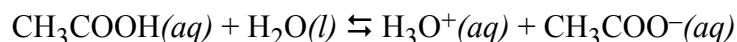
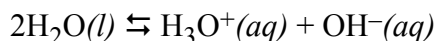


## Why We Ignore Water's Dissociation When Solving pH Problems

Our treatment of equilibrium chemistry at this point includes several simplifications. For example, when finding the pH of a solution of acetic acid,  $\text{CH}_3\text{COOH}$ , we ignored the contribution of water's dissociation to the total concentration of  $\text{H}_3\text{O}^+$ . In setting up an ICE table, we assumed the initial concentration of  $\text{H}_3\text{O}^+$  was zero, which clearly is not true. We argued that this is a reasonable assumption because the  $\text{H}_3\text{O}^+$  from the dissociation of acetic acid



shifts the equilibrium dissociation of water



to the left, decreasing its contribution from that of  $1.0 \times 10^{-7}$  M for neutral water to a value which is insignificant when compared to that from the dissociation of acetic acid. Let's show that this is reasonable by solving for the pH without making any approximations.

### A Rigorous Solution to the pH of 0.100 M Acetic Acid<sup>1</sup>

When acetic acid dissolves in water it undergoes the dissociation reaction shown above, for which the acid dissociation constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

This equation has three terms –  $[\text{H}_3\text{O}^+]$ ,  $[\text{CH}_3\text{COO}^-]$ , and  $[\text{CH}_3\text{COOH}]$  – whose values are unknown to us. With three variables and one equation we cannot find a unique algebraic solution to this problem unless we can find additional equations. There is, of course, another equilibrium reaction of importance in any aqueous solution – the dissociation of water



Although this adds a second equation, it also introduces a new unknown:  $[\text{OH}^-]$ . We still need, therefore, to find at least two additional equations.

One useful equation is a charge-balance equation, which is simply a statement that any solution is electrically neutral; that is, the total concentration of positive charge must equal the total concentration of negative charge. For a solution of acetic acid, the charge-balance equation is

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] + [\text{OH}^-]$$

Another useful equation is a mass-balance equation, which is simply a statement that mass is conserved. We know, for example, that any acetic acid is present in either its weak acid form,  $\text{CH}_3\text{COOH}$ , or its weak base form,  $\text{CH}_3\text{COO}^-$ ; thus

$$0.10 \text{ M} = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

Now we have four equations and four unknowns, which means there is a unique solution.

---

<sup>1</sup> Although it is useful to understand why we can ignore water as a significant source of  $\text{H}_3\text{O}^+$ , you do not need to know how to do the sort of rigorous calculation outlined here. This is covered in greater detail in Chem 352.

To solve the problem, we first substitute  $K_w/[H_3O^+]$  for  $[OH^-]$  in the charge balance equation and solve for the equilibrium concentration of acetate

$$[H_3O^+] = [CH_3COO^-] + \frac{K_w}{[H_3O^+]}$$

$$[CH_3COO^-] = [H_3O^+] - \frac{K_w}{[H_3O^+]}$$

Next, we solve the mass balance equation for the equilibrium concentration of acetic acid

$$[CH_3COOH] = 0.1 - [CH_3COO^-] = 0.1 - [H_3O^+] + \frac{K_w}{[H_3O^+]}$$

Now, we substitute these equations for the equilibrium concentrations of acetic acid and acetate into the  $K_a$  expression, giving

$$K_a = \frac{[H_3O^+] \left( [H_3O^+] - \frac{K_w}{[H_3O^+]} \right)}{0.1 - [H_3O^+] + \frac{K_w}{[H_3O^+]}}$$

Further manipulation produces a third-order polynomial equation in  $[H_3O^+]$

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (0.1K_a + K_w)[H_3O^+] - K_aK_w = 0$$

that is a mess to solve, but for which we obtain  $[H_3O^+] = 1.333 \times 10^{-3}$  and a pH of 2.875.

### The Approximate Solution to the pH of 0.100 M Acetic Acid

Now, let's approach this problem by assuming that we can ignore the dissociation of water as a significant source of  $H_3O^+$ . Because we know that the pH of a weak acid must be less than 7 we can reasonably assume that  $[OH^-] \ll [H_3O^+]$ . This allows us to simplify the charge balance equation, as shown here

$$[H_3O^+] = [CH_3COO^-] + [OH^-] \approx [CH_3COO^-]$$

Now, we substitute  $[H_3O^+]$  for  $[CH_3COO^-]$  in the mass balance equation and solve for the concentration of acetic acid

$$0.10 \text{ M} = [CH_3COOH] + [H_3O^+] \quad [CH_3COOH] = 0.1 - [H_3O^+]$$

Finally, substituting back into the  $K_a$  expression gives

$$K_a = \frac{[H_3O^+][H_3O^+]}{0.1 - [H_3O^+]} = \frac{X^2}{0.1 - X}$$

which is the simplified solution we developed in class. Solving the quadratic equation gives  $[H_3O^+] = 1.333 \times 10^{-3}$  and a pH of 2.875, which are the same results obtained with the more rigorous approach. Thus, we can ignore the contribution of water as a source of  $H_3O^+$  in this problem (and in any problem of interest to us in this course).