Acid-Base Chemistry: pH Calculations

I. Monoprotic Weak Acid pH Calculation

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = 10^{-4.75}$$

HA = Acetic Acid: CH_3COOH

We can use alpha fractions to make accurate pH calculations with an iteration methodology based on % dissociation.

What is the pH of an acetic acid solution with a total acid concentration of C_{tot}?

Monoprotic Weak Acid: Exact Solution

$$HA \rightleftharpoons H^{+} + A^{-}$$

$$K_a = 10^{-4.75}$$

HA = Acetic Acid: CH_3COOH

What is the pH of an acetic acid solution with a total acid concentration of C_{tot}?

Exact Solution:
four unknowns…

$$[HA] \quad [A^{-}]$$

$$[H^{+}] \quad [OH^{-}]$$

Monoprotic Weak Acid: Exact Solution

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = 10^{-4.75}$$

HA = Acetic Acid: CH_3COOH

What is the pH of an acetic acid solution with a total acid concentration of C^{tot}?

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (1)$$

Exact Solution:
four unknowns…

$$K_w = [H^+][OH^-] \quad (2)$$

Water Autoionization

$$[HA] \quad [A^-]$$

$$[H^+] \quad [OH^-]$$

$$C^{tot} = [HA] + [A^-] \quad (3)$$

Mass Balance

And four equations!

$$[H^+] = [A^-] + [OH^-] \quad (4)$$

Charge Balance

Monoprotic Weak Acid: Iterative pH Calculation

$$HA \rightleftharpoons H^{+} + A^{-} \qquad K_a = 10^{-4.75}$$

$$[H^{+}] = [A^{-}] + [OH^{-}]$$ *Charge Balance Equation*

Instead of finding the four roots of exact quartic solution, we will use a iterative method where we calculate an approximate answer and then repeat (iterate) to make it better.

To get the iteration equations, we start with the:

Charge Balance Equation

Monoprotic Weak Acid: Iterative pH Calculation

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = 10^{-4.75}$$

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

$$[H^+]^2 = [H^+][A^-] + [H^+][OH^-]$$ *Multiply by* [H⁺]

Monoprotic Weak Acid: Iterative pH Calculation

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = 10^{-4.75}$$

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

$$[H^+]^2 = [H^+][A^-] + [H^+][OH^-]$$

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

$$K_w = [H^+][OH^-]$$

Substitute in Ka and Kw;

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

Take the square root.

$$K_a[HA] = [H^+][A^-]$$

Monoprotic Weak Acid: Iterative pH Calculation

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = 10^{-4.75}$$

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

$$[H^+]^2 = [H^+][A^-] + [H^+][OH^-]$$

$$\boxed{[H^+] = \sqrt{K_a[HA] + K_w}}$$

We will use this equation along with iterative guesses of [HA] to find the pH in a repeated set of calculations.

Monoprotic Weak Acid: Iterative pH Calculation

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

First guess: Because Ka is small, we first guess that there is only a very little amount of dissociation (i.e., a very little amount of A^- as compared to HA).

Thus: $\alpha_{HA} \approx 1 \qquad [HA] = \alpha_{HA} C^{tot} \approx C^{tot}$

$$\boxed{[H^+]} = \sqrt{K_a C^{tot} + K_w}$$

First guess

We can use the $[H^+]$ from the first guess in the alpha fraction equation for HA to get a better second guess.

Monoprotic Weak Acid: Iterative pH Calculation

First guess: $[HA] \approx C^{tot}$

$$[H^+] = \sqrt{K_a C^{tot} + K_w}$$

Second guess:

$$[HA] = \alpha_{HA} C^{tot} = \left(1 + \frac{K_a}{[H^+]}\right)^{-1} C^{tot}$$

first guess

$$[H^+] = \sqrt{K_a [HA] + K_w}$$

We use [H+] from the first guess to create a second guess for [HA], and then recalculate to get a second guess of [H+].

