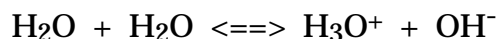


### **K<sub>w</sub>: The Water Ionization Constant**

Important note: all constants referred to: K<sub>c</sub>, K<sub>a</sub>, K<sub>b</sub>, and K<sub>w</sub> are temperature-dependent. All discussions are assumed to be at 25 °C, i.e. standard temperature.

The following equation describes the reaction of water with itself (called autoprotolysis):



The equilibrium constant for this reaction is written as follows:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]} \quad (1)$$

However, in pure liquid water, [H<sub>2</sub>O] is a constant value. To demonstrate this, consider 1000 mL of water with a density of 1.00 g/mL. This 1.00 liter (1000 mL) would weigh 1000 grams. This mass divided by the molecular weight of water (18.0152 g/mol) gives 55.5 moles. The "molarity" of this water would then be 55.5 mol ÷ 1.00 liter or 55.5 M.

Cross-multiplying equation (1) gives:

$$K_c [\text{H}_2\text{O}] [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

Since the term K<sub>c</sub> [H<sub>2</sub>O] [H<sub>2</sub>O] is a constant, let it be symbolized by K<sub>w</sub>, giving:

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \quad (2)$$

This constant, K<sub>w</sub>, is called the water autoprotolysis constant or water autoionization constant. (Sometimes the prefix auto is dropped, as was done in the title of this section.) It can be determined by experiment and has the value 1.011 x 10<sup>-14</sup> at 25 °C. Generally, a value of 1.0 x 10<sup>-14</sup> is used.

From the chemical equation just above equation (1), it can be seen that H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> are in the molar ratio of one-to-one. This means that, in pure water, [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>].

Therefore the values of [H<sub>3</sub>O<sup>+</sup>] and [OH<sup>-</sup>] can be determined by taking the square root of K<sub>w</sub>. Hence, both [H<sub>3</sub>O<sup>+</sup>] and [OH<sup>-</sup>] equal 1.00 x 10<sup>-7</sup>. This leads to several important results in the acid base world.

#### **Result #1: The pH of pure water is 7**

By definition, pH = -log [H<sub>3</sub>O<sup>+</sup>]

The pH of pure water then equals -log 10<sup>-7</sup>, which is 7.

**Result #2: If the pH or the pOH is known, the other can be found.**

Take the negative logarithm of each side of equation (2) as follows:

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

$$-\log 1.00 \times 10^{-14} = -\log [H_3O^+] + -\log [OH^-]$$

Note the use of the add sign on the right side of the equation. The result is usually written as:

$$pK_w = pH + pOH = 14$$

**Result #3: If the  $[H_3O^+]$  or the  $[OH^-]$  is known, the other can be found.**

Using equation 2, simply divide  $K_w$  by the known value to get the other.

Suppose  $[H_3O^+]$  is known, then:

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