Updated: 2 March 2020

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?

10^{-3} M NaOH

Spring Break fun!

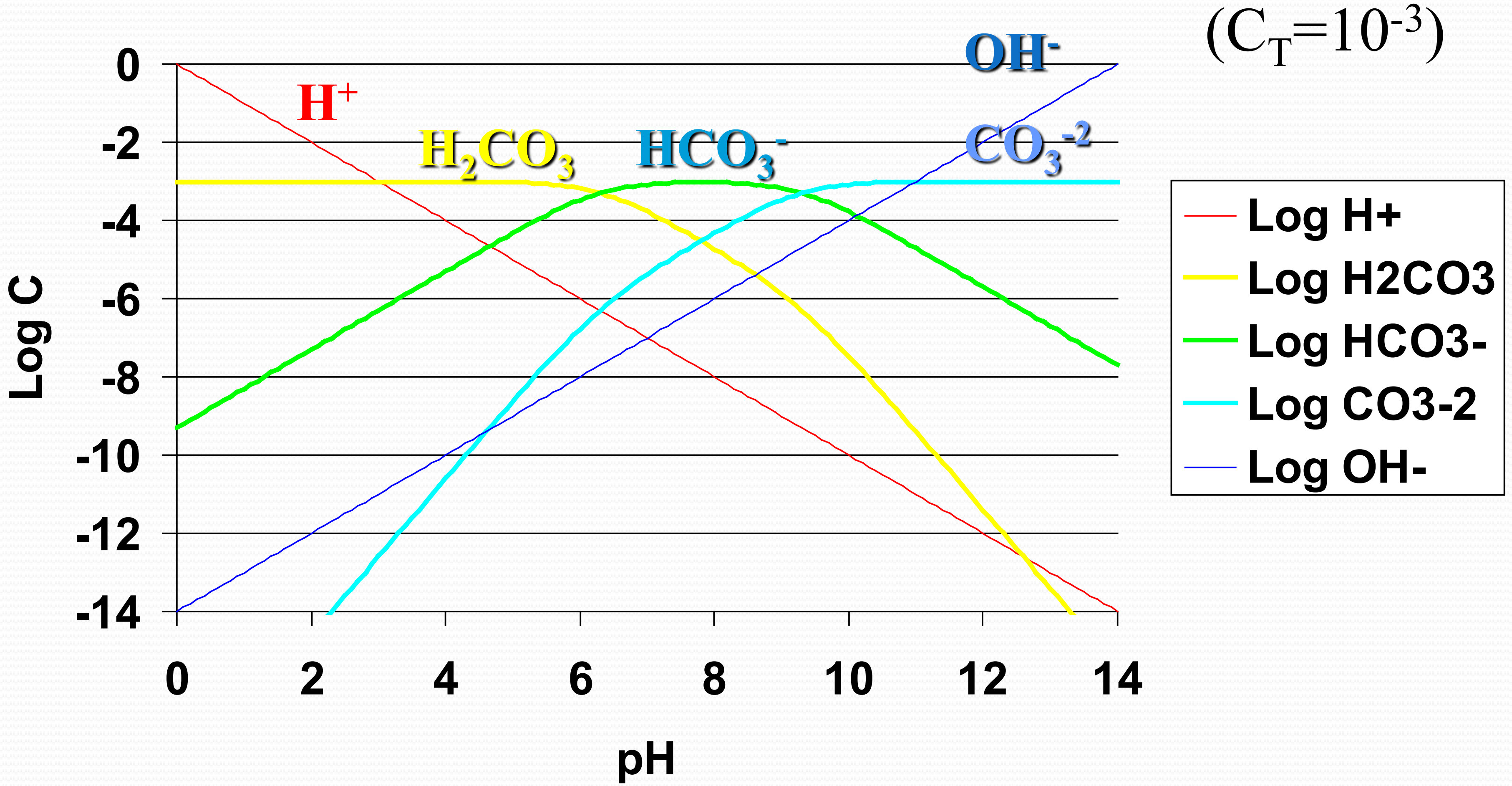
pH 11

pH 8.3

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



See 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

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

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

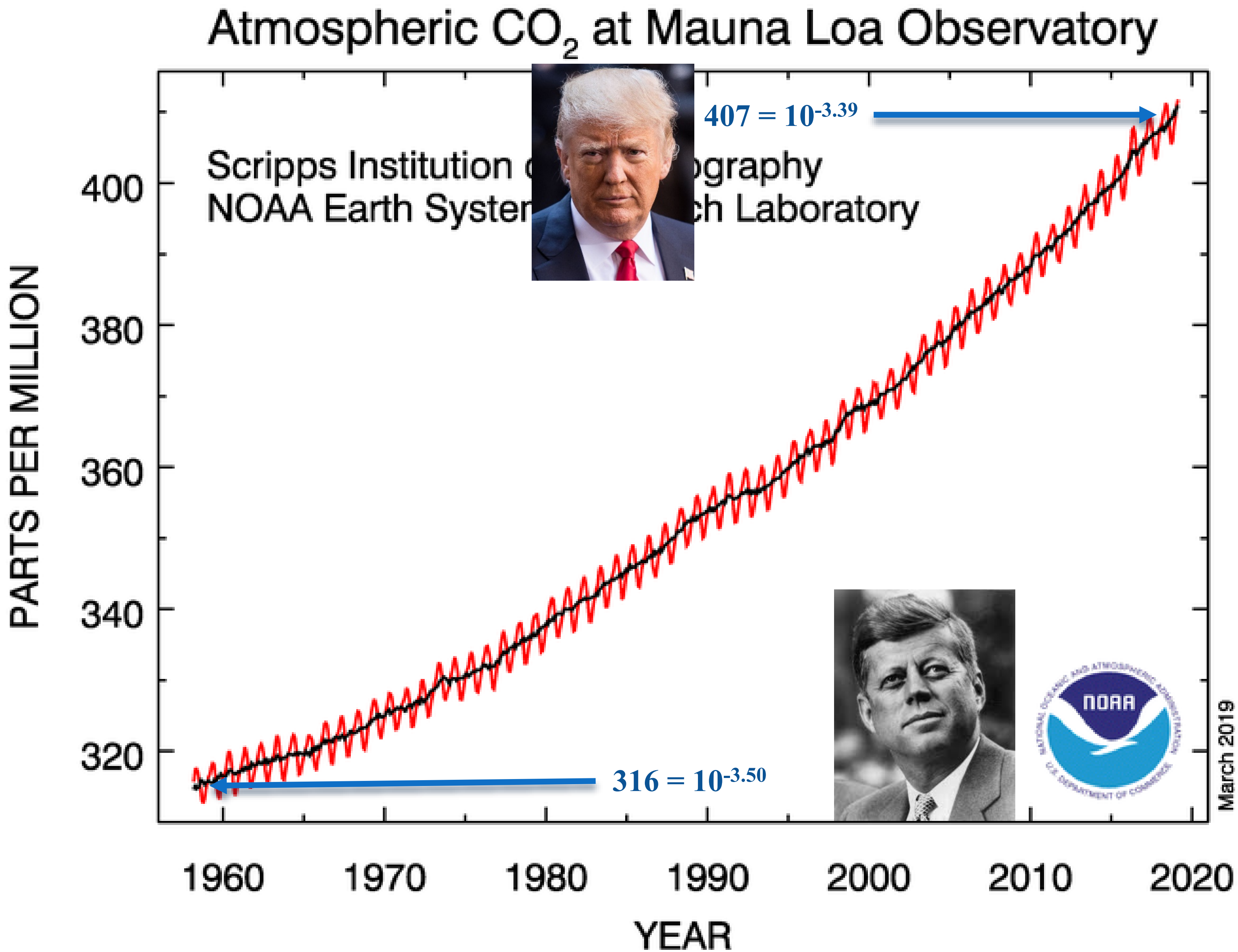
$$K_H = \frac{[H_2CO_3^*]}{p_{CO_2}}$$

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

$10^{-1.5}$ M/atm

$10^{-3.5}$ atm

Typically, for the bulk atmosphere; at least it was


Atmospheric CO_2 at Mauna Loa Observatory
Scripps Institution o... ography
NOAA Earth Syste... ch Laboratory
$407 = 10^{-3.39}$
$316 = 10^{-3.50}$
PARTS PER MILLION
320
340
360
380
400
1960
1970
1980
1990
2000
2010
2020
YEAR
March 2019
NOAA

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:

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

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

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

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

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

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

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

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

Open Systems

- In general the carbonate is determined from:

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

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

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

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

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

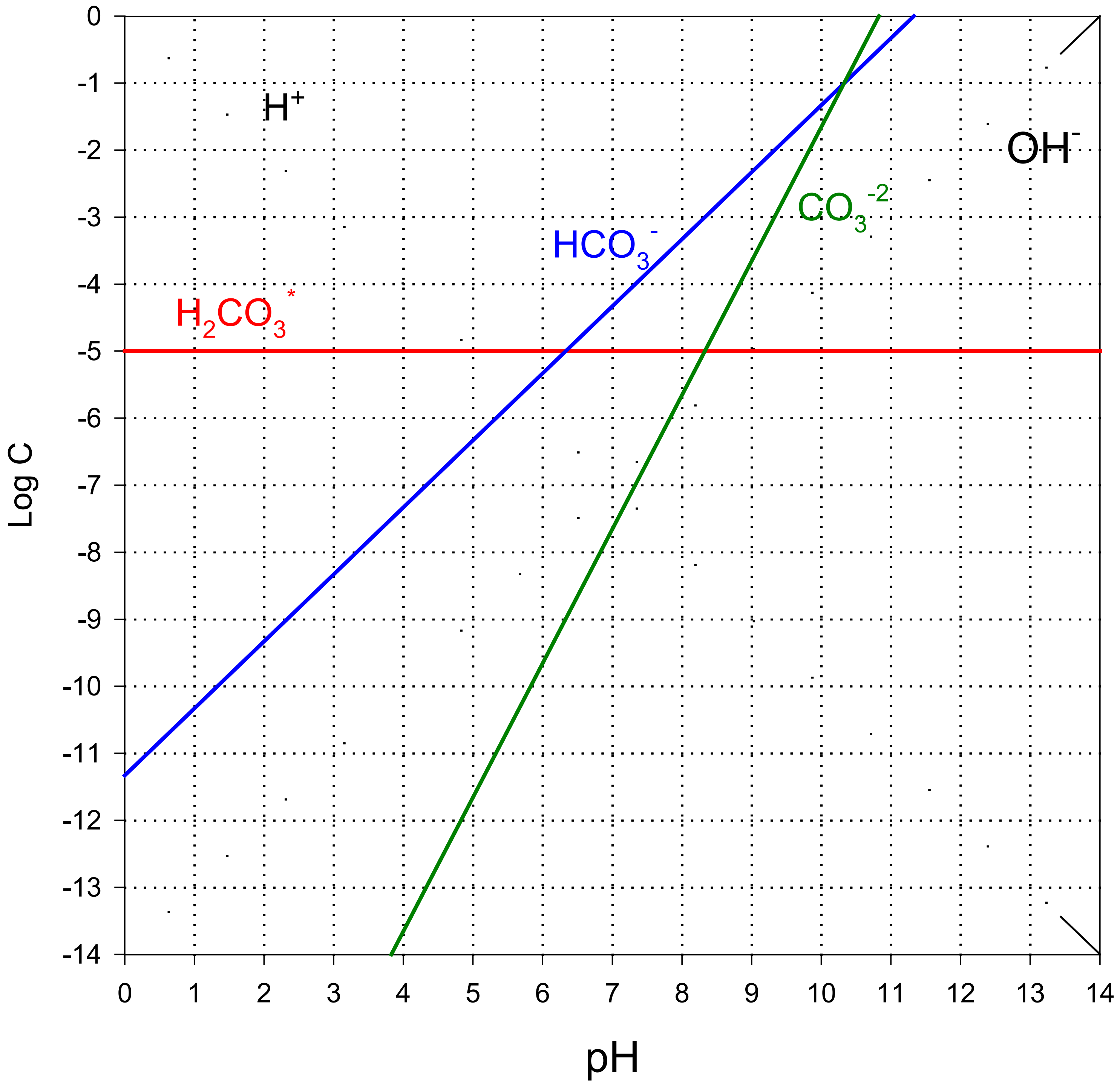
$$= \log K_1 K_2 + 2pH + \log K_H + \log p_{CO_2}$$

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

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

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

Open



H+
OH-
CO3-2
HCO3-
H2CO3*
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

Problems: open & closed

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

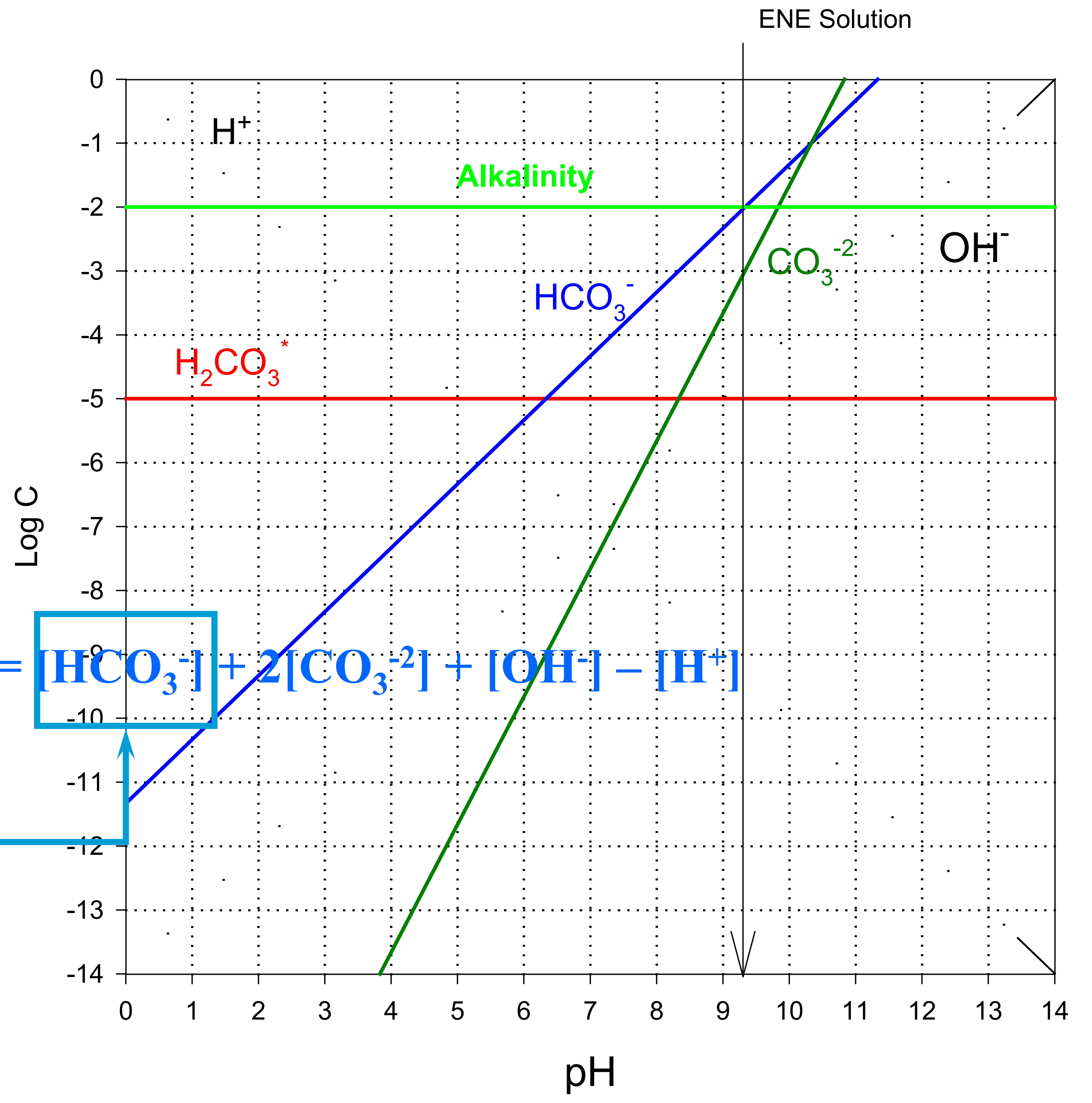
12

9.3

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

$$C_B \left\{ Na^+ + K^+ + 2Ca^{+2} + 2Mg^{+2} \right. \quad = \quad \left. Cl^- + NO_3^- + 2\,SO_4^{-2} \right\} C_A$$

$$+ H^+ \qquad\qquad + HCO_3^- + 2\,CO_3^{-2} + OH^-$$

- 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