10.4: Water as Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, K_w, to calculate concentrations of H_3O^+ and OH^- in aqueous solutions.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.4.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{10.4.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{10.4.3}$$

This process is called the **autoionization of water** (Figure 10.4.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

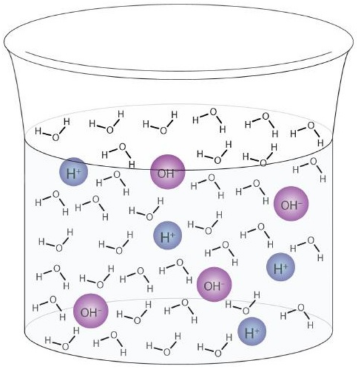

Figure 10.4.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 10.4.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making OH^-(aq). As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming H_3O^+(aq). As the proton acceptor, H_2O is a Brønsted-Lowry base.

Exercise 10.4.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Dissociation of Water

As we have already seen, H_2O can act as an acid or a base. 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:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{10.4.4}$$

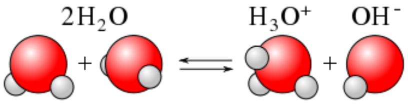

Figure 10.4.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{10.4.5}$$

We often use the simplified form of the reaction:

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

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [H^+][OH^-]$$

The **ion-product constant for water (K_w)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

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

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of K_w is taken.

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

The product of these two concentrations is 1.0×10^{-14}

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

- For acids, the concentration of H^+ or $[H^+]$ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This increases the concentration of H^+ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

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

$$\mathrm{HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)}$$

is **f**orced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH(s) \rightarrow K^+(aq) + OH^-(aq)}$$

The increase in concentration of the OH^- ions will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$ is greater than $[OH^-]$.
- For basic solutions, $[OH-]$ is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH-] = 1.0\times10^{-7}$M

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.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{10.4.6}$$

✓ Example 10.4.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

Step 1: List the known values and plan the problem.

Known

- $[HCl] = 2.0\times10^{-3}$ M
- $Kw = 1.0\times10^{-14}$

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\ \mathrm{M}$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\ \mathrm{M}$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

? Exercise 10.4.2

Sodium hydroxide ($NaOH$) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-] = 0.001M$ or $1 \times 10^{-3}M$; $[H^+]=1\times10^{-11}M$.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.]

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