Updated: 2 April 2020

Print version

CEE 680: Water Chemistry

Lecture #38

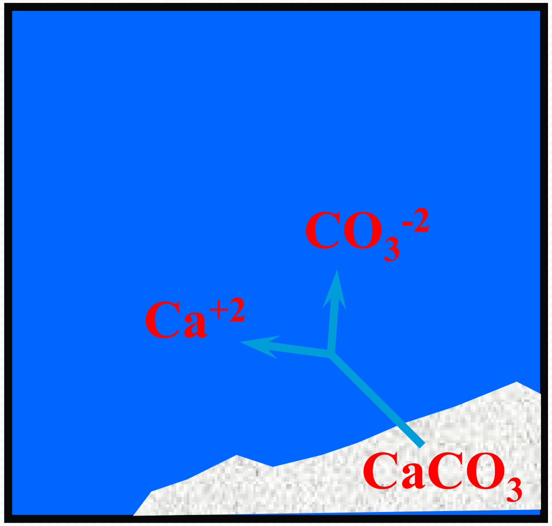
Precipitation and Dissolution: Metal Carbonates & Hydroxides

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Metal Carbonates

- Example of ligands that exist in different forms
- Consider $CaCO_3$ in a closed system
  - Six species: Ca^{+2}, H^+, OH^- CO_3^{-2}, HCO_3^-, $H_2CO_3^*$
  - Need six equations
    - K_1, K_2, K_w
    - K_{so}
    - ENE
    - MBE



Calcium Carbonate

- K_{so}

$$[Ca^{+2}] = \frac{K_{so}}{[CO_3^{-2}]}$$

$$= \frac{K_{so}}{\alpha_2 C_T}$$

- MBE

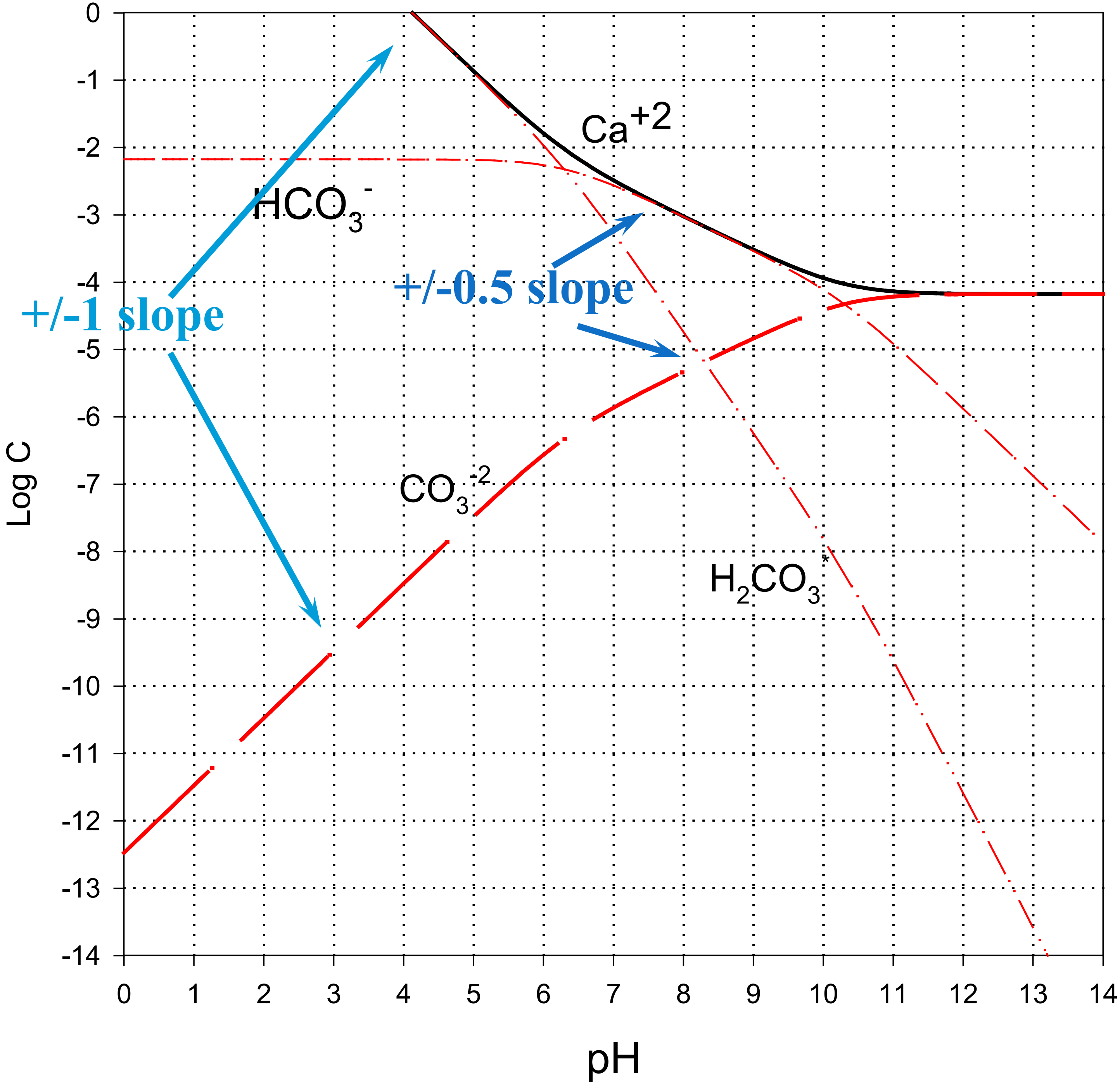
$$[Ca^{+2}] = C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

- combining

$$[Ca^{+2}] = \frac{K_{so}}{\alpha_2 [Ca^{+2}]}$$

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

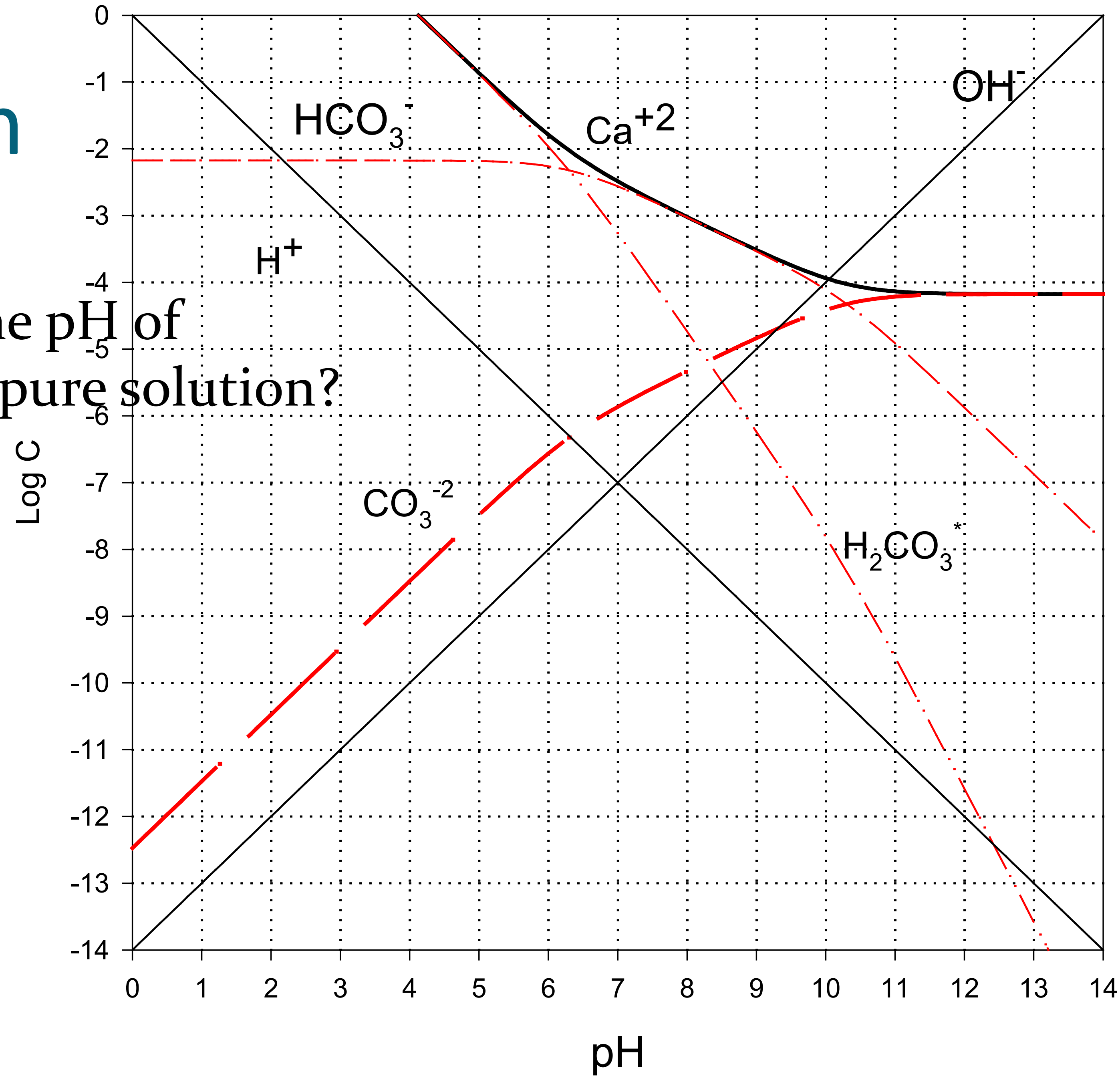
$$[Ca^{+2}] = \sqrt{\frac{K_{so}}{\alpha_2}}$$



