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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

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]}$$

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

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

$$[HA^-] = \frac{K_1[H_2A]}{[H^+]}$$

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

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

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

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

Diprotic acids: calculations (cont.)

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

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \quad \rightarrow \quad \frac{K_1}{[H^+]} = \frac{[HA^-]}{[H_2A]}$$

$$\frac{K_2}{[H^+]} = \frac{[A^{-2}]}{[HA^-]} \quad \leftarrow \quad K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

For distribution diagrams

$$\frac{[HA^-]}{C_T} = \frac{[H_2A]}{C_T}\frac{[HA^-]}{[H_2A]}$$

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

$$\frac{[A^{-2}]}{C_T} = \frac{[HA^-]}{C_T}\frac{[A^{-2}]}{[HA^-]}$$

$$= \frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}}\left(\frac{K_2}{[H^+]}\right)$$

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

α_0

$$\frac{[HA^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}}$$

α_1

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

α_2

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

Diprotic acids: calculations (cont.)

$$\alpha_0 \equiv \frac{[H_2A]}{C_T}$$

$$\alpha_1 \equiv \frac{[HA^-]}{C_T}$$

$$\alpha_2 \equiv \frac{[A^{-2}]}{C_T}$$

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

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

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

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

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

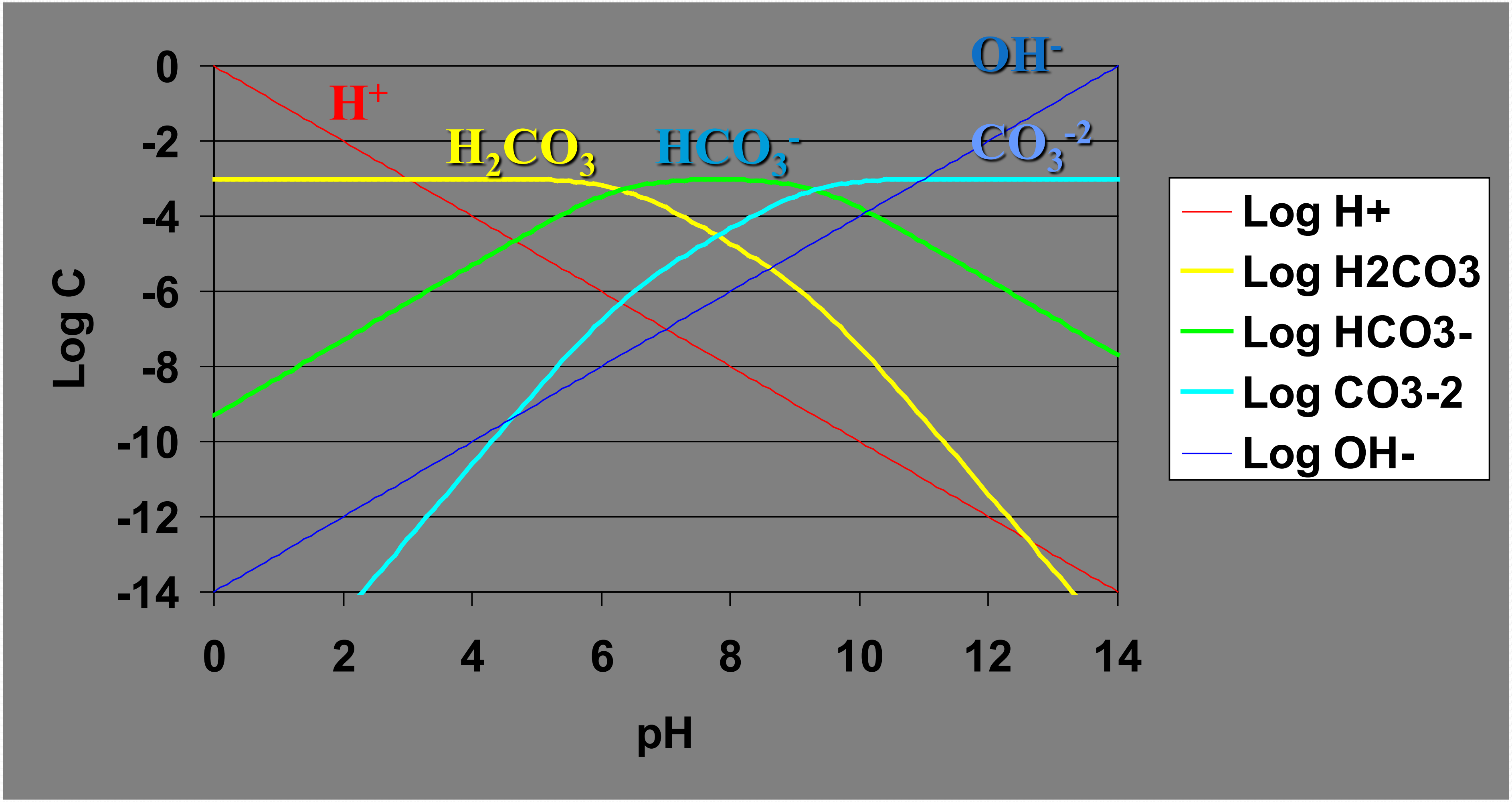
- **If pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$**

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

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

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

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



- To next lecture

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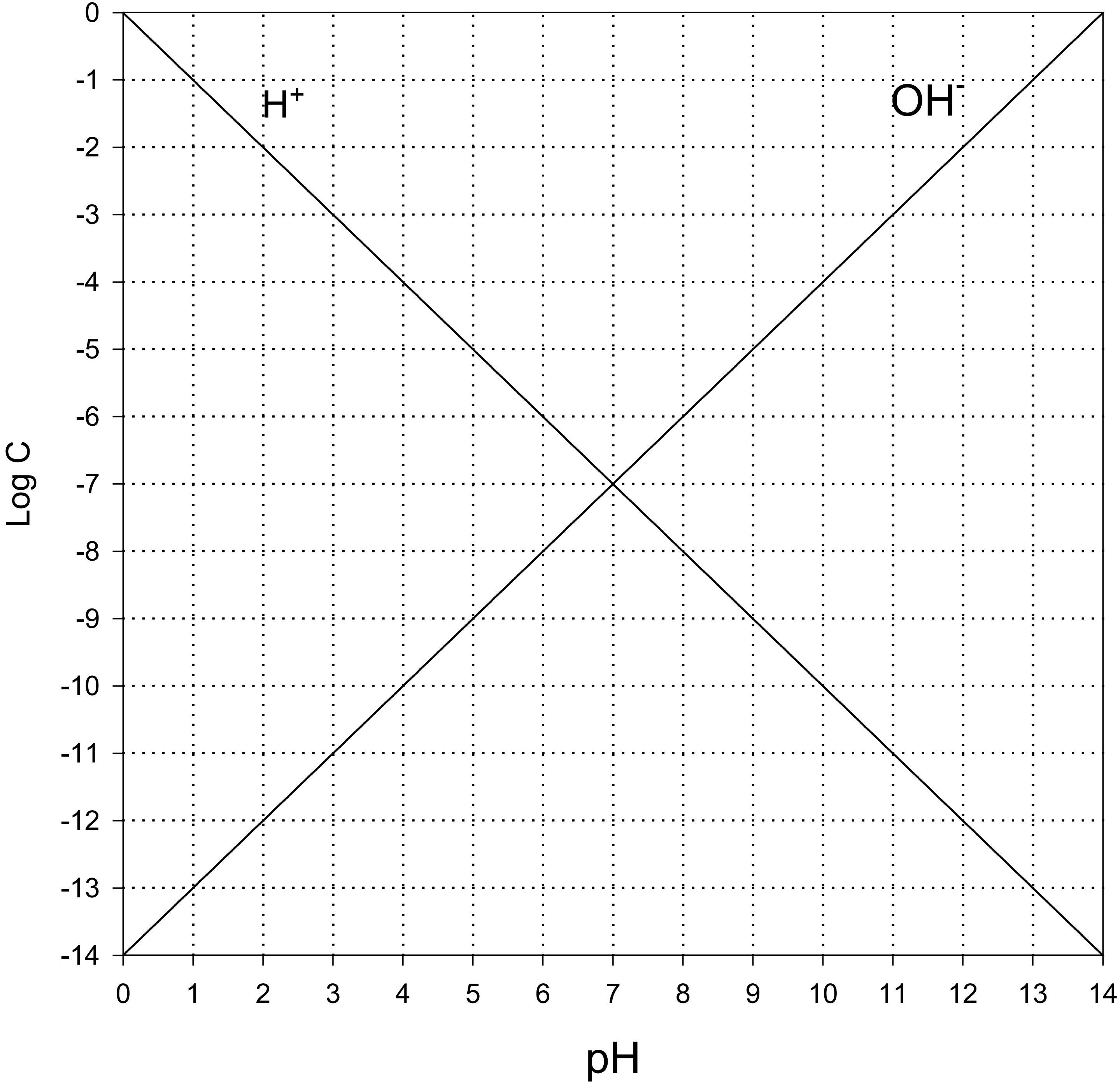
H+
OH-
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14