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CEE 680: Water Chemistry

Lecture #17

Acids/Bases and Buffers: Fundamentals & Buffer Intensity

(Benjamin, Chapter 5)

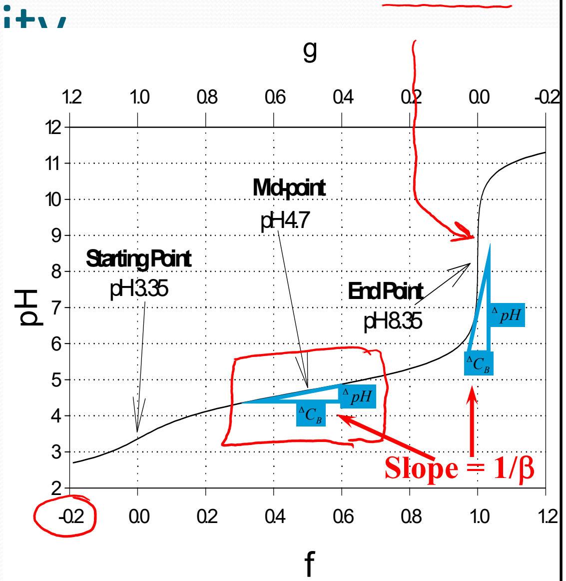
(Stumm & Morgan, Chapt. 3)

Buffer Intensity

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

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH}$$

10^{-2}M HAc



Buffers: Acetic Acid with Acid/Base Addition

- 1. List all species present
  - (use NaOH and HCl as acid/base)
  - H^+, OH^-, HAc, Ac^-, Na^+, Cl^- — Six 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
    - $C_T = [HAc]+[Ac^-]$ (3)
    - $C_A = [Cl^-]$ (5)
    - $C_B = [Na^+]$ (6)
  - electroneutrality: Σ(positive charges) = Σ(negative charges)
    - Note: we can't use the PBE because we're essentially adding an acid and its conjugate base
    - $[Na^+] + [H^+] = [OH^-] + [Ac^-] + [Cl^-]$ (4)

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Acetic Acid with Acid/Base Addition (cont.)

- 3. Use ENE, substitute & solve for C_B-C_A
  - (4) $[Na^+] + [H^+] = [OH^-] + [Ac^-] + [Cl^-]$
  - $C_B + [H^+] = K_w/[H^+] + K_aC_T/\{K_a+[H^+]\} + C_A$
  - $C_B - C_A = K_w/[H^+] - [H^+] + K_aC_T/\{K_a+[H^+]\}$

(1,2,3,4,5,6)

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

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

$C_A = [Cl^-]$ (5)

$C_B = [Na^+]$ (6)

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

$[HAc]= C_T - [Ac^-]$

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

(1+3)

$K_a = [H^+][Ac^-]/\{C_T-[Ac^-]\}$

$K_aC-K_a[Ac^-]= [H^+][Ac^-]$

$K_aC=[Ac^-]\{K_a+[H^+]\}$

$[Ac^-]=K_aC_T/\{K_a+[H^+]\}$

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

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Acetic Acid with Acid/Base Addition (cont.)

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

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

- But this is not exactly what we want
  - Factor out β equation

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

  - 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:

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

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

β 1

$$\alpha_0 = \frac{[HA]}{C_T} = \frac{[H^+]}{K_a+[H^+]}$$

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

$$\beta = 2.303\left([OH^-] + [H^+] + C_T\alpha_0\alpha_1\right)$$

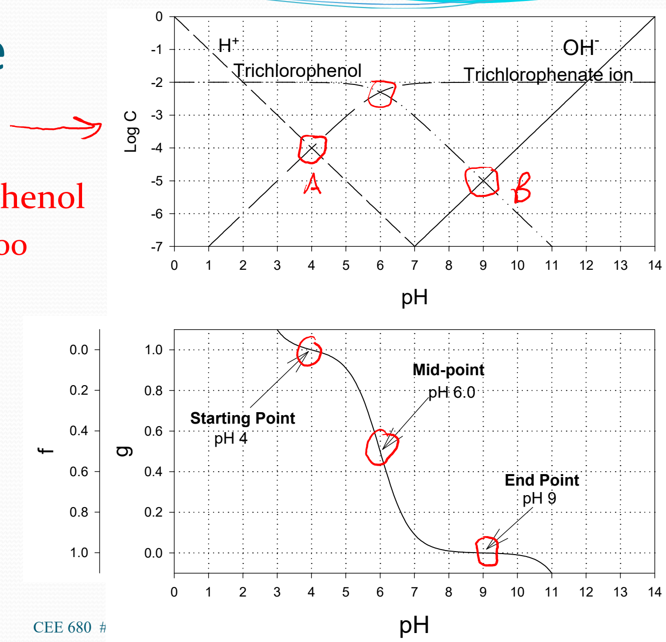
2

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

3

Example

- Trichlorophenol
  - pKa = 6.00
  - $C_T = 10^{-2}$



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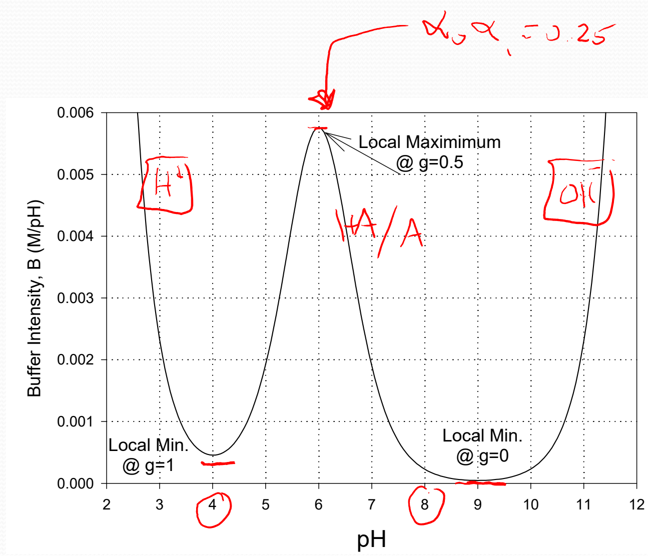
- See also S&M fig 3.10



