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CEE 680: Water Chemistry

Lecture #10

Acids & Bases: Analytical Solutions with simplifying assumptions IV

(Stumm & Morgan, Chapt.3)

(Benjamin, Chapt. 4)

Bases: Sodium Acetate Example

10^{-3} M in 1 L

- 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
    - $C = [HAc]+[Ac^-] = 10^{-3}$ (3)
    - $C_{Na} = [Na^+] = 10^{-3}$ (5)
  - proton balance: Σ(proton rich species) = Σ(proton poor species)
    - Ac⁻ → [HAc]; H_2O → [H⁺], [OH⁻]
    - $[HAc] + [H^+] = [OH^-]$ (4)

NaAc Example (cont.)

$C_{Na} = [Na^+] = 10^{-3}$ (5)

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

- 3. Combine equations and solve for H^+
  - (4) $[H^+] = [OH^-] - [HAc]$
  - (2+4) $[H^+] = K_W/[H^+] - [HAc]$
  - (1+2+3+4) $[H^+] = K_W/[H^+] - [H^+]C/\{K_a+[H^+]\}$
    - $[H^+]^2 = K_W - C[H^+]^2/\{K_a+[H^+]\}$
    - $K_a[H^+]^2 + [H^+]^3 = K_WK_a + K_w[H^+] - C[H^+]^2$
  - **$[H^+]^3 + \{C+K_a\}[H^+]^2 - K_w[H^+] - K_WK_a = 0$**

(3) $C = [HAc]+[Ac^-]$
$[Ac^-] = C-[HAc]$

(1) $K_a = [H^+][Ac^-]/[HAc]$

(1+3)
$K_a = [H^+]\{C-[HAc]\}/[HAc]$
$K_a[HAc] = [H^+]C-[H^+][HAc]$
$[HAc] = C[H^+]/\{K_a+[H^+]\}$

- 4. Solve for other species

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Answer

- $[OH-] = 7.67\ 10\text{-}7$
- pOH = 6.115
- pH = 7.885

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In-class Practice

- 10^{-4}M Sodium Acetate
  - UMass: Alvin & Cielo, Chris
  - UNISA: Sikelelwa
- 10^{-3}M Sodium Cyanide
  - UMass: Ian &JQ
  - UNISA:
- 10^{-3}M Calcium Oxalate
  - UMass:
  - UNISA: Alfred
- 10^{-4}M Sodium Bicarbonate
  - UMass: Laura, Bridgette, Isaac
  - UNISA:

For Oxalic acid,
$H_2Ox \Leftrightarrow HOx^- \Leftrightarrow Ox^{-2}$
pKa1=1.25
pKa2=4.27

Writing PBE's

Note: Alkali metals such as Na and K do not act as acids, so they are ignored here

- Monoprotic Acid
  - same as ENE
- Diprotic Acid
  - same as ENE
- Diprotic: Ampholyte
  - Not ENE
    - e.g., $NaHCO_3$
- Diprotic Base
  - Not ENE

HAc, H_2O
- $[H^+] = [OH^-] + [Ac^-]$

H_2CO_3, H_2O
- $[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{-2}]$

HCO_3^-, H_2O
- $[H_2CO_3] + [H^+] = [OH^-] + [CO_3^{-2}]$

CO_3^{-2}, H_2O
- $2[H_2CO_3] + [HCO_3^-] + [H^+] = [OH^-]$

Guide to Simplified Acid/Base Solutions #1

- Neutral $[H^+] \approx \sqrt{K_w}$
  - if $C<10^{-8}$
- Acid Addition, $C>10^{-6.5}$
  - Acidic $[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2}$
    - if $K_aC > 10^{-13}$
  - Strong Acid $[H^+] \approx \frac{C + \sqrt{C^2 + 4K_w}}{2}$
    - if $K_a > 10C$
  - Weak Acid $[H^+] \approx \sqrt{K_aC + K_w}$
    - if $C > 100K_a$

$[H^+] \approx C$

$[H^+] \approx \sqrt{K_aC}$

Guide to Simplified Acid/Base Solutions #2

- Base Addition, $C>10^{-6.5}$
  - Basic $[OH^-] \approx \frac{-K_b + \sqrt{K_b^2 + 4K_bC}}{2}$
    - if $K_bC > 10^{-13}$
  - Strong Base $[OH^-] \approx \frac{C + \sqrt{C^2 + 4K_w}}{2}$
    - if $K_b > 10C$
  - Weak Base $[OH^-] \approx \sqrt{K_bC + K_w}$
    - if $C > 100K_b$

$[OH^-] \approx C$

$[OH^-] \approx \sqrt{K_bC}$

- Very Dilute Systems
  - if $10^{-8} < C < 10^{-6.5}$
  - try strong acid/base or weak acid/base assumption
  - otherwise may need to use general solution

Exact Solutions: Summary

- Monoprotic
  - Acids: $[H^+]^3 + K_a[H^+]^2 - \{K_w + K_aC\}[H^+] - K_WK_a = 0$
  - Bases: $[H^+]^3 + \{C+K_a\}[H^+]^2 - K_w[H^+] - K_WK_a = 0$
- Diprotic
  - Acids:
    - $[H^+]^4 + K_1[H^+]^3 + \{K_1K_2\text{-}K_w\text{-} K_1C\}[H^+]^2 - K_1\{2CK_2+K_w\}[H^+] - K_WK_1K_2 = 0$
  - Ampholytes:
    - $[H^+]^4 + \{C+K_1\}[H^+]^3 + \{K_1K_2\text{-}K_w\}[H^+]^2 - K_1\{CK_2+K_w\}[H^+] - K_WK_1K_2 = 0$
  - Bases:
    - $[H^+]^4 + \{2C+K_1\}[H^+]^3 + \{CK_1+K_1K_2\text{-}K_w\}[H^+]^2 - K_1K_w[H^+] - K_WK_1K_2 = 0$

- To next lecture