Monoprotic Weak Acid: Iterative pH Calculation

First guess: $[HA] \approx C^{tot}$

Second guess: $[HA] = \alpha_{HA} C^{tot}$ $\quad \boxed{[H^+]} = \sqrt{K_a C^{tot} + K_w}$

Third guess: $$\boxed{[HA] = \alpha_{HA} C^{tot}} = \left(1 + \frac{K_a}{\boxed{[H^+]}}\right)^{-1} C^{tot}$$

second guess

$$\boxed{[H^+] = \sqrt{K_a [HA] + K_w}}$$

We then use [H+] from the second guess to create a third guess for [HA], and then recalculate to get a third guess of [H+].

Monoprotic Weak Acid: Iterative pH Calculation

First guess: $[HA] \approx C^{tot}$

Second guess: $[HA] = \alpha_{HA} C^{tot}$ $\quad \boxed{[H^+]} = \sqrt{K_a C^{tot} + K_w}$

Third guess: $[HA] = \alpha_{HA} C^{tot}$

Fourth guess: $\boxed{[HA] = \alpha_{HA} C^{tot}} = \left(1 + \frac{K_a}{\boxed{[H^+]}}\right)^{-1} C^{tot}$

third guess

$$\boxed{[H^+] = \sqrt{K_a [HA] + K_w}}$$

Et cetera…We keep on iterating until [H⁺] is unchanged.

Monoprotic Weak Acid: Iterative pH Calculation

First Example: Acetic Acid where $C^{tot} = 1.00 \times 10^{-4} M$

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

$$K_a = 10^{-4.75}$$

$$[HA] = \alpha_{HA} C^{tot} = \left(1 + \frac{K_a}{[H^+]}\right)^{-1} C^{tot}$$

% Dissociation

$$(1 - \alpha_{HA}) \times 100$$

First guess:	$\alpha_{HA} = 1$	$pH = 4.37$	0%
Second guess:	$\alpha_{HA} = 0.703$	$pH = 4.45$	29.7%
Third guess:	$\alpha_{HA} = 0.665$	$pH = 4.46$	33.5%
Fourth guess:	$\alpha_{HA} = 0.659$	$pH = 4.47$	34.1%

34% Dissociation!

Monoprotic Weak Acid: Iterative pH Calculation

First Example: Acetic Acid where C^{tot} = 1.00 x 10^{-4}M

$$[H^+] = \sqrt{K_a[HA] + K_w} \qquad K_a = 10^{-4.75}$$

$$[HA] = \alpha_{HA}C^{tot} = \left(1 + \frac{K_a}{[H^+]}\right)^{-1} C^{tot}$$

We will build a spreadsheet to make this iterative calculation very easy!

	A	B	C	D	E	F	G	H
1	[HA]	[H+]	pH	alpha HA	alpha A-			
2	1.00E-04	4.217E-05	4.37	1	0.00E+00		C0HA=	1.00E-04
3	7.03386E-05	3.537E-05	4.45	0.7033856	2.97E-01		pKa=	4.75
4	6.65421E-05	3.44E-05	4.46	0.6654213	3.35E-01			
5	6.59217E-05	3.424E-05	4.47	0.6592169	3.41E-01		Kw	1.00E-14
6	6.58164E-05	3.421E-05	4.47	0.6581638	3.42E-01			
7	6.57984E-05	3.421E-05	4.47	0.657984	3.42E-01			
8	6.57953E-05	3.421E-05	4.47	0.6579532	3.42E-01			
9	6.57948E-05	3.421E-05	4.47	0.657948	3.42E-01			
10	6.57947E-05	3.421E-05	4.47	0.6579471	3.42E-01			

Monoprotic Weak Acid: Iterative pH Calculation

pH Calculation: Acetic Acid where C^{tot} = 1.00 x 10^{-X}M

Concentration	pH	% Dissociation
$C^{tot} = 1 \times 10^{-1} M$	$pH = 2.88$	1.3%
$C^{tot} = 1 \times 10^{-3} M$	$pH = 3.90$	12.5%
$C^{tot} = 1 \times 10^{-5} M$	$pH = 4.45$	71.4%
$C^{tot} = 1 \times 10^{-7} M$	$pH = 6.79$	99.1%
$C^{tot} = 1 \times 10^{-9} M$	$pH = 7.00$	99.4%

Kw is driving the pH to 7.00
where the % Dissociation is almost 100%.

Monoprotic Weak Acid: Simple pH Calculation

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

You have actually already seen this equation before…

First guess: $[HA] \approx C^{tot}$ → $[H^+] = \sqrt{K_a C^{tot} + K_w}$

$$[H^+] = \sqrt{K_a C^{tot}}$$

If C^{tot} is large compared to K_a and K_w, we can use this simple equation.

Monoprotic Weak Acid: Simple pH Calculation

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

You have actually already seen this equation before…

First guess: $[HA] \approx C^{tot}$ → $[H^+] = \sqrt{K_a C^{tot} + K_w}$

$$[H^+] = \sqrt{K_a C^{tot}}$$

We used this as the initial pH in the acid-base titration

High School Calculation

$$HA \rightleftharpoons H^+ + A^-$$

C^{tot} x x

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{x^2}{C^{tot}}$$

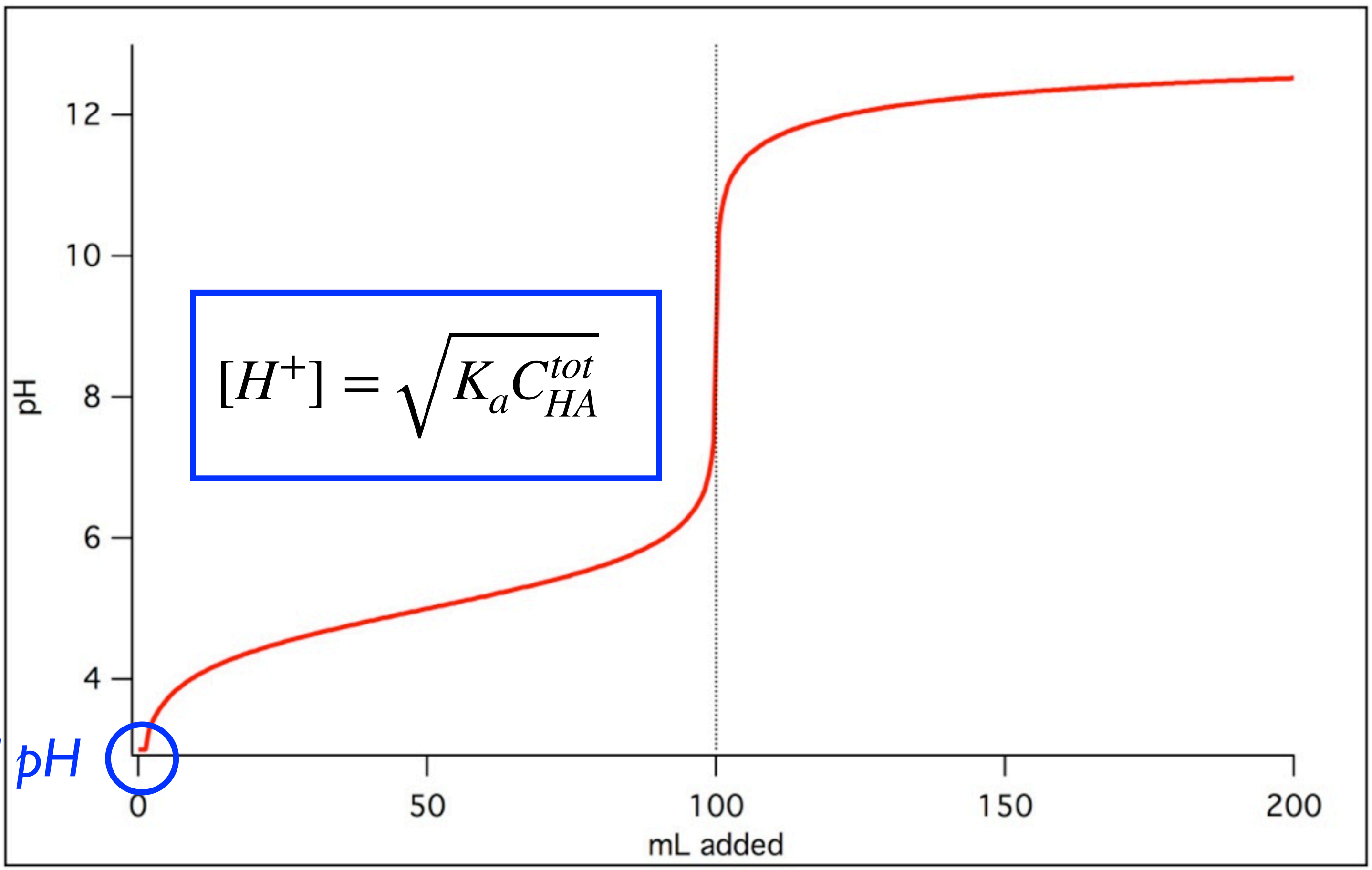
$$[H^+] = x = \sqrt{K_a C^{tot}}$$

Acid-Base Titrations: II. Weak Acid Titration

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad K_t = \frac{K_a}{K_w} \gg 1$$

100.0 mL of 0.100M HA titrated with x mL of 0.100M NaOH

Initial pH. x = 0 mL $\qquad$ V_{tot} *= 100 mL*



$$[H^+] = \sqrt{K_a C_{HA}^{tot}}$$

Acid-Base Chemistry: pH Calculations

We can create iterative pH calculations for many other pH calculations. These additional calculations are explained in the "Iterative Equations" Handout:

II. Diprotic Weak Acid (H_2A) pH calculation

III. Monoprotic Weak Acid Salt (NaA) pH calculation

IV. Diprotic Weak Acid Salt (Na_2A) pH calculation

V. Ampholyte (NaHA) pH calculation

Acid-Base Chemistry: Second Example of a pH Calculation

II. Diprotic Weak Acid (H_2A) pH Calculation

H_2A = Oxalic Acid

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_1 = \frac{[H^+][HA^-]}{[H_2A]} \qquad pK_1 = 1.25$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]} \qquad pK_2 = 4.14$$

What is the pH of an oxalic acid solution with a total acid concentration of C^{tot}?

II. Diprotic Weak Acid (H_2A) pH Calculation

Iterative Equation (see the Handout for derivation):

$$[H^+] = \sqrt{K_1[H_2A] + 2K_2[HA^-] + K_w}$$

Same as HA calculation, but we replace K_a[HA] with

$$K_1[H_2A] + 2K_2[HA^-]$$

Use diprotic alpha fractions

$$[H_2A] = \alpha_{H_2A} C^{tot}$$

$$[HA^-] = \alpha_{HA^-} C^{tot}$$

First guess: $\alpha_{H_2A} = 1 \quad [H_2A] = C^{tot}$

$$\alpha_{HA^-} = 0 \quad [HA^-] = 0$$

$$[H^+] = \sqrt{K_1 C^{tot} + K_w}$$

Second Guess

Acid-Base Chemistry: Third Example of a pH Calculation

III. Monoprotic Weak Acid Salt (NaA) pH Calculation

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_b = \frac{K_w}{K_a} = 10^{-9.25}$$

NaA = Sodium Acetate $NaCH_3COO$
Na^+ and A^- - 100% dissociation

What is the pH of an sodium acetate solution with a total acetic acid concentration of C^{tot}?

III. Monoprotic Weak Acid Salt (NaA) pH Calculation

Iterative Equation (see the Handout for derivation):

$$[OH^-] = \sqrt{K_b[A^-] + K_w} \qquad K_b = \frac{K_w}{K_a}$$

Similar to HA calculation, but [OH-] iteration instead of [H+]

$$pH = 14 - pOH$$

Use alpha fraction for A^-:

$$[A^-] = \alpha_{A^-} C^{tot}$$

$$[OH^-] = \sqrt{K_b C^{tot} + K_w}$$

First guess:

