Topic 8.1

Introduction to Acids and Bases

Learning Objectives

- Define the autoionization constant of water (K_w) and describe its relationship to [H_3O^+] and [OH^-].
- Explain the relationship between K_w and temperature.
- Explain how acid strength is related to pH and how base strength is related to pOH.
- Calculate the pH, pOH, [H_3O^+], or [OH^-] in any neutral solution, given only the value of K_w.
- Calculate pH, pOH, [H_3O^+], or [OH^-] in an acidic or basic solution when given any of those values and K_w.

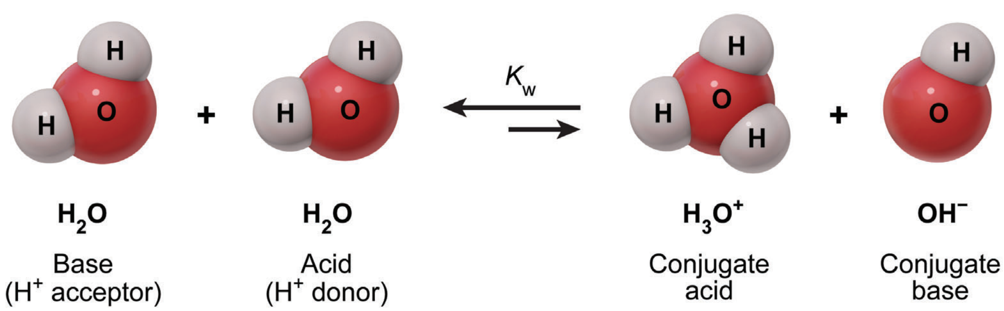
Topic Questions

- What is the autoionization constant water (K_w) and how is it related to [H_3O^+] and [OH^-]?
- How does K_w change with temperature?
- How is acid strength related to pH? How is base strength related to pOH?
- How are pH, pOH, [H_3O^+], or [OH^-] calculated in a neutral solution, given only the value of K_w?
- How are pH, pOH, [H_3O^+], or [OH^-] calculated in acidic or basic solution when given any one of those values and K_w?

8.1.01 Autoionization, pH, and pOH

[SAP-9.A.1 SAP-9.A.2 SAP-9.A.3 SAP-9.A.4]

As explained in Sub-Topic 4.8.01, water is amphoteric (ie, capable of acting either as an acid or as a base). This is true even for the interactions between water molecules. As such, water molecules react with each other (via proton transfer) to form hydronium ions (H_3O^+) and hydroxide ions (OH^-) in a process called **autoionization** (ie, self-ionization), as illustrated in Figure 8.1.



$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Water molecules interact and ionize into hydronium and hydroxide ions

- Water is amphoteric (can act as either an acid or a base)
- [H_3O^+] is a proton shuttle (source of H$^+$): [H$^+$] = [H_3O^+]

Figure 8.1 Self-ionization of water.

The autoionization constant, Kw, is the equilibrium constant for this process, and the value of Kw depends on the temperature. Pure water at 25 °C has $K_w = 1.0 \times 10^{-14}$, which gives it a $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M. As temperature increases, the water autoionizes to a greater extent, which increases $[H_3O^+]$, $[OH^-]$, and the value of K_w (Figure 8.2). However, $[H_3O^+]$ and $[OH^-]$ are always equal and the water remains neutral (ie, not acidic or basic) because there is no excess acid or base.

