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CEE 680: Water Chemistry

Lecture #16

Buffers & Titrations

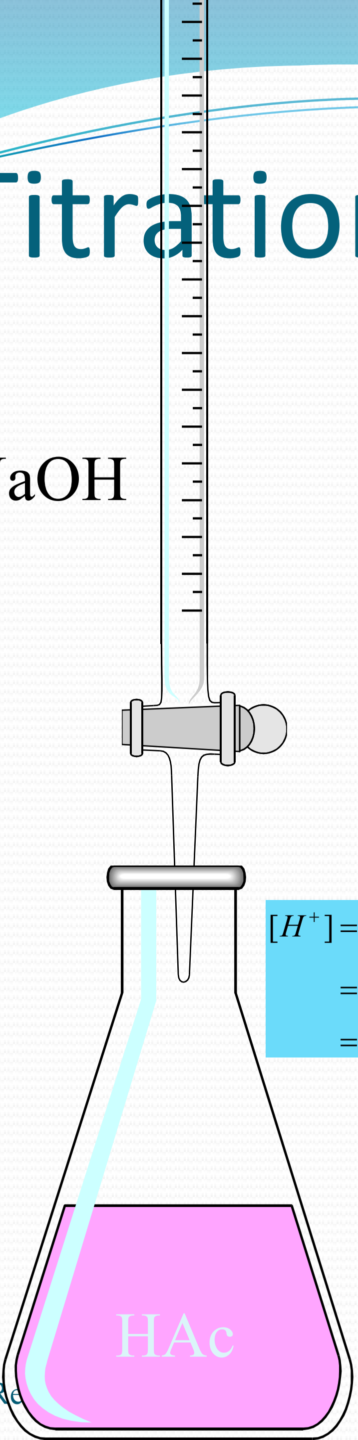
(Benjamin, Chapter 5)

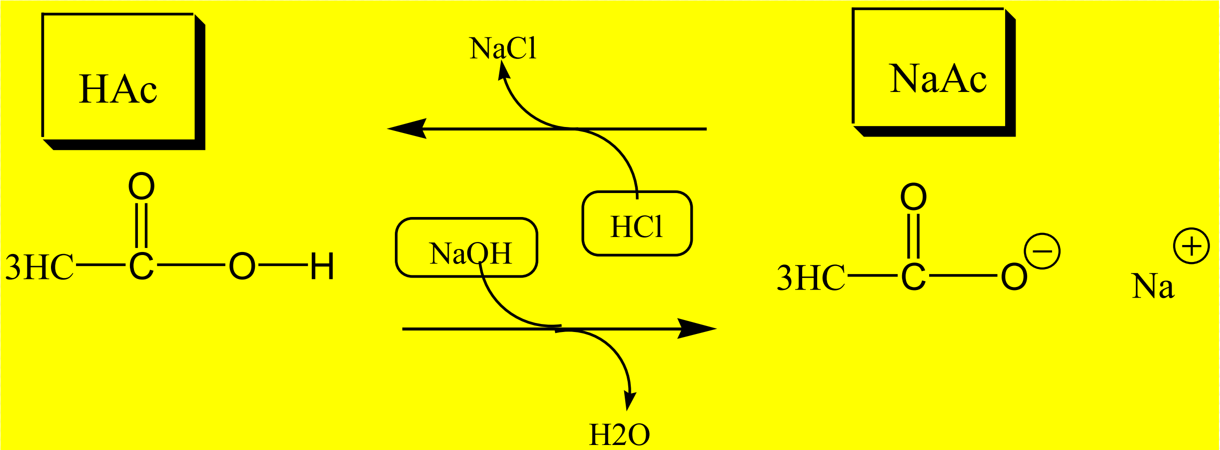
(Stumm & Morgan, Chapt.1-3)

Titrations of Acids and Bases

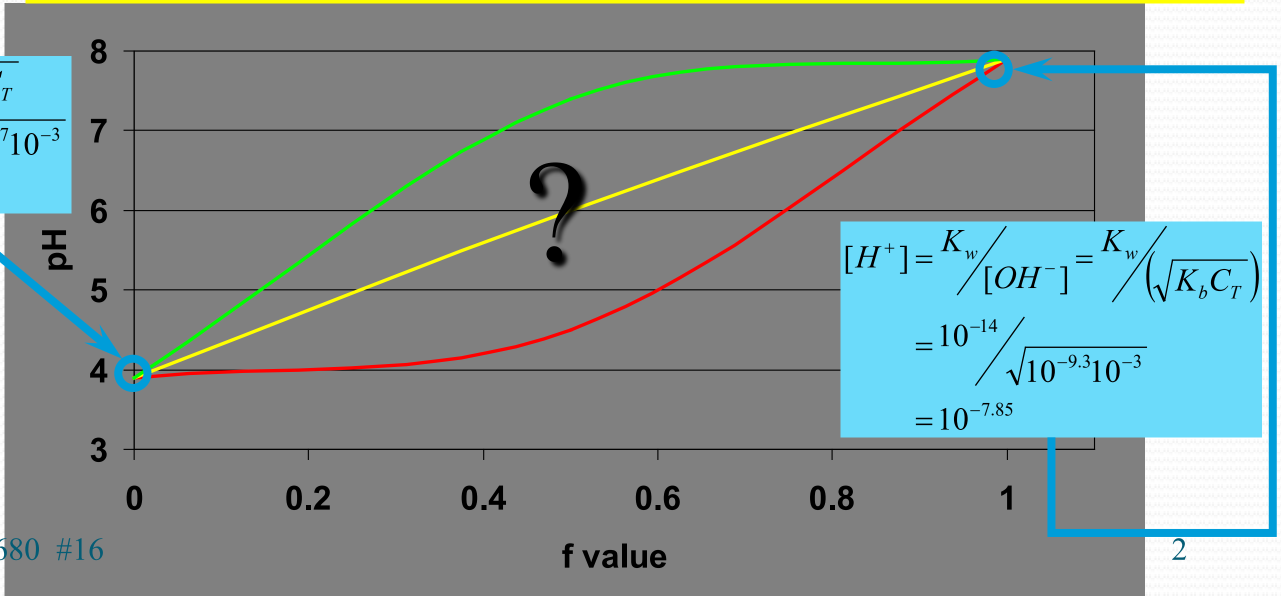
- Weak acid with a strong base

NaOH





$$[H^+] = \sqrt{K_a C_T} = \sqrt{10^{-4.7}10^{-3}} = 10^{-3.85}$$



$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{\left(\sqrt{K_b C_T}\right)} = \frac{10^{-14}}{\sqrt{10^{-9.3}10^{-3}}} = 10^{-7.85}$$

Defining the Titration Curve

- A titration is complete when the equivalents of titrant (t) added equals the equivalents of sample (s) originally present
  - $equ_t = equ_s$
  - $V_tN_t = V_sN_s$
- we can define the extent of a base titration as:

$$f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s}$$

- At any point from the start of the titration, we have a mixed solution of the acid and conjugate base
  - We must use the ENE in place of the PBE

Defining the Titration Curve (cont.)

- The ENE is:
  - for this problem (titration of HAc with NaOH):
    - $[Na^+] + [H^+] = [Ac^-] + [OH^-]$
  - and in general, for a base titration:
    - $C_B \equiv [Na^+] = [A^-] + [OH^-] - [H^+]$
- and combining with the definition for f:

$$f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s} = \frac{C_B}{C_T}$$

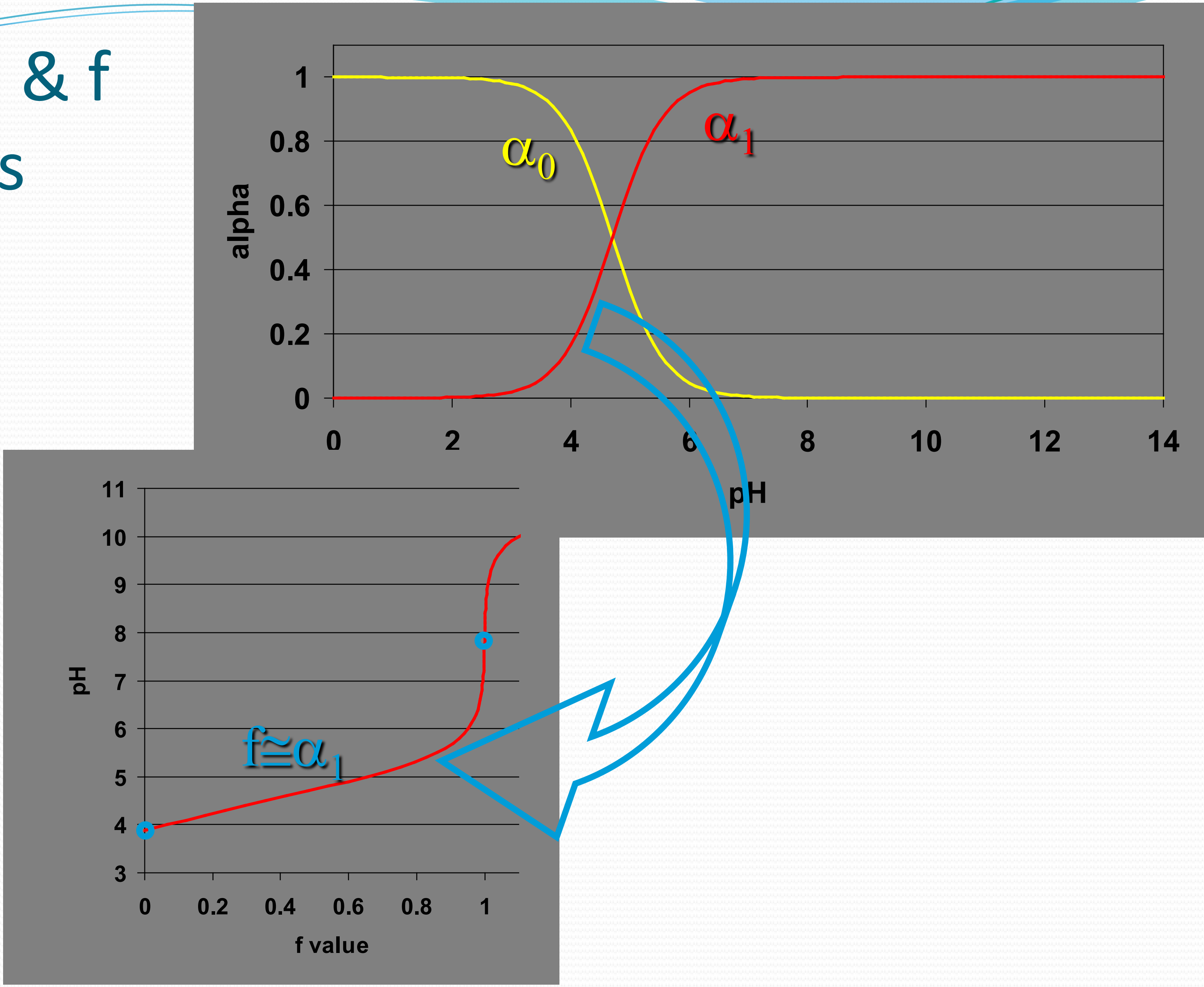
$$= \frac{[A^-]+[OH^-]-[H^+]}{C_T}$$

$$= \alpha_1 + \frac{[OH^-]-[H^+]}{C_T}$$

C_B: Amount of base added at any point during the titration in equivalents/liter

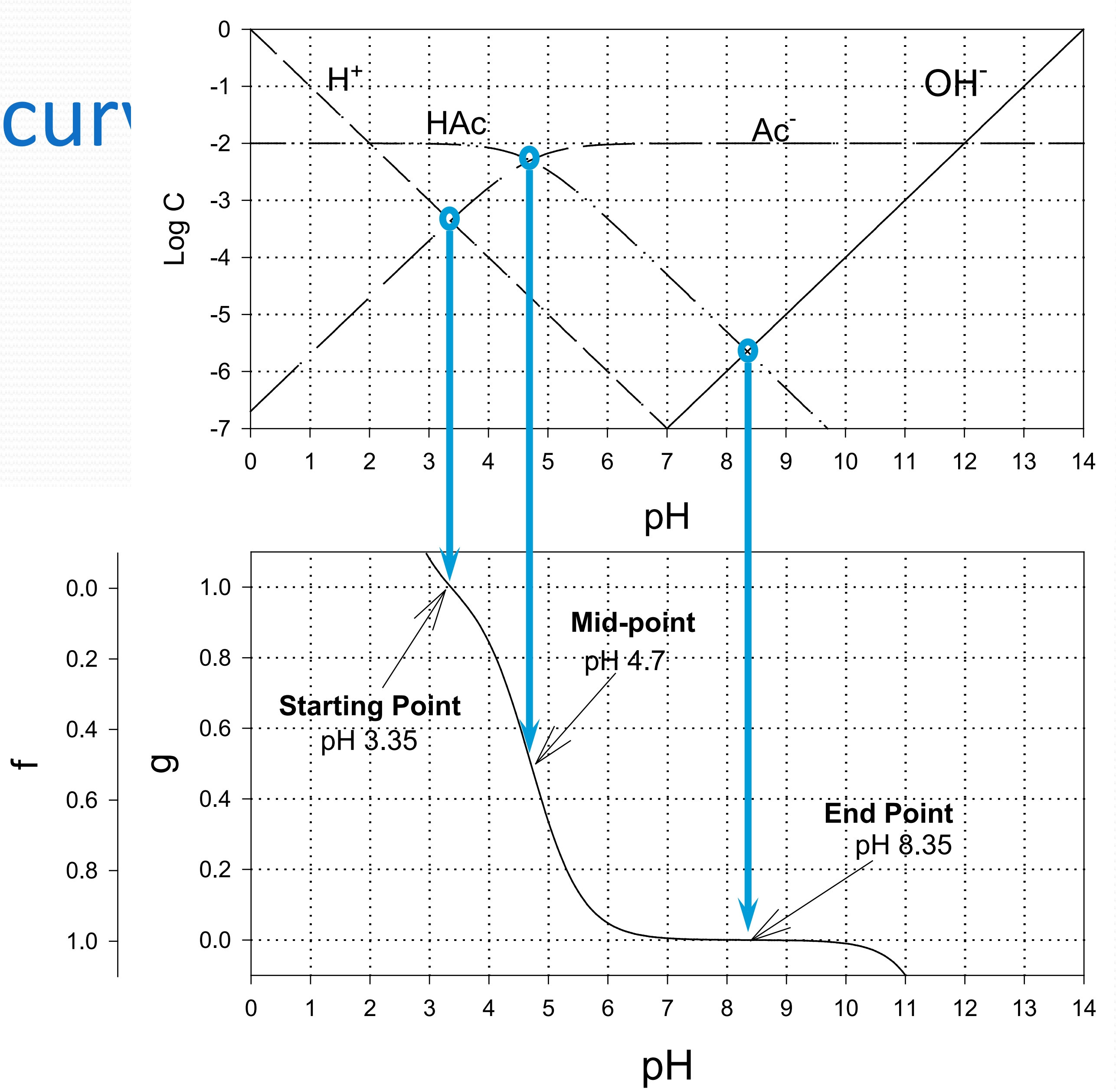
C_T: Amount of acid originally present in moles/liter (which is the same as the total of acid + conjugate base present throughout)

Alpha & f curves



Log C and f cur

- Titration of 10^{-2} M HAc
  - compare to Stumm & Morgan's Figure 3.3



Reverse Titration (acid)

- The reverse titration is the addition of a strong acid (e.g., HCl) to the fully titrated acetic acid (e.g., NaAc). This re-forms the original HAc and produces NaCl too.
- we can define the extent of an acid titration as:

$$g = \frac{V_A N_A}{V_s M_s} = \frac{equ_A}{moles_s}$$

- As with the forward titration, we have a mixed solution of the acid and conjugate base
  - We must use the ENE in place of the PBE

Reverse titration (cont.)

- The ENE is:
  - for this problem (titration of NaAc with HCl):
    - $[Na^+] + [H^+] = [Ac^-] + [OH^-] + [Cl^-]$ $\longrightarrow$ $[Cl^-] = [Na^+] - [Ac^-] + [H^+] - [OH^-]$
  - and for an acid titration of a pure base (Na form):
    - $C_T \equiv [HA] + [A^-] = [Na^+]$ $\longrightarrow$ $C_A \equiv [Cl^-] = [HA] + [H^+] - [OH^-]$
- and combining with the definition for g:

$$g = \frac{V_A N_A}{V_s M_s} = \frac{equ_A}{moles_s} = \frac{C_A}{C_T}$$

$$= \frac{[HA] + [H^+] - [OH^-]}{C_T}$$

$$= \alpha_0 + \frac{[H^+] - [OH^-]}{C_T}$$

C_A: Amount of acid added at any point during the titration in equivalents/liter

C_T: Amount of base originally present in moles/liter (which is the same as the total of acid + conjugate base present throughout)

- For a monoprotic acid/base:
  - f + g equals 1 throughout a titration

$$\begin{aligned} f+g &= \alpha_1 + \frac{[OH]-[H^+]}{C_T} + \alpha_0 + \frac{[H^+]-[OH^-]}{C_T} \\ &= \alpha_1 + \alpha_0 \\ &= 1 \end{aligned}$$

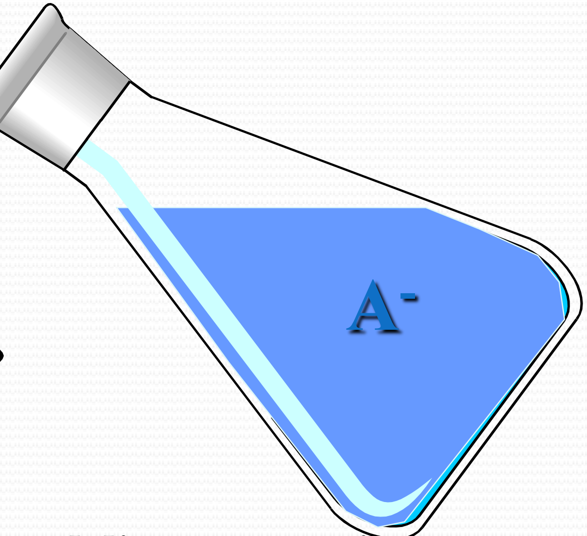
pH Buffers & Buffer Intensity

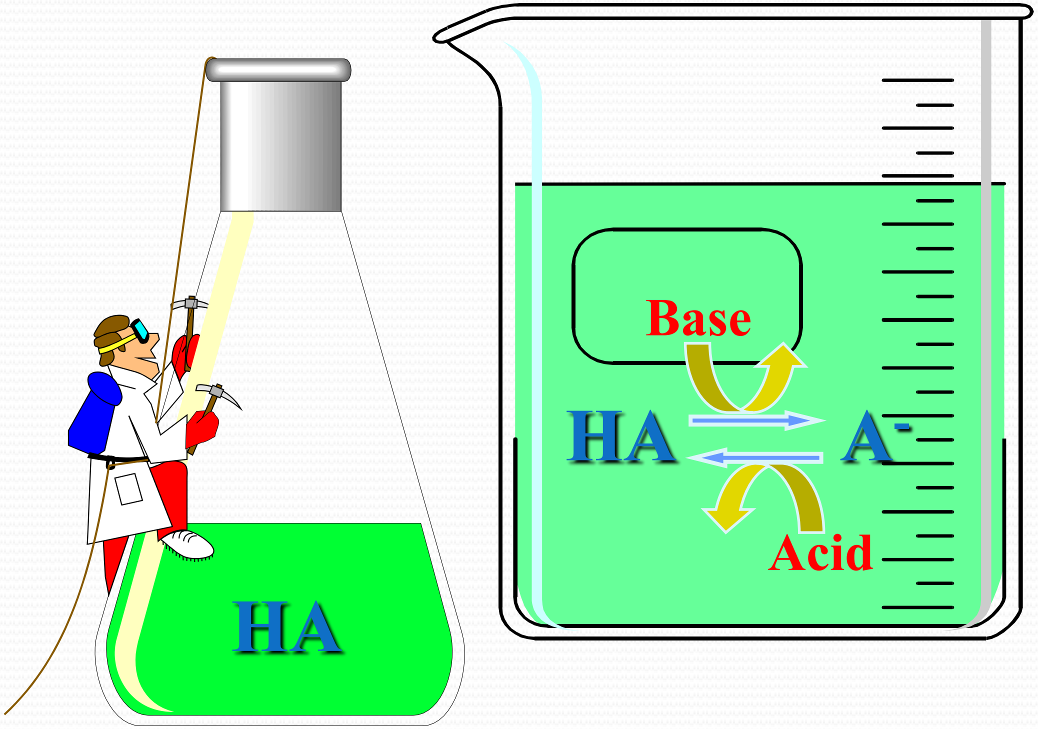
- Definitions
  - Buffer: a solution that resists large pH changes when a base or acid is added
    - commonly a mixture of an acid and its conjugate base
  - Buffer Intensity: the amount of strong acid or strong base required to cause a small shift in pH
- Significance
  - Natural Waters
    - wide range
    - poorly buffered waters are susceptible to acid precipitation

- Engineered Processes
  - certain treatments need large pH shifts (e.g., softening)
  - others need to resist large shifts (e.g., biotreatment)
- Laboratory
  - buffers needed to calibrate pH meters
  - used in experimentation to maintain constant pH. This simplifies data analysis and interpretation

Making a Buffer

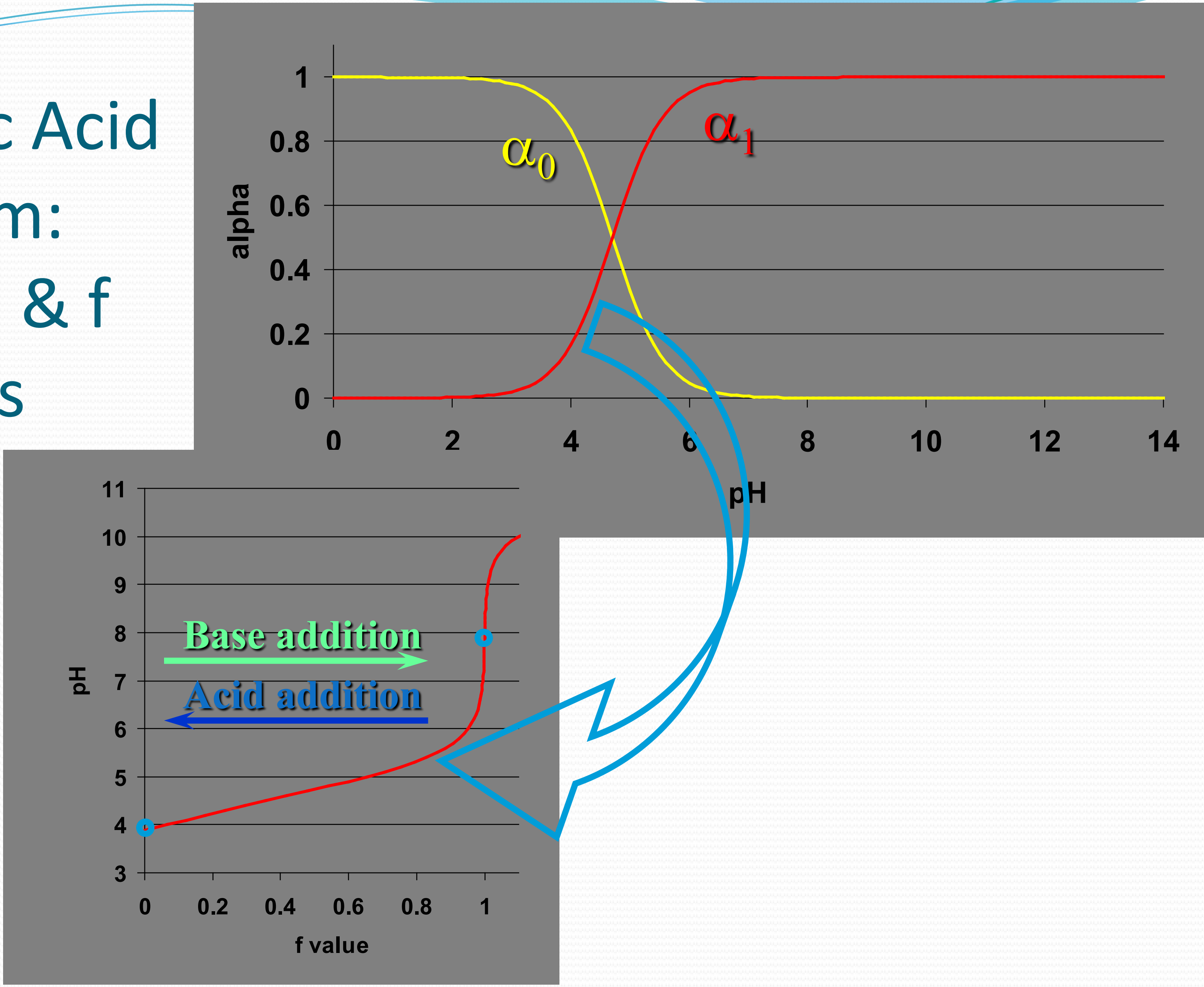
- Acid & conjugate base
  - best to have a reservoir of each so there is resistance to change in both directions





- Mirror questions
  - Given a desired pH, what should the buffer composition be?
  - Given an acid/conjugate base mixture, what will the pH be?

Acetic Acid System: Alpha & f curves



Buffers: Acetic Acid & Sodium Acetate Example

- 1. List all species present
  - H^+, OH^-, HAc, Ac^-, Na^+ Five total
- 2. List all independent equations
  - equilibria
    - $K_a = [H^+][Ac^-]/[HAc] = 10^{-4.77}$ ①
    - $K_w = [H^+][OH^-] = 10^{-14}$ ②
  - mass balances
    - $C_{HAc} + C_{NaAc} = [HAc]+[Ac^-]$ ③ **$C_{NaAc} = [Na^+]$** ⑤
  - electroneutrality: Σ(positive charges) = Σ(negative charges)
    - Note: we can't use the PBE because we're adding an acid and its conjugate base
    - $[Na^+] + [H^+] = [OH^-] + [Ac^-]$ ④

Simplified HAc/NaAc Example

- 3. Use simplified ENE & solve for Ac^- and HAc
  - ④ $[Na^+] + [H^+] = [OH^-] + [Ac^-]$
  - $[Na^+] \approx [Ac^-]$ **Assumes $[Na^+] >> [H^+]$, and $[Ac^-] >> [OH^-]$**
  - (4+5) $\boxed{C_{NaAc}} \approx [Ac^-]$

$\boxed{C_{NaAc}} = [Na^+]$ ⑤

- 4. Plug back in to K_a equation and solve for H^+
  - ① $K_a = [H^+][Ac^-]/[HAc]$
  - $K_a = [H^+]\boxed{C_{NaAc}}/\boxed{C_{HAc}}$
  - $[H^+] = K_a C_{HAc}/C_{NaAc}$
  - $pH = pK_a + \log(C_{NaAc}/C_{HAc})$
- or more generally
  - $\boxed{pH = pK_a + \log(C_A/C_{HA})}$

(1+3+4+5)

③ $C_{HAc} + C_{NaAc} = [HAc] + [Ac^-]$

(3+4+5) $C_{HAc} + C_{NaAc} = [HAc] + C_{NaAc}$

$\boxed{C_{HAc}} = [HAc]$

② $K_w = [H^+][OH^-]$

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

Henderson-Hasselbalch Equation

- Classic H-H equation
  - Just a re-arrangement of equilibrium equation
    - Always correct

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

- Empirical H-H
  - Assumes buffer salts swamp H^+ and OH^-

$$pH = pK_a + \log\frac{C_A}{C_{HA}}$$

Lawrence Henderson was a biochemist, born 3 Jun 1878 in Lynn MA, established the fatigue lab at Harvard

Simplified HAc/NaAc Example (cont.)

- Solution #1
  - C_{NaAc} (= C_A) = 10 mM
  - C_{HAc} (= C_{HA}) = 10 mM

$$pH = pK_a + \log\frac{C_A}{C_{HA}}$$

$$= 4.7 + \log\frac{10}{10}$$

$$= 4.7$$

- Solution #2
  - C_{NaAc} (= C_A) = 20 mM
  - C_{HAc} (= C_{HA}) = 2 mM

$$pH = pK_a + \log\frac{C_A}{C_{HA}}$$

$$= 4.7 + \log\frac{20}{2}$$

$$= 5.7$$

Check Assumptions

Observations

1. pH = pK_a, when equal amounts of acid and conjugate base are added
2. pH is independent of C_T (eventually at low C_T this breaks down)

Exact Solutions: Summary

- Monoprotic
  - Acids:
    - $[H^+]^3 + \{K_a\}[H^+]^2 - \{K_w + K_aC\}[H^+] - K_WK_a = 0$
  - Bases:
    - $[H^+]^3 + \{C+K_a\}[H^+]^2 - \{K_w\}[H^+] - K_WK_a = 0$
  - Mixed Acid/Bases (i.e., buffers):
    - $[H^+]^3 + \{C_A+K_a\}[H^+]^2 - \{K_w + K_aC_{HA}\}[H^+] - K_WK_a = 0$

- To next lecture