Ca+2
HCO3-
+/-1 slope
+/-0.5 slope
CO3-2
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

Problem

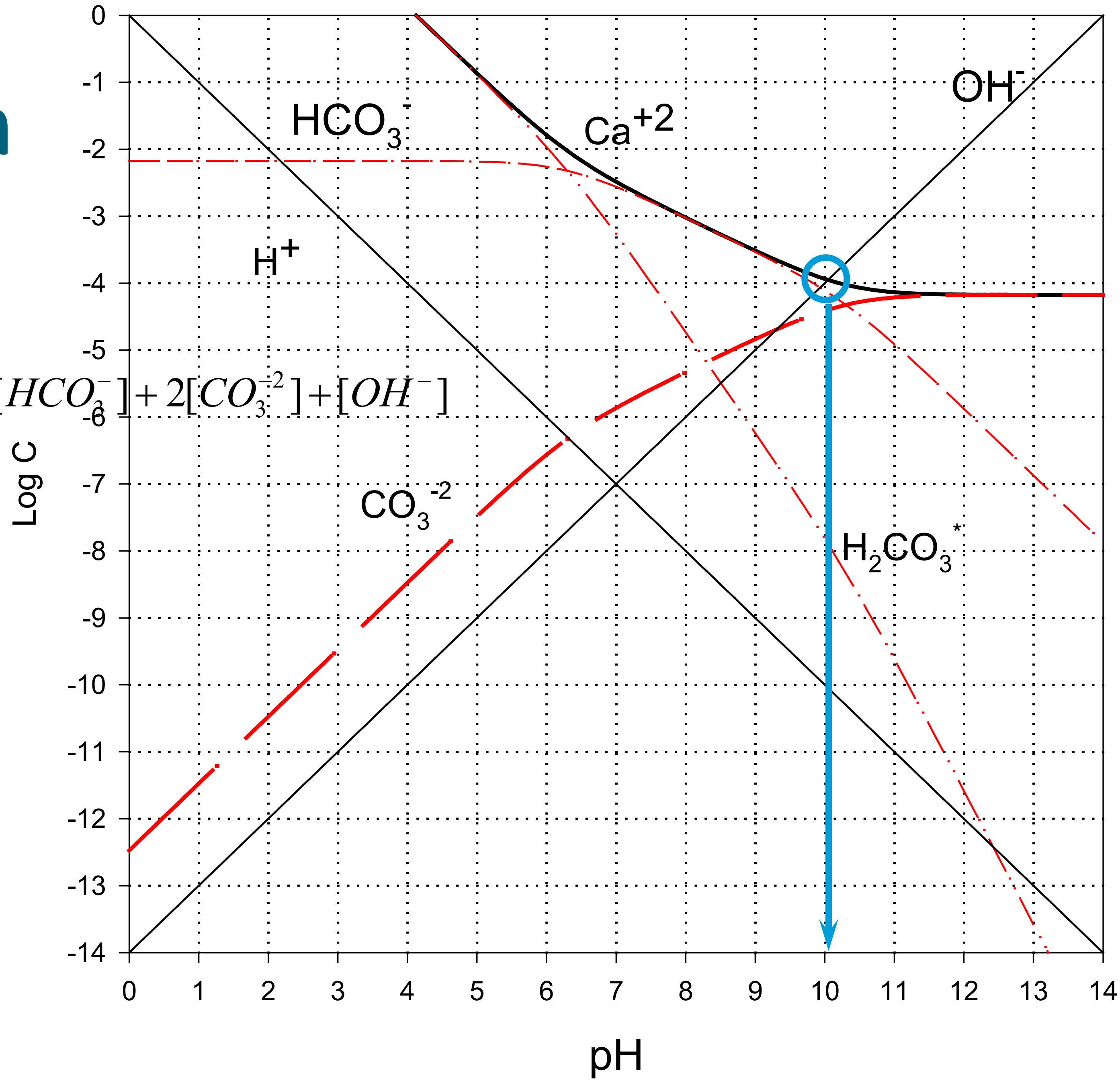
- What is the pH of CaCO3 in pure solution?



