CARBONATE EQUILIBRIA

$CO_{2(g)}$

$\uparrow\downarrow$

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

CARBONIC ACID — BICARBONATE

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

CARBONATE

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

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

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

FINALLY... $CaCO_{3(s)}$ LIMESTONE $\rightleftharpoons Ca^{2+} + CO_3^{2-}$; "SOLUBILITY PRODUCT" $K_{sp} = [Ca^{2+}][CO_3^{2-}]$, $10^{-8.3}$

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

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

LAB REPORT TELLS US TOTAL...

BUT NEED EQUILIBRIUM CALCULATIONS TO IDENTIFY AMOUNT OF EACH SPECIES.

SOMETIMES WATER NOT in EQUILIBRIUM WITH AIR, but in "INTERNAL" EQUILBM

NIGHT:

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

$[H_2CO_3^*] = 10^{-1.5}\,10^{-3.5} = 10^{-5}$

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

DAY:

Rapid photosynthesis

- Algae take up CO_2 quickly
- Mixing with air at top is slow.

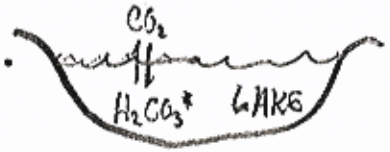
$P_{CO_2}^{WATER} = 10^{-5.2}$

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

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

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.

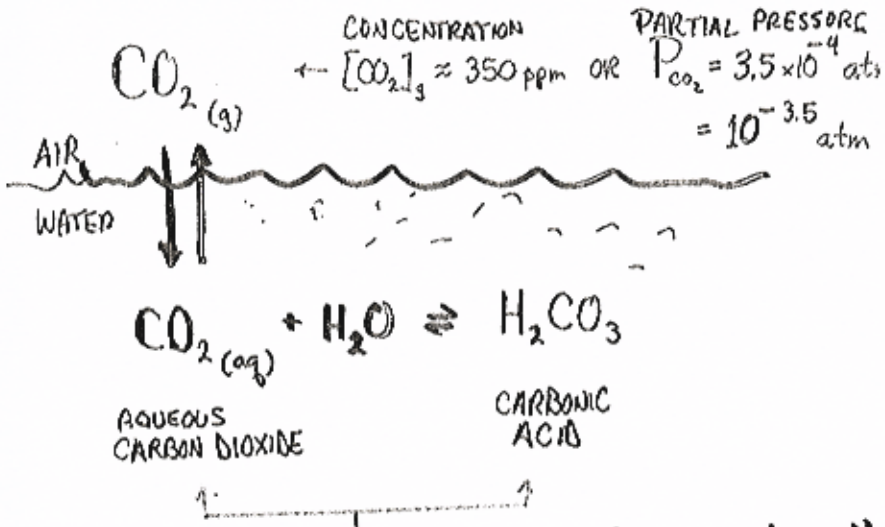
$P_{CO_2} = 10^{-1.5}$ atm

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

$= 10^{-3.0} M$

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

$\therefore$ 100x more carbonic acid in soil water than lake



Convenient to lump these 2 together

Call it: $H_2CO_3^* = CO_{2\,(aq)} + H_2CO_3$

Overall Rxn:

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

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

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

"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 ↑

$$\frac{1}{1} = \frac{10^{-6.3}}{10^{-6.3}} \Leftrightarrow \begin{cases} \text{AT } pH = 6.3 \\ = pK_{a_1} \\ [HCO_3^-] = [H_2CO_3^*] \end{cases}$$

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: