Acid-base systems II

Polyprotic acids

- **Carbonic acid**

$$H_2CO_3{}^* \;=\; H^+ + HCO_3{}^- \;=\; 2H^+ + CO_3{}^{2-}$$

pK$_{a1}$=6.3 pK$_{a2}$=10.3 (at 25°C)

*H_2CO_3** = sum of true *H_2CO_3* and *CO_2*(*aq*)

- **Phosphoric acid**

$$H_3PO_4 \;=\; H^+ + H_2PO_4{}^- \;=\; 2H^+ + HPO_4{}^{2-} \;=\; 3H^+ \;+\; PO_4{}^{3-}$$

pK$_{a1}$=2.1 pK$_{a2}$=7.2 pK$_{a2}$=12.7 (at 25°C)

Analyzing polyprotic acid/base system

Let's work with a <u>di</u>protic acid, H_2A:

Species involved (5):

H^+, OH^-, H_2A, HA^-, A^{2-}

Equilibrium constants:

$$K_w = [H^+][OH^-] \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

Mass balance:

$$C_T = [H_2A] + [HA^-] + [A^{2-}]$$

Charge balance:

Analyzing polyprotic acid/base system

From equilibrium constants & mass balance, we get

$$[H_2A] = C_T \times \left(\frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}}{[H^+]} + 1\right)^{-1}$$

$$[HA^-] = C_T \times \left(\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}\right)^{-1}$$

$$[A^{2-}] = C_T \times \left(1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}}\right)^{-1}$$

Analyzing polyprotic acid/base system

$$[H_2A] = C_T \times \left(\frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}}{[H^+]} + 1\right)^{-1}$$

$pH < pK_{a1}$: $[H_2A] \cong C_T$ ➡ $p[H_2A] \cong pC_T$ *slope: 0*

$pK_{a1} < pH < pK_{a2}$: $[H_2A] \cong C_T\left(\frac{K_{a1}}{[H^+]}\right)^{-1}$

➡ $p[H_2A] \cong pC_T - pK_{a1} + pH$ *slope: 1*

$pK_{a2} < pH$: $[H_2A] \cong C_T\left(\frac{K_{a1}K_{a2}}{[H^+]^2}\right)^{-1}$

➡ $p[H_2A] \cong pC_T - pK_{a1} - pK_{a2} + 2pH$

slope: 2

Analyzing polyprotic acid/base system

$$[HA^-] = C_T \times \left(\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}\right)^{-1}$$

