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CEE 680: Water Chemistry

Lecture #17

Acids/Bases and Buffers: Fundamentals & Buffer Intensity

(Benjamin, Chapter 5)

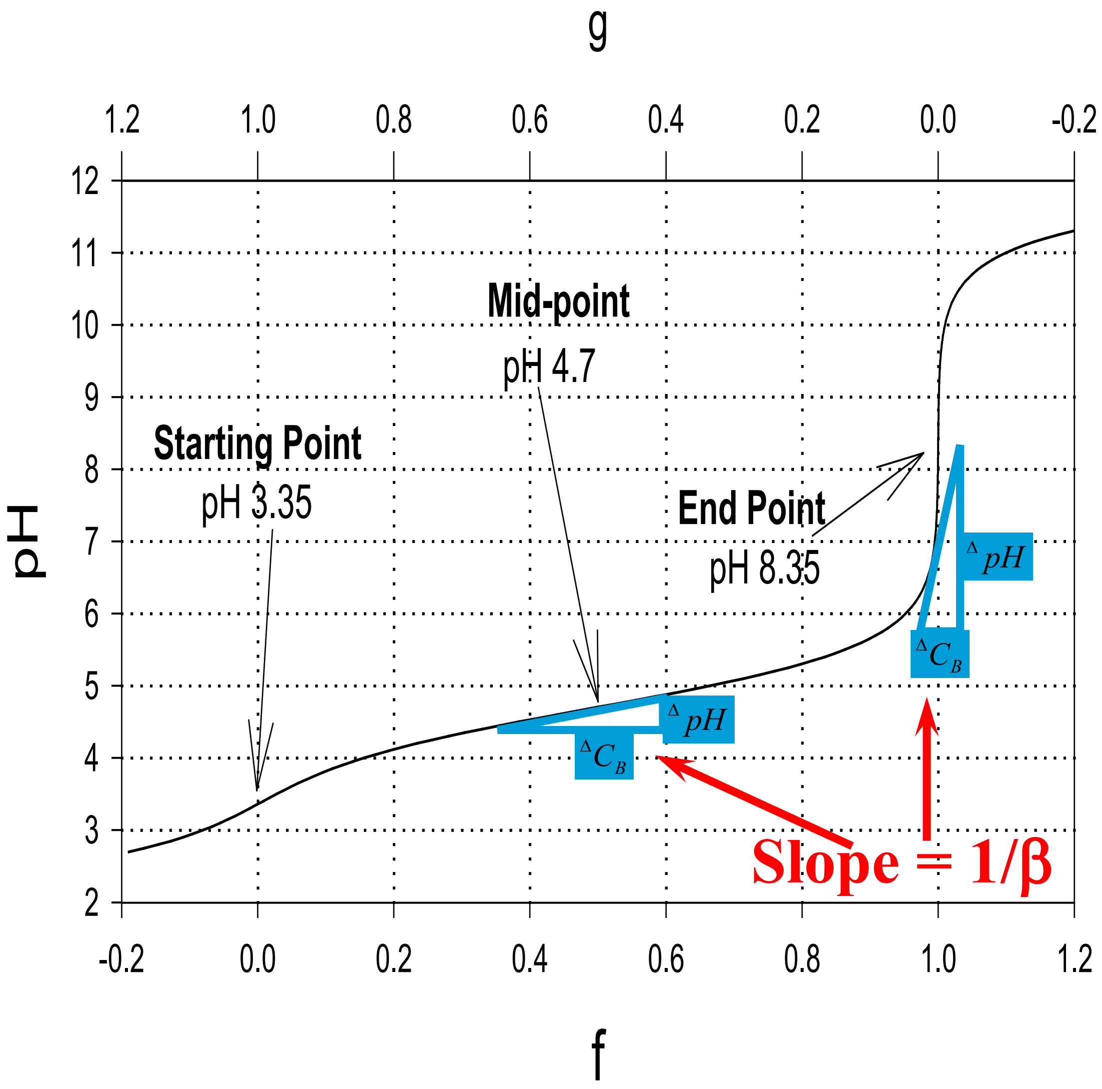
(Stumm & Morgan, Chapt. 3)

Buffer Intensity

10^{-2}M HAc

- 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)
    - 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

Acetic Acid with Acid/Base Addition (cont.)

