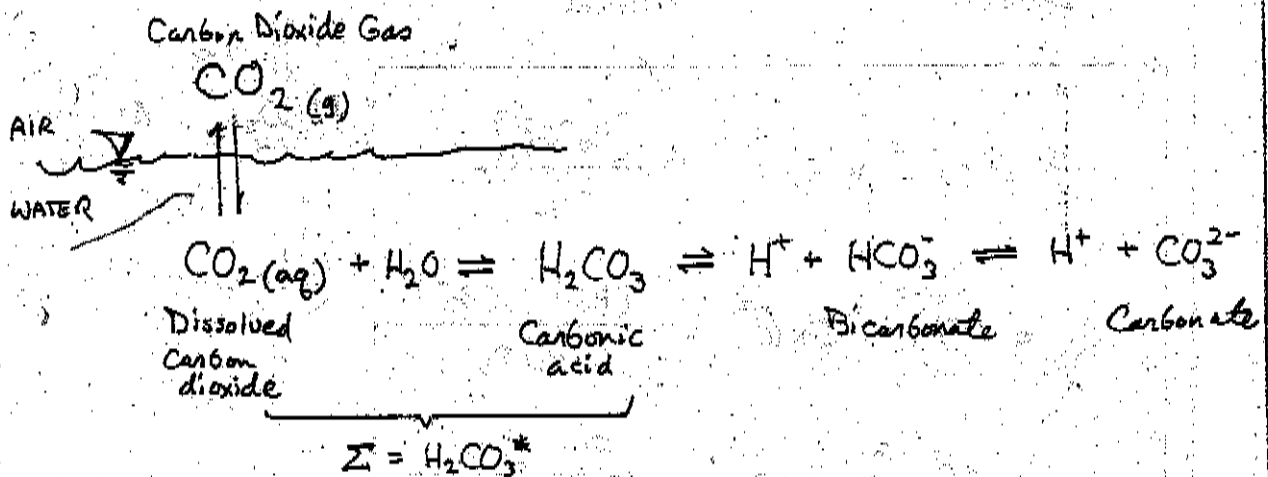


SUMMARY OF CARBONATE CHEMISTRY



I. GAS/WATER EXCHANGE

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

$$K_H^{\text{CO}_2} = 10^{-1.5} \text{ M atm}^{-1}$$

$$P_{\text{CO}_2}^{\text{air}} = 10^{-3.5} \text{ atm}$$

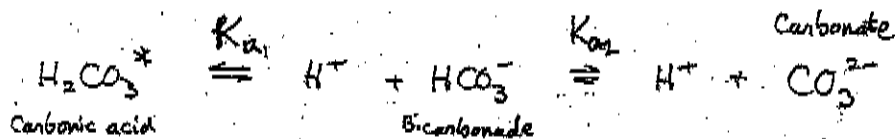
(for normal air)

$K_H^{\text{CO}_2}$ = Henry's Law Constant for CO_2 solubility in H_2O
(is fn of Temp, like all K 's)

P_{CO_2} = partial pressure of CO_2 in the relevant gas phase.

- P_{CO_2} can be considerably higher in the subsurface, esp. if there is biological activity.
- P_{CO_2} can be lower in waters where algae or other plants are photosynthesizing and thus taking CO_2 out of the water.
- If the P_{CO_2} is fixed (e.g., by equilibrium that is "open" to the atmosphere, then (at equilibrium), $[\text{H}_2\text{CO}_3^*]$ is also fixed.
- Hence often is important to decide if water system is "open" or closed with respect to atmospheric CO_2
 - A well mixed river, pond, shallow lake: \sim OPEN ($P_{\text{CO}_2} \sim$ const.)
 - Shallow groundwater: Partially open; open to soil-gas CO_2
 - Deep groundwater: Closed in most cases (P_{CO_2} varies)
 - Water in a distribution (pipe) system; \sim closed unless vented.