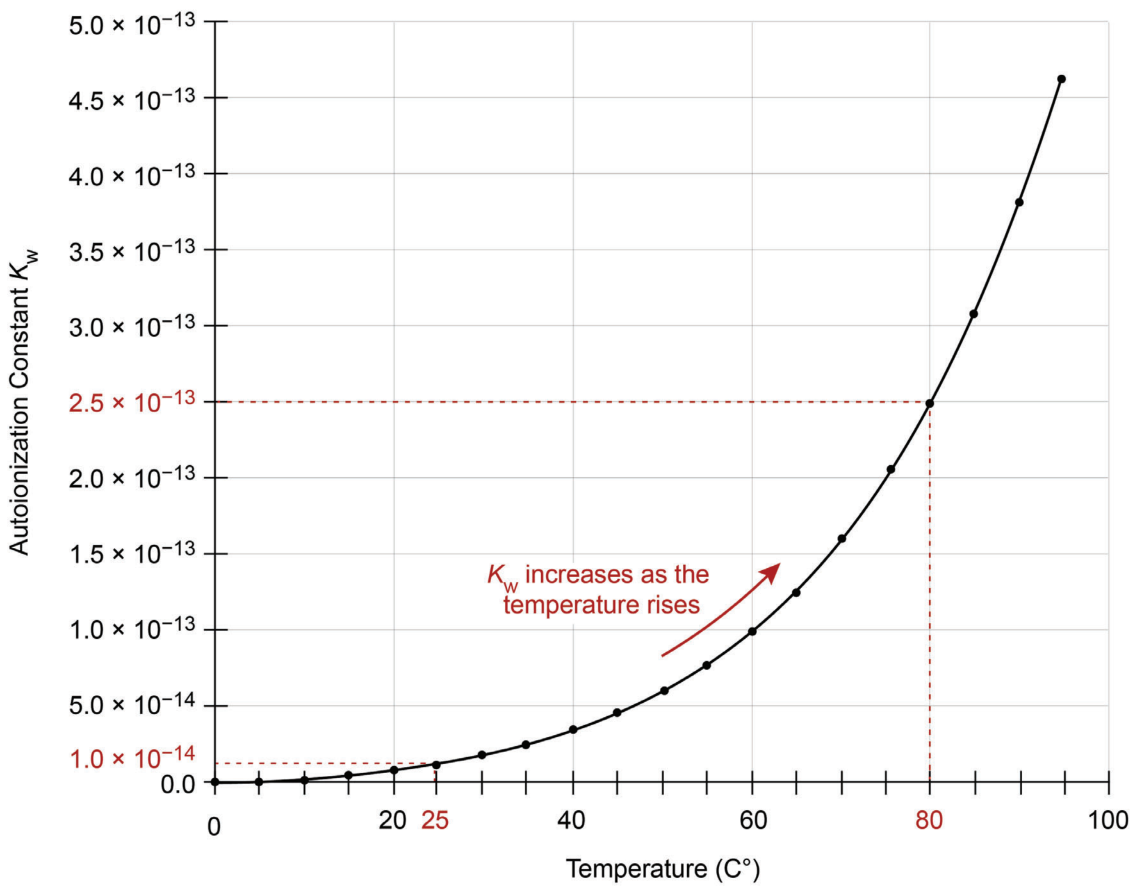


Figure 8.2 The K_w of pure water depends on the temperature.

The K_w equation (see Figure 8.1) shows that the hydronium concentration $[H_3O^+]$ is inversely proportional to the hydroxide concentration $[OH^-]$. When an acid ionizes in water to produce H_3O^+ ions, the OH^- concentration drops proportionally (and vice versa), as Figure 8.3 illustrates.