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Equations for polyprotic acids

- Analogous to the monoprotic systems
  - monoprotic $\beta = 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1\right)$
  - diprotic $\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2\right)$
  - triprotic

$$\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2+C_T\alpha_2\alpha_3\right)$$

Buffer example

- Design a buffer using phosphate that will hold its pH at 7.0 ±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

$$\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2+C_T\alpha_2\alpha_3\right)$$

0 0 0 0

Buffer example (cont.)

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

$$C_T \approx \beta / 2.303(\alpha_1\alpha_2)$$

$$\approx 0.02 / 2.303\left[\left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} + \frac{K_2K_3}{[H^+]^2}\right)^{-1}\left(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1 + \frac{K_3}{[H^+]}\right)^{-1}\right]$$

0 0 0 0

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

$$\approx 0.02 / 2.303(4.22)^{-1}$$

$$\approx 0.037M$$

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Acid Neutralizing Capacity

- Net deficiency of protons
  - with respect to a proton reference level
    - when the reference level is H_2CO_3, the ANC=Alkalinity
  - conservative, not affected by T or P
  - In a monoprotic system:
    - $[ANC] = [A^-] + [OH^-] - [H^+]$
    - $= C_T\alpha_1 + [OH^-] - [H^+]$

$$[ANC] = \int_{f=n}^{f=x} \beta dpH$$

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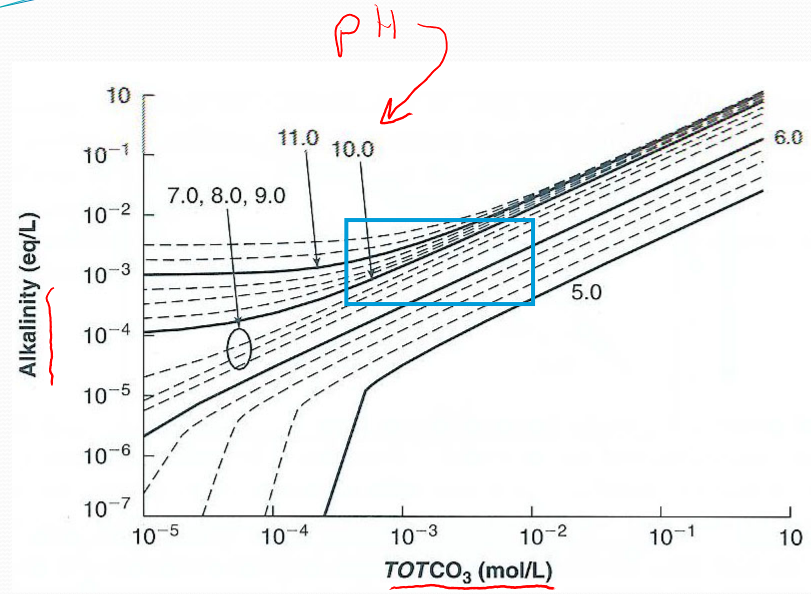
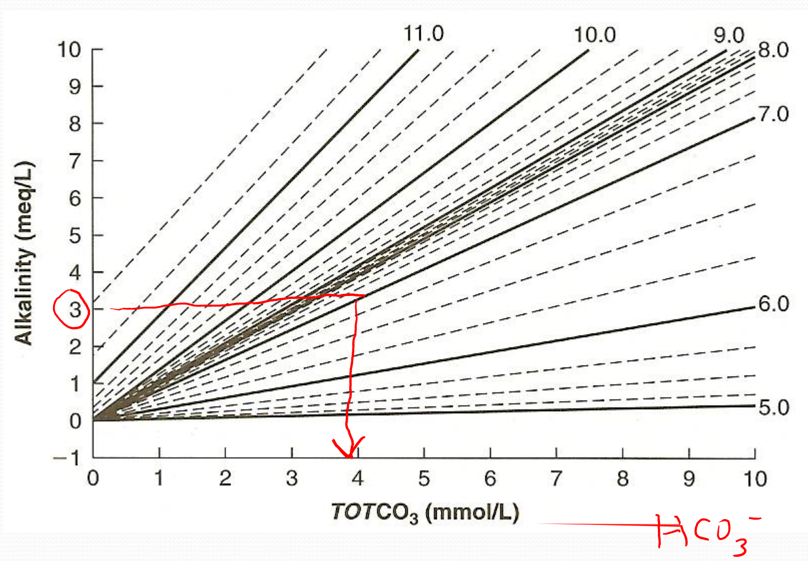

pH
Alkalinity (eq/L)
TOTCO$_3$ (mol/L)
11.0
10.0
7.0, 8.0, 9.0
6.0
5.0
10
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10


Alkalinity (meq/L)
TOTCO$_3$ (mmol/L)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
HCO_3^-

- To next lecture