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

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

② $K_w = [H^+][OH^-]$

$[OH^-] = \boxed{K_w/[H^+]}$

$\boxed{C_A} = [Cl^-]$ ⑤

$\boxed{C_B} = [Na^+]$ ⑥

$C_T = [HAc]+[Ac^-]$ ③

$[HAc] = \boxed{C_T - [Ac^-]}$

① $K_a = [H^+][Ac^-]/[HAc]$

(1+3)

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

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

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

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

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

Acetic Acid with Acid/Base Addition (cont.)

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

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

- 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:

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

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

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

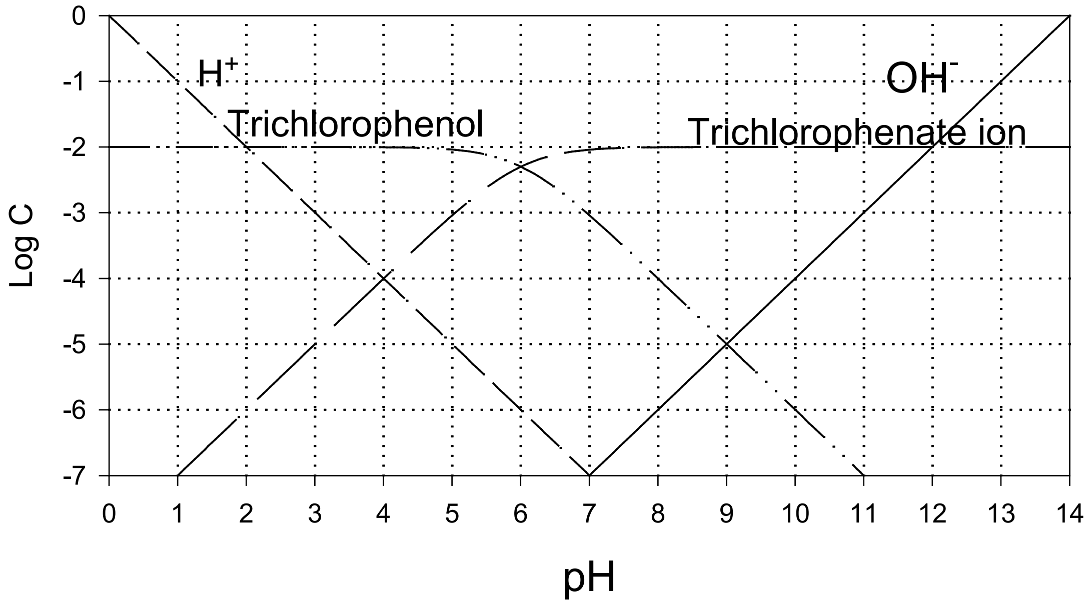
$$\alpha_1 = \frac{[A^-]}{C_T} = \frac{K_a}{K_a + [H^+]}$$

