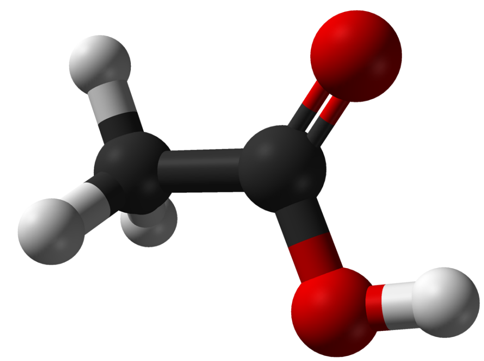
# Acid-Base Chemistry: Alpha Fractions, Titrations, Exact Solutions

## I. Monoprotic Weak Acid Alpha Fractions

HA = Acetic Acid: $CH_3COOH$



$$pK_a = -\,logK_a = 4.75$$

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

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

Two Acid Species: HA and $A^-$

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

Alpha Fractions only depend on pH and $pK_a$

$$pH = -\,log[H^+]$$

Robert Corn Chem M3LC

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

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

$$C_{tot} = [HA] + [A^-]$$

$$C_{tot} = [HA]\,(1 + K_a/[H^+])$$

$$\alpha_{HA} = [HA]/C_{tot} = (1 + K_a/[H^+])^{-1}$$

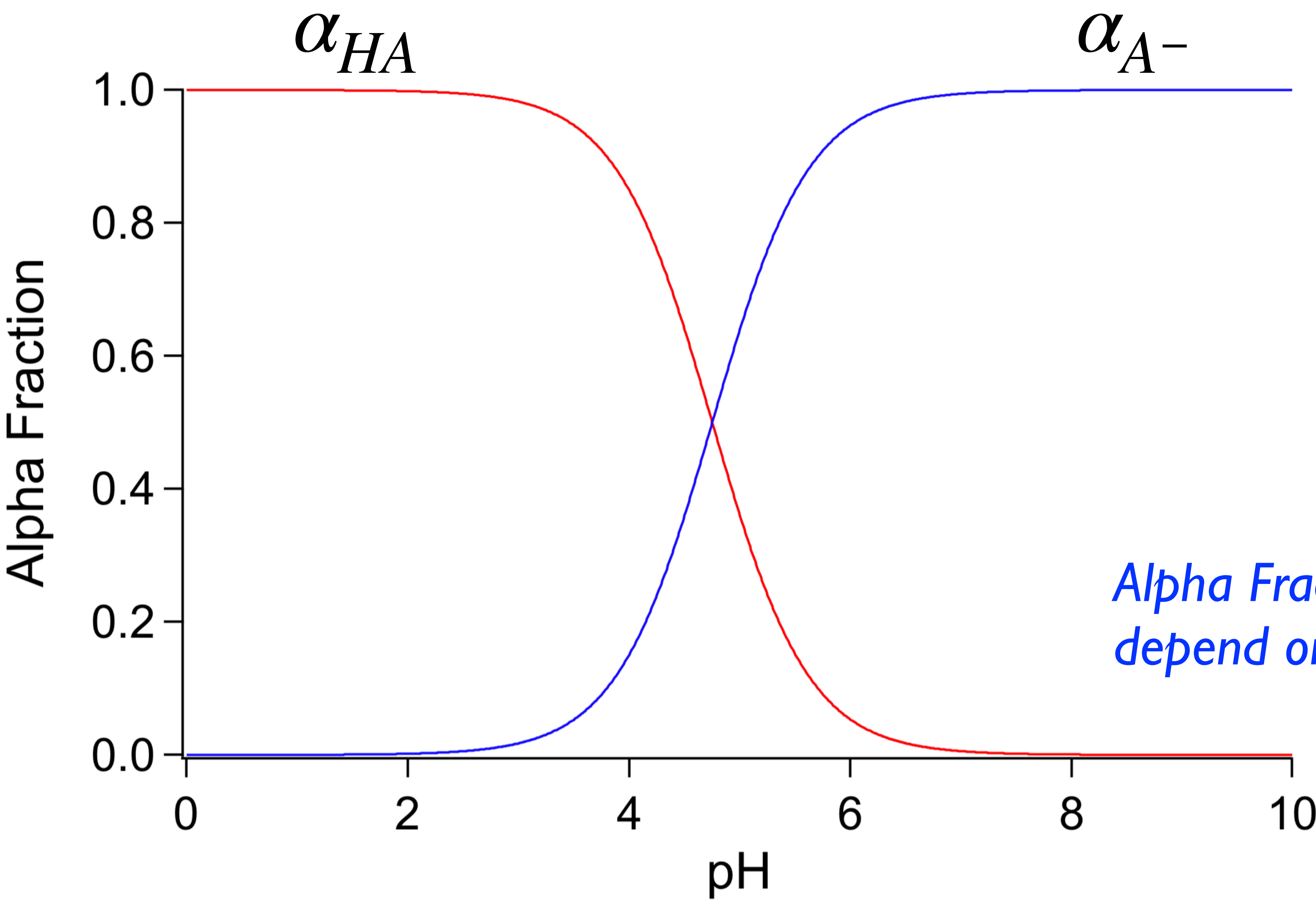
$$\alpha_{A^-} = 1 - \alpha_{HA} = = (1 + [H^+]/K_a)^{-1}$$

Two Acid Species: HA and $A^-$

Alpha Fractions only depend on pH and $pK_a$

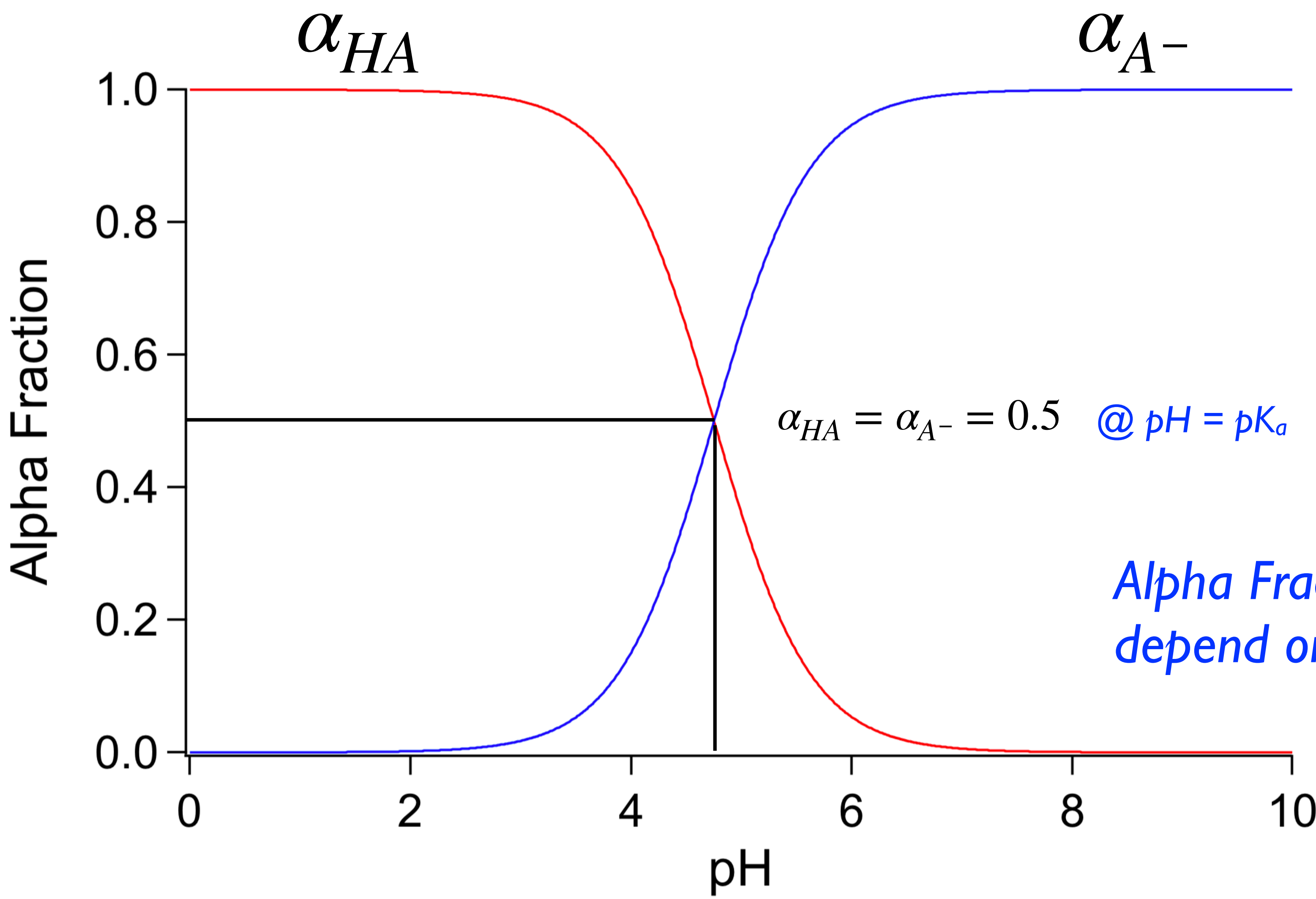
$$pH = -\log[H^+]$$

# *Alpha Fraction Plot for Acetic Acid*




*Alpha Fractions only depend on pH and $pK_a$*

# *Alpha Fraction Plot for Acetic Acid*




*Alpha Fractions only depend on pH and pK$_a$*

## II. Diprotic Weak Acid Alpha Fractions

$H_2A$ = Oxalic Acid: $C_2H_2O_4$

$$pK_1 = 1.25$$

$$pK_2 = 4.14$$

$C_{tot} = [H_2A] + [HA^-] + [A^{2-}]$

$C_{tot} = [H_2A]\ (1 + K_1/[H^+] + K_1K_2/[H^+]^2)$

$\alpha_{H_2A} = [H_2A]/C_{tot} = (1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1}$

$C_{tot} = [HA^-]\ ([H^+]/K_1 + 1 + K_2/[H^+])$

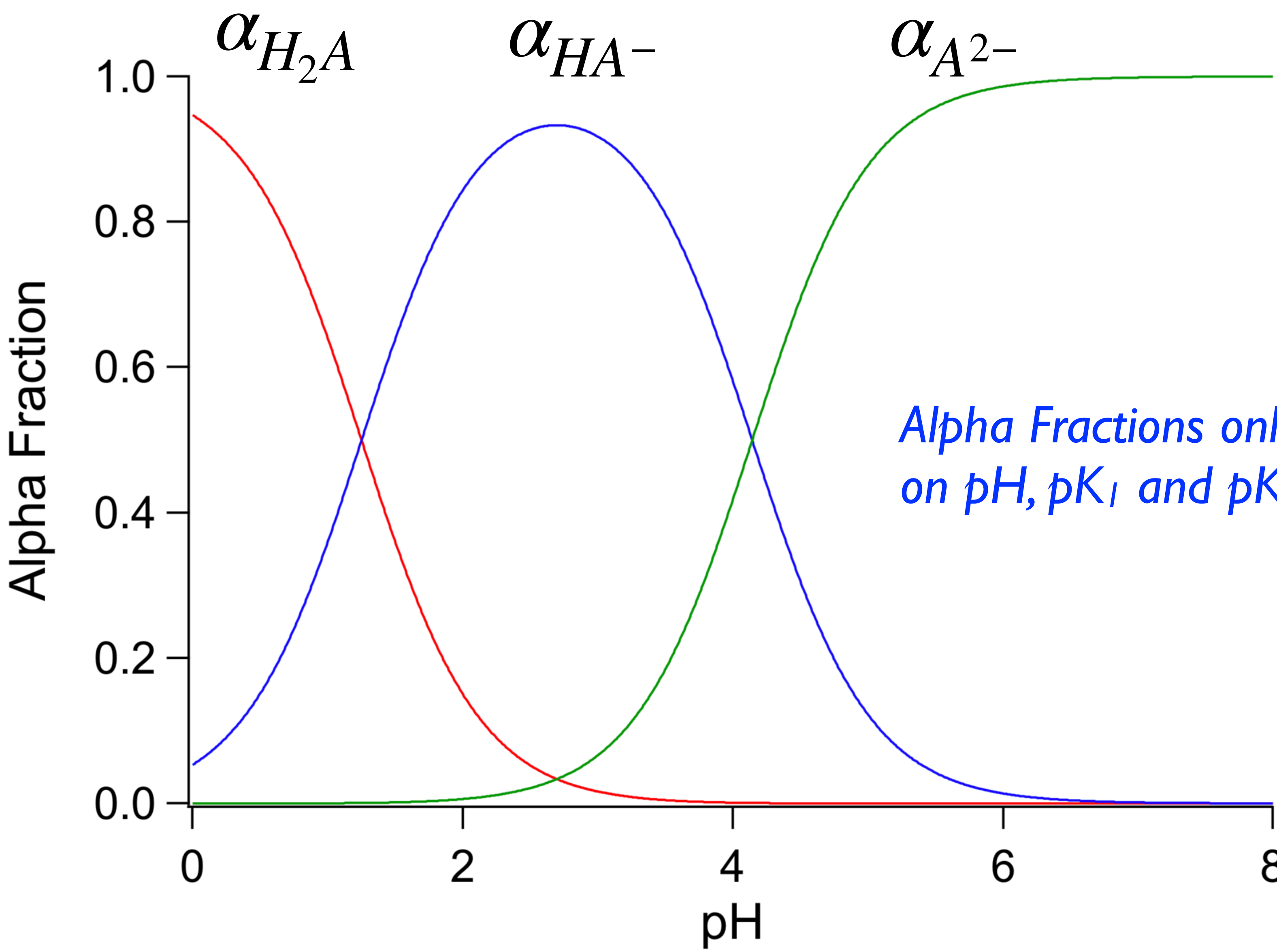
$\alpha_{HA^-} = [HA^-]/C_{tot} = ([H^+]/K_1 + 1 + K_2/[H^+])^{-1}$

$\alpha_{A^{2-}} = 1 - \alpha_{H_2A} - \alpha_{HA^-} = (1 + [H^+]/K_2 + [H^+]^2/K_1K_2)^{-1}$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]}$$

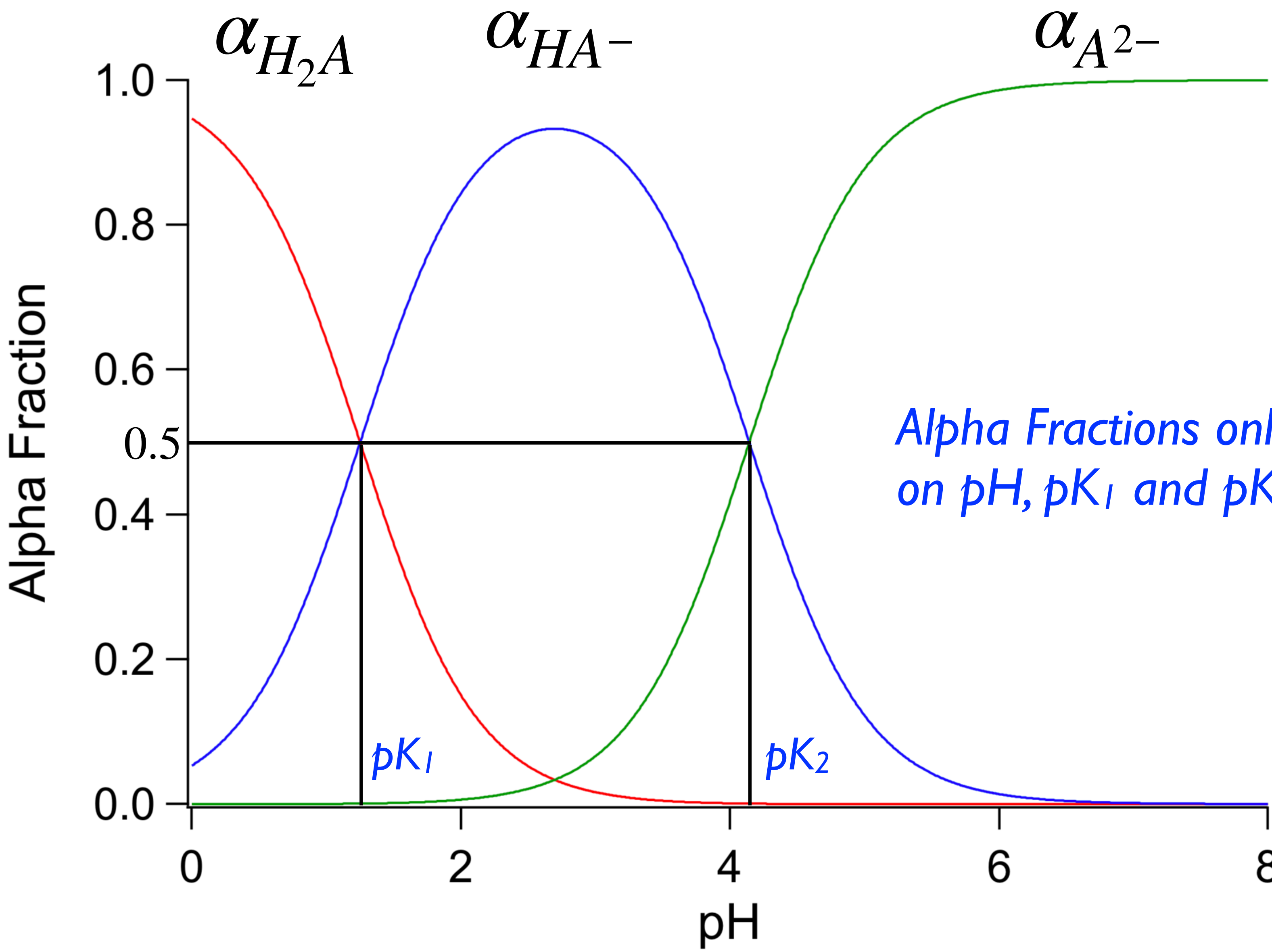
$$K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

# *Alpha Fraction Plot for Oxalic Acid*



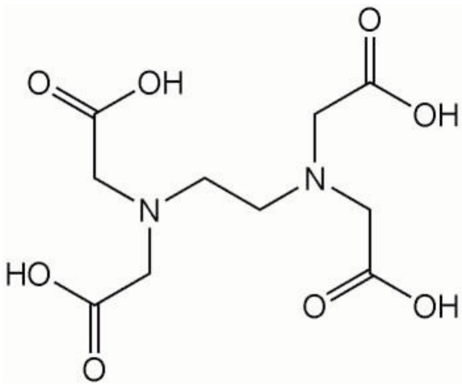

*Alpha Fractions only depend on pH, $pK_1$ and $pK_2$*

# Alpha Fraction Plot for Oxalic Acid




Alpha Fractions only depend on pH, $pK_1$ and $pK_2$

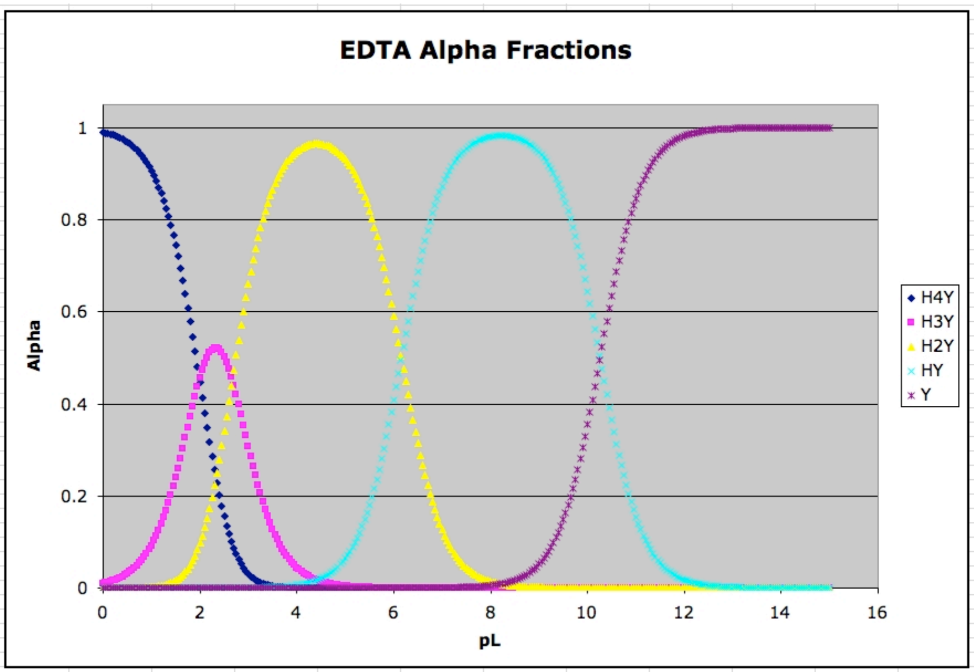
# EDTA Metal Ion Complexation Equilibria