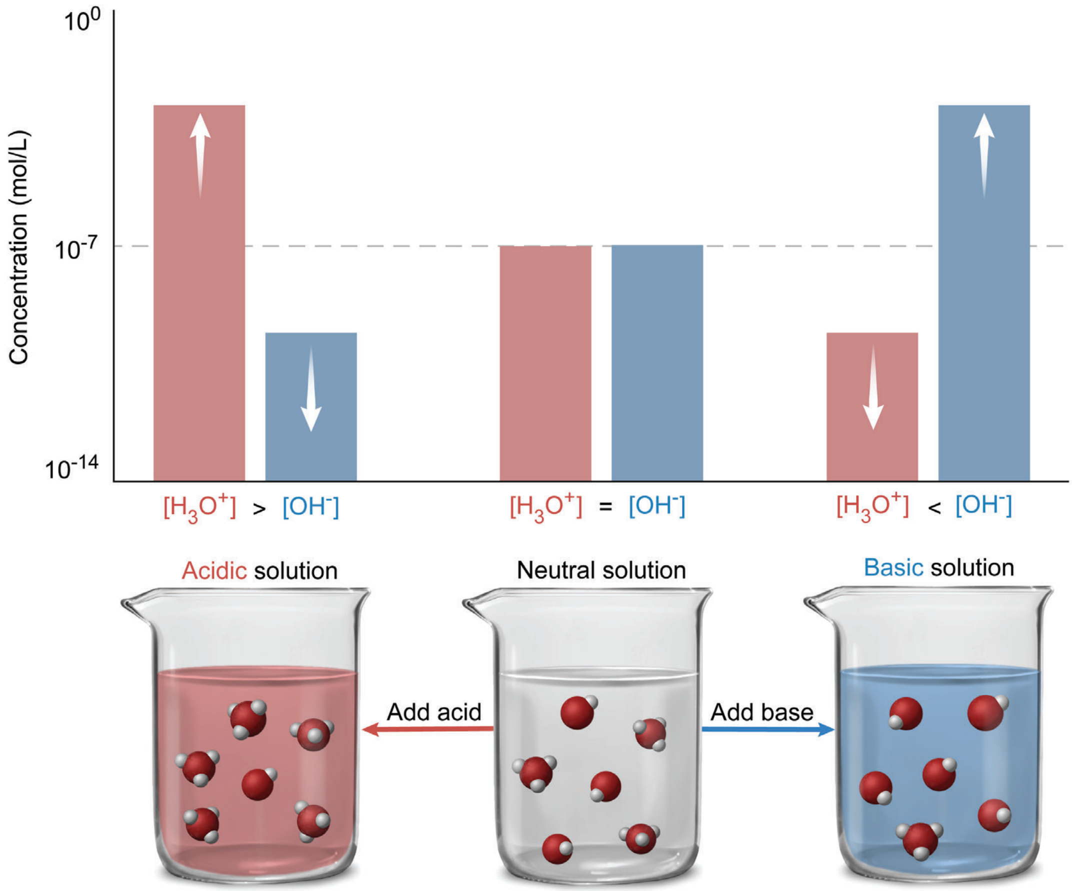


Figure 8.3 Balance of $[H_3O^+]$ and $[OH^-]$ in aqueous solutions.

Consider the example of an acid solution at 25 °C with a hydronium concentration $[H_3O^+]$ of 0.0010 M. The concentration of hydroxide ion $[OH^-]$ in this solution can be determined using the K_w equation:

$$K_w = [H_3O^+][OH^-]$$

Rearranging this equation to solve for $[OH^-]$ and substituting in the values for $[H_3O^+]$ and K_w (1.0×10^{-14} at 25 °C) gives:

$$[OH^-] = \frac{K_w}{[H_3O^+]} \quad \Longrightarrow \quad [OH^-] = \frac{1.0 \times 10^{-14}}{0.0010\ M} = 1.0 \times 10^{-11}\ M$$

The concentrations involved in measuring the acidity of a solution are often extremely small. Using the logarithmic **pH scale** makes the task of expressing these values easier. The pH of a solution relates to the hydronium ion concentration $[H_3O^+]$ (which is sometimes expressed as hydrogen ion concentration $[H^+]$) and is given by the relationship:

$$pH = -\log[H_3O^+] = -\log[H^+]$$

Because pH is a negative logarithmic function, *lower* pH values correspond to *higher* hydronium concentrations and greater acidity (and vice versa), as Figure 8.4 illustrates.

