14.7: Autoionization of Water

Learning Objectives

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

We have already seen that H_2O can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ (}H_2O\text{ acts as an acid)}$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ (}H_2O\text{ acts as a base)}$$

It may not be surprising to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both H^+(aq) and OH^-(aq) in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

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

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

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

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

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

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_w:

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

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$, you can calculate $[H^+]$. 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_w.

Example 14.7.1

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

Solution

Using the expression and known value for K_w,

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

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

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

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

Exercise 14.7.1

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

Answer

$1.0 \times 10^{−5}$ 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 × 0.0044 M = 0.0088 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:

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

[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

$1.6 \times 10^{−11}$ 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 × 0.0788 = 0.00236 M

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

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

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 (C_5H_5N) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and OH^- ions. What are $[OH^-]$ and $[H^+]$ for this solution?

Answer

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

Summary

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