Updated: 3 April 2020

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CEE 680: Water Chemistry

Lecture #38

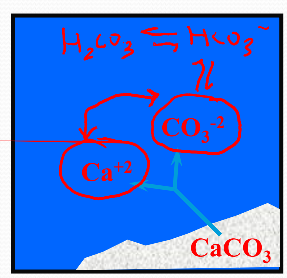
Precipitation and Dissolution: Metal Carbonates & Hydroxides

(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}

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

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

$10^{-8.34}$

- MBE

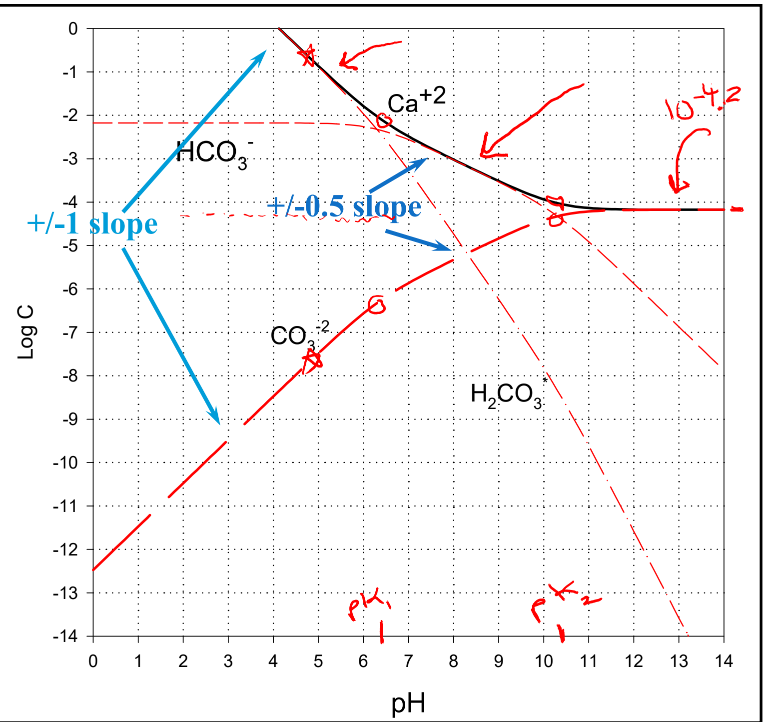
$$[Ca^{+2}] = C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

- combining

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

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

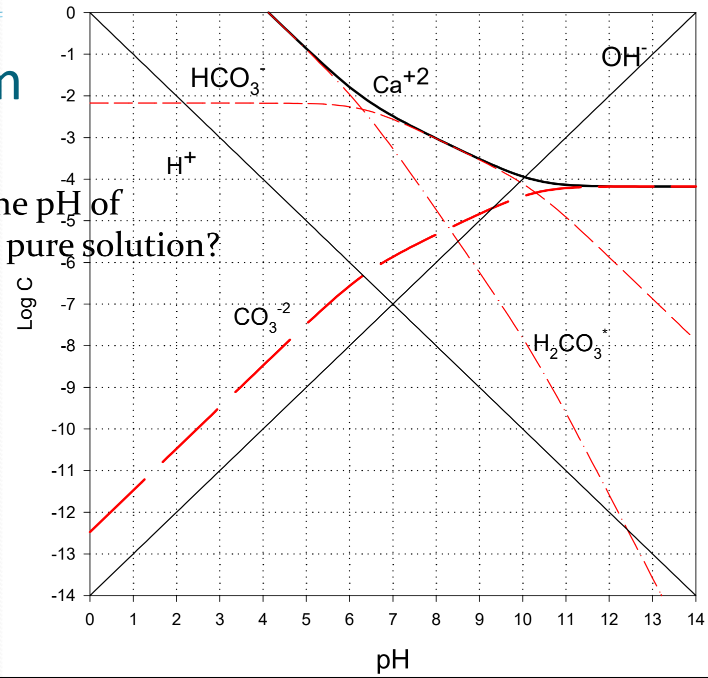
$$\frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$



Problem

- What is the pH of $CaCO_3$ in pure solution?

