ESSENTIALS OF AQUEOUS CARBONATE CHEMISTRY

MOTIVATION: Why do we care?

CO_2 + carbonate minerals are the most important components regulating the pH of natural waters.

CAN ANSWER/UNDERSTAND:

- Why is ocean water almost *always* about pH 8.3?
- Why are some lakes easily acidified by acid rain & others are ~immune?
- What are the impacts of acid-mine drainage or acidic effluents on receiving waters?
- Why do algal blooms cause wild fluctuations in the pH of eutrophic lakes?
- How can we manipulate pH in a treatment system?

$CO_{2(g)}$ ← CONCENTRATION $[CO_2]_g \approx 350$ ppm OR PARTIAL PRESSURE $P_{CO_2} = 3.5 \times 10^{-4}$ a[tm] $= 10^{-3.5}$ at[m]

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3$$

AQUEOUS CARBON DIOXIDE — CARBONIC ACID

Convenient to lump these 2 toge[ther]

Call it: $H_2CO_3^* = CO_{2(aq)} + H_2C[O_3]$

OVERALL RXN:

$$CO_{2(g)} + H_2O \overset{K_H^{CO_2}}{\rightleftharpoons} H_2CO_3^*$$

$$\frac{[H_2CO_3^*]}{P_{CO_2}} = K_H = 10^{-1.5}\ M \cdot atm^{-1}$$

CARBONIC ACID FORMS BICARBONATE AND CARBONATE IONS

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H$$

In laboratory can measure TOTAL INORGANIC CARBON

$$TIC = C_T$$

TIC ↑ LAB USAGE; C_T ↑ CHEMIST'S TERM

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

C_T ↑ LAB REPORT TELLS US TOTAL...

$[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ ↑ BUT NEED EQUILIBRIUM CALCULATIONS TO IDENTIFY AMOUNT OF EACH SPECIES.

CARBONATE EQUILIBRIA

$$CO_{2(g)}$$

$$\upharpoonleft\downharpoonright$$

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$$

CARBONIC ACID — BICARBONATE

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

CARBONATE

$$K_H = \frac{[H_2CO_3^*]}{P_{CO_2}} = 10^{-1.5}$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.3}$$

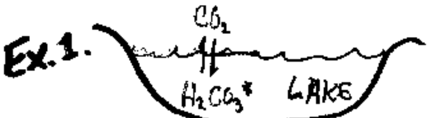
$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

FINALLY...

$\rightleftharpoons Ca^{2+} + CO_3^{2-}$; $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 10^{-8.3}$ "SOLUBILITY PRODUCT"

So AT EQUILIBRIUM amount of CO_2 in the air regulates amount of weak acid $H_2CO_3^*$ in water

Ex.1.



$P_{CO_2} = 10^{-3.5}$ atm

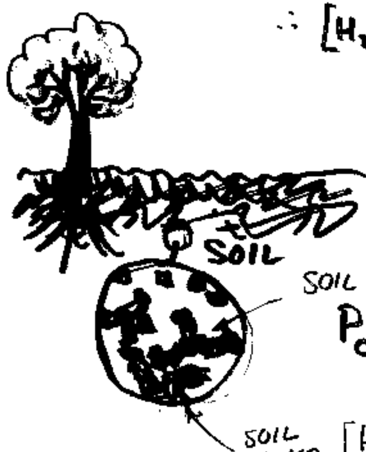
$K_H = 10^{-1.5}$

$\therefore [H_2CO_3^*] = 10^{-1.5}\,10^{-3.5}$

$= 10^{-5.0}$ M

$(= 1 \times 10^{-5}$ M$)$

Ex.2.



SOIL AIR ENRICHED IN CO_2

$P_{CO_2} = 10^{-1.5}$ atm

SOIL WATER $[H_2CO_3^*] = 10^{-1.5} \cdot 10^{-1.5}$

$= 10^{-3.0}$ M

$(= 1 \times 10^{-3}$ M$)$

∴ 100 x more Carbonic acid in soil water than lake

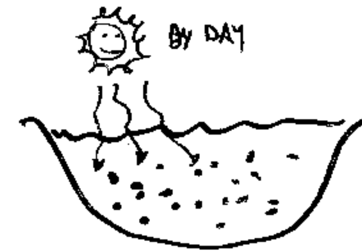
SOMETIMES WATER NOT in EQUILIBRI WITH AIR, but in "INTERNAL" EQUI

NIGHT:

$P_{CO_2} = 10^{-3.5}$

$[H_2CO_3^*] = 10^{-1.5}\,10^{-3.5}$

$= 1 \times 10^{-5}$



DAY:

Rapid photosyn

- Algae take up C quickly
- Mixing with air top is slow.

$P_{CO_2}^{WATER} = 10^{-5.2}$

$[H_2CO_3^*] = 10^{-1.5} \cdot 10^{-5.2} = 10^{-6.7}$

$= 2 \times 10^{-7}$ M

50x less Carbonic

∴ 50x less carbonic acid due to alga

"DOMINANT SPECIES"

Usually only one, maybe two species are important at any pH:

Ex: $K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.3}$

$$\frac{[HCO_3^-]}{[H_2CO_3^*]} = \frac{10^{-6.3}}{10^{-pH}}$$

↑ FOR EQUAL AMTS

$$\frac{1}{1} = \frac{10^{-6.3}}{10^{-6.3}} \Leftarrow$$

At $pH = 6.3 = pK_{a_1}$

$[HCO_3^-] = [H_2CO_3^*]$

At pH 7.3: $\frac{[HCO_3^-]}{[H_2CO_3^*]} = \frac{10^{-6.3}}{10^{-7.3}} = 10$ 10X MORE HCO_3^-

At pH 5.3: $\frac{[HCO_3^-]}{[H_2CO_3^*]} = \frac{10^{-6.3}}{10^{-5.3}} = 0.1$ 10X MORE $H_2CO_3^*$

SAME IS TRUE FOR $\frac{[CO_3^{2-}]}{[HCO_3^-]}$

around $pH = pK_{a_2} = 10.3$

IN GENERAL: