Dissociation of Water

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1 Introduction

Water can dissociate into ions, and this paper discusses the ionic product of water.

2   Theory

Water molecules can function as both acids and bases. One water molecule (acting as a base) can accept a hydrogen ion from a second one (acting as an acid). This will be happening anywhere there is even a trace of water even if it is not pure. Consider the following reaction:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

A hydroxonium ion and a hydroxide ion are formed in the reaction shown above. However, the hydroxonium ion is a very strong acid, and the hydroxide ion is a very strong base. As fast as they are formed, they react to produce water again. At any one time, there are incredibly small numbers of hydroxonium ions and hydroxide ions present. This equilibrium is usually written in a simplified form:

$$H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)}$$

Now that we know that water is in a constant state of dynamic equilibrium, we can consider its equilibrium constant, K_c:

$$K_c = \frac{[H_3O^+{}_{(aq)}][OH^-{}_{(aq)}]}{[H_2O_{(l)}]^2} \tag{1}$$

We can remove the $[H_2O_{(l)}]^2$ term since we know that the water molecules hardly dissociate, meaning it is virtually a constant. This leaves an equation that is known as the ionic product of water, K_w:

$$K_w = [H_3O^+{}_{(aq)}][OH^-{}_{(aq)}] \tag{2}$$

As you can see, this equation is just a specific form of the general equilibrium constant equation. But like any other equilibrium constant, the value of K_w varies with temperature. Its value is usually taken to be 1.00×10^{-14} mol^{2}dm^{-6} at room temperature. Like most calculations involving low concentrations, there is a method to make the values for K_w more readable by calculating pK_w. The relationship between K_w and pK_w is exactly the same as that between K_a and pK_a, or $[H^+]$ and pH:

$$pK_w = -log_{10}K_w \tag{3}$$

The K_w value of 1.00×10^{-14} mol^{2}dm^{-6} at room temperature gives you a pK_w value of 14. The pH of pure water is 7 at just below 25°C.

To find the pH you need to first find the hydrogen ion concentration (or hydroxonium ion concentration). Then you convert it to pH. In pure water at room temperature the Kw value tells you that:

$$[H^+][OH^-] = 1.00 \times 10^{-14} \tag{4}$$

But in pure water, the hydrogen ion (hydroxonium ion) concentration must be equal to the hydroxide ion concentration. For every hydrogen ion formed, there is a hydroxide ion formed as well. That means that you can replace the $[OH^-]$ term in the K_w expression by another $[H^+]$.

$$[H^+]^2 = 1.00 \times 10^{-14} \tag{5}$$

Taking the square root of each side gives:

$$[H^+] = 1.00 \times 10^{-7} mol dm^{-3} \tag{6}$$

Converting that into pH:

$$pH = -log_{10}[H^+] \tag{7}$$

$$pH = 7 \tag{8}$$

That's where the familiar value of 7 comes from. The dissociation of water is an endothermic process, meaning that the forward reaction absorbs heat. According to Le Chatelier's Principle, if you make a change to the conditions of a reaction in dynamic equilibrium, the position of equilibrium moves to counter the change you have made. Which means that if you increase the temperature of the water, the equilibrium will move to lower the temperature again. It will do that by absorbing the extra heat. That means that the forward reaction will be favoured, and more hydrogen ions and hydroxide ions will be formed. This means that the value of K_w increases with temperature, as can be sen by the following table:

T(°C)	K_w(mol^{2}dm^{-6})	pH
0	0.114E -14	7.47
10	0.293E -14	7.27
20	0.681E -14	7.08
25	1.008E -14	7.00
30	1.471E -14	6.92
40	2.916E -14	6.77
50	5.476E -14	6.63
100	51.3E -14	6.14

As you can see, the pH of pure water falls as the temperature increases. Although the pH of pure water changes with temperature, it is important to realise that it is still neutral. In the case of pure water, there are always going to be the same number of hydrogen ions and hydroxide ions present. That means that the pure water remains neutral, even if its pH changes. Remember that you calculate the neutral value of pH from K_w. If that changes, then the neutral value for pH changes as well. At 100°C, the pH of pure water is 6.14. That is the neutral point on the pH scale at this higher temperature.

A solution with a pH of 7 at this temperature is slightly alkaline because its pH is a bit higher than the neutral value of 6.14. Similarly, you can argue that a solution with a pH of 7 at 0°C is slightly acidic, because its pH is a bit lower than the neutral value of 7.47 at this temperature.