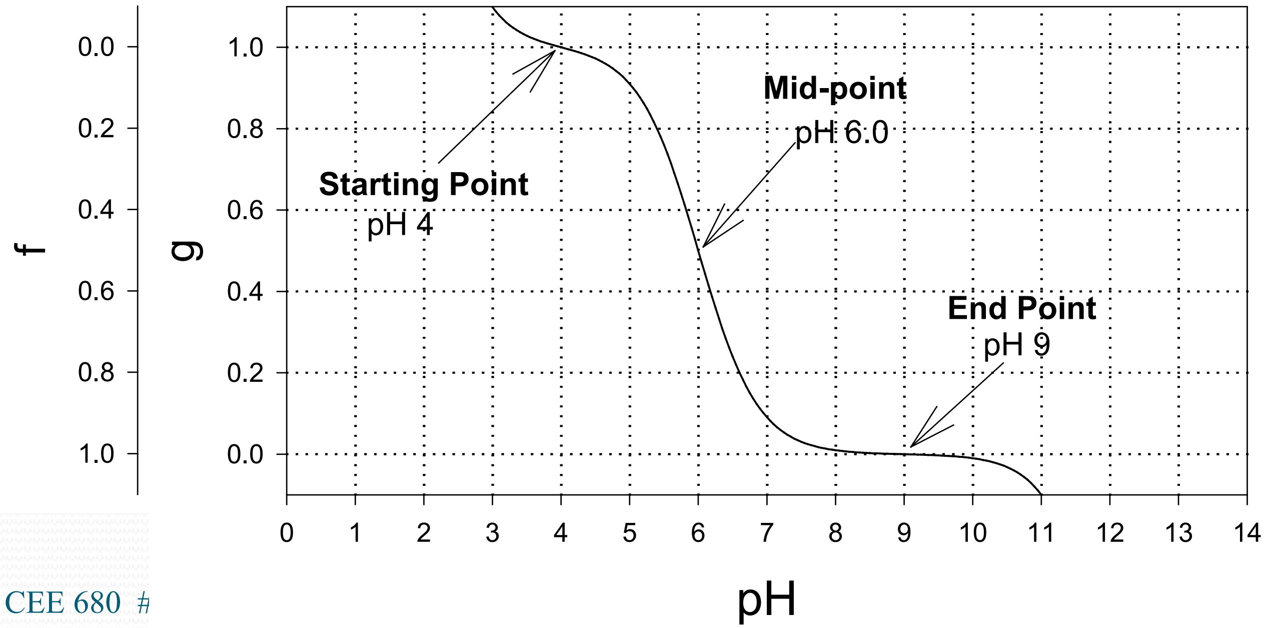
$$\boxed{\beta = 2.303\left([OH^-] + [H^+] + C_T\alpha_0\alpha_1\right)}$$

