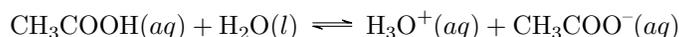


Ignoring Water's Dissociation When Solving for pH

Our treatment of equilibrium chemistry at this point includes several simplifications. For example, when we calculated the pH of a solution of acetic acid, CH_3COOH , we ignored the contribution of water's dissociation to the total concentration of H_3O^+ . In setting up an ICE table, we assumed the initial concentration of H_3O^+ was zero, which clearly is not true. We argued that this is a reasonable assumption because the H_3O^+ from the dissociation of acetic acid



shifts the equilibrium dissociation of water



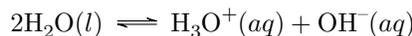
to the left, decreasing its contribution from that of 1.0×10^{-7} M for neutral water to a much smaller value that likely is insignificant when compared to that from the dissociation of acetic acid. Let's show that this is reasonable by solving for the pH without making any approximations.¹

A Rigorous Solution to the pH of 0.100 M Acetic Acid

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 unless we can write additional equations that relate these terms to each other. The dissociation of water, of course, is another equilibrium reaction of importance in any aqueous solution



for which the equilibrium constant expression is

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Although this provides us with 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 simply is 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

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

¹Although it is useful to understand why we can ignore water as a significant source of H_3O^+ , 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: Analytical Equilibria.

Another useful equation is a *mass-balance equation*, which simply is a statement that mass is conserved. We know that acetic acid is present in either its weak acid form, CH_3COOH , or in its weak base form, CH_3COO^- , and that although their relative concentrations depend upon pH, their combined concentration is a constant (in this case, 0.100 M); thus

$$0.100 \text{ M} = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

Now we have four equations and four unknowns, which means we can find a unique solution.

To complete the calculation, first, we solve the K_w equation for $[\text{OH}^-]$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

substitute this into the charge balance equation

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

and solve for the equilibrium concentration of acetate

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

Next, we solve the mass balance equation for the equilibrium concentration of acetic acid, substituting in our equation for CH_3COO^-

$$[\text{CH}_3\text{COOH}] = 0.100 - [\text{CH}_3\text{COO}^-]$$

$$[\text{CH}_3\text{COOH}] = 0.100 - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}$$

Now, we substitute these equations into the K_a expression for acetic acid

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}_3\text{O}^+] \left([\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]} \right)}{0.100 - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}}$$

which we simplify to a third-order polynomial equation in $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+]^3 + K_a[\text{H}_3\text{O}^+]^2 - (0.100 \times K_a + K_w)[\text{H}_3\text{O}^+] - K_a K_w = 0$$

that is a mess to solve, but for which the solution is $[\text{H}_3\text{O}^+] = 1.33 \times 10^{-3} \text{ M}$, or a pH of 2.88.

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 is less than 7 we can reasonably assume that $[\text{OH}^-] \ll [\text{H}_3\text{O}^+]$. This allows us to simplify the charge balance equation, as shown here

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

Next, we substitute $[\text{H}_3\text{O}^+]$ for $[\text{CH}_3\text{COO}^-]$ in the mass balance equation and solve for the concentration of acetic acid

$$0.100M = [\text{CH}_3\text{COOH}] + [\text{H}_3\text{O}^+]$$

$$[\text{CH}_3\text{COOH}] = 0.100 - [\text{H}_3\text{O}^+]$$

Finally, we substitute back into the K_a expression

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+]}{0.100 - [\text{H}_3\text{O}^+]} = \frac{X^2}{0.100 - X}$$

which is the simplified solution we developed in class. Solving the quadratic equation gives $[\text{H}_3\text{O}^+] = 1.33 \times 10^{-3}$ M, or a pH of 2.88, which is the same result obtained above when we used 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).