Lecture #9

Acids & Bases: Analytical Solutions with simplifying assumptions II

(Stumm & Morgan, Chapt. 3)

(Benjamin, Chapt. 3)
Exact Solution: Is it really necessary?

- Can we simplify?

\[
[H^+]^3 + K_a[H^+]^2 - K_w[H^+] - K_aC[H^+] - K_wK_a = 0
\]

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| 1.82E-12 | 2.53E-13 | 1.22E-18 | 2.07E-12 | 1.70E-19 | 0 |
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- What about the PBE?
  - \([H^+] = [OH^-] + [Ac^-]\)
Simplified HAc Example

3. Use simplified PBE & solve for \( H^+ \)
   - \([H^+] = [OH^-] + [Ac^-]\)
   - \([H^+] \approx [Ac^-]\)  \textbf{Assumes } [H^+] \gg [OH^-]

4. Solve for other species
   - \([H^+] \approx \frac{K_a C}{\{K_a + [H^+]\}}\)
   - \([H^+]^2 \approx \frac{K_a C [H^+]}{\{K_a + [H^+]\}}\)
   - \(K_a [H^+]^2 + [H^+]^3 \approx K_a C [H^+]\)
   - \(K_a C - K_a [Ac^-] = [H^+][Ac^-]\)
   - \([Ac^-] = \frac{K_a C}{\{K_a + [H^+]\}}\)

\[
K_w = [H^+][OH^-] \quad [OH^-] = K_w/[H^+]
\]

\[
C = [HAc] + [Ac^-] \quad [HAc] = C - [Ac^-]
\]

\[
K_a = \frac{[H^+][Ac^-]}{[HAc]} \quad K_a = \frac{[H^+][Ac^-]}{\{C - [Ac^-]\}}
\]

\[
K_a C - K_a [Ac^-] = [H^+][Ac^-] \quad K_a C = [Ac^-] \{K_a + [H^+]\}
\]
Simplified solution #1

- Exact solution: \( \text{pH} = 3.9132779 \)
  - \([H^+] = 1.22 \times 10^{-4}\)
  - \([OH^-] = 8.19 \times 10^{-11}\)
  - \([Ac^-] = 1.22 \times 10^{-4}\)
  - \([HAc] = 8.78 \times 10^{-4}\)

\[\text{OH}^- = \frac{K_w}{[H^+]}\]
\[\text{Ac}^- = \frac{K_aC}{K_a + [H^+]}\]
\[\text{HAc} = C - [\text{Ac}^-]\]

Same as exact to at least 3 significant figures!
So how do we know when to use a simplified method?

- Use both & Compare answers
  - Exact: pH = 3.9132777
  - Simplified: pH = 3.9132779
- Use simplified equation, and check assumptions!
  - \([\text{OH}^-] \ll [\text{H}^+]\)
  - \(8.19 \times 10^{-11} \ll 1.22 \times 10^{-4}\)
    - yes!
Types of Simplifying Assumptions for Acids

- Basis: one additive term is negligible
  - MBE: $C = [HA] + [A]$
  - PBE: $[H^+] = [A] + [OH^-]$

- Combinations
  - Acidic Solution: $[OH^-] \ll [H^+]$
  - Weak Acid: $[HA] \gg [A]$
  - Strong Acid: $[A] \gg [HA]$
  - Weak Acid & Acidic Solution
  - Strong Acid & Acidic Solution
Simplified HAc Example #2

3. Use simplified PBE & MBE
   - \([H^+] = [OH^-] + [Ac^-]\)
   - \([H^+] \approx [Ac^-]\)  \textbf{Assumes} \([H^+] \gg [OH^-]\)

4. Solve for other species

2. \(K_w = [H^+][OH^-]\)
   \([OH^-] = K_w/[H^+]\)

1. \(K_a = [H^+][Ac^-]/[HAc]\)
   \(K_a \approx [H^+][Ac^-]/C\)

3. \(C = [HAc]+[Ac^-]\)
   \([HAc] \approx C\)  \textbf{Assumes} \([HAc] \gg [Ac^-]\)

1+3

\([Ac^-] \approx K_a C/[H^+]\)

1+3+4

\([H^+] \approx K_a C/[H^+]\)

\(\text{ Assumes } [HAc] \gg [Ac^-]\)

\([H^+]^2 \approx K_a C\)

\([H^+] \approx (K_a C)^{0.5}\)
Simplified solution #2

- Solution: pH = 3.885
  - $[H^+] = 1.3 \times 10^{-4}$
  - $[OH^-] = 7.7 \times 10^{-11}$
  - $[Ac^-] = 1.3 \times 10^{-4}$
  - $[HAc] = 8.7 \times 10^{-4}$

\[
[OH^-] = K_w/[H^+]
\]
\[
[Ac^-] = K_a C/[H^+]
\]
\[
[HAc] = C - [Ac^-]
\]
Assumptions

- Use both & Compare answers
  - Exact: \( \text{pH} = 3.9132777 \)
  - Simplified: \( \text{pH} = 3.885 \)
- Use simplified equation, and check assumptions!
  - \([\text{OH}^-] \ll [\text{H}^+]\)
    - \(7.7 \times 10^{-11} \ll 1.3 \times 10^{-4} \) yes!
  - \([\text{Ac}^-] \ll [\text{HAc}]\)
    - \(1.3 \times 10^{-4} \ll 8.7 \times 10^{-4} \) probably OK
To next lecture