$$\alpha_{A^-} = 1$$

$$[A^-] = C^{tot}$$

$$[OH^-] \approx \sqrt{K_b C^{tot}}$$

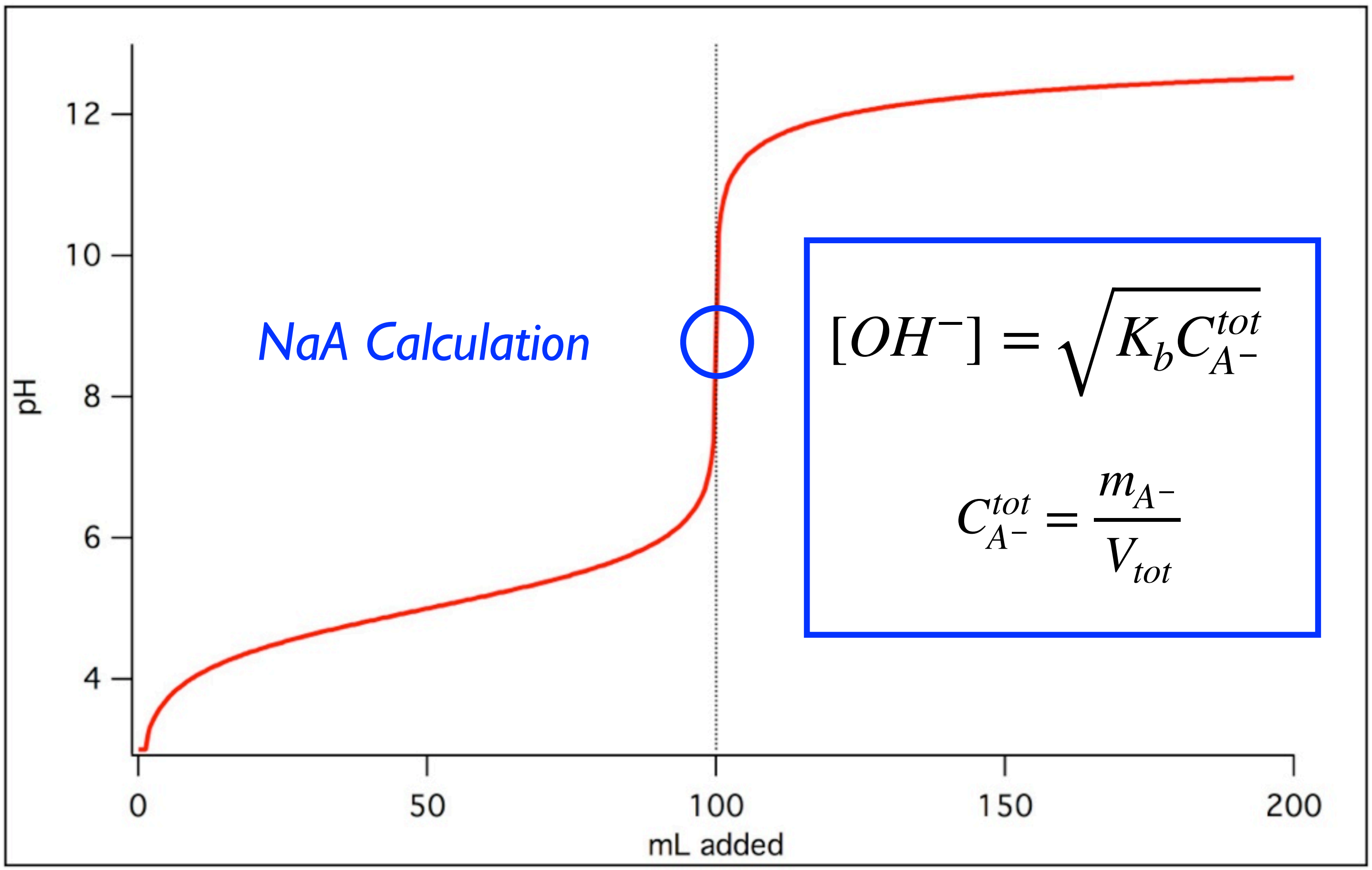
We used this simple equation for the equivalence point calculation.

Acid-Base Titrations: Weak Acid Titration Equivalence Point

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad K_t = \frac{K_a}{K_w} \gg 1$$

100.0 mL of 0.100M HA titrated with x mL of 0.100M NaOH

Equivalence Point: x = 100 mL. $\qquad$ V_{tot} *= 200 mL*



Other iterative pH calculations described in the Handout:

IV. Diprotic Weak Acid Salt pH calculation

Na_2A, e.g., sodium oxalate

V. Ampholyte pH calculation

NaHA, e.g., sodium bicarbonate

$$pH \approx \frac{pK_1 + pK_2}{2}$$