Acid-Base Chemistry: Weak Acid Alpha Fractions

Strong Acids

$$HCl \rightleftharpoons H^+ + Cl^-$$ $$K_a \approx \infty$$ 100% Dissociation

Weak Acids

$$HA \rightleftharpoons H^+ + A^-$$ $$K_a \ll 1$$ % Dissociation?

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

$$pK_a = -\,logK_a$$

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

pH dependence on
% Dissociation?

Two Acid Species: HA and A^-

Robert Corn
Chem M3LC

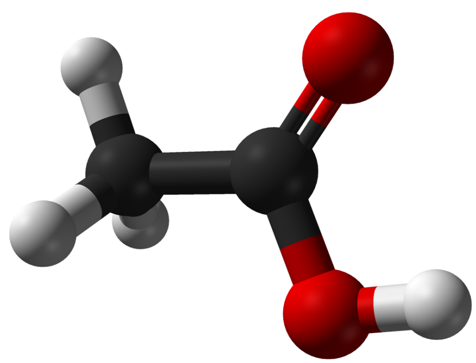
Acid-Base Chemistry: Monoprotic Weak Acid Alpha Fractions

Acetic Acid: CH_3COOH - A Monoprotic Weak Acid

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

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

$$pK_a = 4.75$$



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

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

Two Acid Species: HA and A^-

$HA = CH_3COOH$

$A^- = CH_3COO^-$

pH dependence on
% Dissociation?

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Henderson-Hasselbach Eqn.

Acid-Base Chemistry: Monoprotic Weak Acid Alpha Fractions

We will use Alpha Fractions to describe % Dissociation

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

C^{tot} is the total acid concentration

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

fraction of C^{tot} in the HA form

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

fraction of C^{tot} in the A^- form

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

% Dissociation = $\alpha_{A^-} \times 100$

All alpha fractions must range between 0 and 1: $0 \leq \alpha \leq 1$

Acid-Base Chemistry: Monoprotic Weak Acid Alpha Fractions

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

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

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

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

$$\alpha_{A^-} = \frac{[A^-]}{C^{tot}} = 1 - \alpha_{HA}$$

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

$$\frac{1 - \alpha_{HA}}{\alpha_{HA}} = \frac{K_a}{[H^+]}$$

$$\frac{1 - \alpha_{HA}}{\alpha_{HA}} = \frac{1}{\alpha_{HA}} - 1 = \frac{K_a}{[H^+]} \longrightarrow$$

$$\boxed{\alpha_{HA} = \frac{1}{1 + \frac{K_a}{[H^+]}}}$$

Acid-Base Chemistry: Monoprotic Acid Alpha Fractions

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

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

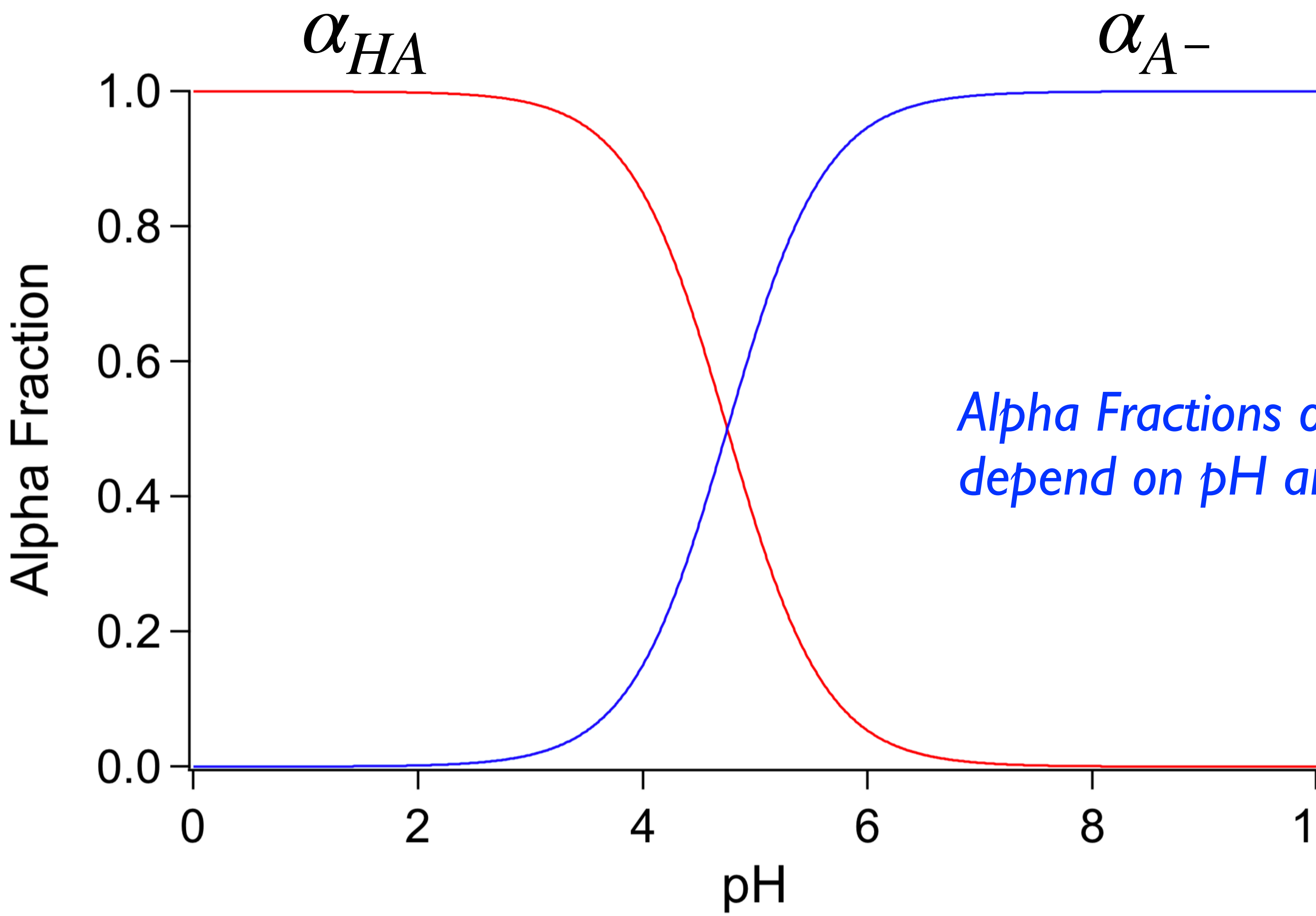
$$C^{tot} = [HA] + [A^-]$$

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

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

Alpha Fractions DO NOT depend on C^{tot} - only pH and pKa!

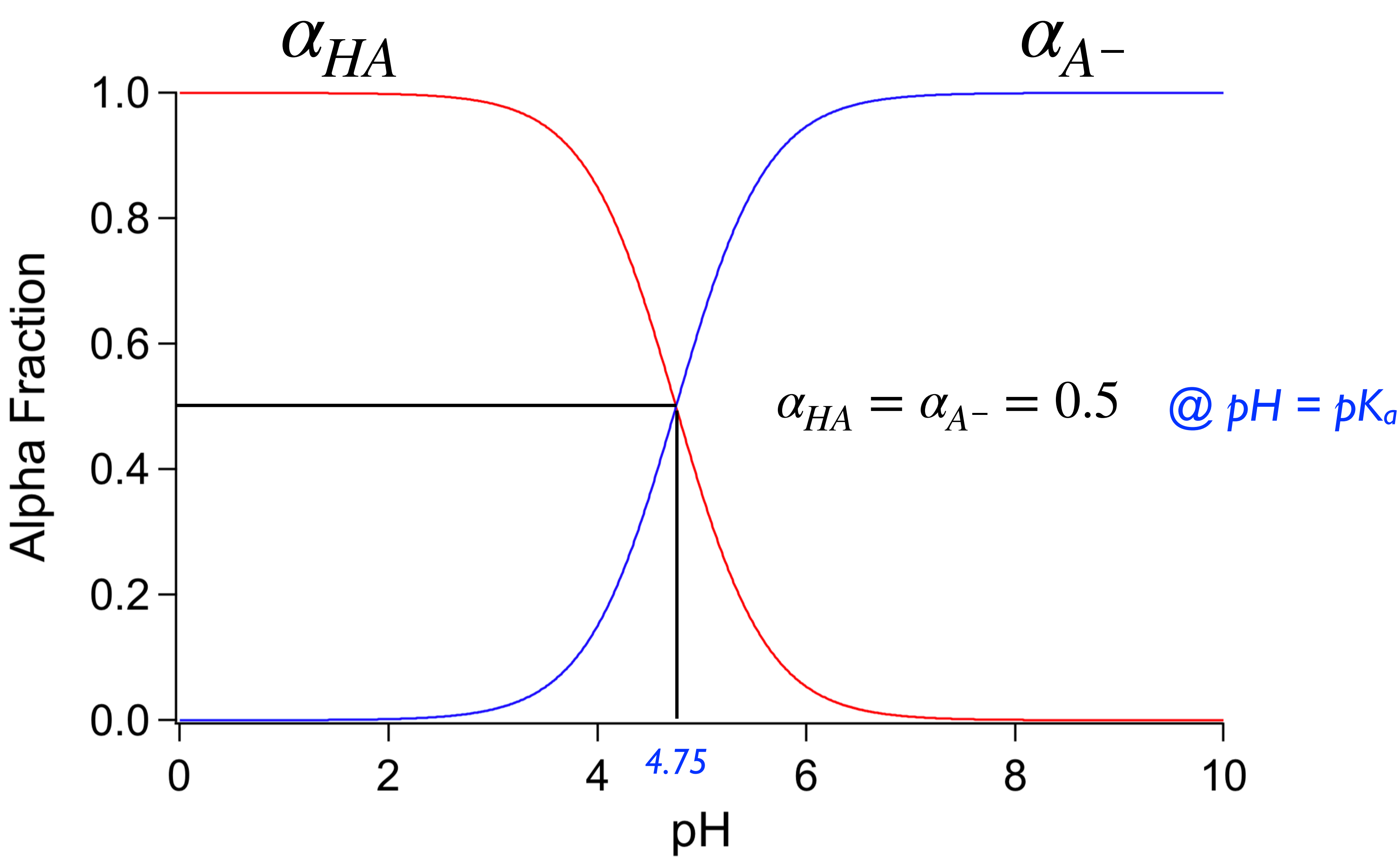
Alpha Fraction Plot for Acetic Acid (pK_a = 4.75)



Alpha Fractions only depend on pH and pK_a

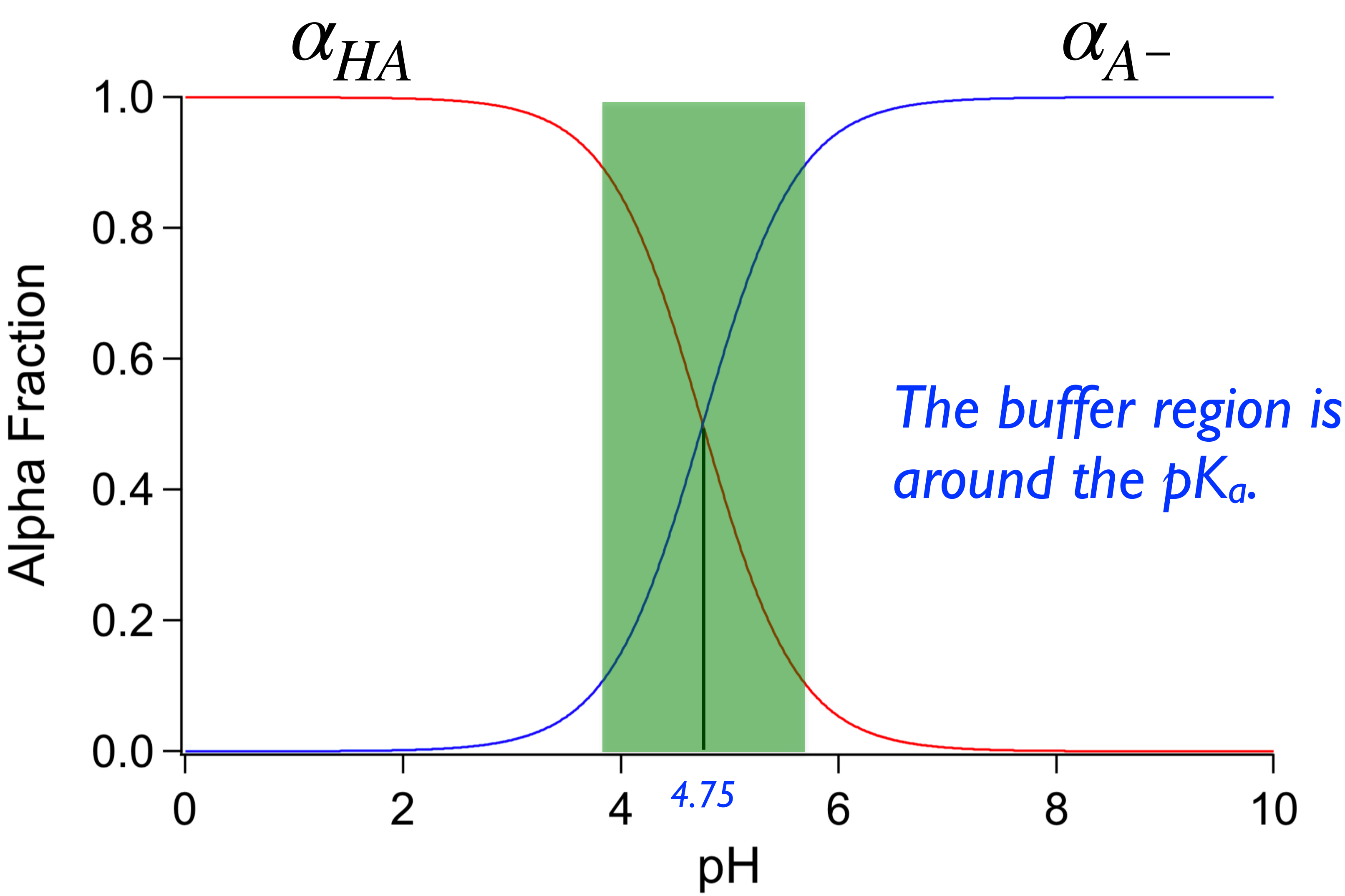
$$0 \le \alpha \le 1$$

Alpha Fraction Plot for Acetic Acid (pK_a = 4.75)



Alpha Fractions only depend on pH and pK_a

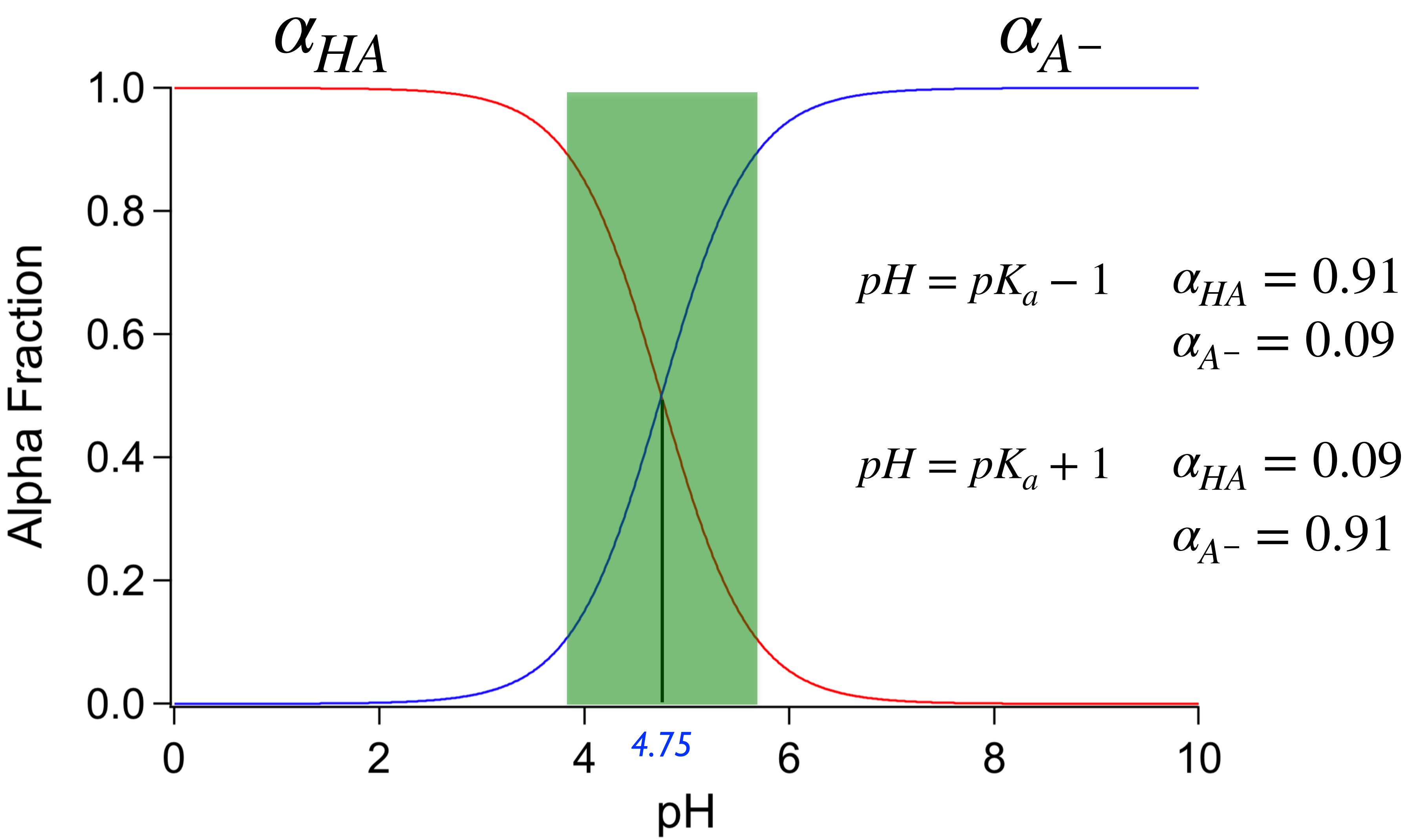
A buffer is a mixture of a conjugate weak acid and its conjugate base: HA and A^-



A buffered solution resists changes in pH when acids or bases are added or when dilution occurs.

In the buffer region, addition of strong acid or base only changes pH by <1 unit.

Buffer Region: $pK_a \pm 1$



The alpha fractions change significantly but the pH does not.

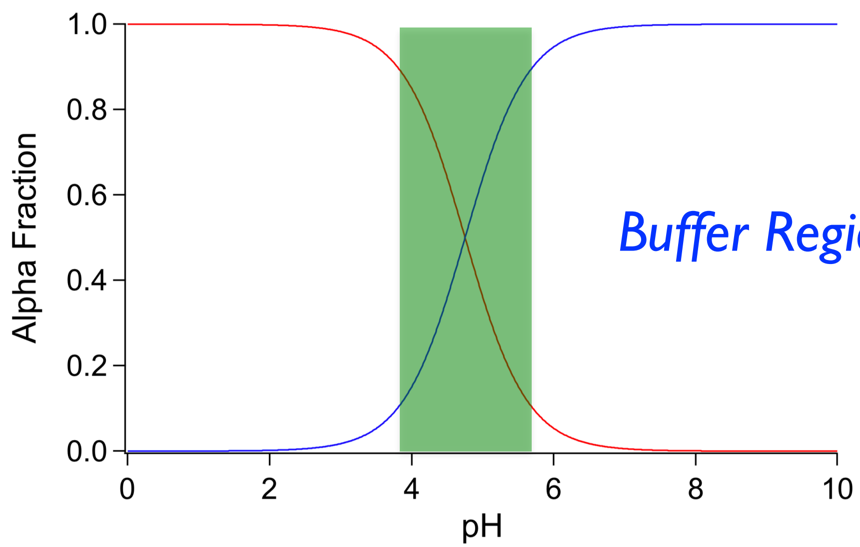
Buffer Capacity

General Definition:

"The amount of a strong acid or base that can be added to a volume of a buffer solution before its pH changes significantly."

"Amount" can be in moles, grams or concentration.

"Significantly" typically means ± 1 pH unit.



Buffer Region: $pK_a \pm 1$

$$pH = pK_a - 1 \qquad \alpha_{HA} = 0.91 \qquad \alpha_{A^-} = 0.09$$

$$pH = pK_a + 1 \qquad \alpha_{HA} = 0.09 \qquad \alpha_{A^-} = 0.91$$

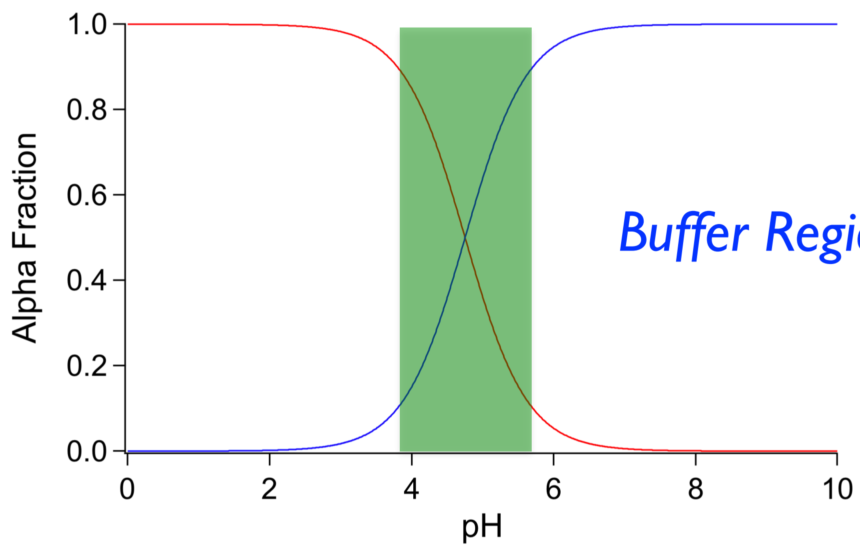
Buffer Capacity

Specific Definition (beta):

$$\beta = \frac{dC_b}{d(pH)} = 2.303\left(\frac{K_w}{[H^+]} + [H^+] + C^{tot}\frac{K_a[H^+]}{\left(K_a + [H^+]\right)^2}\right)$$

C_b is the concentration of strong base added.

See the Handout on Buffer Capacity for Derivation.



Buffer Region: $pK_a \pm 1$

$pH = pK_a - 1$ $\qquad \alpha_{HA} = 0.91$

$\alpha_{A^-} = 0.09$

$pH = pK_a + 1$ $\qquad \alpha_{HA} = 0.09$

$\alpha_{A^-} = 0.91$

Acid-Base Chemistry: Diprotic Acid Alpha Fractions

Oxalic Acid: $C_2H_2O_4$

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

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

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

$$\alpha_{H_2A} = \frac{[H_2A]}{C^{tot}} \qquad \alpha_{HA^-} = \frac{[HA^-]}{C^{tot}} \qquad \alpha_{A^-} = \frac{[A^{2-}]}{C^{tot}}$$

$$\alpha_{H_2A} + \alpha_{HA^-} + \alpha_{A^{2-}} = 1$$

$0 \leq \alpha \leq 1$ *Still true!*

Acid-Base Chemistry: Diprotic Acid Alpha Fractions

II. Diprotic Weak Acid Alpha Fractions

H_2A = Oxalic Acid: $C_2H_2O_4$

$$pK_1 = 1.25$$

$$pK_2 = 4.14$$

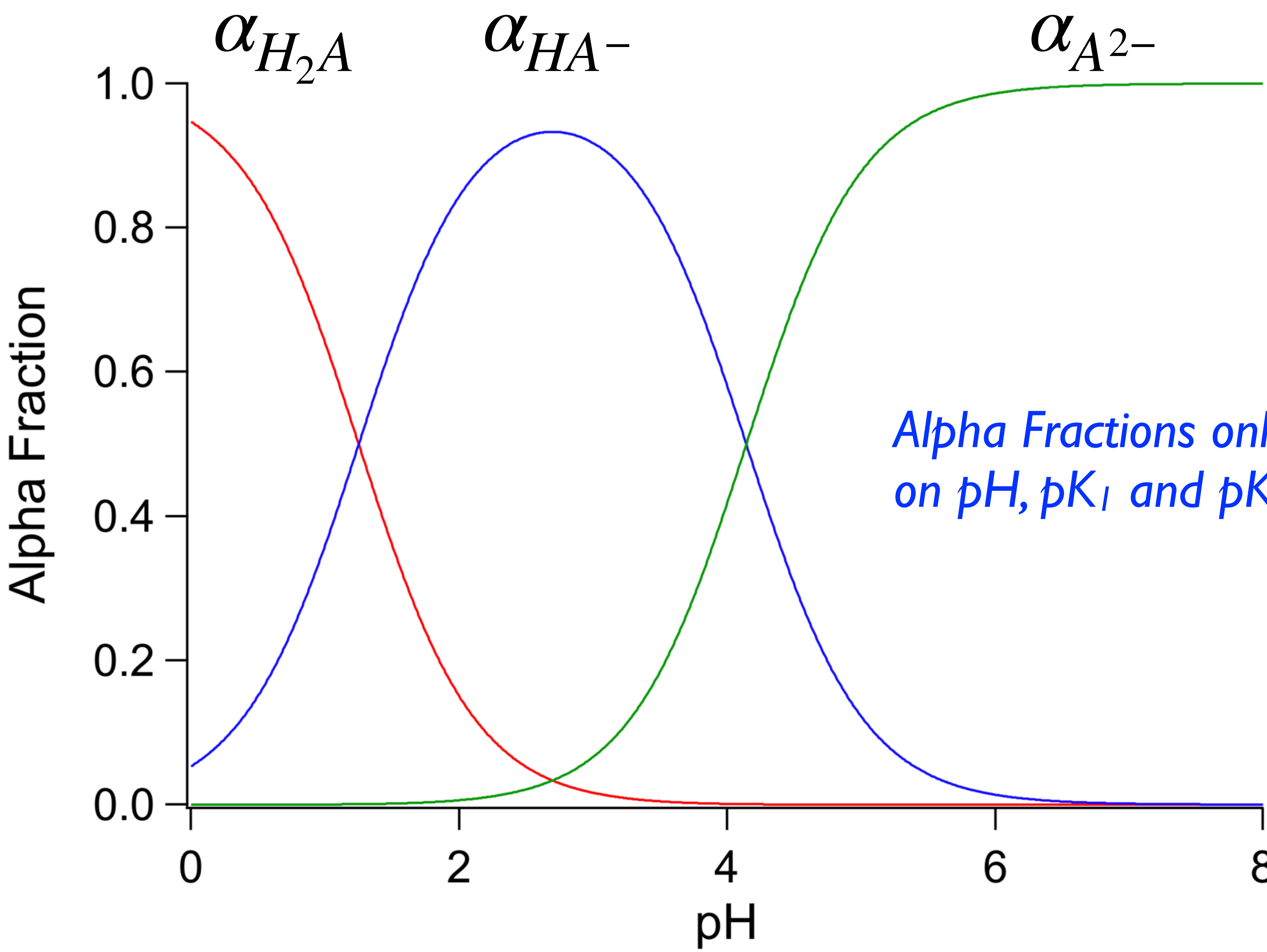
$$\alpha_{H_2A} = \frac{[H_2A]}{C^{tot}} = \left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)^{-1}$$

$$\alpha_{HA^-} = \frac{[HA^-]}{C^{tot}} = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)^{-1}$$

$$\alpha_{A^{2-}} = \frac{[A^{2-}]}{C^{tot}} = \left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)^{-1}$$

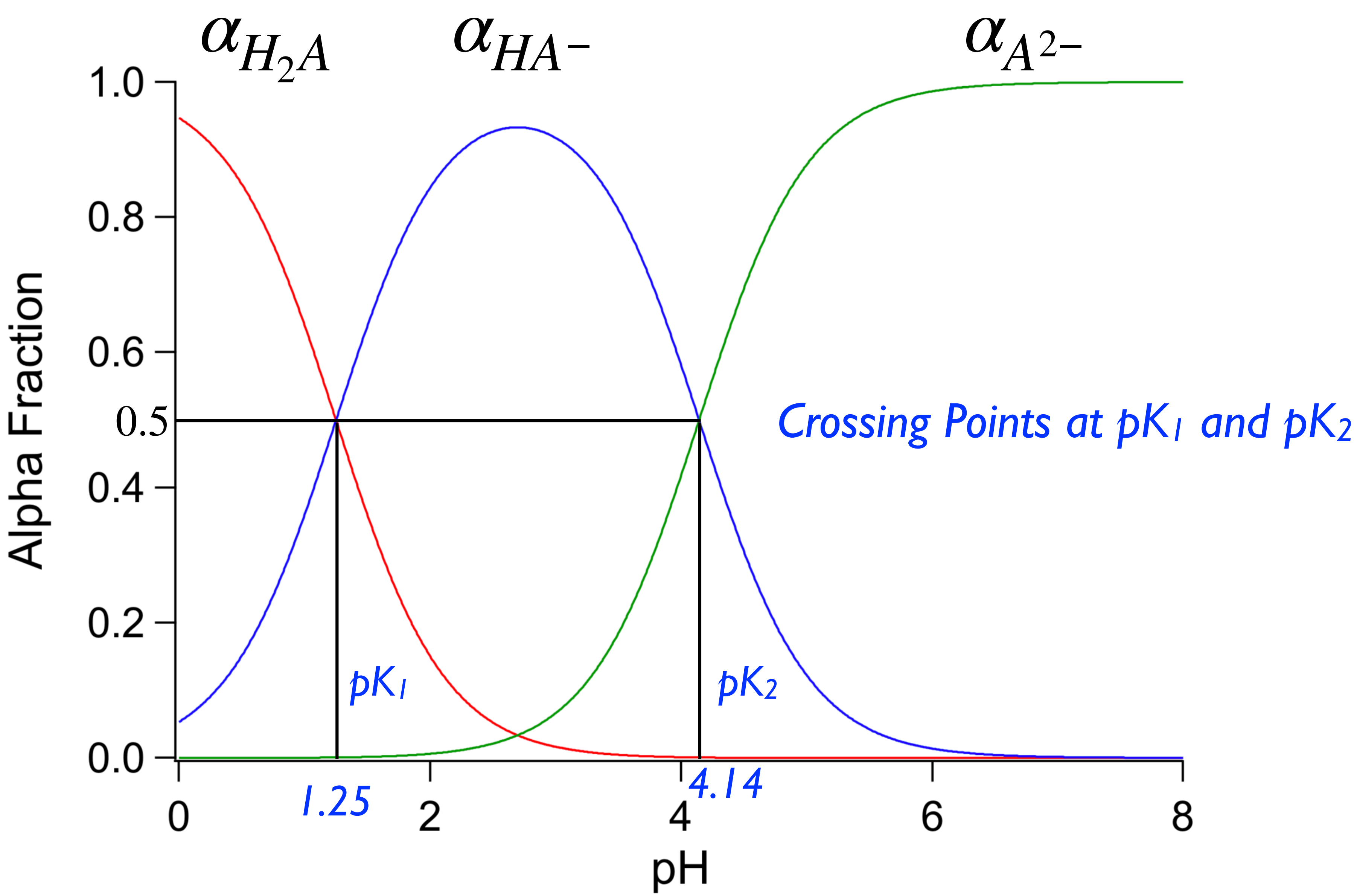
$$\alpha_{H_2A} + \alpha_{HA^-} + \alpha_{A^{2-}} = 1$$

Alpha Fraction Plot for Oxalic Acid

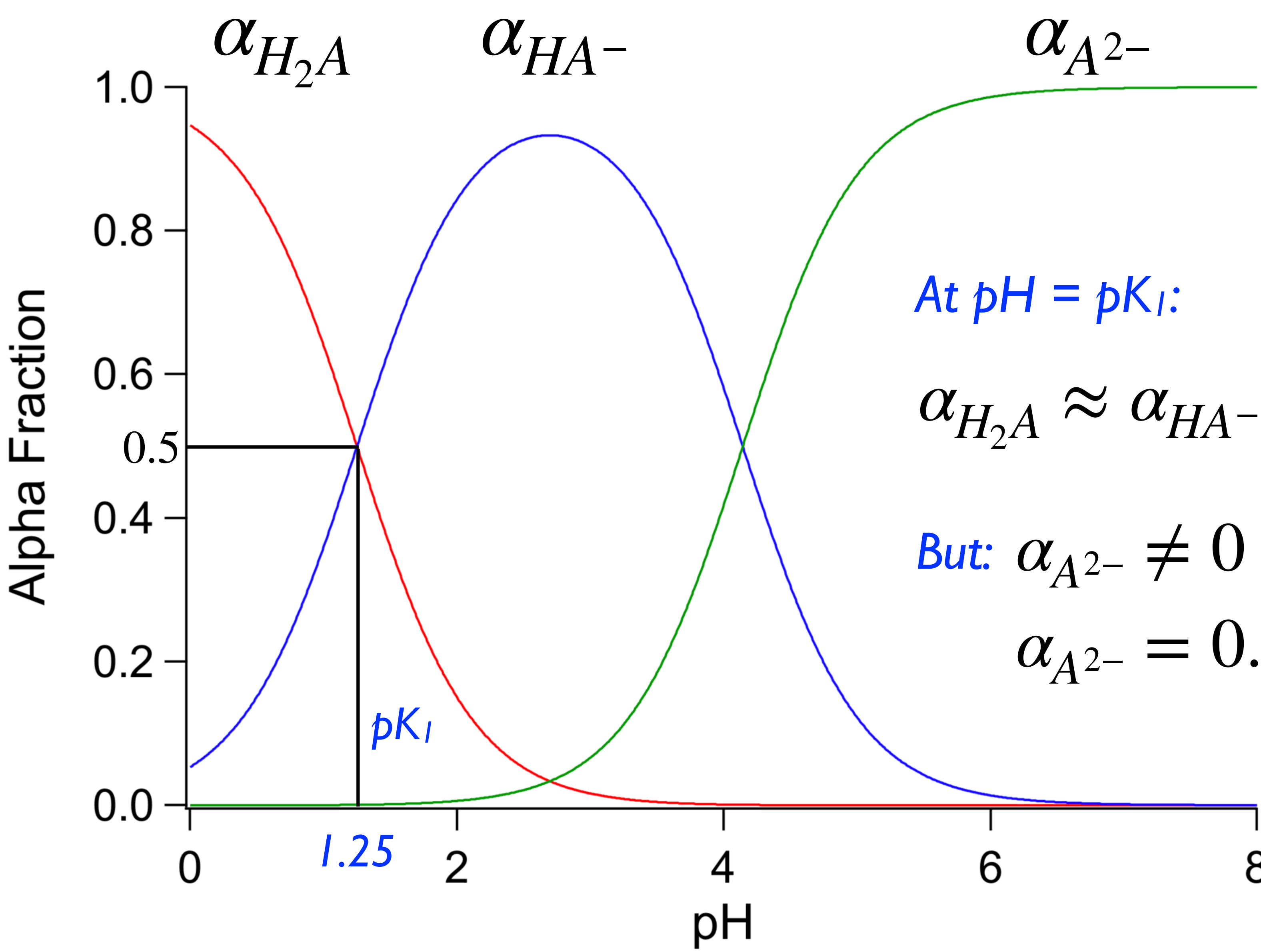


Alpha Fractions only depend on pH, pK_1 and pK_2

Alpha Fraction Plot for Oxalic Acid



Alpha Fraction Plot for Oxalic Acid



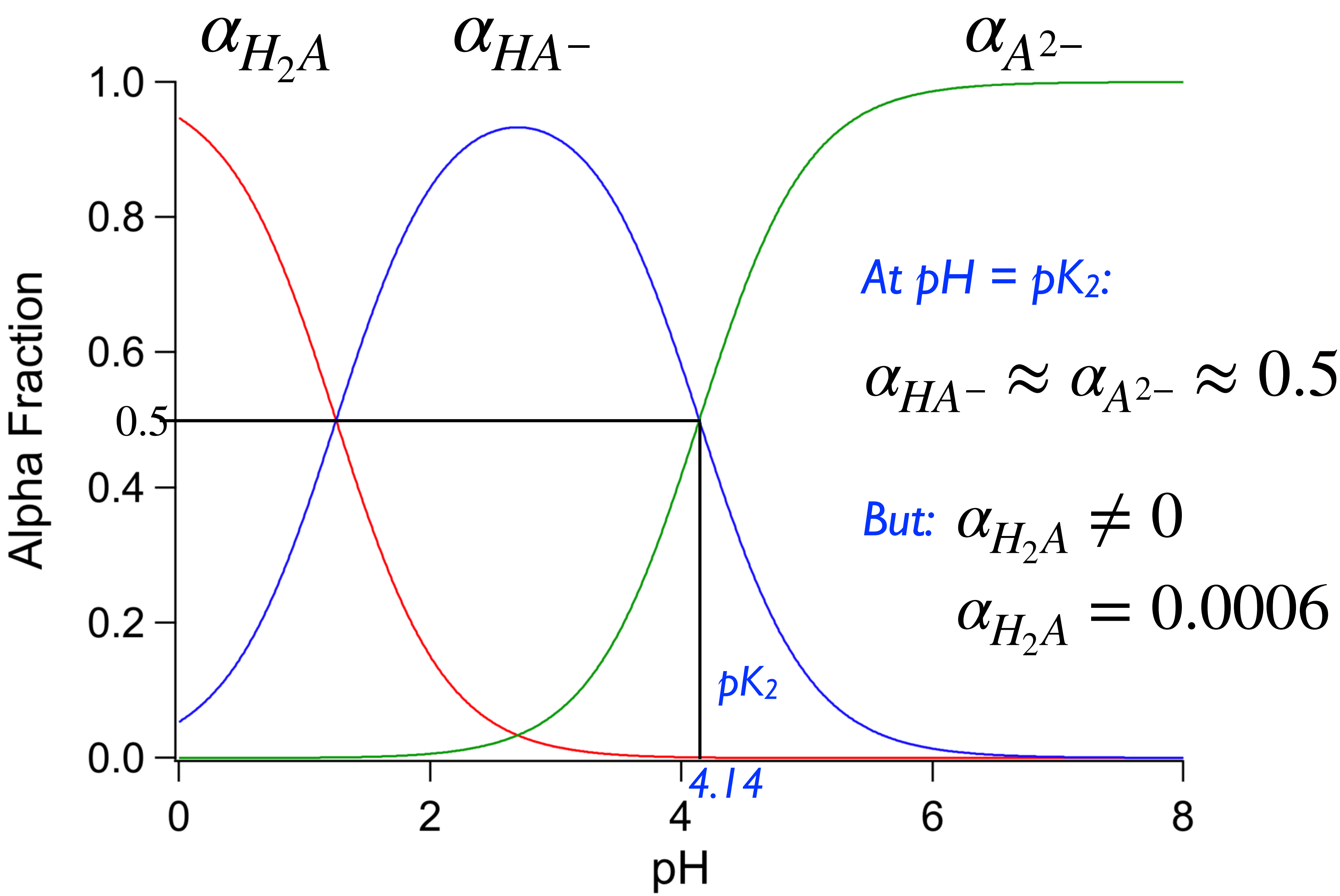
At $pH = pK_1$:

$$\alpha_{H_2A} \approx \alpha_{HA^-} \approx 0.5$$

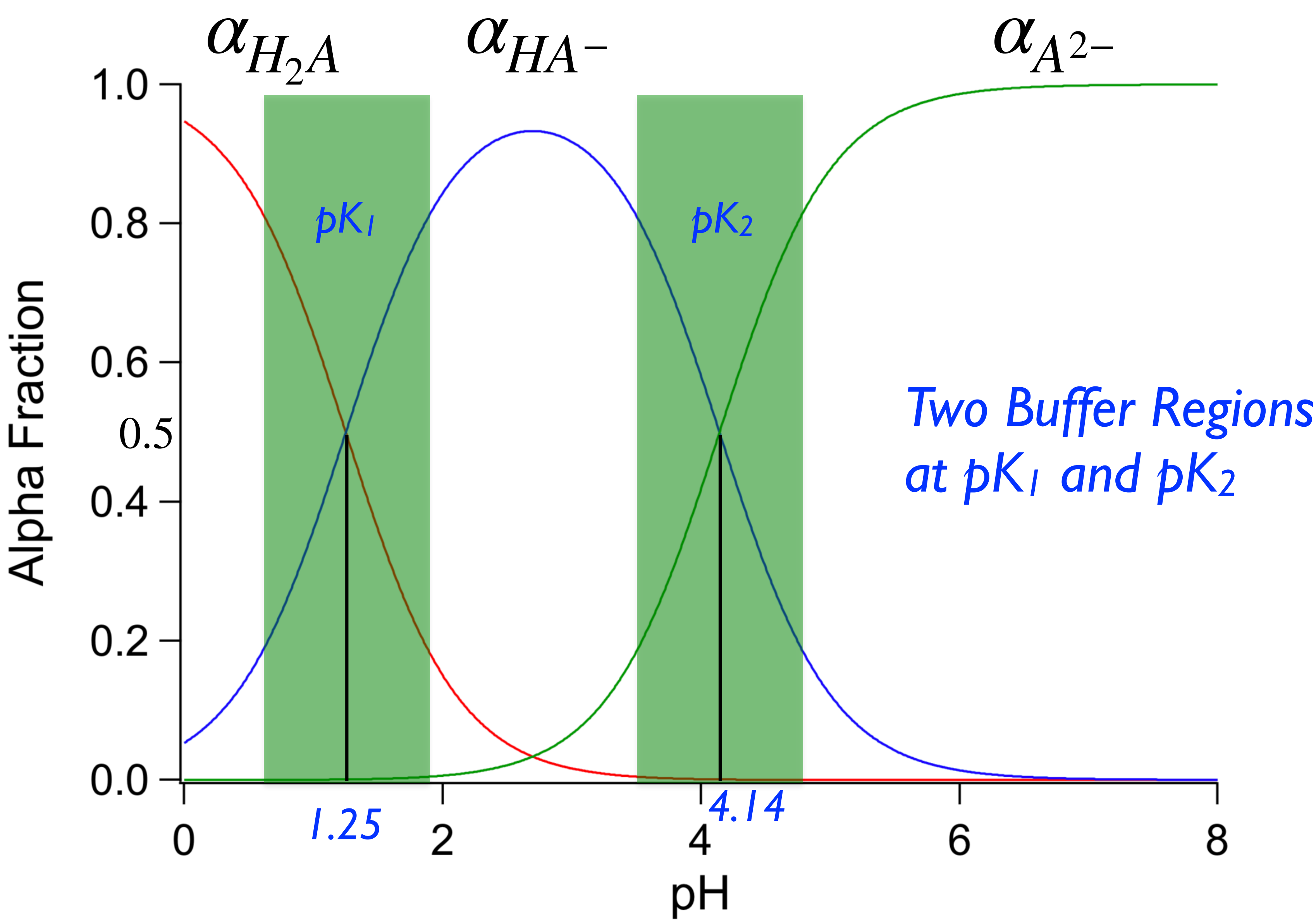
But: $\alpha_{A^{2-}} \neq 0$

$$\alpha_{A^{2-}} = 0.0006$$

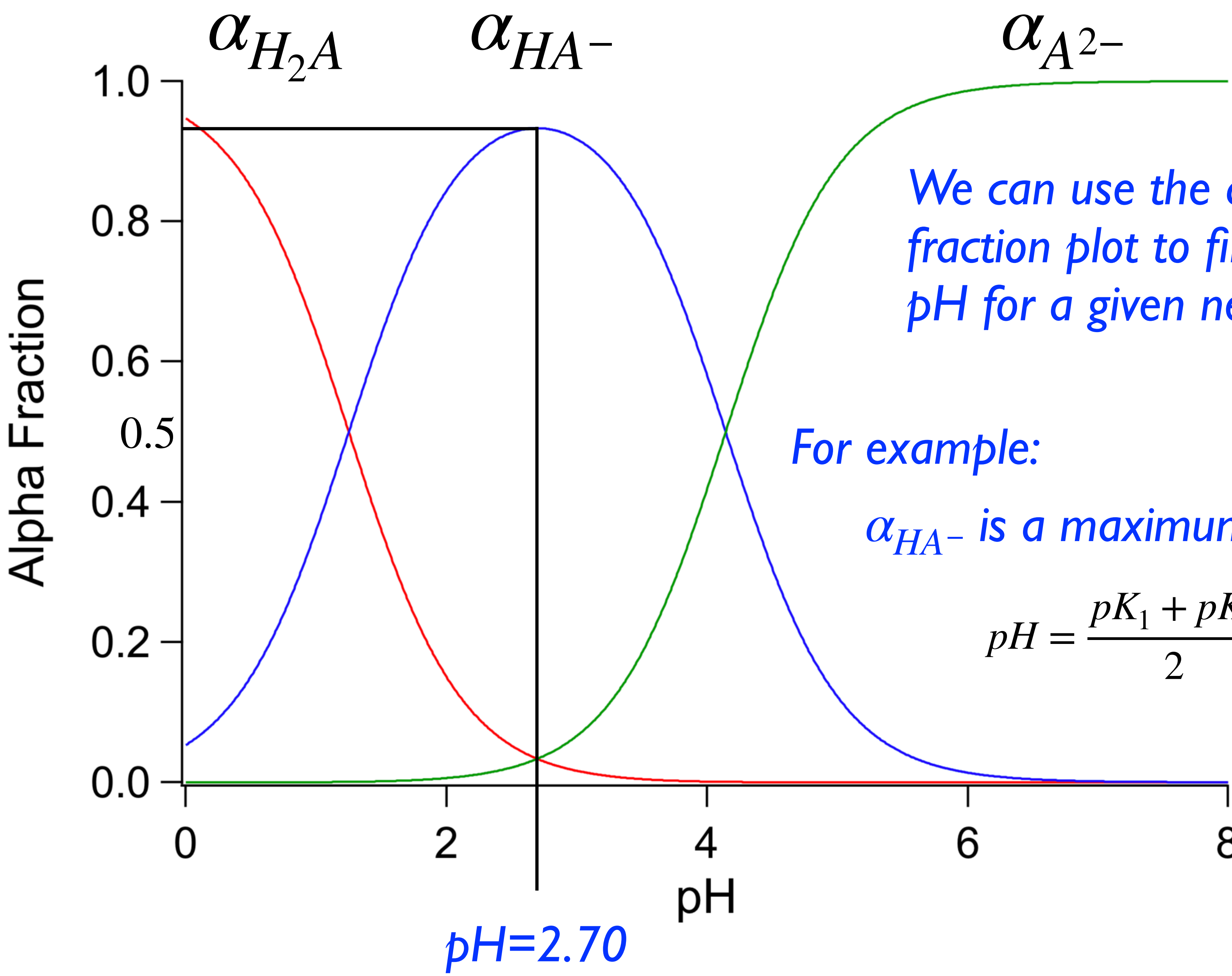
Alpha Fraction Plot for Oxalic Acid



Alpha Fraction Plot for Oxalic Acid



Alpha Fraction Plot for Oxalic Acid



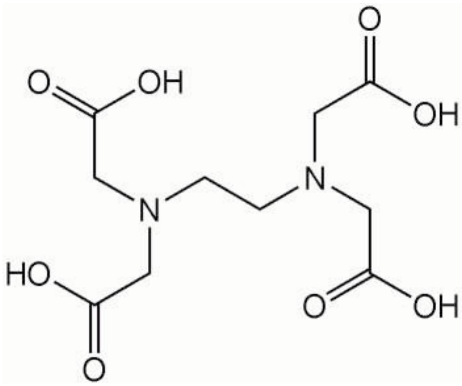
We can use the alpha fraction plot to find the best pH for a given need.

For example:

α_{HA^-} *is a maximum (0.93) at:*

$$pH = \frac{pK_1 + pK_2}{2} = 2.70$$

EDTA Metal Ion Complexation Equilibria



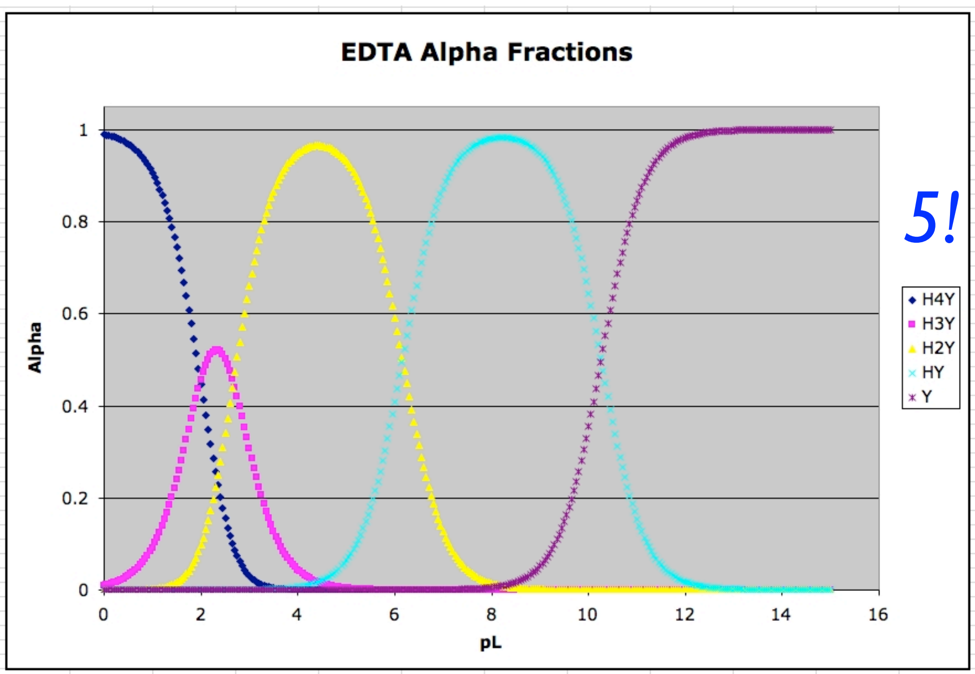
Ethylene Diamine Tetra-acetic Acid (H_4Y)

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

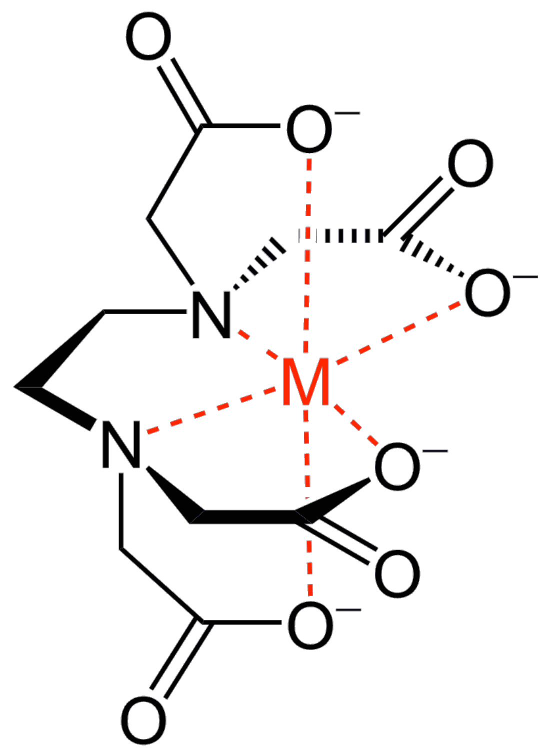
@ pH =10:

$$\alpha_{Y^{4-}} \approx 0.36$$

EDTA - the world's best metal ion chelator



5!



Y^{4-}

EDTA titrations are in basic buffers