II. SOLUTION EQUILIBRIA



$$\begin{aligned}
 K_{\text{CO}_2} &= 10^{-1.5} = 5 \times 10^{-2} = \frac{[\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2}} \\
 K_{a1} &= 10^{-6.3} = 5 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \\
 K_{a2} &= 10^{-10.3} = 5 \times 10^{-11} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \\
 K_{\text{sp}} &= 10^{-8.3} = 5 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]
 \end{aligned}$$

$\text{MCO}_3(\text{s}) \rightleftharpoons \text{M}^{2+} + \text{CO}_3^{2-}$ K_{sp}
 Solid CO₂ mineral (like calcite, CaCO₃(s))
 (For example if you have calcite in sediment from $K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.3}$)

We can see some general relationships among these species as follows:

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = \frac{10^{-6.3}}{[\text{H}^+]}$$

so at pH 6.3, $[\text{H}^+] = 10^{-6.3}$ and

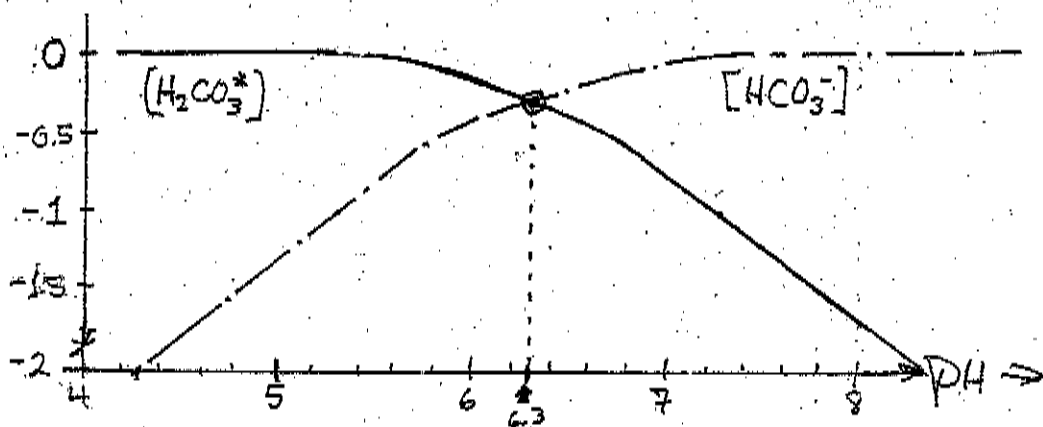
$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = 1.0 \quad \therefore [\text{HCO}_3^-] = [\text{H}_2\text{CO}_3^*]$$

For pH < 6.3 : $[\text{HCO}_3^-] < [\text{H}_2\text{CO}_3^*]$

For pH > 6.3 : $[\text{HCO}_3^-] > [\text{H}_2\text{CO}_3^*]$

We can draw this on a convenient log-log plot:

$C_i = [\text{H}_2\text{CO}_3^*] \text{ or } [\text{HCO}_3^-]$
 $C_T = \text{Total}$



We see that: $H_2CO_3^*$ is dominant if pH much below 6.3
 HCO_3^- " " " " " " above 6.3

Right at 6.3 the two are equal

REPEAT for $[HCO_3^-] \rightleftharpoons [CO_3^{2-}]$

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

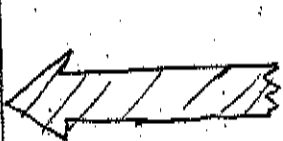
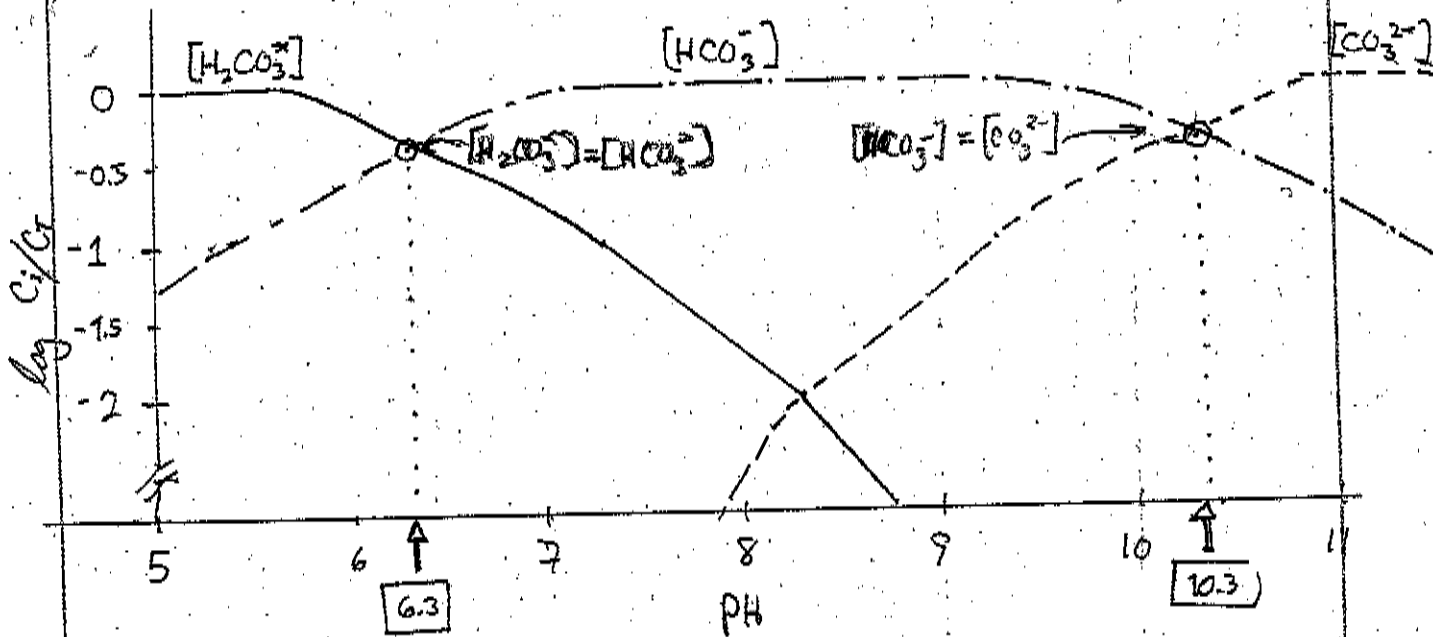
At pH 10.3 $[CO_3^{2-}] = [HCO_3^-]$

pH < 10.3 $[CO_3^{2-}] < [HCO_3^-]$

pH > 10.3 $[CO_3^{2-}] > [HCO_3^-]$

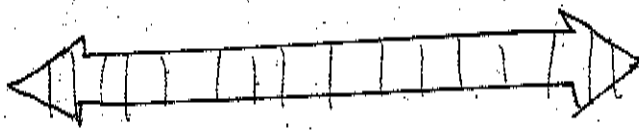
$2 = 0.3 \log$ units

Add this info to our prior chart:



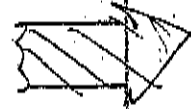
$H_2CO_3^*$
DOMINANT

$$[H_2CO_3] \approx C_T$$



HCO_3^-
DOMINANT

$$[HCO_3^-] \approx C_T$$



CO_3^{2-}
DOMINANT

$$[CO_3^{2-}] \approx C_T$$

Where $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = \text{Total Inorganic Carbon (TIC)}$

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Keep this general framework in mind. It can give you a practical, "engineer's" view of the carbonate chemistry.

EXAMPLES: 1. Routine water samples often analyzed for "DIC" or dissolved inorganic carbon. That's the same as C_T on the previous page.

If a lab report tells you a wastewater sample has: PH 8.3

$$\text{DIC} = 6 \times 10^{-4} \text{ M}$$

You can work out the carbonate speciation easily on the back of an envelope (or even off the top of your head, with experience.)

(A) At PH 8.3 $[\text{HCO}_3^-]$ dominates

$$\text{so } [\text{HCO}_3^-] \approx C_T = 6 \times 10^{-4} \text{ M} \\ = 10^{-3.2} \text{ M}$$

ANS.

$$\text{(B)} \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = \frac{10^{-6.3}}{10^{-\text{pH} - 8.3}} \Rightarrow [\text{H}_2\text{CO}_3^*] = \frac{1}{100} [\text{HCO}_3^-] = 6 \times 10^{-6} \text{ M}$$

ANS.

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{10^{-10.3}}{10^{-8.3}} \Rightarrow [\text{CO}_3^{2-}] = \frac{1}{100} [\text{HCO}_3^-] = 6 \times 10^{-6} \text{ M}$$

ANS.

And $[\text{HCO}_3^-]$ is ~100 times more important than either $[\text{H}_2\text{CO}_3^*]$ or $[\text{CO}_3^{2-}]$

⇒ Even if you use MINTQA2, this would be a quick check to see that you set up the problem right. ("Reality Check")

2. You have an industrial waste with PH 4.6 and only source of C_T is the air. What is the DIC if the water is in equilibrium w/ air?

(A) At PH 4.6, $C_T = [\text{H}_2\text{CO}_3^*]$

$$\text{(B)} [\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2} = 10^{-1.5} 10^{-3.5} = 10^{-5} = 1 \times 10^{-5} \text{ M}$$

ANS.