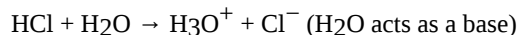
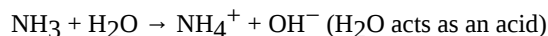


## 14.7: Autoionization of Water

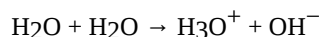
### Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in solutions, knowing the other concentration.

We have already seen that  $\text{H}_2\text{O}$  can act as an acid or a base:



It may not be surprising to learn, then, that within any given sample of water, some  $\text{H}_2\text{O}$  molecules are acting as acids, and other  $\text{H}_2\text{O}$  molecules are acting as bases. The chemical equation is as follows:



This occurs only to a very small degree: only about 6 in  $10^8$   $\text{H}_2\text{O}$  molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  in a sample of pure  $\text{H}_2\text{O}$  is about  $1.0 \times 10^{-7}$  M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because  $\text{H}_2\text{O}$  can act as both an acid and a base. The product of these two concentrations is  $1.0 \times 10^{-14}$ :

$$[\text{H}^+] \times [\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of  $\text{H}^+(\text{aq})$ — $[\text{H}^+]$ —is greater than  $1.0 \times 10^{-7}$  M, while for bases the concentration of  $\text{OH}^-(\text{aq})$ — $[\text{OH}^-]$ —is greater than  $1.0 \times 10^{-7}$  M. However, the *product* of the two concentrations— $[\text{H}^+][\text{OH}^-]$ —is *always* equal to  $1.0 \times 10^{-14}$ , no matter whether the aqueous solution is an acid, a base, or neutral:

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

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted  $K_{\text{w}}$ :

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

This means that if you know  $[\text{H}^+]$  for a solution, you can calculate what  $[\text{OH}^-]$  has to be for the product to equal  $1.0 \times 10^{-14}$ , or if you know  $[\text{OH}^-]$ , you can calculate  $[\text{H}^+]$ . This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of  $K_{\text{w}}$ .

### ✓ Example 14.7.1

What is  $[\text{OH}^-]$  of an aqueous solution if  $[\text{H}^+]$  is  $1.0 \times 10^{-4}$  M?

#### Solution

Using the expression and known value for  $K_{\text{w}}$ ,

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[\text{OH}^-]$$

We solve by dividing both sides of the equation by  $1.0 \times 10^{-4}$ :

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ M}$$

It is assumed that the concentration unit is molarity, so  $[\text{OH}^-]$  is  $1.0 \times 10^{-10}$  M.

### ? Exercise 14.7.1

What is  $[H^+]$  of an aqueous solution if  $[OH^-]$  is  $1.0 \times 10^{-9} \text{ M}$ ?

**Answer**

$$1.0 \times 10^{-5} \text{ M}$$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of  $H^+$  or  $OH^-$  ions in the formula unit because  $[H^+]$  or  $[OH^-]$  may not be the same as the concentration of the acid or base itself.

### ✓ Example 14.7.2

What is  $[H^+]$  in a 0.0044 M solution of  $Ca(OH)_2$ ?

**Solution**

We begin by determining  $[OH^-]$ . The concentration of the solute is 0.0044 M, but because  $Ca(OH)_2$  is a strong base, there are two  $OH^-$  ions in solution for every formula unit dissolved, so the actual  $[OH^-]$  is two times this, or  $2 \times 0.0044 \text{ M} = 0.0088 \text{ M}$ . Now we can use the  $K_w$  expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088 \text{ M})$$

Divide both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} \text{ M}$$

$[H^+]$  has decreased significantly in this basic solution.

### ? Exercise 14.7.2

What is  $[OH^-]$  in a 0.00032 M solution of  $H_2SO_4$ ? (Hint: assume both  $H^+$  ions ionize.)

**Answer**

$$1.6 \times 10^{-11} \text{ M}$$

For strong acids and bases,  $[H^+]$  and  $[OH^-]$  can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine  $[H^+]$  and  $[OH^-]$ .

### ✓ Example 14.7.3

A 0.0788 M solution of  $HC_2H_3O_2$  is 3.0% ionized into  $H^+$  ions and  $C_2H_3O_2^-$  ions. What are  $[H^+]$  and  $[OH^-]$  for this solution?

**Solution**

Because the acid is only 3.0% ionized, we can determine  $[H^+]$  from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$$[H^+] = 0.030 \times 0.0788 = 0.00236 \text{ M}$$

With this  $[H^+]$ , then  $[OH^-]$  can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} \text{ M}$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

### ? Exercise 14.7.3

A 0.0222 M solution of pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) is 0.44% ionized into pyridinium ions ( $\text{C}_5\text{H}_5\text{NH}^+$ ) and  $\text{OH}^-$  ions. What are  $[\text{OH}^-]$  and  $[\text{H}^+]$  for this solution?

#### Answer

$$[\text{OH}^-] = 9.77 \times 10^{-5} \text{ M}; [\text{H}^+] = 1.02 \times 10^{-10} \text{ M}$$

### Summary

In any aqueous solution, the product of  $[\text{H}^+]$  and  $[\text{OH}^-]$  equals  $1.0 \times 10^{-14}$  (at room temperature).

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