Solution

- Use ENE

$$2[Ca^{+2}]+[H^{+}]=[HCO_3^{-}]+2[CO_3^{-2}]+[OH^{-}]$$



Analytical Solution

- Start with ENE and substitute

$$2[Ca^{+2}]+[H^+]=[HCO_3^-]+2[CO_3^{-2}]+[OH^-]$$

$$2\sqrt{\frac{K_{so}}{\alpha_2}}+[H^+]=\alpha_1 C_T+2\alpha_2 C_T+\frac{K_w}{[H^+]}$$

$$2\sqrt{\frac{K_{so}}{\alpha_2}}+[H^+]=\alpha_1\sqrt{\frac{K_{so}}{\alpha_2}}+2\alpha_2\sqrt{\frac{K_{so}}{\alpha_2}}+\frac{K_w}{[H^+]}$$

$$\boxed{[H^+]+\sqrt{\frac{K_{so}}{\alpha_2}}\left(2-\alpha_1-2\alpha_2\right)-\frac{K_w}{[H^+]}=0}$$

S&M, equation #30
Pg. 376

- For $CaCO_3$: pH=9.91

With other acy/alk

- $CaCO_3$ system with addition of:
  - Strong acid (C_A)
  - Strong base (C_B)

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

$$\boxed{[H^+] + \sqrt{\frac{K_{so}}{\alpha_2}}\left(2 - \alpha_1 - 2\alpha_2\right) - \frac{K_w}{[H^+]} = \left(C_A - C_B\right)}$$

S&M, equation #31
Pg. 376

$CaCO_3$ in open system

$$[Ca^{+2}] = \frac{K_{so}}{[CO_3^{-2}]}$$

$$= \frac{K_{so}}{\alpha_2 \boxed{C_T}}$$

- Applying the open system C_T:
- And substituting into the ENE:

$$[Ca^{+2}] = \frac{K_{so}}{\alpha_2}\boxed{\left(\frac{\alpha_0}{K_H p_{CO_2}}\right)}$$

$$2[Ca^{+2}] + [H^+] = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-]$$

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

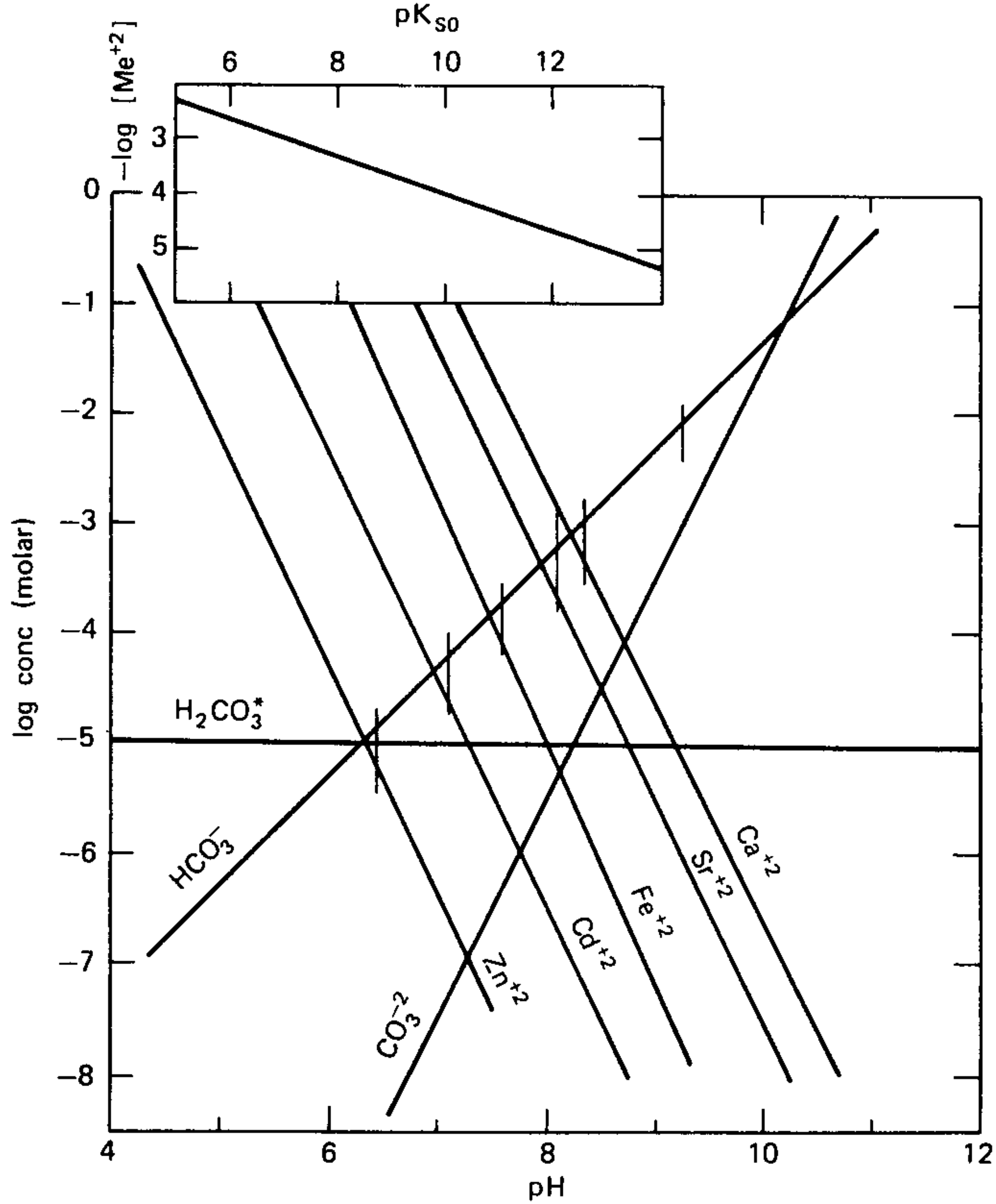
$$2\frac{K_{so}\alpha_0}{\alpha_2 K_H p_{CO_2}} + [H^+] - \alpha_1 \frac{K_H p_{CO_2}}{\alpha_0} - 2\alpha_2 \frac{K_H p_{CO_2}}{\alpha_0} - \frac{K_w}{[H^+]} = 0$$

- The pH is calculated to be:
  - pH = 8.27

Quite similar to surface water processes

Open System

- Assuming equilibrium with a constant partial pressure of CO_2 ($10^{-3.5}$ atm)



Stumm & Morgan, 1996, Figure 7.10, pg. 379

Open system with other acy/alk

- $CaCO_3$ system with addition of:
  - Strong acid (C_A)
  - Strong base (C_B)

