Lecture #17

Acids/Bases and Buffers: Fundamentals & Buffer Intensity

(Benjamin, Chapter 5)

(Stumm & Morgan, Chapt. 3)
Buffer Intensity

- Amount of strong acid or base required to cause a specific small shift in pH

\[ \beta = \frac{dC_B}{dpH} = - \frac{dC_A}{dpH} \]
Buffers: Acetic Acid with Acid/Base Addition

1. List all species present
   - (use NaOH and HCl as acid/base)
   - $\text{H}^+$, $\text{OH}^-$, $\text{HAc}$, $\text{Ac}^-$, $\text{Na}^+$, $\text{Cl}^-$

2. List all independent equations
   - **equilibria**
     - $K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = 10^{-4.77}$
     - $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$
   - **mass balances**
     - $C_T = [\text{HAc}]+[\text{Ac}^-]$
   - **electroneutrality:** $\Sigma$(positive charges) = $\Sigma$(negative charges)
     - Note: we can’t use the PBE because we’re essentially adding an acid and its conjugate base
     - $[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{Ac}^-] + [\text{Cl}^-]$
Acetic Acid with Acid/Base Addition (cont.)

3. Use ENE, substitute & solve for $C_B - C_A$

- $[Na^+] + [H^+] = [OH^-] + [Ac^-] + [Cl^-]$

- $C_B + [H^+] = \frac{K_w}{[H^+]} + \frac{K_a C_T}{K_a + [H^+]} + C_A$

- $C_B - C_A = \frac{K_w}{[H^+]} - [H^+] + \frac{K_a C_T}{K_a + [H^+]}$

4. Take derivative
   - with respect to $[H^+]$

$K_w = [H^+][OH^-]$
$[OH^-] = \frac{K_w}{[H^+]}$
$C_A = [Cl^-]$
$C_B = [Na^+]$
$C_T = [HAc] + [Ac^-]$
$[HAc] = C_T - [Ac^-]$
$K_a = \frac{[H^+][Ac^-]}{[HAc]}$
$K_a = \frac{[H^+][Ac^-]}{[C_T - [Ac^-]]}$
$K_a C - K_a [Ac^-] = [H^+][Ac^-]$
$K_a C = [Ac^-] \frac{K_a + [H^+]}{K_a C_T}$
$[Ac^-] = K_a C_T \frac{K_a + [H^+]}{K_a C_T}$
Acetic Acid with Acid/Base Addition (cont.)

- Take the derivative with respect to $[H^+]$ of:
  
  \[ CB = C_A + K_w/[H^+] - [H^+] + K_aC_T/[K_a+[H^+]] \]

  \[
  \frac{dC_B}{d[H^+]} = -\frac{K_w}{[H^+]^2} - 1 - \frac{C_TC_a}{(K_a+[H^+])^2}
  \]

- But this is not exactly what we want

- Factor out $\beta$ equation

  \[
  \beta = \frac{dC_B}{dpH} = \frac{dC_B}{d[H^+]} \times \frac{d[H^+]}{dpH}
  \]

- and recall:

  \[
  pH = -\log[H^+] = -\frac{\ln[H^+]}{2.303}
  \]

  \[
  dpH = -\frac{d \ln[H^+]}{2.303} = \frac{d[H^+]}{2.303[H^+]} \]

  \[
  \frac{d[H^+]}{dpH} = -2.303[H^+] \]
Acetic Acid with Acid/Base Addition (cont.)

- so:

\[ \beta = -2.303[H^+] \frac{dC_B}{d[H^+]} \]

- and combining:

\[ \beta = -2.303[H^+] \left( -\frac{K_w}{[H^+]^2} - 1 - \frac{C_T K_a}{(K_a + [H^+]^2)^2} \right) \]
\[ = 2.303 \left( \frac{K_w}{[H^+]^2} + [H^+] + \frac{C_T K_a [H^+]}{(K_a + [H^+]^2)^2} \right) \]

\[ \beta = 2.303 ( [OH^-] + [H^+] + C_T \alpha_0 \alpha_1 ) \]
\[ \beta = 2.303 \left( [OH^-] + [H^+] + C_T \frac{[HA][A^-]}{([HA] + [A^-])^2} \right) \]
Example

- Trichlorophenol
  - pKa = 6.00
  - $C_T = 10^{-2}$
See also S&M fig 3.10
Equations for polyprotic acids

- Analogous to the monoprotic systems
  
  - **monoprotic**
    \[
    \beta = 2.303 ([OH^-] + [H^+] + C_T \alpha_0 \alpha_1 )
    \]
  
  - **diprotic**
    \[
    \beta \approx 2.303 ([OH^-] + [H^+] + C_T \alpha_0 \alpha_1 + C_T \alpha_1 \alpha_2 )
    \]
  
  - **triprotic**
    \[
    \beta \approx 2.303 ([OH^-] + [H^+] + C_T \alpha_0 \alpha_1 + C_T \alpha_1 \alpha_2 + C_T \alpha_2 \alpha_3 )
    \]
Buffer example

- Design a buffer using phosphate that will hold its pH at \(7.0 \pm 0.05\) even when adding \(10^{-3}\) moles per liter of a strong acid or base
  - first determine the required buffer intensity
    \[
    \beta = \frac{dC_B}{dpH} = \frac{10^{-3}}{0.05} = 0.02
    \]
  - Next look at the buffer equation and try to simplify based on pH range of interest
    \[
    \beta \approx 2.303\left(\left[OH^-\right] + \left[H^+\right] + C_T\alpha_0\alpha_1 + C_T\alpha_1\alpha_2 + C_T\alpha_2\alpha_3\right)
    \]

\[0 \quad 0 \quad 0 \quad 0 \quad 0\]
Buffer example (cont.)

- This gives us the simplified version that can be further simplified

\[
C_T \approx \beta / 2.303(\alpha_1 \alpha_2)
\]

\[
\approx 0.02 / 2.303 \left[ \left( \frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+] + \frac{K_2 K_3}{[H^+]^2}} \right)^{-1} \left( \frac{[H^+]}{K_1 K_2} + \frac{[H^+]}{K_2} + 1 + \frac{K_3}{[H^+] \right)^{-1} \right]
\]

\[
\approx 0.02 / 2.303 \left[ \left( 1 + \frac{K_2}{[H^+]} \right)^{-1} \left( \frac{[H^+]}{K_2} + 1 \right)^{-1} \right]
\]

\[
\approx 0.02 / 2.303 \left( 4.22 \right)^{-1}
\]

\[
\approx 0.037 M
\]
Acid Neutralizing Capacity

- Net deficiency of protons
  - with respect to a proton reference level
    - when the reference level is $\text{H}_2\text{CO}_3$, the ANC=Alkalinity
  - conservative, not affected by T or P

- In a monoprotic system:
  - $[\text{ANC}] = [A^-] + [\text{OH}^-] - [H^+]$
  - $= C_T \alpha_1 + [\text{OH}^-] - [H^+]$

\[
[\text{ANC}] = \int_{f=n}^{f=x} \beta dpH
\]
• To next lecture