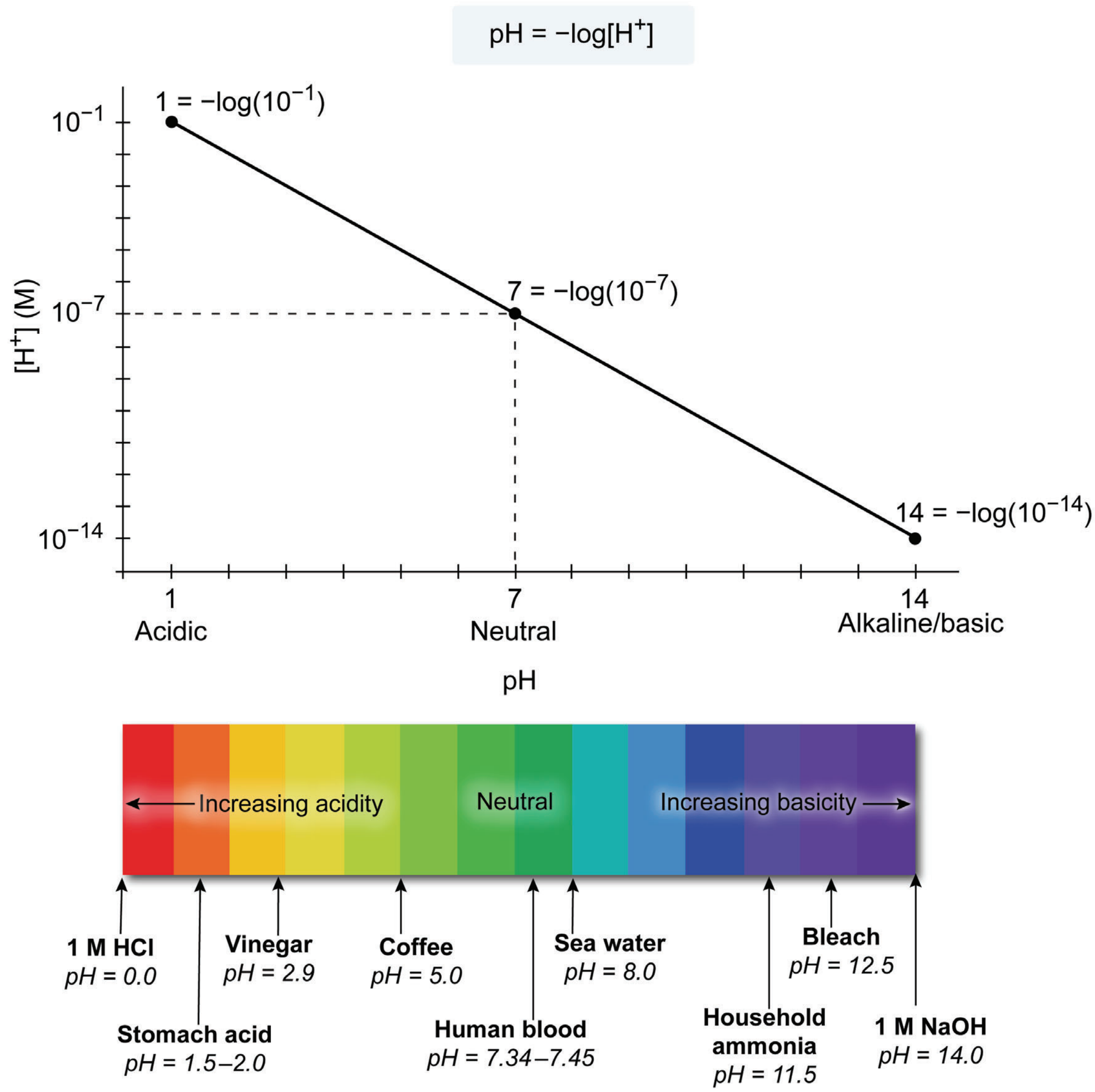


Figure 8.4 The pH scale.

At 25 °C, pure water (without any added acid or base) is neutral and has pH = 7.0 because its $K_w = 1.0 \times 10^{-14}$, which gives $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M. As the temperature increases, the water autoionizes more, which increases its K_w (Figure 8.2) and decreases its pH. Because of this, pure water at temperatures other than 25 °C has a pH that is slightly higher or lower than 7.0.

In the same way that the pH scale expresses the degree of acidity of a solution, the pOH scale indicates the degree of basicity of a solution. The pOH is expressed mathematically as the negative logarithm of the molar concentration of OH^- in solution:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-]$$

The relationship between pH and pOH is derived from the K_w equilibrium expression as shown in Figure 8.5.

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

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

$$-\log[H^+] - \log[OH^-] = 14$$

$$-\log(10^{-pH}) - \log(10^{-pOH}) = 14$$

$$\mathbf{pH + pOH = 14}$$

Figure 8.5 The relationship between pH and pOH derived from K_w.

Consider the example of a basic solution with an OH^- ion concentration of 4.5×10^{-4} M. The pH of this solution can be determined using the pOH, given that pOH = $-\log[OH^-]$ and pH + pOH = 14. By this method, the calculation of the pOH is given by:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(4.5 \times 10^{-4}\ \mathrm{M}) = 3.35$$

Using this pOH value to find the pH gives:

$$\mathrm{pH} = (14 - \mathrm{pOH}) = (14 - 3.35) = 10.65$$

Topic 8.1 Introduction to Acids and Bases
Check for Understanding Quiz

1. Autoionization is a process in which water molecules:
   A. react with each other to form H_3O^+ and OH^- ions
   B. react with other species to form only H_3O^+ ions
   C. react with each other to form only OH^- ions
   D. react with other species to form H_3O^+ and OH^- ions

2. What is the hydronium ion concentration of a solution at 25 °C with a pOH of 9.34?
   A. 9.34
   B. 4.66
   C. 4.6×10^{-10}
   D. 2.2×10^{-5}

Note: Answers to this quiz are in the back of the book (appendix).