

Acid-base systems II

Polyprotic acids

- **Carbonic acid**



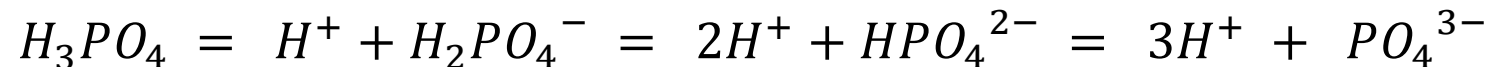
$pK_{a1}=6.3$

$pK_{a2}=10.3$

(at 25°C)

$H_2CO_3^* = \text{sum of true } H_2CO_3 \text{ and } CO_2(aq)$

- **Phosphoric acid**



$pK_{a1}=2.1$

$pK_{a2}=7.2$

$pK_{a3}=12.7$

(at 25°C)

- Others of potential interest: arsenic acid (H_3AsO_4), EDTA (ethylenediaminetetraacetic acid, gives 4 H^+ in total), pyrophosphoric acid ($H_4P_2O_7$), dichromic acid ($H_2Cr_2O_7$), chromic acid (H_2CrO_4), Oxalic acid ($H_2C_2O_4$), Succinic acid ($H_2C_4H_4O_4$)

Analyzing polyprotic acid/base system

Let's work with a diprotic acid, H_2A :

Species involved (5):

Equilibrium constants:

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

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

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

$pH < pK_{a1}$: $[H_2A] \cong C_T \quad \rightarrow \quad p[H_2A] \cong pC_T \quad \text{slope: } 0$

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

$\rightarrow \quad p[H_2A] \cong pC_T - pK_{a1} + pH \quad \text{slope: } 1$

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

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

slope: 2

Analyzing polyprotic acid/base system

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

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

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

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

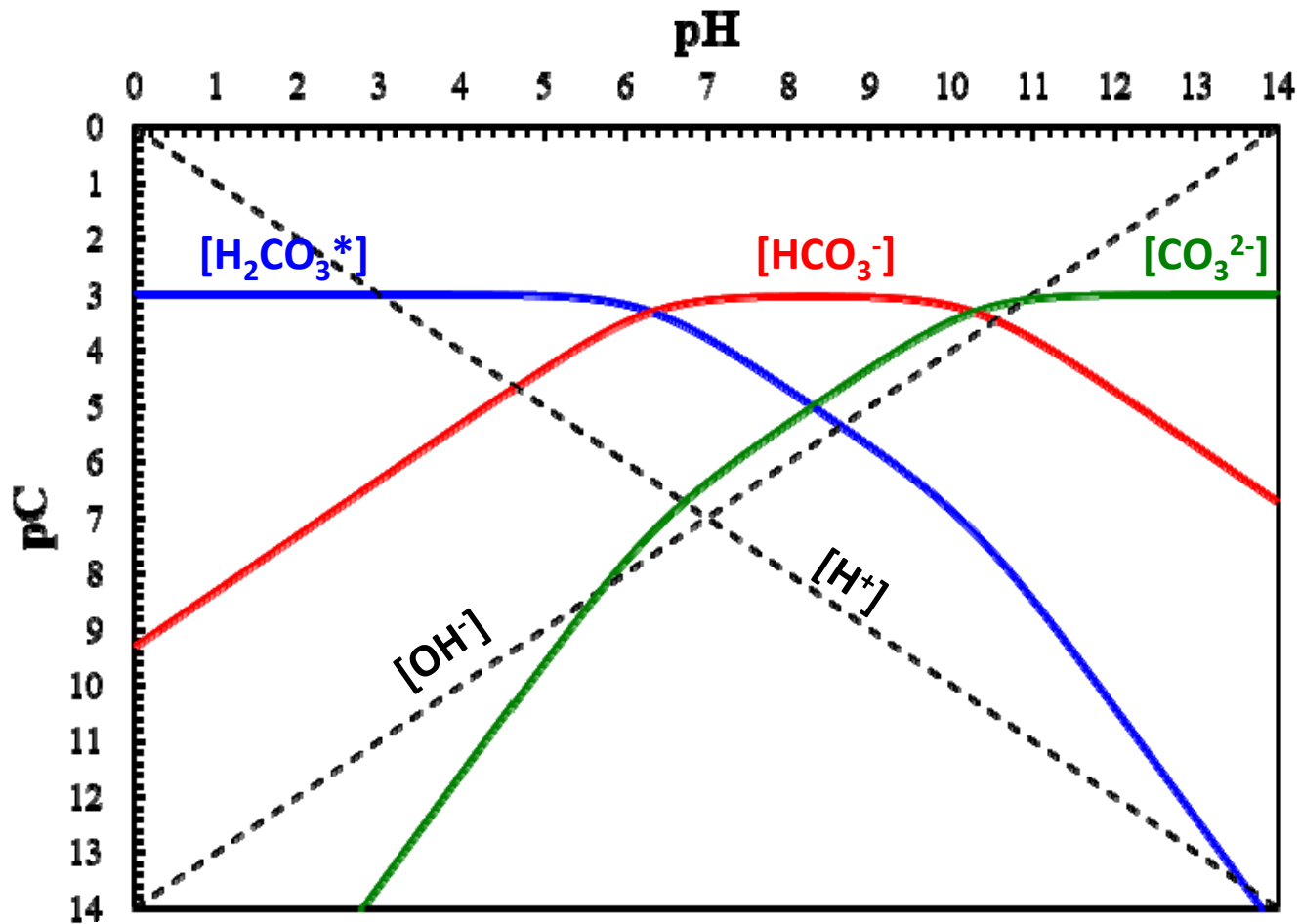
$$[A^{2-}] = C_T \times \left(1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}} \right)^{-1}$$

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

$$pK_{a1} < pH < pK_{a2}: \quad p[A^{2-}] \cong pC_T + pK_{a2} - pH \quad \text{slope: } -1$$

$$pK_{a2} < pH: \quad p[A^{2-}] \cong pC_T \quad \text{slope: } 0$$

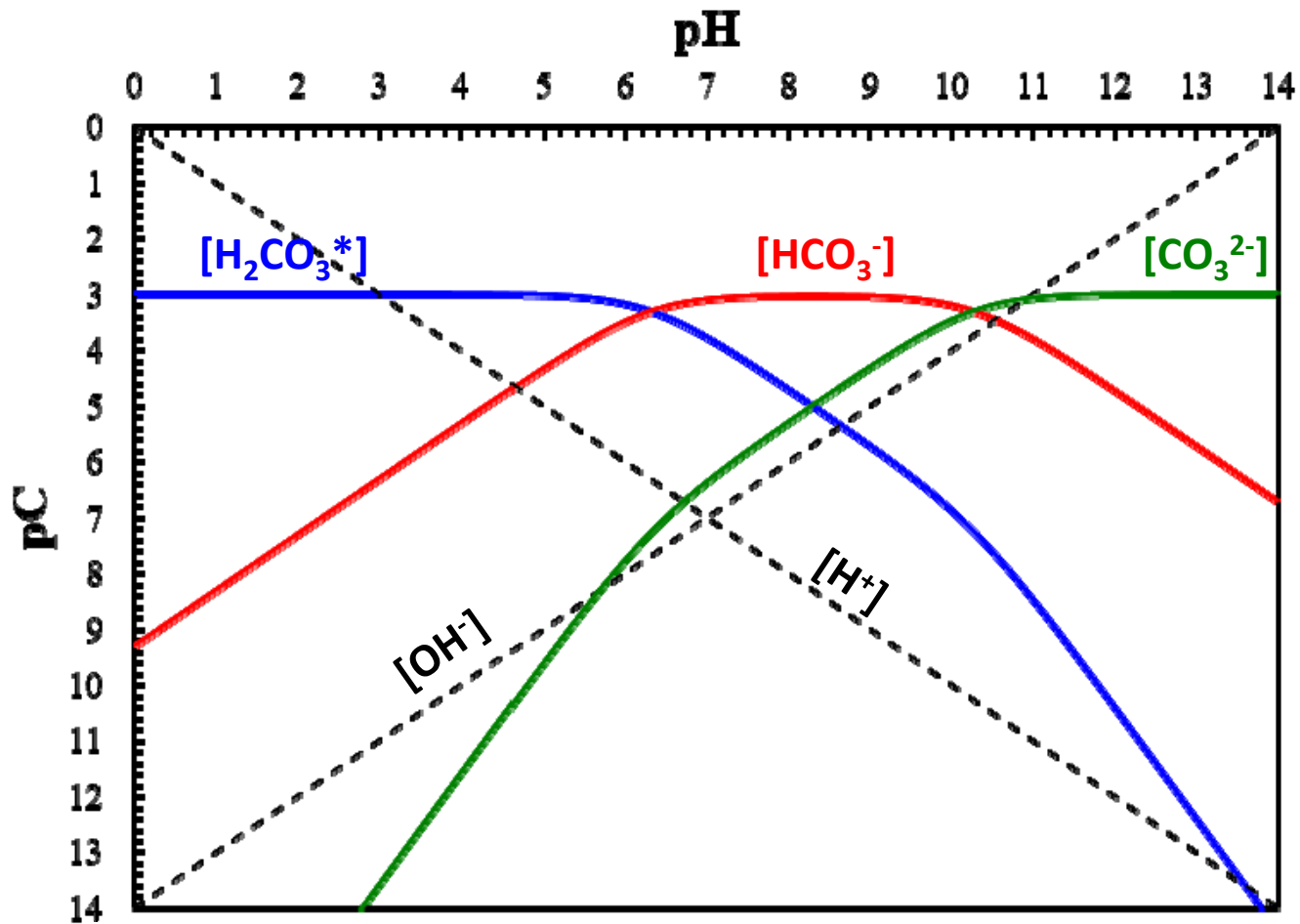
Analyzing polyprotic acid/base system



H_2CO_3 ,
 $C_T = 10^{-3} \text{ M}$
 $\text{pK}_{a1} = 6.3$
 $\text{pK}_{a2} = 10.3$

Apply charge
balance here to
get pH for this
 C_T !

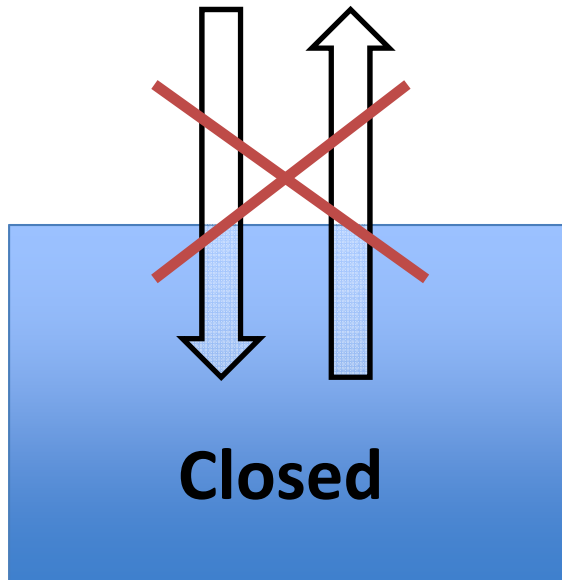
Analyzing polyprotic acid/base system



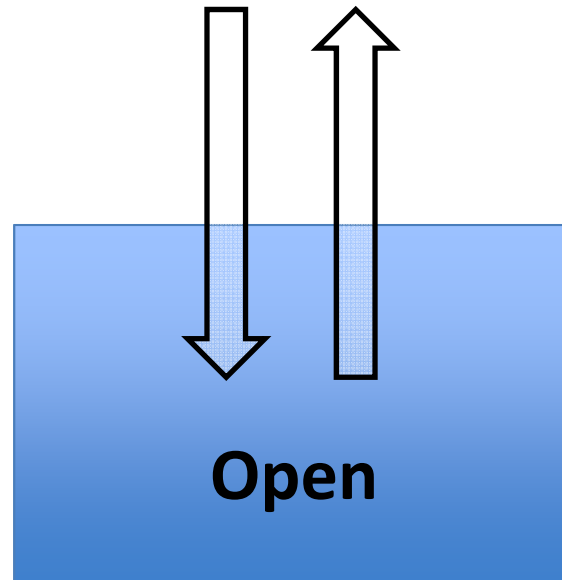
pH of...
 10^{-3} M $NaHCO_3$?
 10^{-3} M Na_2CO_3 ?

