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CEE 680: Water Chemistry

Lecture #13

Acids & Bases: Polyprotics

Benjamin, Chapter 4

(Stumm & Morgan, Chapt.3)

Rapid Method for Log C vs. pH Graph

- 1. Plot diagonal $[H^+]$ and $[OH^-]$ lines
- 2. Draw a light horizontal line corresponding to log C_T
- 3. Locate System Point
  - i.e., pH = pK_a, log C = log C_T
  - make a mark 0.3 units below system point
- 4. Draw 45º lines (slope = ±1) below log C_T line, and aimed at system point
- 5. Approximate curved sections of species lines ±1 pH unit around system point
- 6. Repeat steps as necessary for more complex graphs
  - #3-#5 for additional pK_as of polyprotic acids
  - #2-#5 for other acid/base pairs

Diprotic acids: calculations

- Start with C_T and K_a equations

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \qquad K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

$$C_T = [H_2A] + [HA^-] + [A^{-2}]$$

$$[HA^-] = \frac{K_1[H_2A]}{[H^+]} \qquad [A^{-2}] = \frac{K_2[HA^-]}{[H^+]} = \frac{K_1K_2[H_2A]}{[H^+]^2}$$

$$C_T = [H_2A] + \frac{K_1[H_2A]}{[H^+]} + \frac{K_1K_2[H_2A]}{[H^+]^2}$$

$$C_T = [H_2A]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)$$

$$\alpha_0 \equiv \frac{[H_2A]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$

Diprotic acids: calculations (cont.)

- Use $[H_2A]/C_T$ and K_a equations to get other α's

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \rightarrow \frac{K_1}{[H^+]} = \frac{[HA^-]}{[H_2A]} \qquad \frac{K_2}{[H^+]} = \frac{[A^{-2}]}{[HA^-]} \leftarrow K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

For distribution diagrams

$$\frac{[HA^-]}{C_T} = \frac{[H_2A]}{C_T}\frac{[HA^-]}{[H_2A]} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}\left(\frac{K_1}{[H^+]}\right)$$

$$\frac{[A^{-2}]}{C_T} = \frac{[HA^-]}{C_T}\frac{[A^{-2}]}{[HA^-]} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}\left(\frac{K_2}{[H^+]}\right)$$

$$\frac{[H_2A]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} \qquad \frac{[HA^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}} \qquad \frac{[A^{-2}]}{C_T} = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

α_0 α_1 α_2

Note: $\alpha_0 + \alpha_1 + \alpha_2 = 1$

Diprotic acids: calculations (cont.)

$$\alpha_0 \equiv \frac{[H_2A]}{C_T} \qquad \alpha_1 \equiv \frac{[HA^-]}{C_T} \qquad \alpha_2 \equiv \frac{[A^{-2}]}{C_T}$$

$$\frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}} \qquad \frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}} \qquad \frac{1}{\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1}$$

- If pH << pK_1, or $[H^+] >> K_1$

1 $\quad K_1/[H^+] \quad K_1K_2/[H^+]^2$

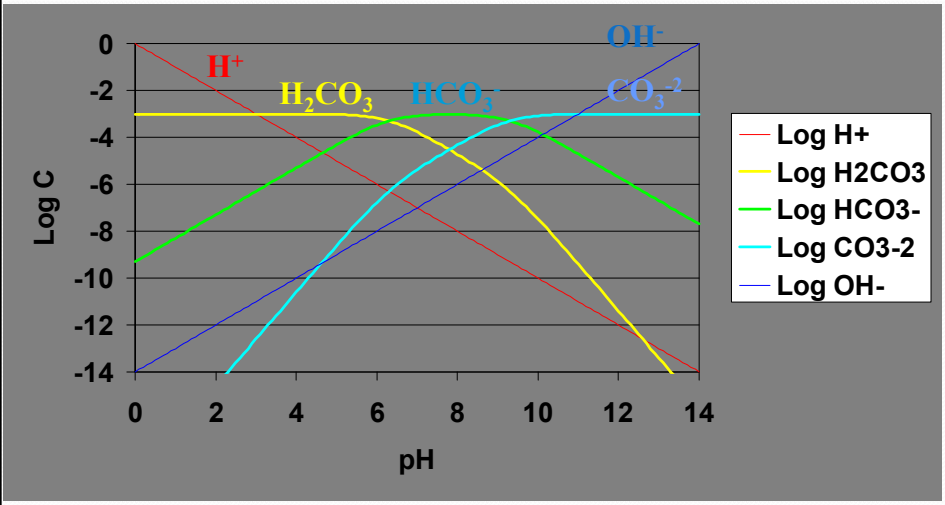
- If pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$

$[H^+]/K_1 \quad 1 \quad K_2/[H^+]$

- If pK_2 << pH, or $K_2 >> [H^+]$

$[H^+]^2/K_1K_2 \quad [H^+]/K_2 \quad 1$

Carbonate System ($C_T=10^{-3}$)



- To next lecture

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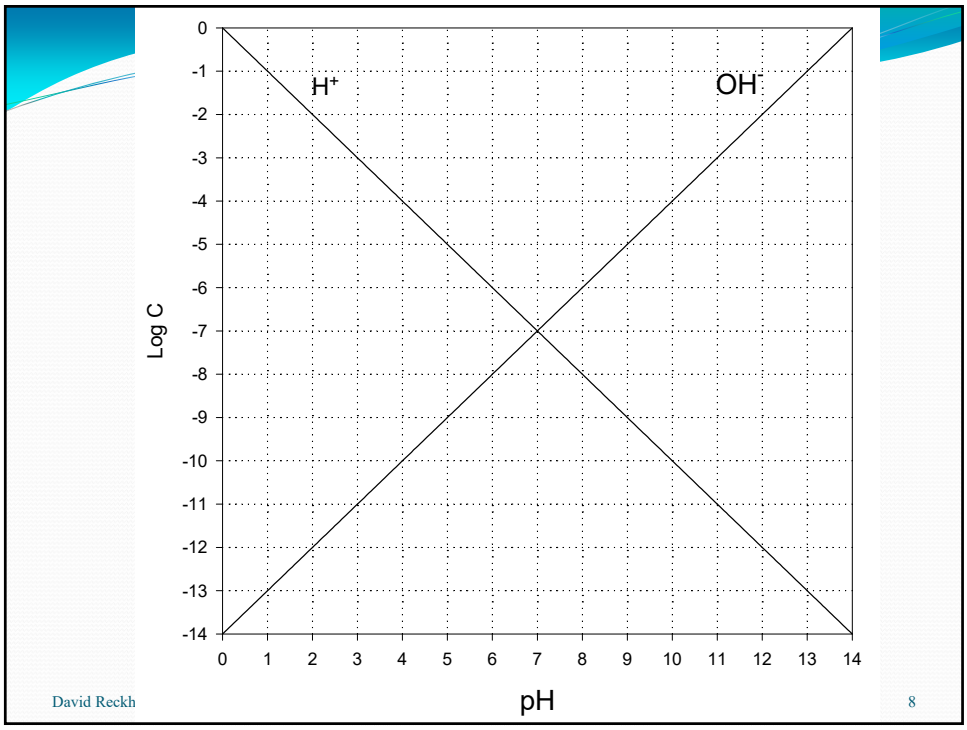

David Reckh 8