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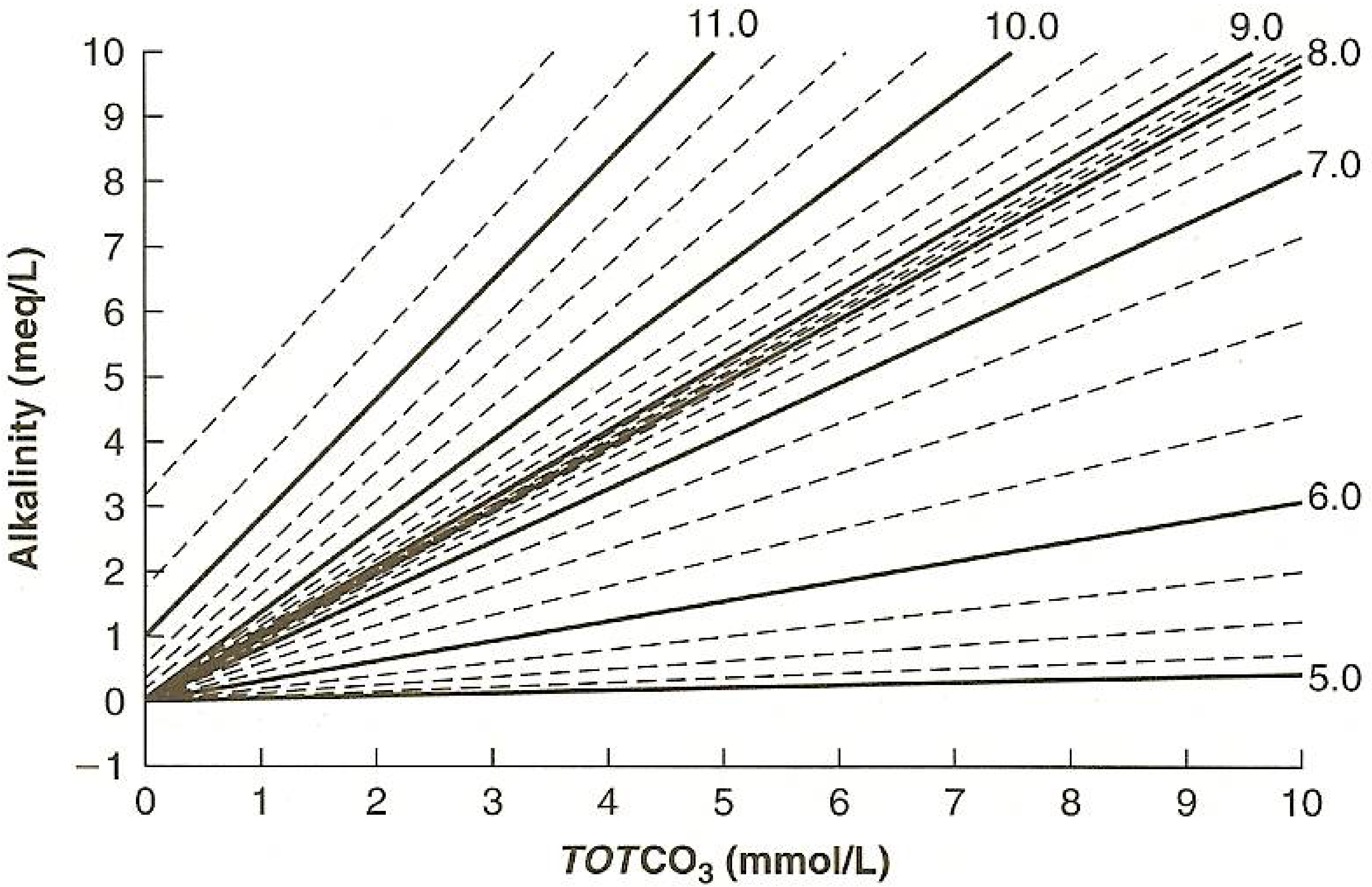
CEE 680: Water Chemistry

Lecture #21

Dissolved Carbon Dioxide: Closed & Open Systems

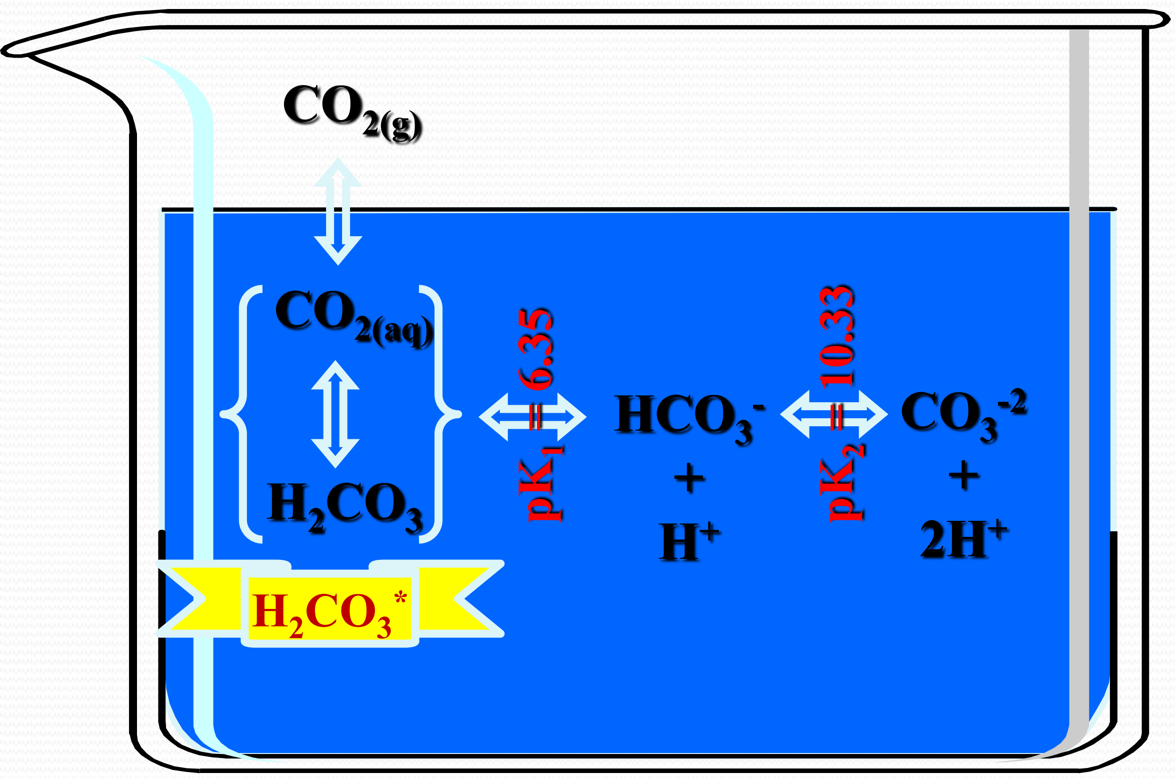
(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 5.4 & 7



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)

Major homogeneous reactions



- Gas transfer
- Acid/Base Reactions
  - Diprotic Acid
  - Fully-protonated form exits as two species
    - dissolved CO_2
    - true carbonic acid
    - we use $H_2CO_3^*$ to signify the sum of the two

Carbonic Acid

- The true acidity constant:

$$K_{H_2CO_3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-3.5}$$

- Hydration equilibrium

$$K_{CO_2} = \frac{[H_2CO_3]}{[CO_{2(aq)}]} = 10^{-2.8}$$

$$[CO_{2(aq)}] = 630[H_2CO_3]$$

- Total analytical concentration is essentially the dissolved carbon dioxide
- Then, the effective constant, K_1, is:

$$[H_2CO_3^*] \equiv [CO_{2(aq)}] + [H_2CO_3] \cong [CO_{2(aq)}]$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \cong K_{H_2CO_3} K_{CO_2} = 10^{-6.3}$$

Equilibria & Mass Balance

- For the carbonate system:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

$$\alpha_0 \equiv \frac{[H_2CO_3^*]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$

$$\alpha_1 \equiv \frac{[HCO_3^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}$$

$$\alpha_2 \equiv \frac{[CO_3^{-2}]}{C_T} = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

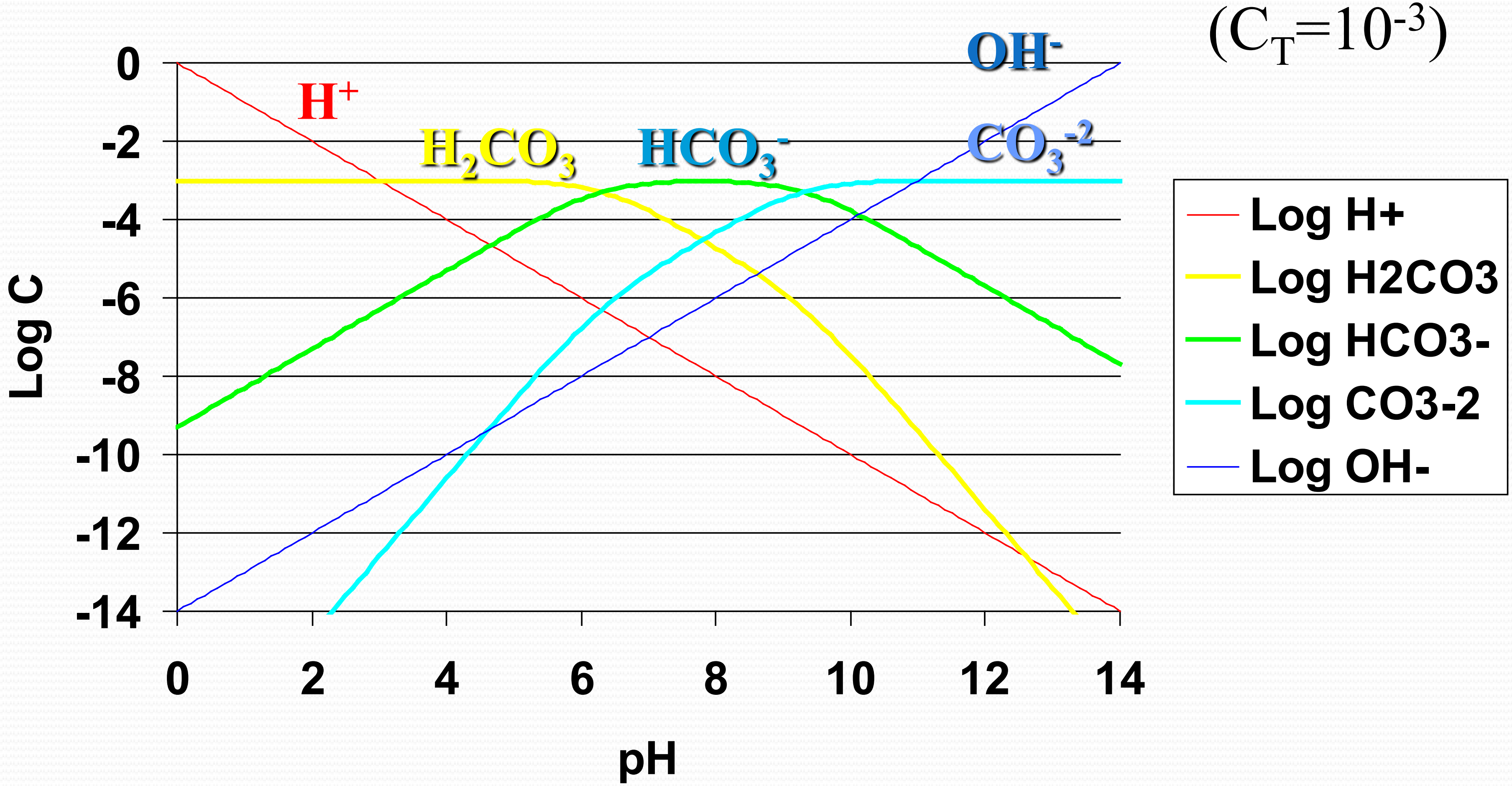
  - where for closed systems C_T is constant
    - e.g., groundwaters, water distribution systems, rapid laboratory titrations
  - for open system C_T is variable
    - surface fresh waters, ocean waters

Topics Covered

- Open system equations
  - log transforms for Log C vs. pH diagram
- Preparation and use of open system Log C vs. pH diagram
  - Note major features
  - problems
    - pure rainwater
    - waters with alkalinity
    - 10^{-2}M KOH solution left on bench over weekend

The Closed Carbonate System

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



Similar to S&M, pg. 158

Tableaux

Components		H_2CO_3	H^+	Log K
Species	H_2CO_3	0	0	0
	HCO_3^-	1	-1	-6.35
	CO_3^{-2}	1	-2	-16.68
	OH^-	0	-1	-14
	H^+	0	1	0
Total		10^{-3}	0	

$$10^{-6.35} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$[HCO_3^-] = [H_2CO_3]^1[H^+]^{-1}10^{-6.35}$$

Open System: Gas Transfer Equilibrium

- Dimensionless Partition Coefficient, K_D
- From which we get the Henry's Law Constant, K_H
  - using the ideal gas law
  - and applying it to CO_2
  - and substituting back in to the K_D equation

$$K_D = \frac{[CO_{2(aq)}]}{[CO_{2(g)}]}$$

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$[CO_{2(g)}] = \frac{p_{CO_2}}{RT}$$

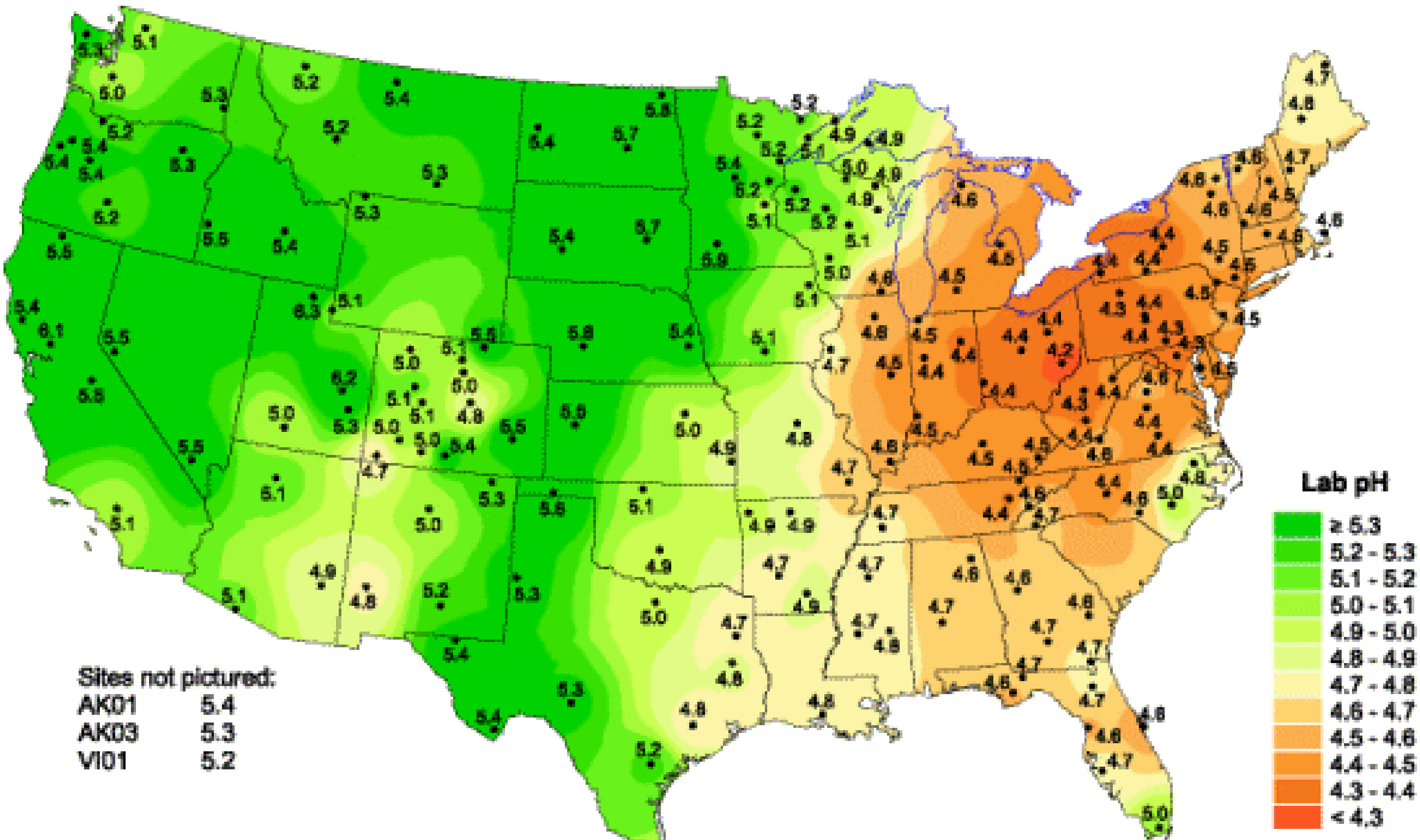
$$K_D = \frac{[CO_{2(aq)}]}{p_{CO_2}} RT$$

$$K_H \equiv \frac{K_D}{RT} = \frac{[CO_{2(aq)}]}{p_{CO_2}} = 10^{-1.5} \frac{M}{atm} \qquad @25^oC$$

Rain problem

- What is the composition of pure rain (25ºC)?
  - What is an "abnormal" rainwater pH?
    - i.e., what was its pH in prehistoric times?
    - Should it be pH 7?
  - What are its principal constituents?
    - Ignore those species that do not affect acid/base equilibria
      - N_2, O_2

Acid Rain in the US



National Atmospheric Deposition Program/National Trends Network

Rain Example (cont.)

- 1. List all species present
  - H^+, OH^-, H_2CO_3, HCO_3^-, CO_3^{-2} Five total
- 2. List all independent equations
  - equilibria
    - $K_1 = [H^+][HCO_3^-]/[H_2CO_3] = 10^{-6.3}$ 1
    - $K_2 = [H^+][CO_3^{-2}]/[HCO_3^-] = 10^{-10.3}$ 5
    - $K_w = [H^+][OH^-] = 10^{-14}$ 2
  - mass balances 3
    - $C = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}]$
  - atmospheric equilibria
    - $[H_2CO_3] = K_H p_{CO_2}$
  - charge balance: Σ(cationic species) = Σ(anionic species)
    - $[H^+] = [OH^-] + 2[CO_3^{-2}] + [HCO_3^-]$ 4

Rain Example (cont.)

- 3. Substitute into the Charge Balance
  - $[H^+] = [OH^-] + 2[CO_3^{-2}] + [HCO_3^-]$ ④
  - $[H^+] = [OH^-] + 2\alpha_2 C_T + \alpha_1 C_T$

$$[H^+] = \frac{K_w}{[H^+]} + 2\frac{\alpha_2 K_H p_{CO_2}}{\alpha_0} + \frac{\alpha_1 K_H p_{CO_2}}{\alpha_0}$$

- Solving gives us:
  - pH = 5.65
  - $[H_2CO_3] = 10^{-5}$
  - $[HCO_3^-] = 10^{-5.65} = 2.24\text{x}10^{-6}$
  - $[CO_3^{-2}] = 4.3\text{x}10^{-11}$
- What is C_T and TIC?
  - $C_T = 10^{-5} + 2.24\text{x}10^{-6} + 4.3\text{x}10^{-11} = 1.22\text{x}10^{-5}$
  - TIC = 0.146 mg/L

- But this time let's use the alpha equation in place of the equilibria

$$\alpha_0 \equiv \frac{[H_2CO_3^*]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}$$ ①

$$\alpha_2 \equiv \frac{[CO_3^{-2}]}{C_T} = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$ ⑤

$$\alpha_1 \equiv \frac{[HCO_3^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}$$

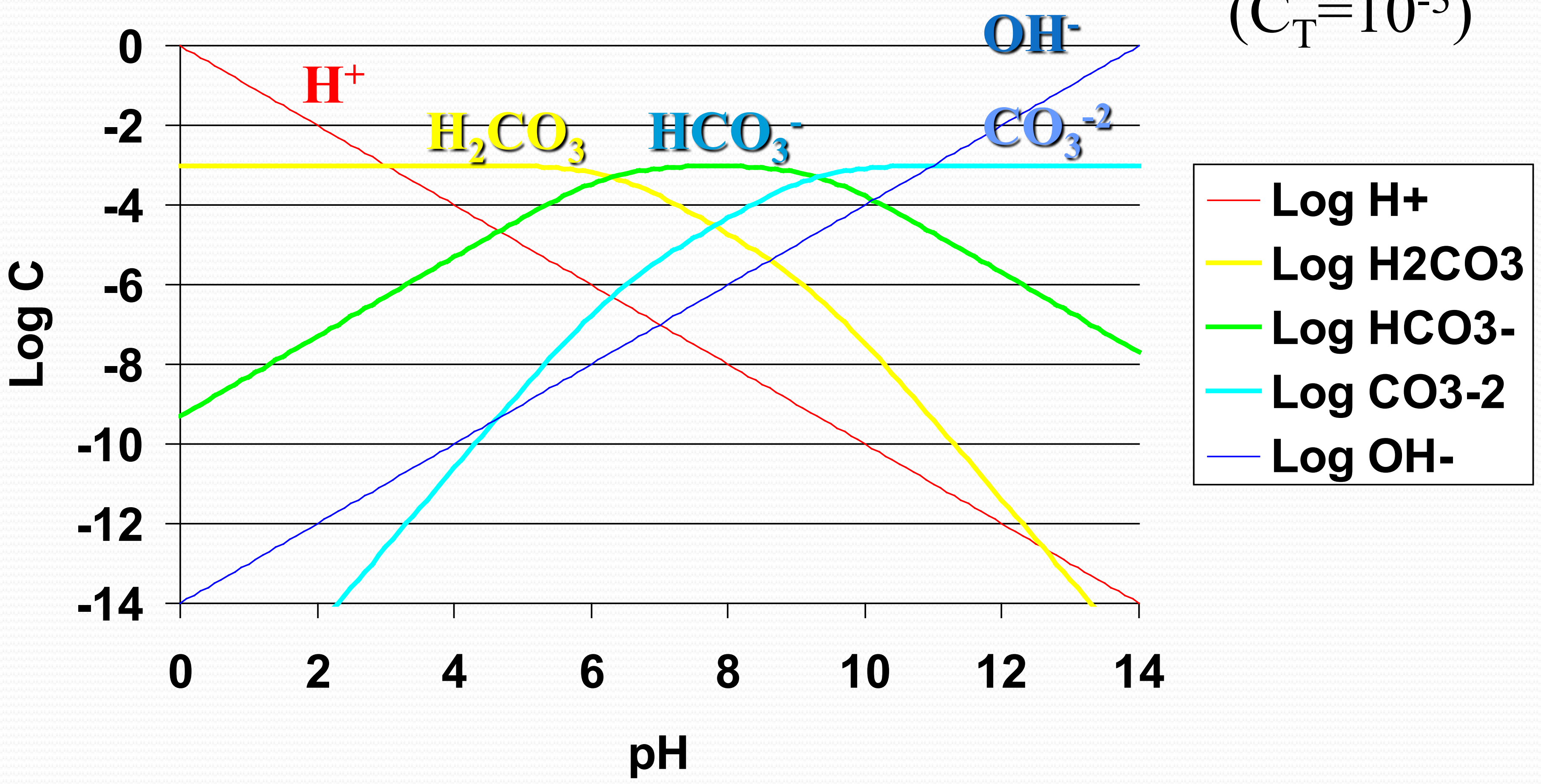
- and the gas transfer
  - $[H_2CO_3] = K_H p_{CO_2}$
  - $\alpha_o C_T = K_H p_{CO_2}$
  - $C_T = K_H p_{CO_2} / \alpha_o$

Pepsi Problem

- pH 2.5 (mostly phosphoric acid)
- 2.5 gas volumes (CO_2)

The Closed Carbonate System

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



- To next lecture