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

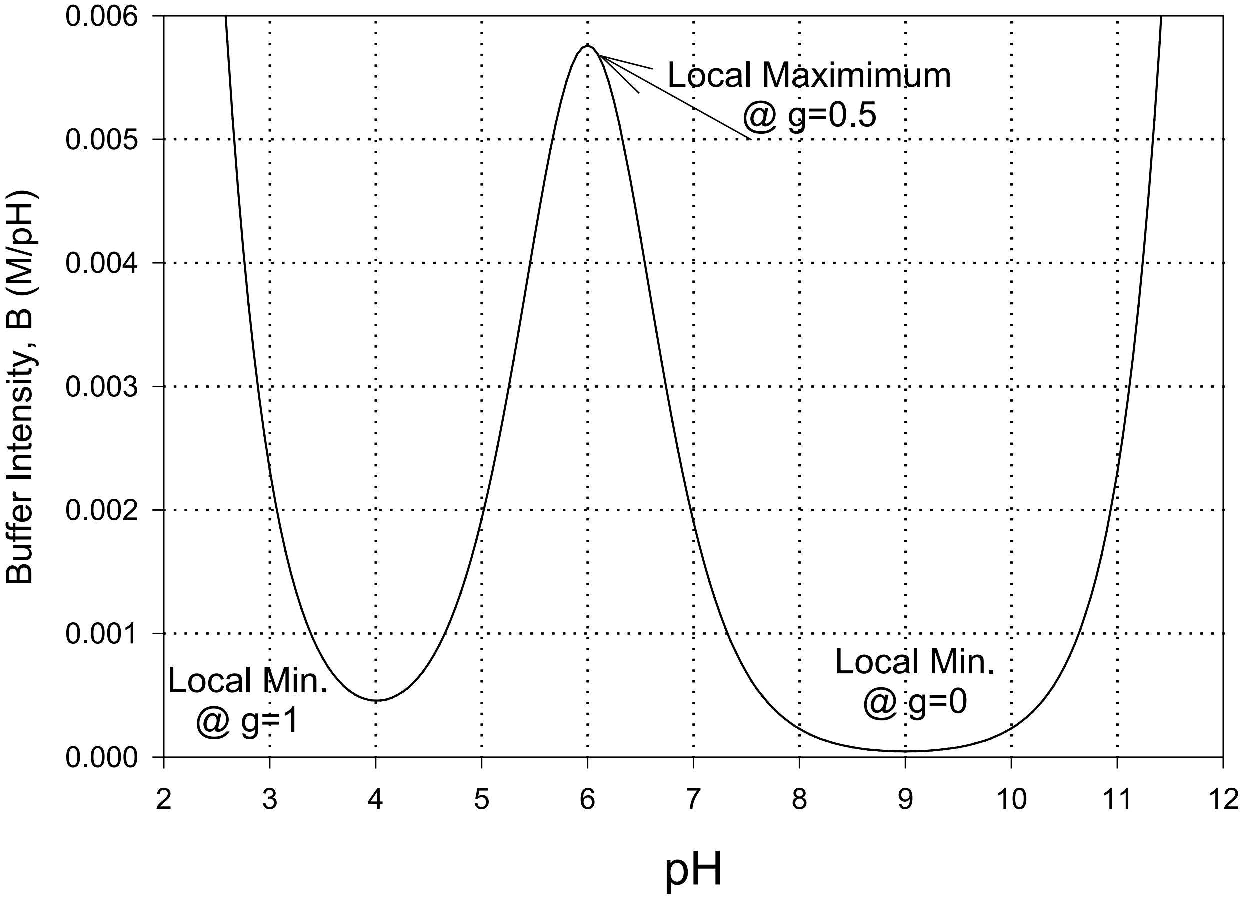
Example

- 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

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

  - diprotic

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

  - triprotic

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

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

$$\boxed{\beta \approx 2.303\left(\underbrace{[OH^-]}_{0} + \underbrace{[H^+]}_{0} + \underbrace{C_T\alpha_0\alpha_1}_{0} + C_T\alpha_1\alpha_2 + \underbrace{C_T\alpha_2\alpha_3}_{0}\right)}$$

Buffer example (cont.)

