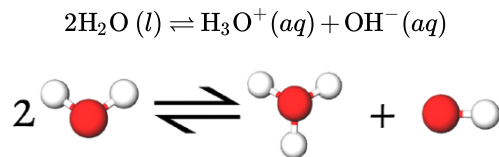


14.2: Ionization of Water

In the section on [amphiprotic species](#), we saw that water can act as a very weak acid and a very weak base, donating protons to itself to a limited extent:



The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^2} \approx \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{(1)^2} = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (14.2.1)$$

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 solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{\text{eq}}[\text{H}_2\text{O}]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{\text{eq}}(a_{\text{H}_2\text{O}})$. Because $a_{\text{H}_2\text{O}} = 1$ for a dilute solution, $K_a = K_{\text{eq}}(1)$, or $K_a = K_{\text{eq}}$.

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 as 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:

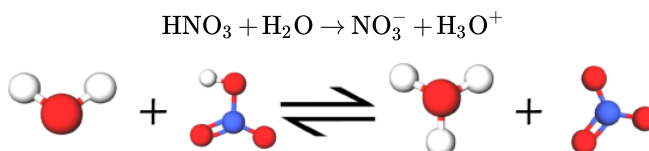
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (14.2.2)$$

Measurements of the electrical conductivity of carefully purified water indicate that at 25°C $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol/L}$, so that

$$\begin{aligned} K_w &= 1.00 \times 10^{-7} \text{ mol L}^{-1} \times 1.00 \times 10^{-7} \text{ mol L}^{-1} \\ &= 1.00 \times 10^{-14} \text{ mol}^2 \text{L}^{-2} \end{aligned} \quad (14.2.3)$$

(Since the equilibrium law is not obeyed exactly, even in dilute solutions, results of most equilibrium calculations are rounded to three significant figures. Hence the value of $K_w = 1.00 \times 10^{-14} \text{ mol}^2/\text{L}^2$ is sufficiently accurate for all such calculations.)

The equilibrium constant K_w applies not only to pure water but to any aqueous solution at 25°C. Thus, for example, if we add 1.00 mol of the strong acid HNO_3 to H_2O to make a total volume of 1 L, essentially all the HNO_3 molecules donate their protons to H_2O :



and a solution in which $[\text{H}_3\text{O}^+] = 1.00 \text{ mol/L}$ is obtained. Although this solution is very acidic, there are still hydroxide ions present. We can calculate their concentration by rearranging Eq. ??? :

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{1.00 \text{ mol L}^{-1}} \quad (14.2.4)$$

$$(14.2.5)$$

$$= 1.00 \times 10^{-14} \text{ mol L}^{-1} \quad (14.2.6)$$

The addition of the HNO_3 to H_2O not only increases the hydronium-ion concentration but also reduces the hydroxide-ion concentration from an initially minute 10^{-7} mol/L to an even more minute 10^{-14} mol/L .

✓ Example 14.2.2: Ion Concentration

Calculate the hydronium-ion concentration in a solution of 0.306 M Ba(OH)_2 .

Solution

Since 1 mol Ba(OH)_2 produces 2 mol OH^- in solution, we have

$$[\text{OH}^-] = 2 \times 0.306 \frac{\text{mol}}{\text{L}} = 0.612 \frac{\text{mol}}{\text{L}}$$

Then

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{0.612 \text{ mol L}^{-1}} \quad (14.2.7)$$

$$= 1.63 \times 10^{-14} \text{ mol L}^{-1}$$

📌 Note

Note that since strong acids like HNO_3 are completely converted to H_3O^+ in aqueous solution, it is a simple matter to determine $[\text{H}_3\text{O}^+]$, and from it, $[\text{OH}^-]$. Similarly, when a strong base dissolves in H_2O it is entirely converted to OH^- , so that $[\text{OH}^-]$, and from it $[\text{H}_3\text{O}^+]$ are easily obtained.

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