

Introduction to Weak Acid Equilibrium

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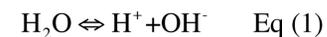
Summary

Students are asked to calculate the pH of a weak acid aqueous solution. The problems involve a series of generic acids with assigned equilibrium constants (K_a) and total concentrations (C_t). Initially, students are required to hand calculate all problems by algebraic manipulation of the mathematical relationships of the system. The solution is a cubic equation. Through a series of assumptions, the solution is simplified. The assumptions are based on the chemistry of the system given the K_a and C_t for the problem. The problems are then graphically solved. Ultimately, the students develop an Excel worksheet to solve the problems and a Bjerrum plot to display the speciation as a function of pH.

Exercise

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.



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

$$K_w = [H^+][OH^-] \quad \text{Eq (3)} \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{Eq (4)}$$

Finally a Mass Balance and Charge Balance for the system are identified.

$$C_t = HA + A^- \quad \text{Eq (5)} \quad H^+ = OH^- + A^- \quad \text{Eq (6)}$$

Mass Balance Assumption (Eq 5)

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:

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

Charge Balance Assumption (Eq 6)

The assumption in the charge balance is based on the relative concentration 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:

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

$C_t \gg K_a$ -- Approximation in the Mass Balance equation. Assumes that the reaction does not go far to the right thus the reactant concentration can be approximated by the total concentration of the acid. Thus $C_t = HA$		
$C_t K_a \gg K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the acid dissociation and deprotonated concentration is greater than the OH^- conc. Thus $H^+ = A^-$.	Solution: $H^+ = \sqrt{CK_a}$
$C_t K_a \approx K_w$	No Charge Balance approximation.	Solution: $H^+ = \sqrt{K_w + CK_a}$
$C_t K_a \ll K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the water equilibrium. Thus $OH^- \gg A^-$ and $H^+ = OH^-$.	Solution: $pH = 7$

$C_t \ll K_a$ -- Approximation in the Mass Balance equation. Assumes that the reaction goes far to the right thus the deprotonated concentration can be approximated by the total concentration of the acid. Thus $C_t = A^-$		
$C_t K_a \gg K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the acid dissociation and deprotonated conc. Is greater than the OH^- conc. Thus $H^+ = A^-$. This is valid only if $pC \ll 7$.	Solution: $H^+ = A^- = C_t$ Not valid when C is close to 10^{-7}. Because, OH^- would be close to A^- .
$C_t K_a \approx K_w$	No Charge Balance approximation.	Solution: $(H^+)^2 - C(H^+) - K_w = 0$
$C_t K_a \ll K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the water equilibrium. Thus $OH^- \gg A^-$ and $H^+ = OH^-$.	Solution: $pH = 7$

$C_t = K_a$ -- No approximation in the Mass Balance equation. Thus $C_t = HA + A^-$		
$C_t K_a \gg K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the acid dissociation and deprotonated concentration. Is greater than the OH^- conc. Thus $H^+ = A^-$	Solution: $(H^+)^2 + K_a(H^+) - K_a C = 0$
$C_t K_a \approx K_w$	No Charge Balance approximation	Solution: $(H^+)^2 + K_a(H^+)^2 - (K_w + K_a C)(H^+) - K_w K_a = 0$
$C_t K_a \ll K_w$	Approximation in the Charge Balance. Assumes the source of hydrogen ions in the system is from the water equilibrium. Thus $OH^- \gg A^-$ and $H^+ = OH^-$.	Solution: $pH = 7$

