$ . Calculate  $pK_w$  and the pH and the pOH of a neutral solution at 37°C. Report pH and pOH values to two decimal places.

**Answer:**  $pK_w = 13.45$   $pH = pOH = 6.73$

Summary

Water is **amphiprotic**: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion ( $H_3O^+$ ). The *autoionization* of liquid water produces  $OH^-$  and  $H_3O^+$  ions. The equilibrium constant for this reaction is called the **ion-product constant of liquid water ( $K_w$ )** and is defined as  $K_w = [H_3O^+][OH^-]$ . At 25°C,  $K_w$  is  $1.01 \times 10^{-14}$ ; hence  $pH + pOH = pK_w = 14.00$ .

Key Takeaway

- For any neutral solution,  $pH + pOH = 14.00$  (at 25°C) and  $pH = 1/2 pK_w$ .

Key Equations

**Ion-product constant of liquid water**

Equation 16.1.7:  $K_w = [H_3O^+][OH^-]$

**Definition of pH**

Equation 16.1.9:  $pH = -\log_{10}[H^+]$

Equation 16.1.10:  $[H^+] = 10^{-pH}$

**Definition of pOH**

Equation 16.1.11:  $pOH = -\log_{10}[OH^-]$

Equation 16.1.12:  $[OH^-] = 10^{-pOH}$

**Relationship among pH, pOH, and  $pK_w$**

Equation 16.1.13:  $pK_w = pH + pOH$

## Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water ( $K_w$ )?
2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause  $K_w$  to increase or decrease? Why?
3. Show that water is amphoteric by writing balanced chemical equations for the reactions of water with  $\text{HNO}_3$  and  $\text{NH}_3$ . In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
  1. Nitric acid is added to water.
  2. Potassium hydroxide is added to water.
  3. Calcium hydroxide is added to water.
  4. Sulfuric acid is added to water.
5. Show that  $K$  for the sum of the following reactions is equal to  $K_w$ .



2.

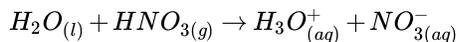
## Answers

1. 
$$K_{\text{auto}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

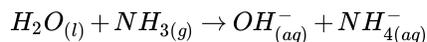
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = K_{\text{auto}}[\text{H}_2\text{O}]^2$$

2.

3. water is the base:



water is the acid:

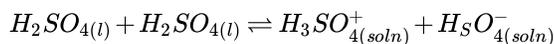


4.

5.

## Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:



At 25°C,  $K = 3 \times 10^{-4}$ . Write an equilibrium constant expression for  $K(\text{H}_2\text{SO}_4)$  that is analogous to  $K_w$ . The density of  $\text{H}_2\text{SO}_4$  is 1.8 g/cm<sup>3</sup> at 25°C. What is the concentration of  $\text{H}_3\text{SO}_4^+$ ? What fraction of  $\text{H}_2\text{SO}_4$  is ionized?

2. An aqueous solution of a substance is found to have  $[\text{H}_3\text{O}^+] = 2.48 \times 10^{-8}$  M. Is the solution acidic, neutral, or basic?
3. The pH of a solution is 5.63. What is its pOH? What is the  $[\text{OH}^-]$ ? Is the solution acidic or basic?
4. State whether each solution is acidic, neutral, or basic.
  1.  $[\text{H}_3\text{O}^+] = 8.6 \times 10^{-3}$  M
  2.  $[\text{H}_3\text{O}^+] = 3.7 \times 10^{-9}$  M
  3.  $[\text{H}_3\text{O}^+] = 2.1 \times 10^{-7}$  M
  4.  $[\text{H}_3\text{O}^+] = 1.4 \times 10^{-6}$  M
5. Calculate the pH and the pOH of each solution.

1. 0.15 M HBr

2. 0.03 M KOH
  3.  $2.3 \times 10^{-3}$  M HNO<sub>3</sub>
  4.  $9.78 \times 10^{-2}$  M NaOH
  5. 0.00017 M HCl
  6. 5.78 M HI
6. Calculate the pH and the pOH of each solution.
1. 25.0 mL of  $2.3 \times 10^{-2}$  M HCl, diluted to 100 mL
  2. 5.0 mL of 1.87 M NaOH, diluted to 125 mL
  3. 5.0 mL of 5.98 M HCl added to 100 mL of water
  4. 25.0 mL of 3.7 M HNO<sub>3</sub> added to 250 mL of water
  5. 35.0 mL of 0.046 M HI added to 500 mL of water
  6. 15.0 mL of 0.0087 M KOH added to 250 mL of water.
7. The pH of stomach acid is approximately 1.5. What is the [H<sup>+</sup>]?
8. Given the pH values in parentheses, what is the [H<sup>+</sup>] of each solution?
1. household bleach (11.4)
  2. milk (6.5)
  3. orange juice (3.5)
  4. seawater (8.5)
  5. tomato juice (4.2)
9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?
10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

### Answers

1. 
$$K_{H_2SO_4} = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]_2$$
  

$$[H_3SO_4^+] = 0.3M$$
  
 [H<sub>3</sub>SO<sub>4</sub><sup>+</sup>] = 0.3 M; the fraction ionized is 0.02.
- 2.
3. pOH = 8.37; [OH<sup>-</sup>] =  $4.3 \times 10^{-9}$  M; acidic
- 4.
5.
  1. pH = 0.82; pOH = 13.18
  2. pH = 12.5; pOH = 1.5
  3. pH = 2.64; pOH = 11.36
  4. pH = 12.990; pOH = 1.010
  5. pH = 3.77; pOH = 10.23
  6. pH = -0.762; pOH = 14.762
- 6.
- 7.
- 8.
9. 2.9 mg HCl
- 10.

### Contributors

- Anonymous

Modified by Joshua B. Halpern

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