pH<pK_{a1}: $p[HA^-] \cong pC_T + pK_{a1} + pH$ *slope: -1*

pK_{a1}<pH<pK_{a2}: $p[HA^-] \cong pC_T$ *slope: 0*

pK_{a2}<pH: $p[HA^-] \cong pC_T - pK_{a2} + pH$ *slope: 1*

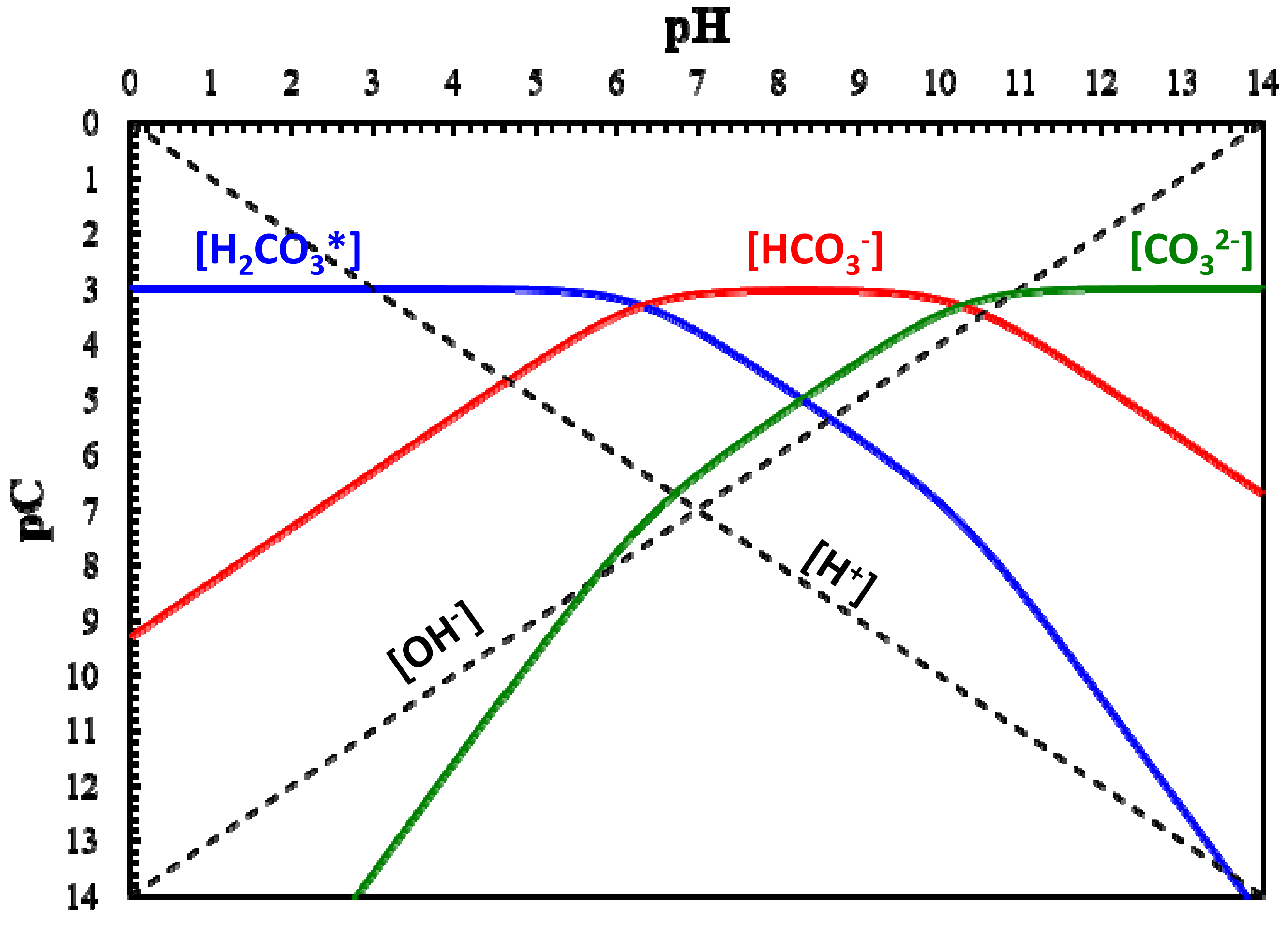
$$[A^{2-}] = C_T \times \left(1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}}\right)^{-1}$$

pH<pK_{a1}: $p[A^{2-}] \cong pC_T + pK_{a1} + pK_{a2} - 2pH$ *slope: -2*

pK_{a1}<pH<pK_{a2}: $p[HA^-] \cong pC_T + pK_{a2} - pH$ *slope: -1*

pK_{a2}<pH: $p[HA^-] \cong pC_T$ *slope: 0*

Analyzing polyprotic acid/base system



H_2CO_3,

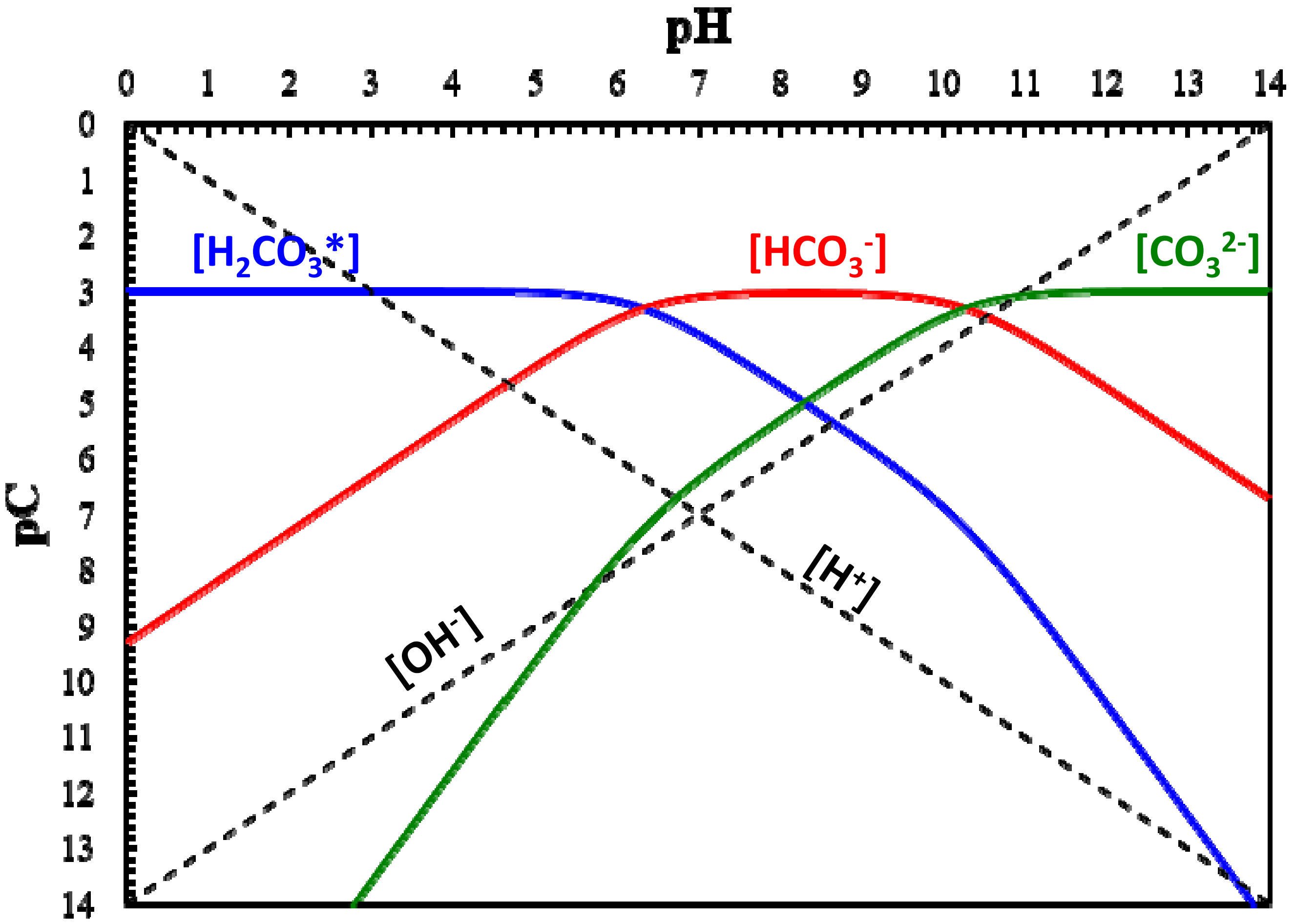
$C_T = 10^{-3}$ M

$pK_{a1} = 6.3$

$pK_{a2} = 10.3$

Charge balance:

Analyzing polyprotic acid/base system

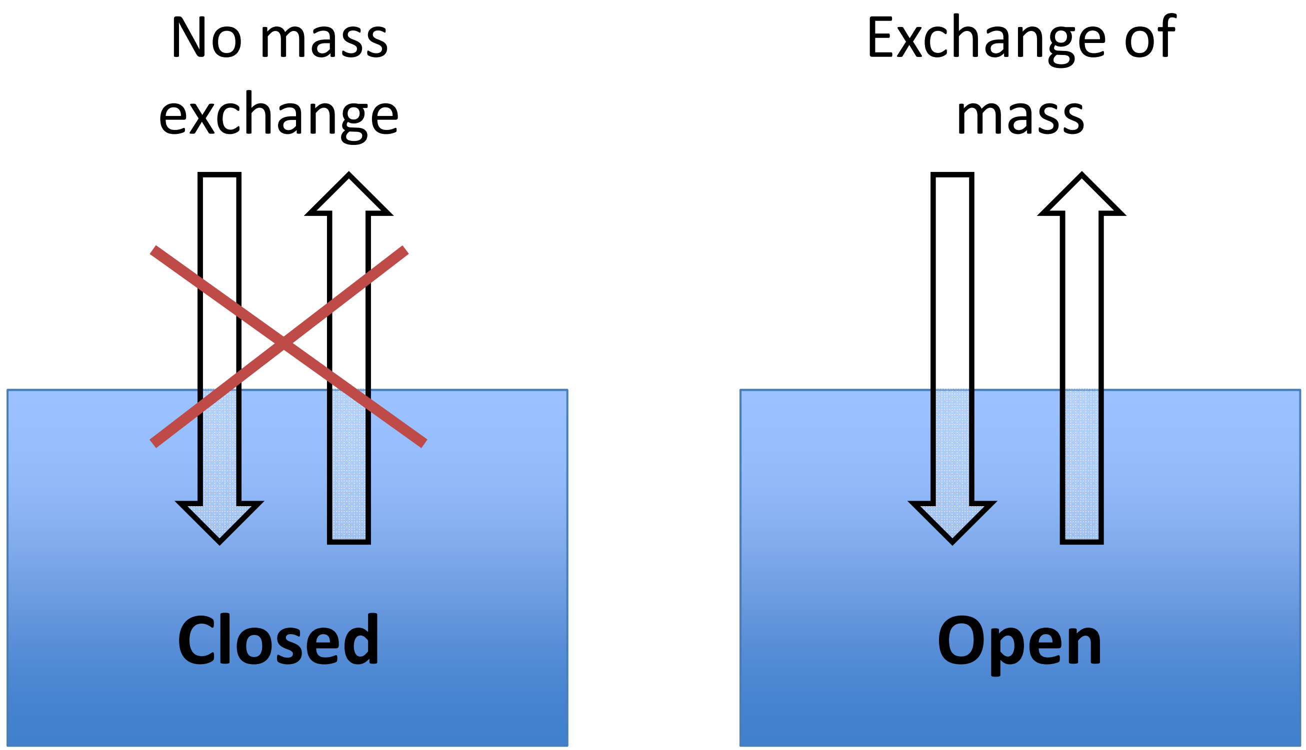


pH of…

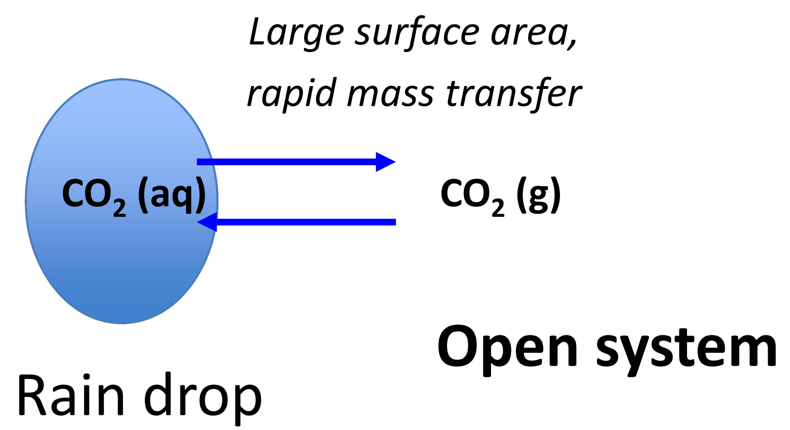
10^{-3} M $NaHCO_3$?

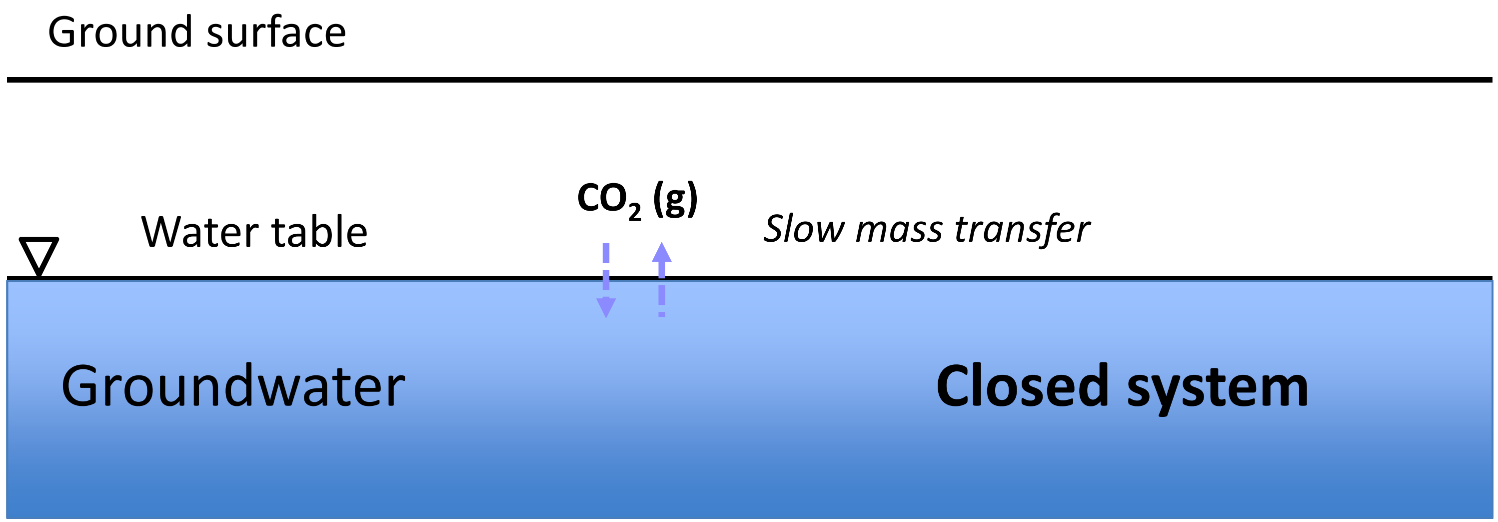
10^{-3} M Na_2CO_3?

Open vs. Closed system



Open & Closed systems in natural waters

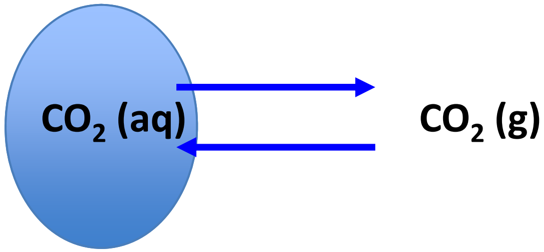




Open & Closed systems for carbonates

- **Closed system: C_T = constant**
  (we have a solution already!)

- **Open system (ex: rain drop)**



– Equilibrium between gas & aqueous phase:
"Henry's Law"

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

K_H = Henry's law constant (M/atm)
P_{CO_2} = partial pressure of CO_2 (atm)

