General Solution for Weak Acid pH - Derivation

$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$ $\quad K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ $\quad K_w = [H_3O^+][OH^-]$

mass balance: $[HA]_o = [HA] + [A^-]$

charge balance: $[H_3O^+] = [A^-] + [OH^-]$ read this as the concentration of positive charge = the concentration of negative charge

4 equations 4 unknowns ($[H_3O^+]$, $[OH^-]$, $[A^-]$, $[HA]$)
(or as Don Rumsfeld would say 4 equations, 4 known unknowns)

Simplify

$[OH^-] = \dfrac{K_w}{[H_3O^+]}$, substitute into charge balance eqn.

$[H_3O^+] = [A^-] + \dfrac{K_w}{[H_3O^+]}$

$[HA] = [HA]_o - [A^-]$, substitute into K_a

$K_a = \dfrac{[H_3O^+][A^-]}{[HA]_o - [A^-]}$

$[A^-] = [H_3O^+] - \dfrac{K_w}{[H_3O^+]}$, substitute into K_a above

$$K_a = \frac{[H_3O^+]\left([H_3O^+] - \frac{K_w}{[H_3O^+]}\right)}{[HA]_o - \left([H_3O^+] - \frac{K_w}{[H_3O^+]}\right)} \Rightarrow K_a = \frac{[H_3O^+]^2 - K_w}{[HA]_o - \left(\frac{[H_3O^+]^2 - K_w}{[H_3O^+]}\right)}$$