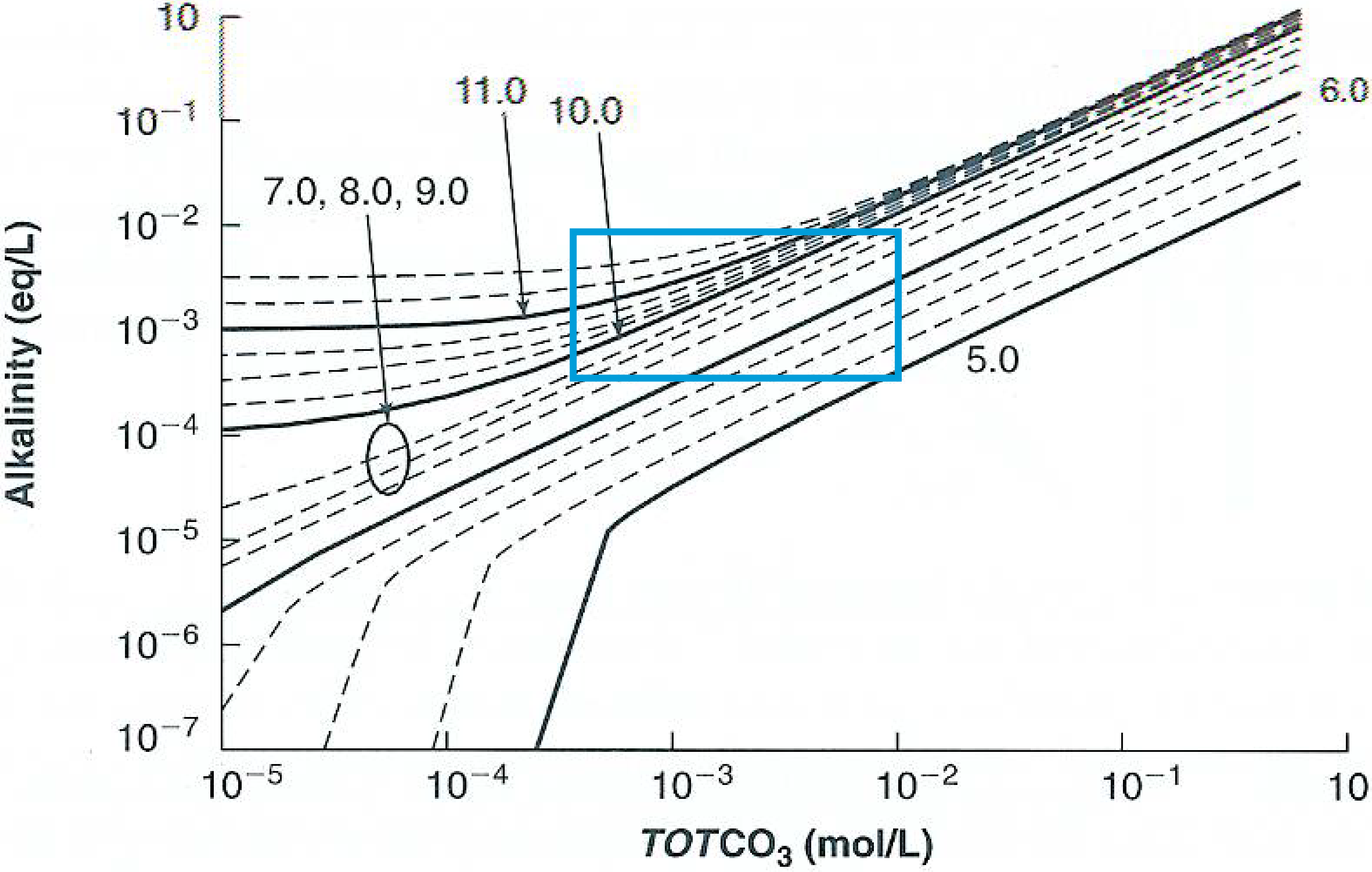
- This gives us the simplified version that can be further simplified

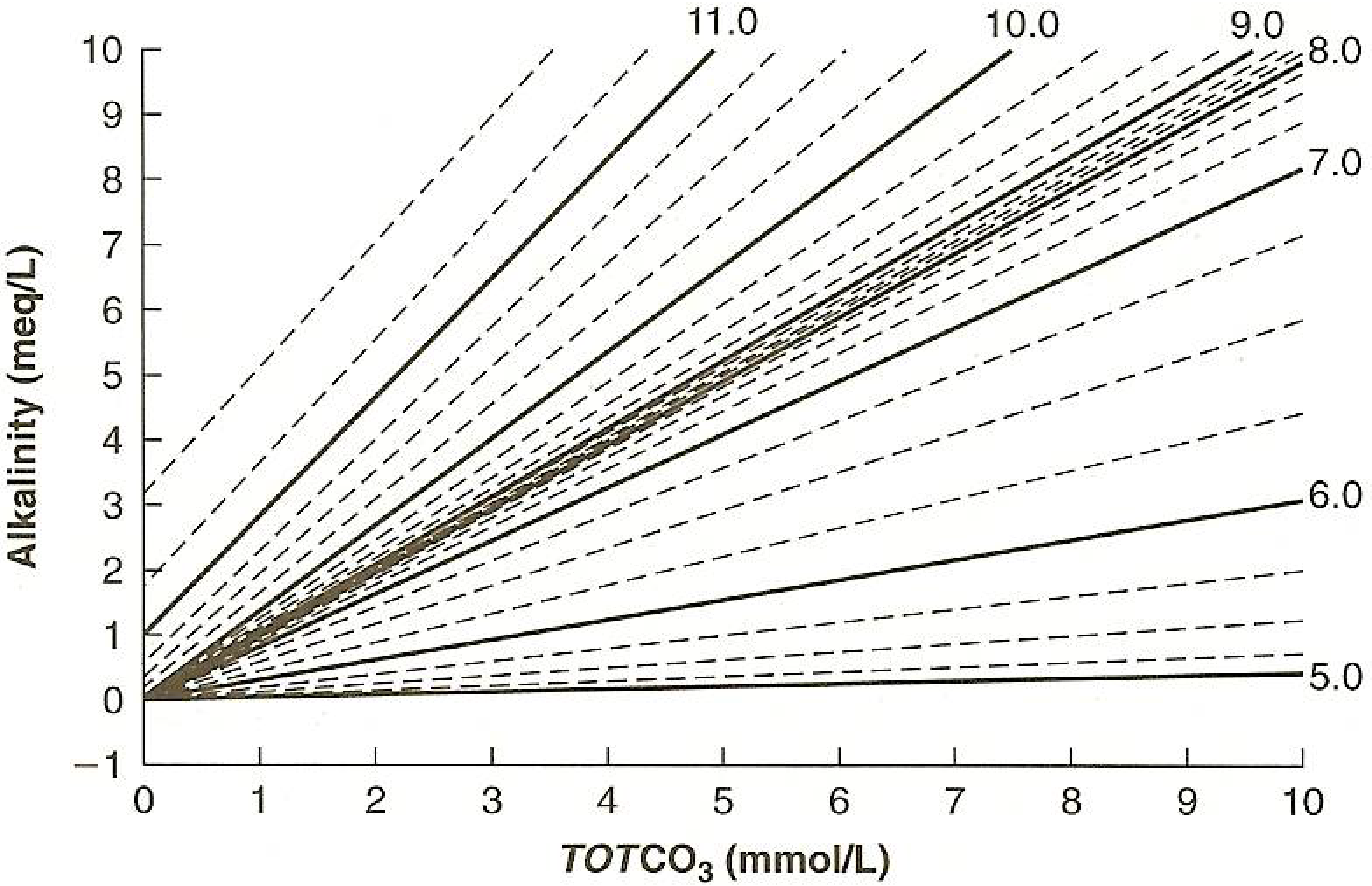
$$
\begin{aligned}
C_T &\approx \beta \Big/ 2.303(\alpha_1\alpha_2) \\
&\approx 0.02 \Big/ 2.303\left[\left(\cancelto{0}{\frac{[H^+]}{K_1}} + 1 + \frac{K_2}{[H^+]} + \cancelto{0}{\frac{K_2K_3}{[H^+]^2}}\right)^{-1}\left(\cancelto{0}{\frac{[H^+]^2}{K_1K_2}} + \frac{[H^+]}{K_2} + 1 + \cancelto{0}{\frac{K_3}{[H^+]}}\right)^{-1}\right] \\
&\approx 0.02 \Big/ 2.303\left[\left(1 + \frac{K_2}{[H^+]}\right)^{-1}\left(\frac{[H^+]}{K_2} + 1\right)^{-1}\right] \\
&\approx 0.02 \Big/ 2.303(4.22)^{-1} \\
&\approx 0.037M
\end{aligned}
$$

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:
    - $[ANC] = [A^-] + [OH^-] - [H^+]$
    - $= C_T\alpha_1 + [OH^-] - [H^+]$

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


10
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
Alkalinity (eq/L)
11.0
10.0
7.0, 8.0, 9.0
6.0
5.0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10
$TOTCO_3$ (mol/L)


11.0
10.0
9.0
8.0
7.0
6.0
5.0
Alkalinity (meq/L)
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
$TOTCO_3$ (mmol/L)

- To next lecture