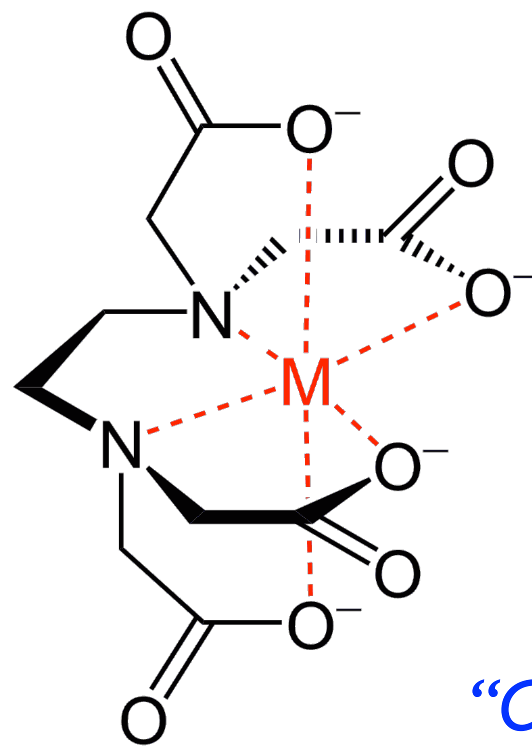

Ethylene Diamine Tetra-acetic Acid ($H_4Y$)

$$\alpha_{Y^{4-}}$$

EDTA - the world's best metal ion chelator




EDTA titrations are in basic buffers



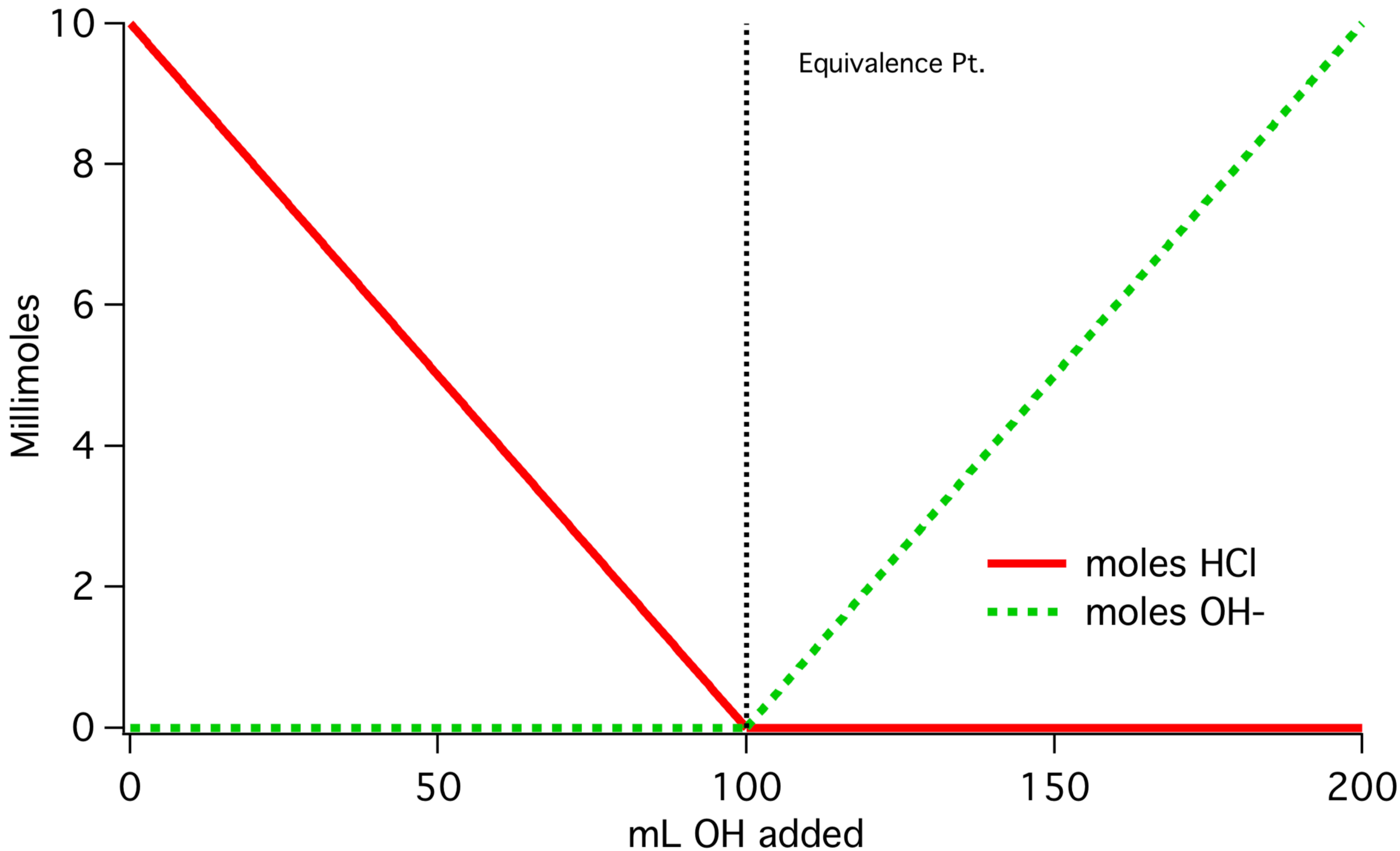

$Y^{4-}$

"Chelate"