$H^+ + 2Ca^{+2} \Leftrightarrow HCO_3^- + 2CO_3^{-2} + OH^-$



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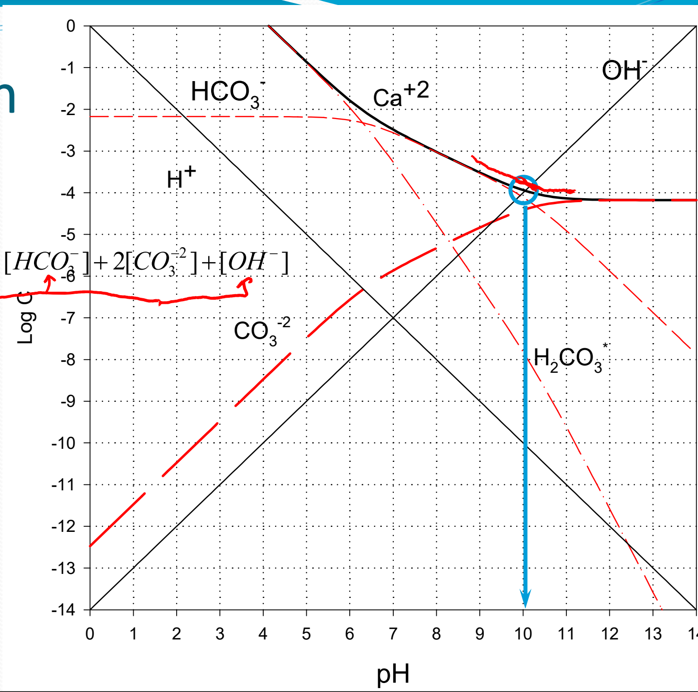
Solution

- Use ENE

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



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Analytical Solution

- Start with ENE and substitute

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

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

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

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

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)

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

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

S&M, equation #31
Pg. 376

$CaCO_3$ in open system

$$[Ca^{+2}] = \frac{K_{so}}{[CO_3^{-2}]} = \frac{K_{so}}{\alpha_2 C_T}$$

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

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

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

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

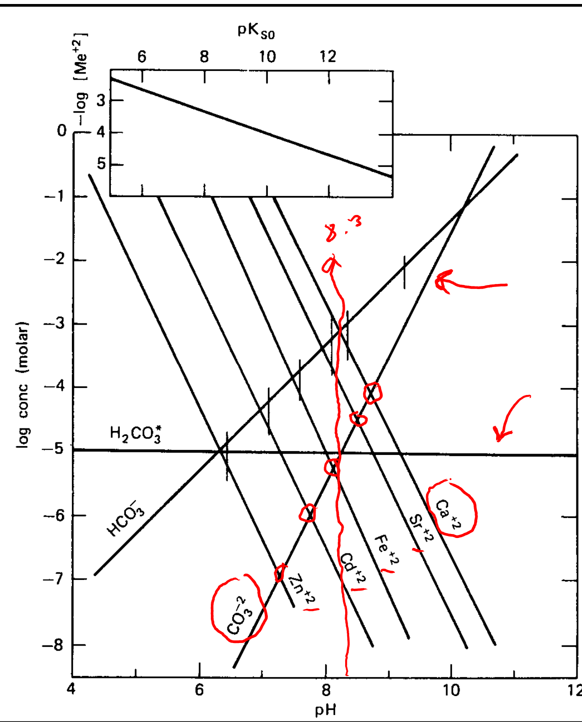
$$2\frac{K_{so}\alpha_0}{\alpha_2 K_H p_{CO_2}} + [H^+] - \alpha_1\frac{K_H p_{CO_2}}{\alpha_0} - 2\alpha_2\frac{K_H p_{CO_2}}{\alpha_0} - \frac{K_w}{[H^+]} = 0$$

- 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)

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

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

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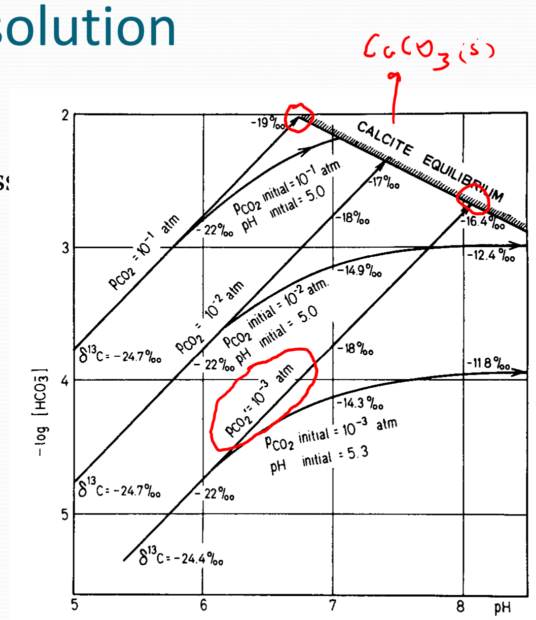
Carbonate dissolution

- Pathways
  - Not covered in class



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

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- To next lecture