Open vs. Closed system

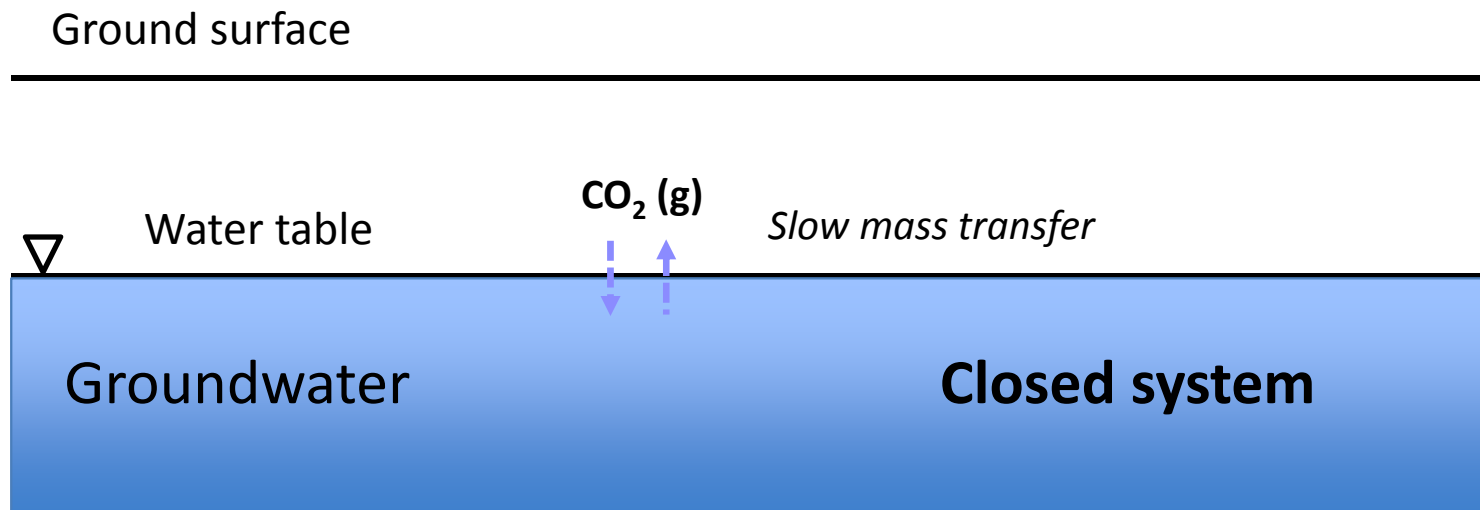
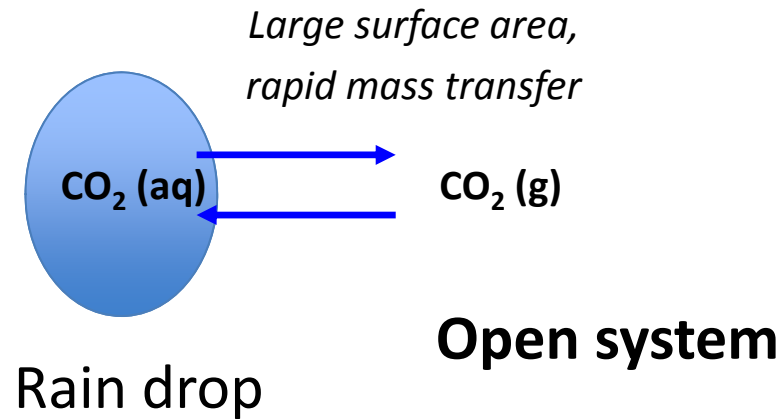
No mass
exchange



Exchange of
mass

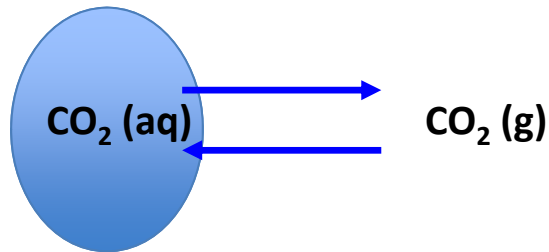


Open & Closed systems in natural waters



Open & Closed systems for carbonates

- **Closed system: $C_T = \text{constant}$**
(we have a solution already!)
- **Open system (ex: rain drop)**



– Equilibrium between gas & aqueous phase:
“Henry’s Law”

$$[\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2}$$

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

K_H = Henry’s law constant (M/atm)

P_{CO_2} = partial pressure of CO_2 (atm)

Open system for carbonates

pH-pC diagram for an open system

Equilibrium constants:

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

~~Mass balance.~~

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

*$C_T \neq \text{constant}$
in an open system*

Air-water CO₂ equilibrium:

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

Open system for carbonates

Equilibrium constants and Air-water equilibrium gives:

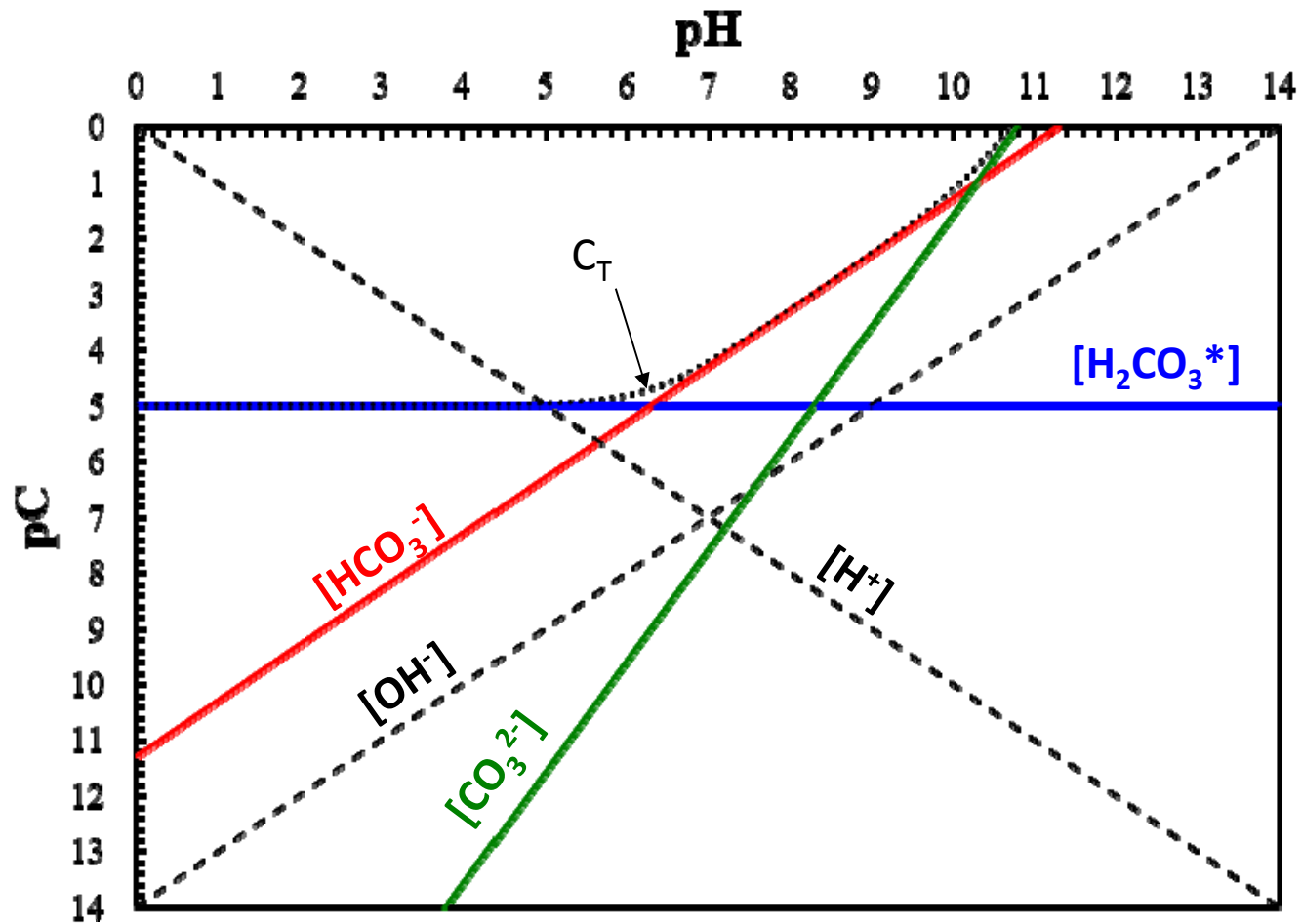
$$p[H_2CO_3] = -\log(K_H P_{CO_2})$$

$$p[HCO_3^-] = -\log(K_H P_{CO_2}) + pK_{a1} - pH$$

$$p[CO_3^{2-}] = -\log(K_H P_{CO_2}) + pK_{a1} + pK_{a2} - 2pH$$

at any pH

Open system for carbonates



$$K_H = 10^{-1.5} \text{ M/atm}$$
$$P_{CO_2} = 10^{-3.5} \text{ atm}$$

(atmospheric air)

Carbonate buffer

- So, rainwater pH can go down to 5.6 in uncontaminated areas
- **Carbonate species ($\text{H}_2\text{CO}_3 - \text{HCO}_3^- - \text{CO}_3^{2-}$)**
 - Most of the time, exist in the highest concentration among 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_{CO_2} may not be $10^{-3.5}$ atm (atmospheric partial pressure) because of biological activities (photosynthesis, respiration)
 - Equilibrium may not be established