

Rigorous Treatment For Finding pH of Weak Acid

We begin with 4 equations; namely

$$\text{acid dissociation: } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

$$\text{charge balance: } [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{A}^-]$$

$$\text{mass balance: } C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$$

Because we want to find the $[\text{H}_3\text{O}^+]$ it is convenient to solve the charge balance equation.

To do so we need to solve for the $[\text{OH}^-]$ and $[\text{A}^-]$ in terms of the $[\text{H}_3\text{O}^+]$. This is easy to do for OH^- using K_w

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

To do the same for A^- we begin solving K_a for HA

$$[\text{HA}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{K_a}$$

and substituting into the mass balance equation

$$C_{\text{HA}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{K_a} + [\text{A}^-]$$

Next we factor out the $[\text{A}^-]$ from the left side of the equation and solve for $[\text{A}^-]$

$$[\text{A}^-] = \frac{C_{\text{HA}} K_a}{[\text{H}_3\text{O}^+] + K_a}$$

Substituting back into the charge balance equation gives

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{H}_3\text{O}^+]} + \frac{C_{\text{HA}} K_a}{[\text{H}_3\text{O}^+] + K_a}$$

After much gory algebra, we get

$$[\text{H}_3\text{O}^+]^3 + K_a[\text{H}_3\text{O}^+]^2 - \{K_w + C_{\text{HA}}K_a\} [\text{H}_3\text{O}^+] - K_aK_w = 0$$