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Print version

CEE 680: Water Chemistry

Lecture #22

Dissolved Carbon Dioxide: Introduction to Open Systems

(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 7

Lab Mystery

- Lab crime scene?

Spring Break fun!

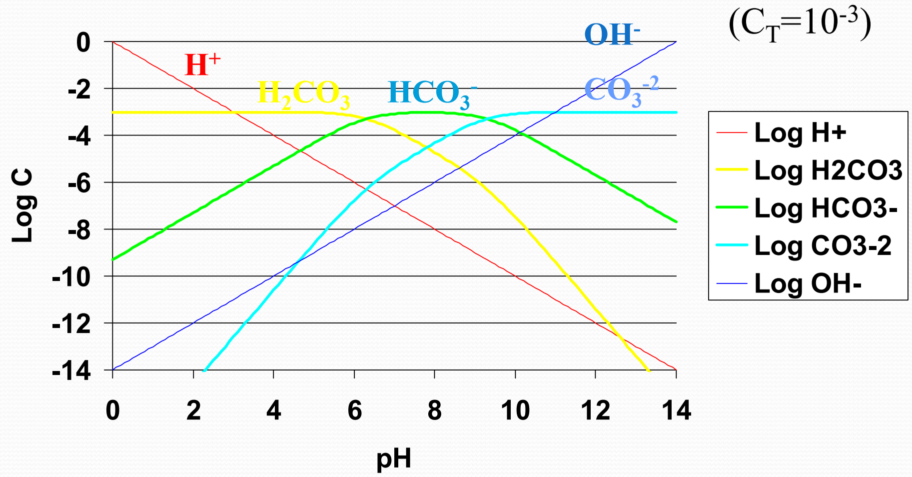
10^{-3} M NaOH

Topics Covered

- Log C vs. pH diagram
  - problems
    - 10^{-2}M $NaHCO_3$ solution left on bench over weekend
- Conservation of Alkalinity and C_T
  - closed/open systems
  - photosynthesis problem

The Closed Carbonate System

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



Tableaux

See pg. 158

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

- $[H_2CO_3]$ is constant, but C_T is not constant
  - Determined only by the partial pressure of CO_2
    - CO_2 (g) = CO_2(aq)
      - CO_2 (aq) + H_2O = $H_2CO_3^*$

$$[CO_2(aq)] + [H_2CO_3] \equiv [H_2CO_3*]$$

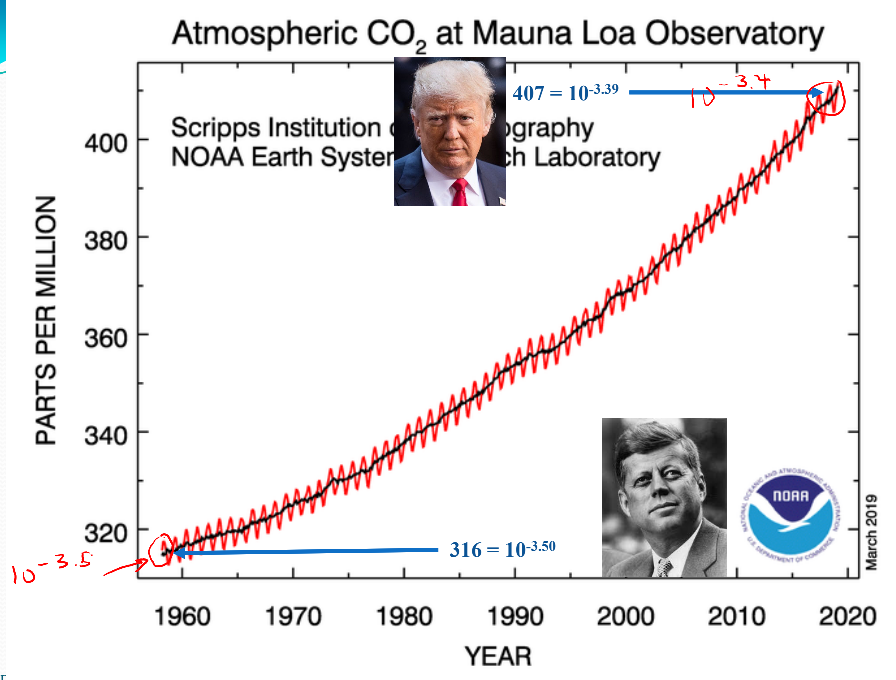
$$K_H = \frac{[H_2CO_3^*]}{p_{CO_2}}$$

$$[H_2CO_3^*] = K_H p_{CO_2}$$

K_H: $10^{-1.5}$ M/atm

p_{CO_2}: $10^{-3.5}$ atm

Typically, for the bulk atmosphere; at least it was



Gas phase concentrations

- Ideal Gas Law $PV = nRT$
  - Allows one to convert between gas-phase concentration in moles/L (C_G) and partial pressure (P)

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

  - And the mole fraction of substance "i" (y_i) is related to partial pressure of "i" (P_i) by:

$$y_i = \frac{P_i}{P_{total}}$$

Open Systems

- In general the bicarbonate is determined from:

$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \qquad [H_2CO_3^*] = K_H p_{CO_2}$$

$$[HCO_3^-] = K_1[H^+]^{-1}[H_2CO_3^*]$$

$$[HCO_3^-] = K_1[H^+]^{-1}K_H p_{CO_2}$$

$$\log[HCO_3^-] = \log K_1 + pH + \log K_H + \log p_{CO_2}$$

$$= -7.8 + pH + \log p_{CO_2}$$

  - And when p_{CO_2} is $10^{-3.5}$, then

$$\log[HCO_3^-] = -11.3 + pH$$

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Open Systems

- In general the carbonate is determined from:

$$K_2 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]} \qquad [HCO_3^-] = K_1[H^+]^{-1}K_H p_{CO_2}$$

$$[CO_3^{-2}] = K_2[H^+]^{-1}[HCO_3^-]$$

$$[CO_3^{-2}] = K_2[H^+]^{-1}K_1[H^+]^{-1}K_H p_{CO_2}$$

$$\log[CO_3^{-2}] = \log K_2 + pH + \log K_1 + pH + \log K_H + \log p_{CO_2}$$

$$= \log K_1K_2 + 2pH + \log K_H + \log p_{CO_2}$$

$$= -18.1 + 2pH + \log p_{CO_2}$$

  - And when p_{CO_2} is $10^{-3.5}$, then

$$\log[CO_3^{-2}] = -21.6 + 2pH$$

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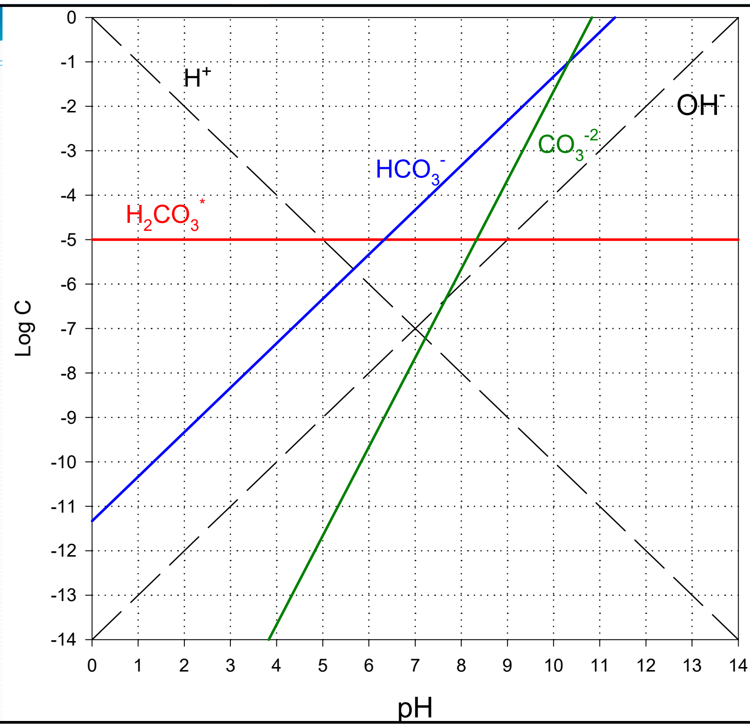
Open



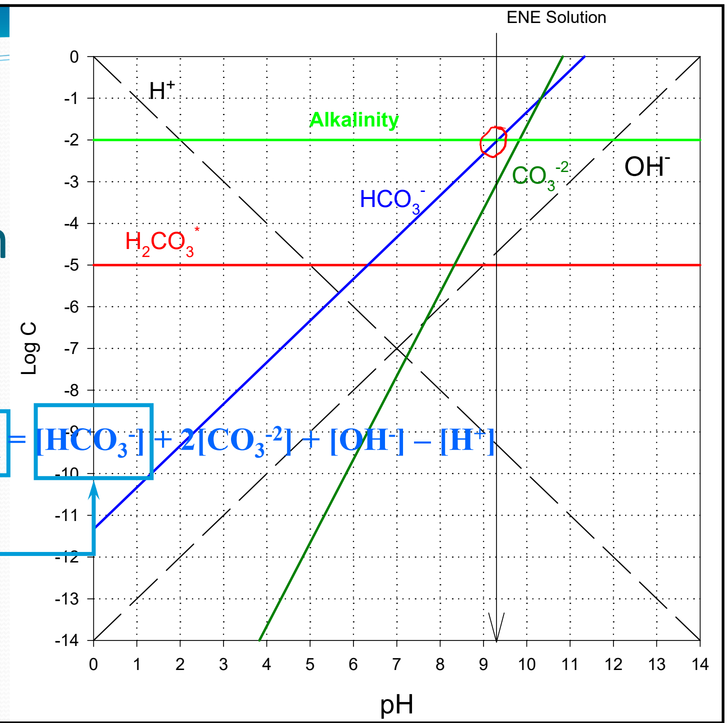
Problems: open & closed

- Example #1: 10^{-2}M KOH
  - What is initial pH?
  - What is pH after equilibrium with CO_2? 12
- Example #2: 10^{-2}M $NaHCO_3$ 9.3
  - What is initial pH?
  - What is pH after equilibrium with CO_2?

8.3

9.3

Open System Solution



$Alk = C_B - C_A = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$

Charge Balance & Alk

- Major Cation Charge = Major Anion Charge

C_B { $Na^+ + K^+ + 2Ca^{+2} + 2Mg^{+2}$ } $+ H^+$ = { $Cl^- + NO_3^- + 2\ SO_4^{-2}$ } C_A $+ HCO_3^- + 2\ CO_3^{-2} + OH^-$

- And simplifying:

$$C_B - C_A = \underbrace{HCO_3^- + 2\ CO_3^{-2} + OH^- - H^+}_{\equiv \text{Alkalinity}}$$

- Now combining with equilibria

$$C_B - C_A \equiv Alk \equiv (\alpha_1 + 2\alpha_2)C_T + K_w/[H^+] - H^+$$

- To next lecture