## I. Strong Acid Titration

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

*100.0 mL of 0.100 HCl titrated with x mL of 0.100 NaOH*



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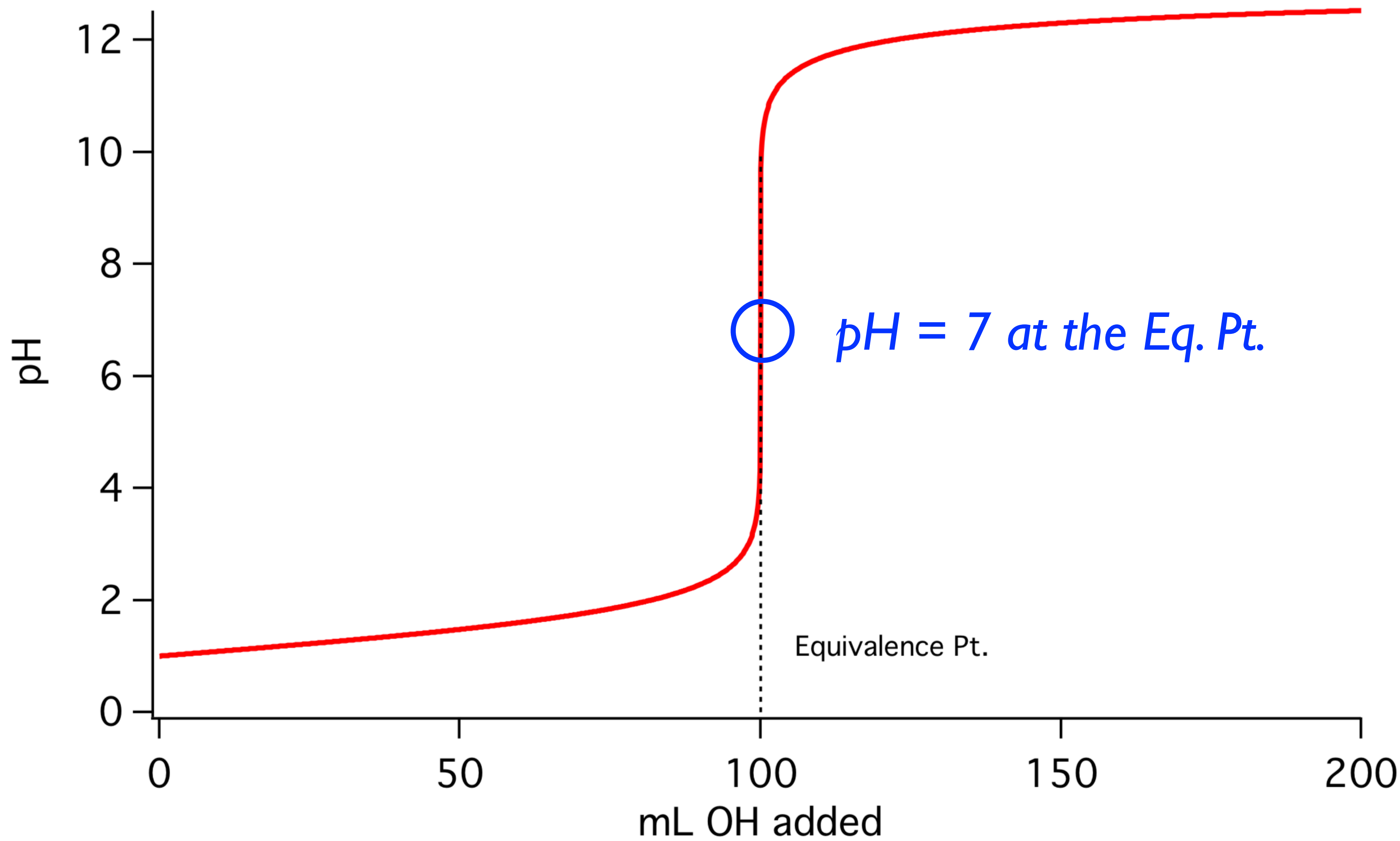


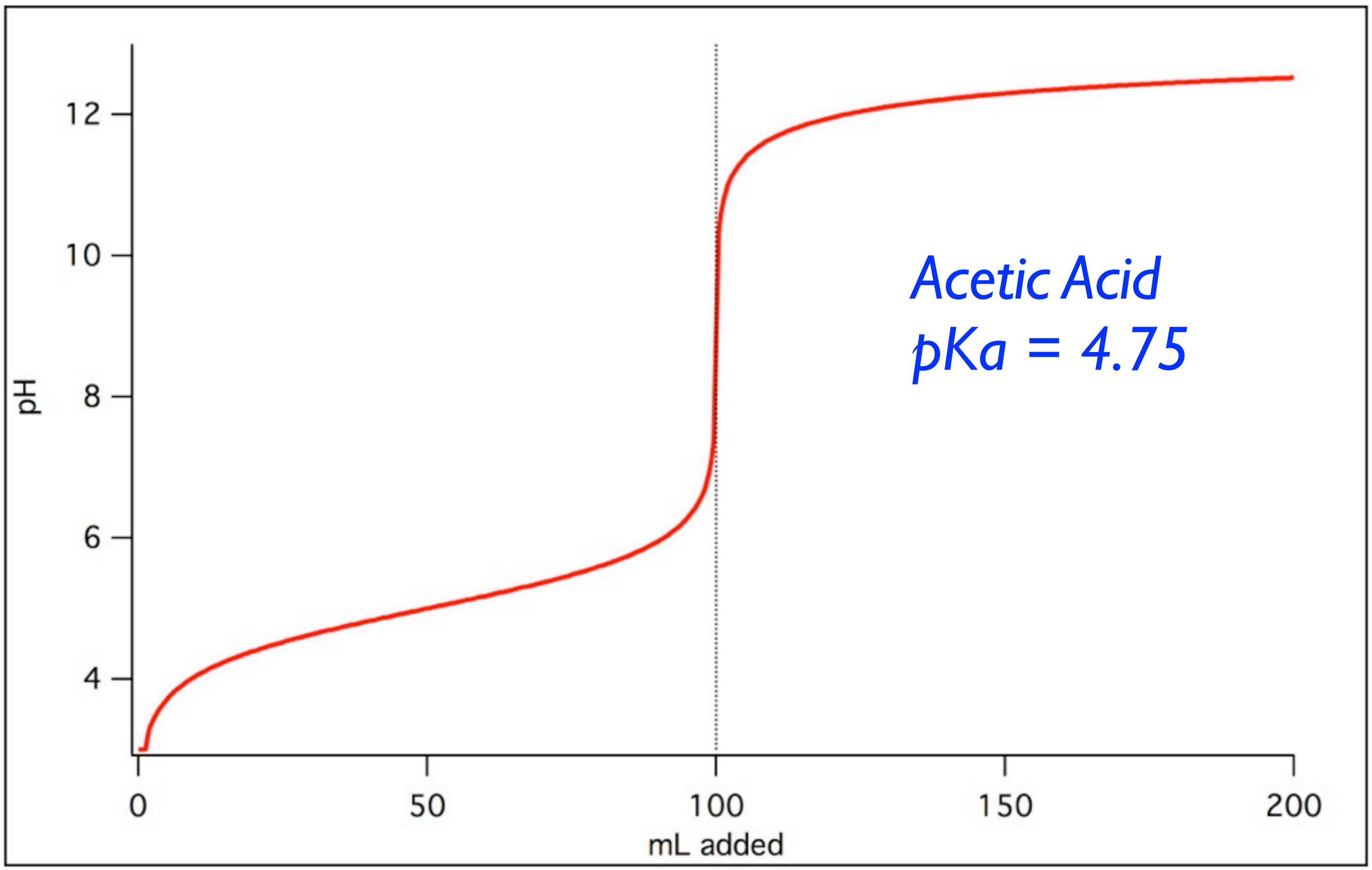
# Acid-Base Chemistry: Alpha Fractions, Titrations, Exact Solutions

## II. Weak Acid Titration

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

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

Calculate the pH of solution at x = 0.0, 50.0, 100.0 and 150.0 mL



# Acid-Base Chemistry: Alpha Fractions, Titrations, Exact Solutions

## II. Weak Acid Titration

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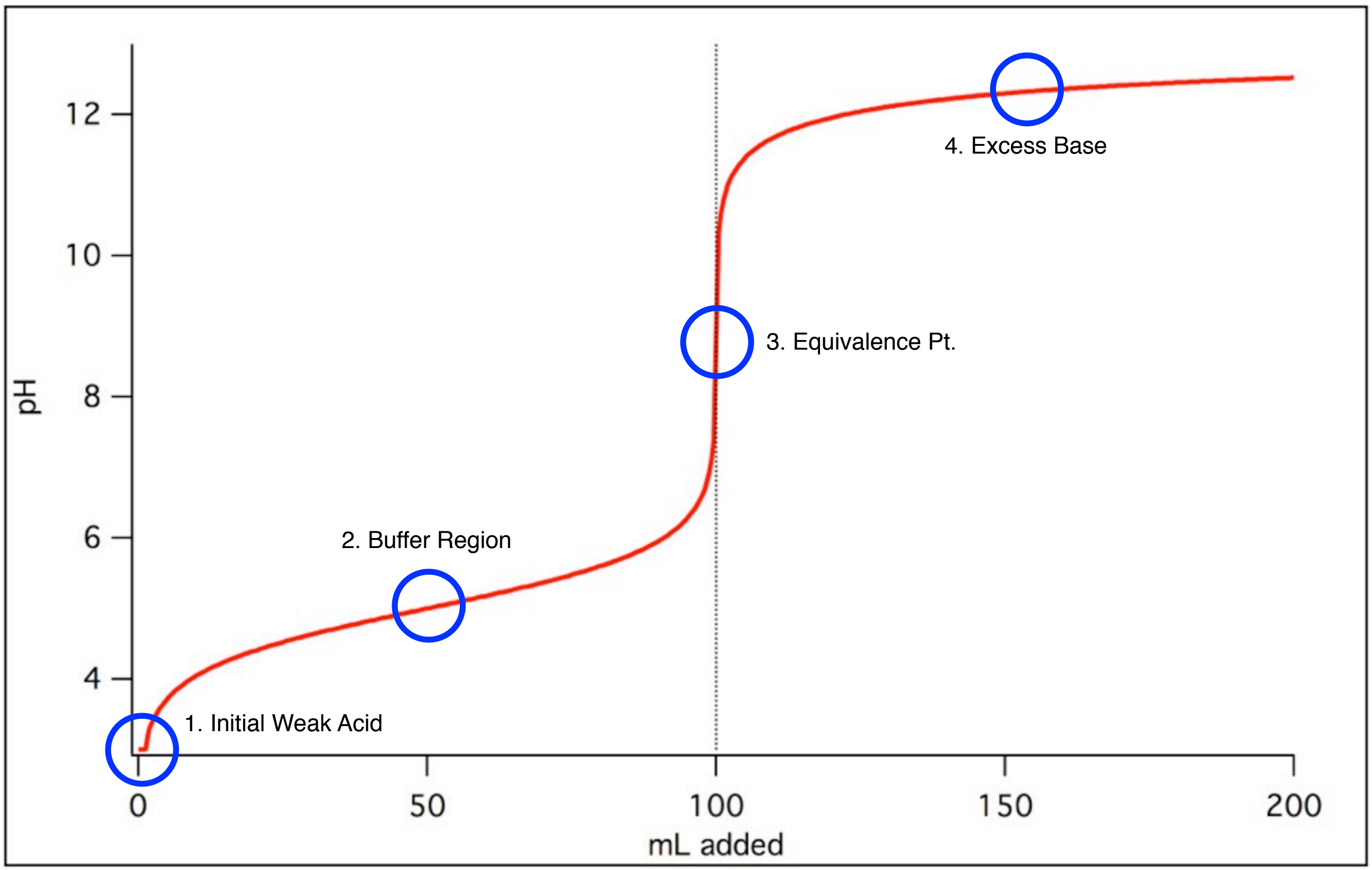

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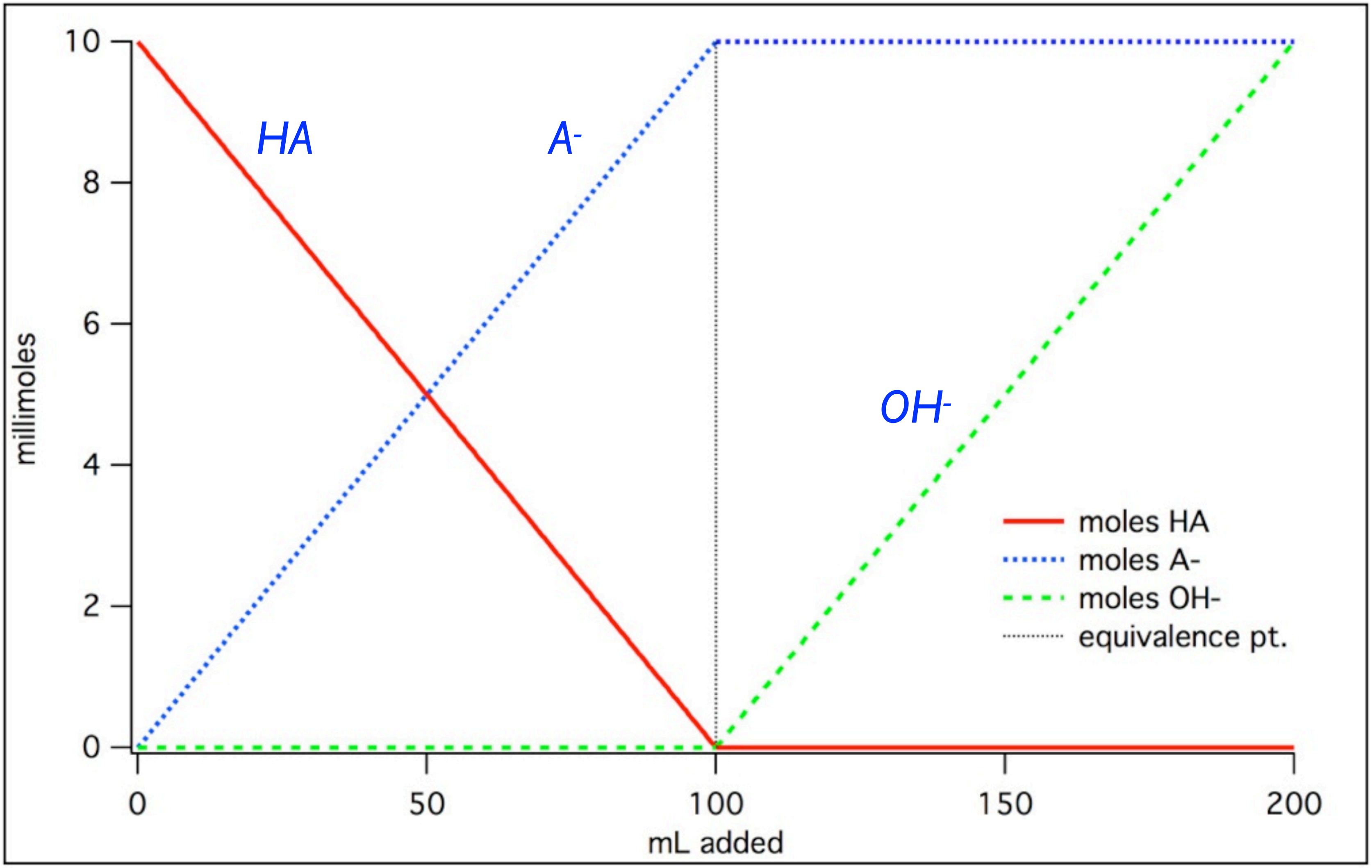

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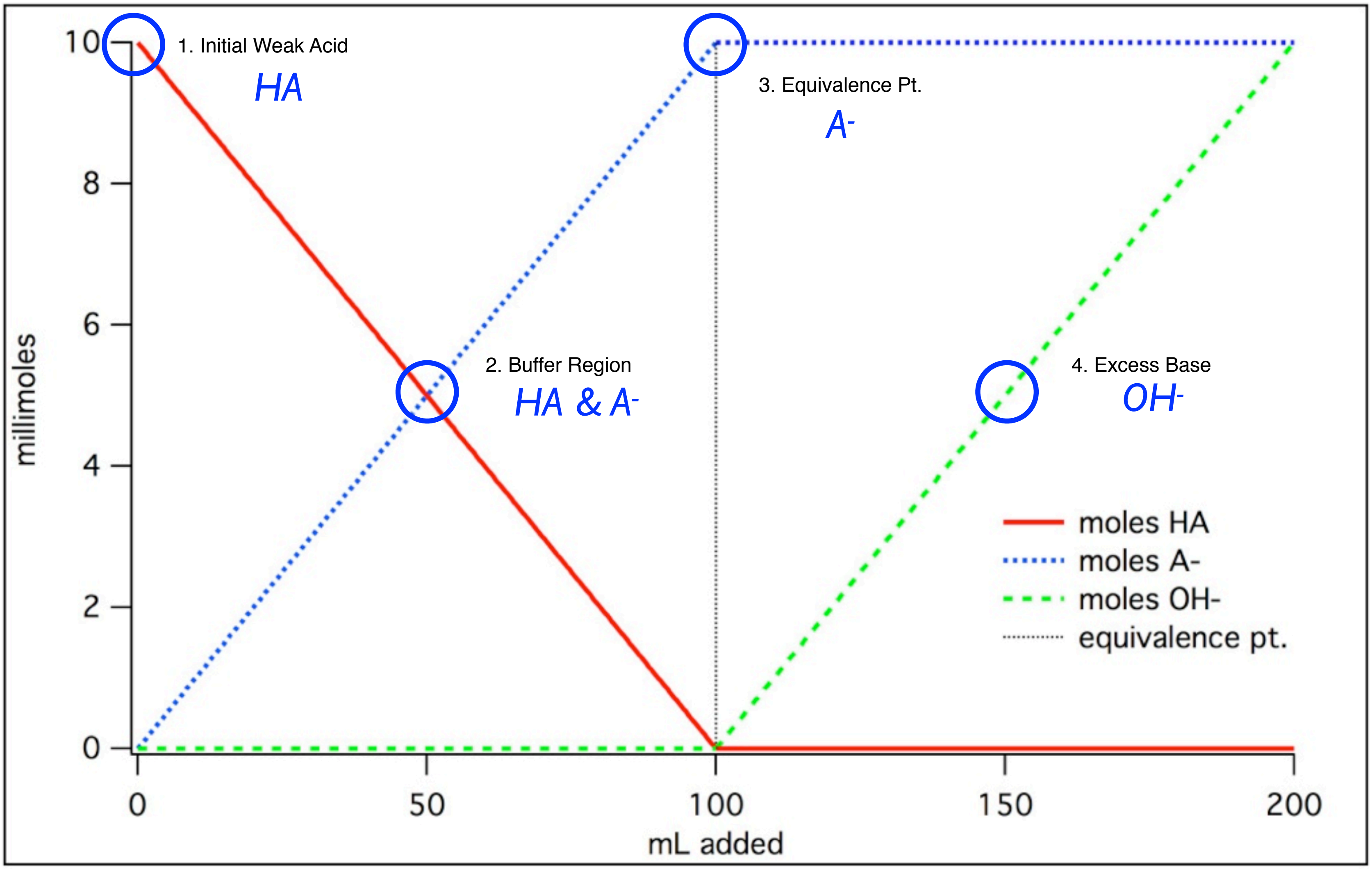

## II. Weak Acid Titration

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

Calculate the pH of the solution at points:

x = 0.0 mL — Initial Weak Acid pH: HA

x = 50.0 mL — Buffer Region: HA & $A^-$

x = 100.0 mL — Equivalence Point: $A^-$ ← weak acid salt calc. "NaA"

x = 150.0 mL — Excess Base $OH^-$

## II. Weak Acid Titration

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

$$pK_a = 4.75 \qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad K_a = 10^{-4.75}$$

x = 0.0 mL — Initial Weak Acid pH: HA

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

x = 50.0 mL — Buffer Region: HA & $A^-$

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

x = 100.0 mL — Equivalence Point: $A^-$

$$[OH^-] = \sqrt{K_b C_{A^-}^{tot}}$$

$$C_{A^-}^{tot} = \frac{m_{HA}}{V_{tot}}$$

x = 150.0 mL — Excess Base $OH^-$

$$[OH^-] = \frac{m_{OH^-}}{V_{tot}}$$

## I. Monoprotic Weak Acid - Exact Solution

Approximate Solution:

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

Monoprotic Weak Acid

Constants: Ka, Kw, Ctot

Four species: [HA], [A-], [H+], [OH-]

| | |
|---|---|
| Ka = [H+][A-]/[HA] | acid dissociation |
| Kw = [H+][OH-] | water dissociation |
| [H+] = [A-] + [OH-] | charge balance |
| Ctot = [HA] + [A-] | mass balance |

## I. Monoprotic Weak Acid - Exact Solution

Full Cubic for [H+]

$[H+][A-] = Ka[HA]$

$[H+]([H+] - [OH-]) = Ka(Ctot - [A-])$

$[H+]^2 - Kw = Ka(Ctot - [H+] + Kw/[H+])$

$[H+]^2 = Ka(Ctot - [H+] + Kw/[H+]) + Kw$

Iterative Equations:

$[HA] = Ctot\ (1 + Ka/[H+])^{-1}$

$[H+] = sqrt(Ka[HA] + Kw)$

## II. Monoprotic Weak Acid Salt - Exact Solution

**Approximate Solution:**

$$[OH^-] = \sqrt{K_b C_{A^-}^{tot}}$$

Monoprotic Weak Acid Salt

Constants: Kb, Kw, Ctot

Five species: [HA], [A-], [H+], [OH-], [Na+]

| | |
|---|---|
| Kb = [OH-][HA]/[A-] | base dissociation |
| Kw = [H+][OH-] | water dissociation |
| [Na+] + [H+] = [A-] + [OH-] | charge balance |
| Ctot = [HA] + [A-] | mass balance 1 |
| Ctot = [Na+] | mass balance 2 |

## II. Monoprotic Weak Acid Salt - Exact Solution

Full Cubic for [OH-]

$[OH^-][HA] = K_b[A^-]$

$[OH^-]([OH^-] - [H^+]) = K_b(C_{tot} - [HA])$

$[OH^-]^2 - K_w = K_b(C_{tot} - [OH^-] + K_w/[OH^-])$

$[OH^-]^2 = K_b(C_{tot} - [OH^-] + K_w/[OH^-]) + K_w$

Iterative Equations:

$[A^-] = C_{tot}(1 + K_b/[OH^-])^{-1}$

$[OH^-] = \mathrm{sqrt}(K_b[A^-] + K_w)$

## III. Diprotic Weak Acid - Exact Solution

Diprotic Weak Acid

Constants: K1, K2, Kw, Ctot

Five species: [H2A], [HA-], [A2-], [H+], [OH-]

| | |
|---|---|
| K1 = [H+][HA-]/[H2A] | acid dissociation 1 |
| K2 = [H+][A2-]/[HA-] | acid dissociation 2 |
| Kw = [H+][OH-] | water dissociation |
| [H+] = [HA-]+ 2[A2-] + [OH-] | charge balance |
| Ctot = [H2A] + [HA-] + [A2-] | mass balance |

## III. Diprotic Weak Acid - Exact Solution

Iterative eqns for [H+]

$[H^+][HA^-] = K_1[H_2A]$

$[H^+]([H^+] - [OH^-] - 2[A^{2-}]) = K_1[H_2A]$

$[H^+]^2 - 2[H^+][A^{2-}] - K_w = K_1[H_2A]$

$[H^+]^2 = K_1[H_2A] + 2K_2[HA^-] + K_w$

Initial Guess: $[H^+] = \mathrm{sqrt}(K_1 \cdot C_{tot} + K_w)$

Calculate $[H_2A]$, $[HA^-]$, $[A^{2-}]$

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

Alpha Fractions

$[H_2A]/C_{tot} = (1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1}$

$[HA^-]/C_{tot} = ([H^+]/K_1 + 1 + K_2/[H^+])^{-1}$

$[A^{2-}]/C_{tot} = ([H^+]/K_2 + [H^+]^2/K_1K_2 + 1)^{-1}$

## IV. Diprotic Ampholyte - Approximate Solution

Ampholyte Disproportionation:

$2HA \rightarrow H_2A + A^{2-}$

$K_d = [H_2A][A^{2-}]/[HA^-]^2 = ([H_2A]/[HA^-][H^+])([H^+][A^{2-}]/[HA^-]) = K_2/K_1 << 1$

$[H_2A] = [A^{2-}] = [HA^-]\text{sqrt}(K_d)$

$[H^+] = K_1[H_2A]/ [HA^-] = K_1\text{sqrt}(K_d) = \text{sqrt}(K_1K_2)$

$pH = (pK_1 + pK_2)/2$

*Approximate Solution:*

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

## IV. Diprotic Ampholyte - Exact Solution

Diprotic Weak Acid Ampholyte

Constants: K1, K2, Kw, Ctot

Six species: [H2A], [HA-], [A2-], [H+], [OH-], [Na+]

| | |
|---|---|
| $K1 = [H^+][HA^-]/[H_2A]$ | acid dissociation 1 |
| $K2 = [H^+][A^{2-}]/[HA^-]$ | acid dissociation 2 |
| $Kw = [H^+][OH^-]$ | water dissociation |
| $[Na^+] + [H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$ | charge balance |
| $Ctot = [H_2A] + [HA^-] + [A^{2-}]$ | mass balance 1 |
| $Ctot = [Na^+]$ | mass balance 2 |

## IV. Diprotic Ampholyte - Exact Solution

Full equations for $[H^+]$

$Ctot = [H_2A] + [HA^-] + [A^{2-}]$ mass balance 1

$Ctot = [Na^+]$ mass balance 2

$[Na^+] + [H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$ charge balance

$$[H^+] = [A^{2-}] - [H_2A] + [OH^-]$$

$$[H^+] = Ka2[HA^-]/[H^+] - [H^+][HA^-]/Ka1 + Kw/[H^+]$$

$$[H^+]^2 = (Ka2[HA^-] + Kw)/(1 + [HA^-]/Ka1)$$

$$[H^+] = \mathrm{sqrt}[(Ka2[HA^-] + Kw)/(1 + [HA^-]/Ka1)]$$

## V. Diprotic Weak Acid Salt - Exact Solution

**Approximate Solution:**

$$[OH^-] = \sqrt{K_{b_2} C_{A^-}^{tot}}$$

Diprotic Weak Acid Salt

Constants: K1, K2, Kw, Ctot

Six species: [H2A], [HA-], [A2-], [H+], [OH-], [Na+]

| | |
|---|---|
| K1 = [H+][HA-]/[H2A] | acid dissociation 1 |
| K2 = [H+][A2-]/[HA-] | acid dissociation 2 |
| Kw = [H+][OH-] | water dissociation |
| [Na+] + [H+] = [HA-]+ 2[A2-] + [OH-] | charge balance |
| Ctot = [H2A] + [HA-] + [A2-] | mass balance 1 |
| 2Ctot = [Na+] | mass balance 2 |

## V. Diprotic Weak Acid Salt - Exact Solution

Iterative Equations for [OH-]

$Kb1 = Kw/K1 = [H2A][OH-]/[HA-]$

$Kb2 = Kw/K2 = [HA-][OH-]/[A2-]$

$[OH-][HA-] = Kb2[A2-]$

$2Ctot + [H+] = [HA-] + 2(Ctot – [HA-] – [H2A]) + [OH-]$

$[HA-] = [OH-] – 2[H2A] – [H+]$

$[OH-]([OH-] – 2[H2A] – [H+]) = Kb2[A2-]$

$[OH-]^2 – 2[OH-][H2A] - Kw = Kb[A2-]$

$[OH-]^2 = Kb2[A2-] + 2[OH-][H2A] + Kw$

$[OH-]^2 = Kb2[A2-] + 2Kb1[HA-] + Kw$

## V. Diprotic Weak Acid Salt - Exact Solution

Iterative Equations:

Initial Guess:

[A2-] = Ctot

[OH-] = sqrt(Kb2Ctot + Kw)

Iterate:

[A2-] = Ctot([H+]/K2 + $[H+]^2$/K1K2 + $1)^{-1}$

[OH-] = sqrt(Kb2[A2-] + 2Kb1[HA-] + Kw)