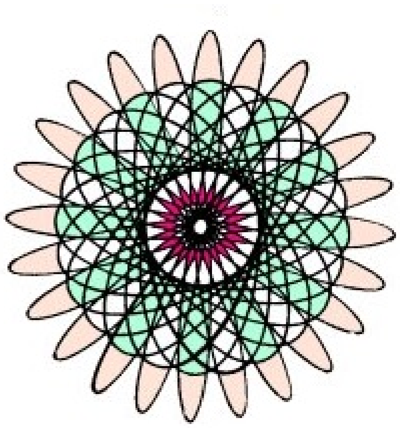

12.5 Autoionization of Water

LEARNING OBJECTIVES

1. Describe the autoionization of water.

2. 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:

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

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

It may not surprise you 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

$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ 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 9

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.

Test Yourself

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

Answer

1.0×10^{-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 10

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:

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

Dividing 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.

Test Yourself

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

Answer

1.6×10^{-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 11

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.

Test Yourself

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

KEY TAKEAWAY

- In any aqueous solution, the product of $[H^+]$ and $[OH^-]$ equals 1.0×10^{-14}.

EXERCISES

1. Does $[H^+]$ remain constant in all aqueous solutions? Why or why not?
2. Does $[OH^-]$ remain constant in all aqueous solutions? Why or why not?
3. What is the relationship between $[H^+]$ and K_w? Write a mathematical expression that relates them.
4. What is the relationship between $[OH^-]$ and K_w? Write a mathematical expression that relates them.
5. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.
6. Write the reverse of the reaction for the autoionization of water. It is still an acid-base reaction? If so, label the acid and base.
7. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-3}$ M, what is $[OH^-]$?
8. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-9}$ M, what is $[OH^-]$?
9. For a given aqueous solution, if $[H^+] = 7.92 \times 10^{-5}$ M, what is $[OH^-]$?

10. For a given aqueous solution, if $[H^+] = 2.07 \times 10^{-11}$ M, what is $[H^+]$?

11. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-5}$ M, what is $[H^+]$?

12. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-12}$ M, what is $[H^+]$?

13. For a given aqueous solution, if $[OH^-] = 3.77 \times 10^{-4}$ M, what is $[H^+]$?

14. For a given aqueous solution, if $[OH^-] = 7.11 \times 10^{-10}$ M, what is $[H^+]$?

15. What are $[H^+]$ and $[OH^-]$ in a 0.344 M solution of HNO_3?

16. What are $[H^+]$ and $[OH^-]$ in a 2.86 M solution of HBr?

17. What are $[H^+]$ and $[OH^-]$ in a 0.00338 M solution of KOH?

18. What are $[H^+]$ and $[OH^-]$ in a 6.02×10^{-4} M solution of $Ca(OH)_2$?

19. If HNO_2 is dissociated only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?

20. If $(C_2H_5)_2NH$ is dissociated only to an extent of 0.077%, what are $[H^+]$ and $[OH^-]$ in a 0.0955 M solution of $(C_2H_5)_2NH$?

ANSWERS

1. $[H^+]$ varies with the amount of acid or base in a solution.

3. $[\mathrm{H}+] = K\mathrm{w}[\mathrm{OH}-]$

5. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-

7. 1.0×10^{-11} M

9. 1.26×10^{-10} M

11. 1.0×10^{-9} M

13. 2.65×10^{-11} M

15. $[H^+] = 0.344$ M; $[OH^-] = 2.91 \times 10^{-14}$ M

17. $[OH^-] = 0.00338$ M; $[H^+] = 2.96 \times 10^{-12}$ M

19$[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M