Weak Acid Equilibrium
Michael Stapleton
Department of Geography, Geology and the Environment
Slippery Rock University of Pennsylvania

Students are asked to determine the pH of an aqueous solution of a monoprotic weak acid (HA). For each problem, they are given the equilibrium constant (K_a) and total concentration (C_t) of the acid. The following provides an approach to understanding and solving the problem.

Initially, they should write all chemical reactions in the system.

$$H_2O \Leftrightarrow H^+ + OH^- \qquad \text{Eq (1)}$$

$$HA \Leftrightarrow H^+ + A^- \qquad \text{Eq (2)}$$

Based on these equations, the associated equilibrium expressions should be derived.

$$K_w = \left[H^+\right]\left[OH^-\right] \qquad \text{Eq (3)}$$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} \qquad \text{Eq (4)}$$

Finally a Mass Balance

$$C_t = HA + A^- \qquad \text{Eq (5)}$$

and Charge Balance for the system are identified.

$$H^+ = A^- + OH^- \qquad \text{Eq (6)}$$

The system has four unknown concentrations (H^+, OH^-, HA, A^-) and four independent equations (Eqs. 3-6). Thus it can be solved. The solution is a cubic equation. However, a solution can be found by making a series of simplifying assumptions about the chemistry in the system. These assumptions are made independently in the mass balance and charge balance. Students are asked to think about the implication of making the assumptions, is the assumption consistent with the chemistry? As an undergraduate, I found the method helpful to understand equilibrium as presented in an intro chemistry by Owen D. Faut, Ph.D.

Mass Balance Assumption
The assumption in the mass balance is based on the relative concentration of the protonated species (HA) to the deprotonated species (A^-). In essence, is the final pH close to the pK_a of the weak acid. As an initial estimate the equilibrium constant (K_a) is compared to the total concentrations (C_t) of the acid. The logic is a weak acid will not dissociate significantly. Thus the protonated species is dominant and is significantly greater than the deprotonated species. However as the solution becomes more dilute, the dissociation is shifted to the right making the

two species similar in concentration. If dilution continues the deprotonated species becomes dominant. This leads to the following;

- $C_t >> K_a$ – leads to assumption $HA >> A^-$ and results in $C_t = HA$, $pH << pK_a$
- $C_t \approx K_a$ – leads to assumption $HA \approx A^-$ and results in $C_t = HA + A^-$, $pH \approx pK_a$
- $C_t << K_a$ – leads to assumption $HA << A^-$ and results in $C_t = A^-$, $pH >> pK_a$

Charge Balance Assumption

The assumption in the charge balance is based on the relative concentration of the deprotonated species (A^-) to the hydroxide (OH^-) concentration. What is the source of hydrogen ions in the system? A high concentration of a relatively "strong" weak acid will drive the pH of the system. But as the concentration of the acid is reduced or the acid becomes weaker (K_a is reduced), the water equilibrium becomes significant. As an initial estimate on the relative contribution of the weak acid and water equilibriums (Eq 1 vs Eq 2) is based on the relative value of the product of the equilibrium constant (K_a) and total concentrations (C_t) of the acid to the equilibrium constant (K_w) for water. This leads to the following;

- $C_t K_a >> K_w$ – leads to assumption $A^- >> OH^-$ and results in $H^+ = A^-$, $pH << 7$
- $C_t K_a \approx K_w$ – leads to assumption $A^- \approx OH^-$ and results in $H^+ = OH^- + A^-$, $pH < 7$
- $C_t K_a << K_w$ – leads to assumption $A^- << OH^-$ and results in $H^+ = OH^-$, $pH = 7$

Note: the potential fault in this approximation is when the $Ct \leq 10^{-7}M$. At this concentration even a strong acid will not have a significant impact on pH. A solution of an acid will not have a basic pH, it will be either neutral or acidic. A nitric acid solution ($10^{-10}M$) will be neutral.

Using these approximations as a guide (along with common sense), the mathematical solution become simpler. Once solved, the assumptions must be checked given the acceptable error in the problem. Students are required to provide hand calculations for all problems on Engineering Paper with all steps and equations written out. Concentrations for all species are calculated and assumptions must be verified based on these results. The following Tables provide the solution for all conditions.