The problem of weak acid equilibrium

Example 1: What is the pH of a 1 mM solution of a weak acid, HA, which dissociates according to

$$HA = H^+ + A^- \qquad K_a = 10^{-5}$$

Four unknowns: $[HA]$, $[A^-]$, $[H^+]$, $[OH^-]$

Need four equations:

1. Mass balance for HA: $HA_T = [HA] + [A^-] = 10^{-3}$
2. Mass law for HA: $K_a = [H^+][A^-]/[HA] = 10^{-5}$
3. Mass law for H_2O: $K_w = [H^+][OH^-]$

Need a fourth equation:

4. Mole balance for H^+: $[H^+] = [OH^-] + [A^-]$*

(*this comes from different sources: electroneutrality, proton condition, TOTH = total of free and bound H^+. We will use the latter.)

Sources of H^+: $1H_2O = 1H^+ + 1OH^-$
$1HA = 1H^+ + 1A^-$

Solve for $[H^+]$ (no short cuts, tricks, assumptions):

Let $[HA] = 10^{-3} - [A^-]$, substitute into mass law for HA:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{10^{-3} - [A^-]}$$

solve for $[A^-]$: $[A^-] = K_a 10^{-3}/([H^+] + K_a)$

Let $[OH^-] = K_w/[H^+]$ and substitute into mole balance for H^+:

$$[H^+] = [OH^-] + [A^-] = K_w/[H^+] + K_a 10^{-3}/([H^+] + K_a)$$

$$[H^+]^3 + K_a[H^+]^2 - (K_a 10^{-3} + K_w)[H^+] - K_a K_w = 0$$

$$[H^+] = 9.513 \times 10^{-5} = 10^{-4.022}\ M$$

Quicker approach: use your chemical intuition to restrict the mole balance equation:

$$[H^+] = [OH^-] + [A^-] \rightarrow [H^+] = [A^-]$$

Substitute into mass law for HA and solve for $[H^+]$:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{10^{-3} - [H^+]}$$

$$[H^+]^2 + K_a[H^+] = 10^{-3}K_a$$

Quadratic solution: $[H^+] = 9.512 \times 10^{-5} = 10^{-4.022}$ M