– Atmosphere: nearly infinite source of CO_2
constant P_{CO_2}

Open system for carbonates

pH-pC diagram for an open system

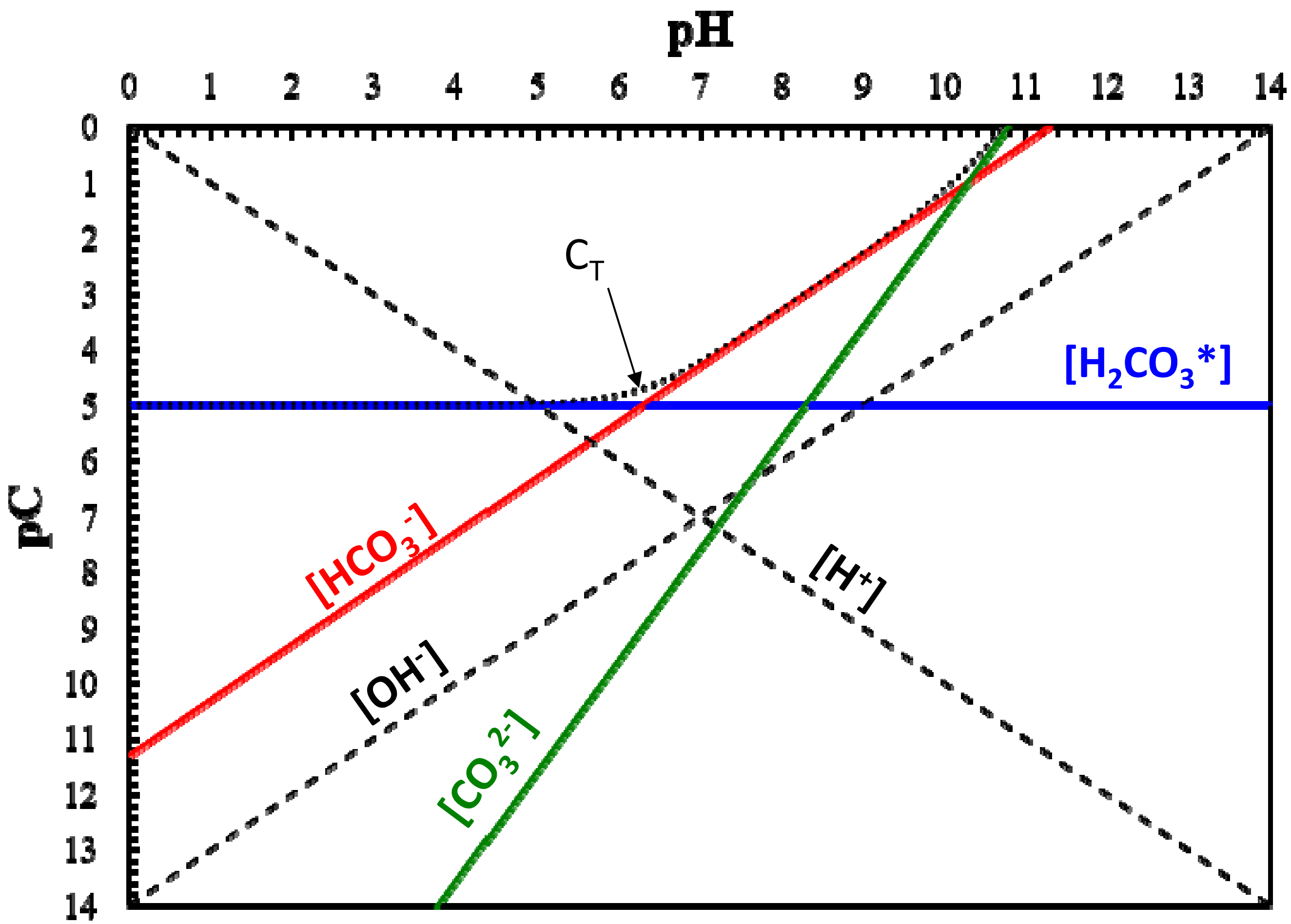
Equilibrium constants:

$$K_w = [H^+][OH^-] \qquad K_{a1} = \frac{[H^+][HCO_3{}^-]}{[H_2CO_3]} \quad K_{a2} = \frac{[H^+][CO_3{}^{2-}]}{[HCO_3{}^-]}$$

Mass balance:

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

Open system for carbonates



Carbonate buffer

- So, rainwater pH ≈ 5.6 in uncontaminated areas

- **Carbonate species (H_2CO_3 – HCO_3^- – CO_3^{2-})**
  - Most of the time, exist in the highest concentration among weak acids in natural waters

    → Controls the pH (others adjust to that pH)

- Freshwater pH range: 6-8; seawater pH range: 7.5-8.5
  - Much more complicated than we calculate in the class
    - Other equilibriums involved: dissolution of carbonate minerals (ex: $CaCO_3$)
    - P_{CO2} may not be $10^{-3.5}$ atm (atmospheric partial pressure) because of biological activities (photosynthesis, respiration)
    - Equilibrium may not be established