8.5: The Meaning of Neutrality - The Autoprotolysis of Water

In the previous section, we described the reaction of an acid and a base to form water. When all of the acid and base have been consumed, we are left with water and an aqueous solution containing an ionic compound. Another way to think of this would be to say that, the acid we began with had a high concentration of hydronium cations (H_3O^+), the base had a high concentration of hydroxide anions (HO^-) and the neutral solution contains only water. This, however, is a little too simplistic. Just like water can promote the ionization of acids, water can also promote the ionization of *itself*. Picture two water molecules sharing a hydrogen bond. Just like for HF , the partially bonded hydrogen can transfer *along* the hydrogen bond to form a hydronium cation and a hydroxide anion. This process occurs very rapidly in pure water, thus, any sample of pure water will *always* contain a small concentration of hydronium and hydroxide ions. How small is "small"? Very small! In pure water at 25 ^oC, the concentration of hydronium ions ($[H_3O^+]$) and hydroxide ions ($[HO^-]$) will both be equal to exactly 1×10^{-7} M. Based on this, we can expand upon our definitions of acidic, basic and neutral solutions:

- A solution is **acidic** if $[H_3O^+] > 1 \times 10^{-7}$ M.
- A solution is **basic** if $[H_3O^+] < 1 \times 10^{-7}$ M.
- A solution is **neutral** if $[H_3O^+] = 1 \times 10^{-7}$ M.

Working with these definitions, if you have a solution with $[H_3O^+] = 4.5 \times 10^{-4}$ M, it will be *acidic* ($4.5 \times 10^{-4} > 1 \times 10^{-7}$). If you have a solution with $[H_3O^+] = 1 \times 10^{-4}$ M, it will be *basic* ($1 \times 10^{-4} < 1 \times 10^{-7}$). Finally, a *neutral* solution is one in which $[H_3O^+]$ and $[HO^-]$ are *both* 1×10^{-7} M.

Recalling our discussion of acid dissociation constants from Section 8.2, we can write the ionization equilibrium for water

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

and the expression for the dissociation constant, K_a, as shown below:

$$\begin{aligned} K_a &= \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \\ &\approx \frac{[H_3O^+][HO^-]}{(1)^2} \\ &= [H_3O^+][HO^-] \end{aligned}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each of the solutes is approximated by the molarity of the solute. In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

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

At neutrality and 25 ^oC, $[H_3O^+]$ and $[HO^-]$ are *both* 1×10^{-7} M, therefore:

$$K_w = [1 \times 10^{-7}][1 \times 10^{-7}] = 1 \times 10^{-14}$$

This simple relationship is actually quite powerful. Because K_W is a constant, if we know *either* a hydronium ion or a hydroxide ion concentration, we can directly calculate the concentration of the other species. For example, if you are *given* that $[H_3O^+]$ is 1×10^{-4} M, $[HO^-]$ can be calculated as:

$$\begin{aligned} K_w &= [H_3O^+][HO^-] \\ &= 1 \times 10^{-14} \\ &= [1 \times 10^{-4}][HO^-] \end{aligned}$$

$$[HO^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10} M$$

? Exercise 8.5.1: Calculating hydronium and hydroxide concentrations

A solution at 25 ^{o}C, is known to have a hydronium ion concentration of 4.5 × 10^{-5} M; what is the concentration of hydroxide ion in this solution?

? Exercise 8.5.2: Calculating hydronium and hydroxide concentrations

A solution at 25 ^{o}C, is known to have a hydroxide ion concentration of 7.5 ×10^{-2} M; what is the concentration of hydronium ion in this solution?

? Exercise 8.5.3: Calculating hydronium and hydroxide concentrations

A solution is known to have a hydronium ion concentration of 9.5 × 10^{-8} M; what is the concentration of hydroxide ion in this solution?