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

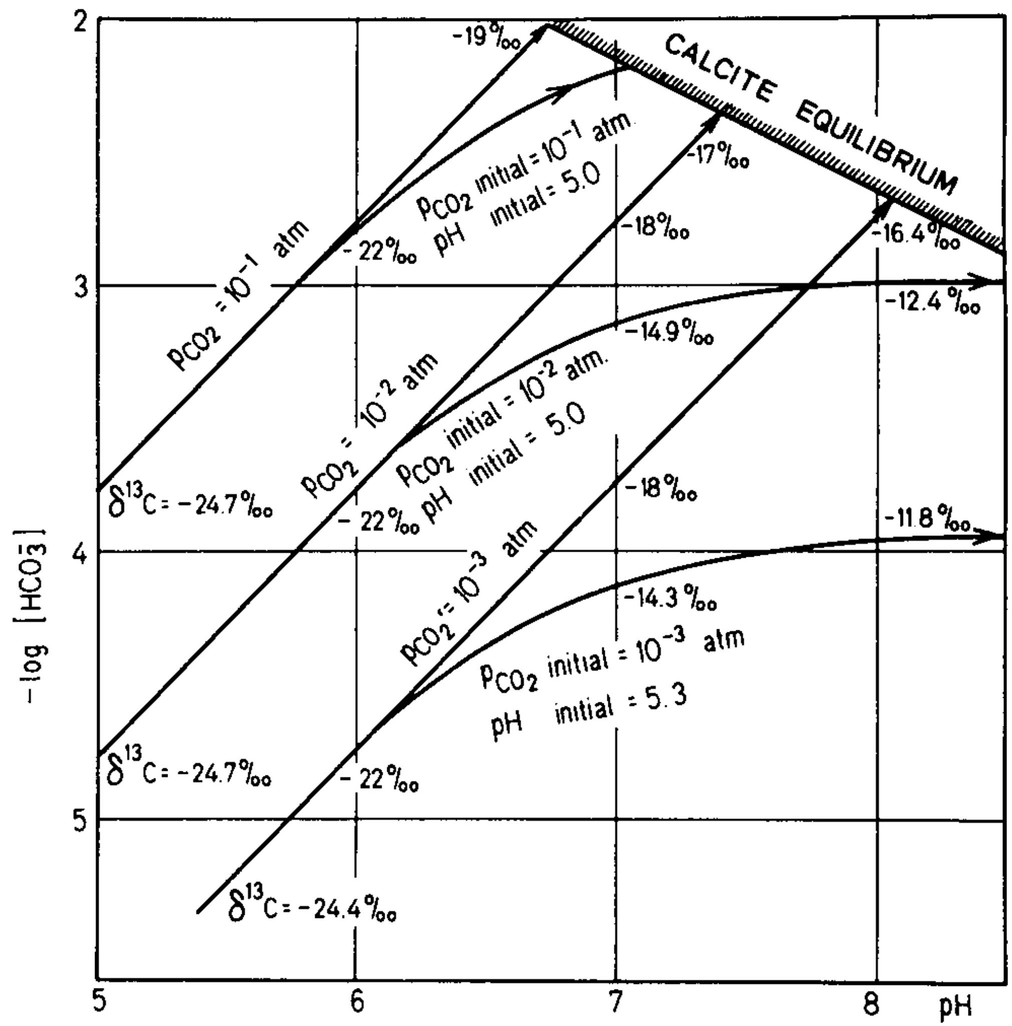
$$\Downarrow$$

$$\Downarrow$$

$$\boxed{2\frac{K_{so}\alpha_0}{\alpha_2 K_H p_{CO_2}} + [H^+] - \alpha_1\frac{K_H p_{CO_2}}{\alpha_0} - 2\alpha_2\frac{K_H p_{CO_2}}{\alpha_0} - \frac{K_w}{[H^+]} = \left(C_A - C_B\right)}$$

Carbonate dissolution

- Pathways
  - Not covered in class



Stumm & Morgan, 1996, Figure 7.12, pg. 385

- To next lecture