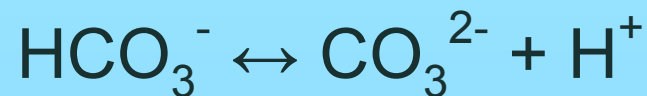# Solubility of CO_2 and Carbonate Equilibrium

"Carbonic acid"

$$CO_2(g) \leftrightarrow CO_2(aq) \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$$

$$CO_2(g) \leftrightarrow CO_2(aq) + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

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

$$H_2O \leftrightarrow H^+ + OH^-$$

Solubility of CO_2 and Carbonate Equilibrium

$$K_H \qquad\qquad K_1 \qquad K_2$$

$$CO_2(g) \leftrightarrow CO_2(aq) \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$$

1. $K_H = [H_2CO_3]/P_{CO2}$ $= 3 \times 10^{-2}$ M atm^{-1} = $10^{-1.5}$ M atm^{-1}

2. $K_1 = [HCO_3^-][H^+]/[H_2CO_3]$ $= 9 \times 10^{-7}$ M = $10^{-6.1}$ M

3. $K_2 = [CO_3^{2-}][H^+]/[HCO_3^-]$ $= 2.7 \times 10^{-10}$ M = $10^{-9.6}$ M

4. $K_w = [H^+][OH^-]$ $= 10^{-14}$ M^2

Note: Values of these equil. constants are sensitive to temperature and ionic strength of the solution; these values are appropriate to seawater.

CO$_2$ Partitioning
Atmosphere - Ocean

pH of Natural Waters
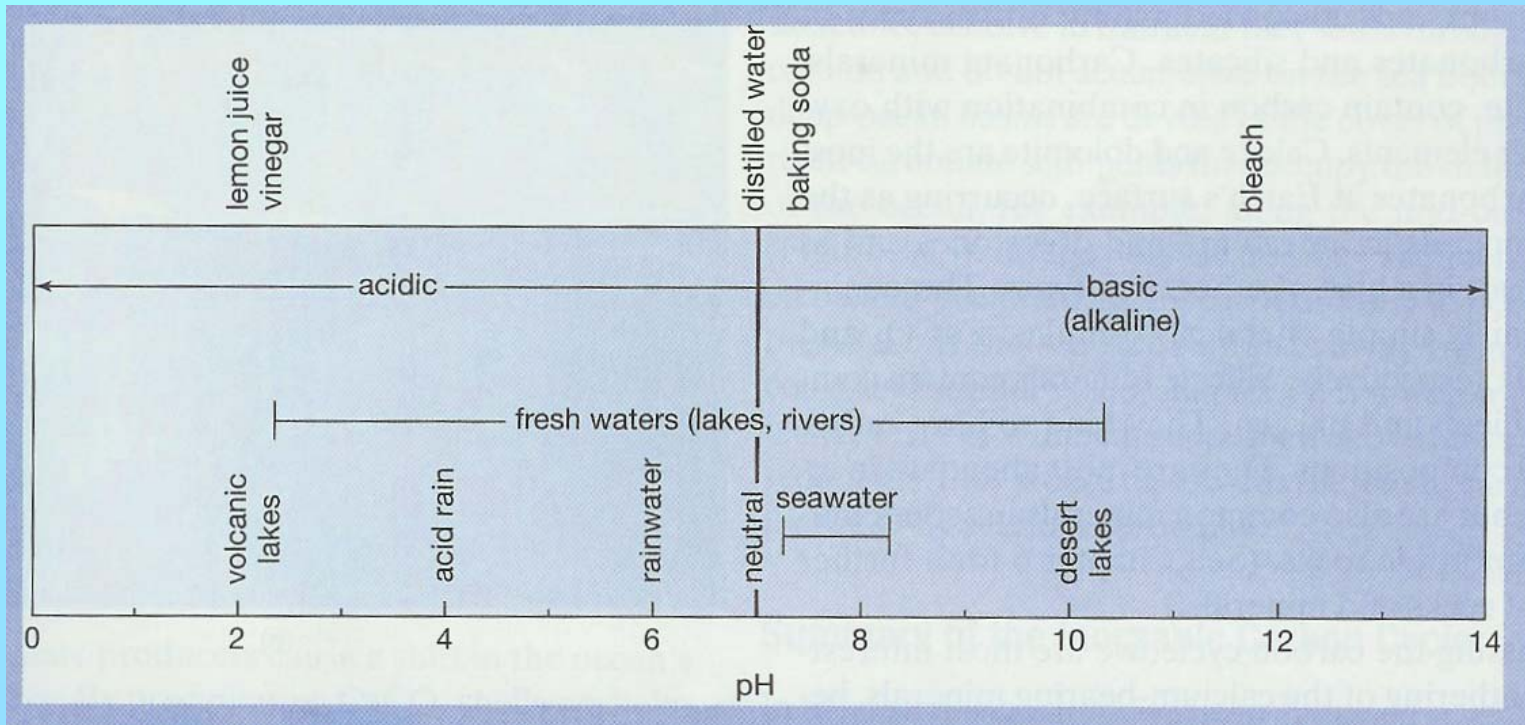
So we want to understand what controls pH…

pH of Natural Waters
General concept…

At least six unknowns:

- H^+, OH^-

- P_{CO2}

- H_2CO_3, HCO_3^-, CO_3^{2-}

∴ Need at least six equations:

- Equilibrium expressions 1 - 4

- Typically, constraint on either P_{CO2} ("open system") or total moles carbon ("closed system")

- Charge balance; $\Sigma n[i^{n+}] = \Sigma m[j^{m-}]$

pH of Natural Waters
Pure water in contact with atmosphere

- Six unknowns

- Equilibrium expressions (4 equations)

- $P_{CO2} = 3.5 \times 10^{-4}$ atm (1 more equation)

- Charge balance (6th equation):

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

- Strategy: Rewrite charge balance equation in terms of $[H^+]$ and known quantities…

pH of Natural Waters
Example: *Pure water in contact with atmosphere*

$$[H^+] = K_1 K_H P_{CO2}/[H^+] + 2K_1 K_2 K_H P_{CO2}/[H^+]^2 + K_w/[H^+]$$

Can solve rigorously for $[H^+]$. Alternatively, make a simplifying assumption:

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

In this case:

$$[H^+] = K_1 K_H P_{CO2}/[H^+] + K_w/[H^+]$$

or

$$[H^+]^2 = K_1 K_H P_{CO2} + K_w$$

This is easily solved:

For pure water @25°C: K_1 = 4.45 x 10^{-7} M; K_H = 3.39 x 10^{-2} M/atm

$\therefore$ [H+] = 2.4 x 10-6 M

pH = 5.62

$\therefore$ "Acid rain" is a term applied to pH < 5

pH of Natural Waters
Assess simplifying assumption…

Is it fair to assume $[CO_3^{2-}] << [HCO_3^-]$?

$K_2 = [CO_3^{2-}][H^+]/[HCO_3^-] = 10^{-10.33}$ (pure water, 25°C)

So: $[CO_3^{2-}]/[HCO_3^-] = 10^{-10.33}/[H^+]$

Clearly, $[CO_3^{2-}]/[HCO_3^-] << 1$ as long as $[H^+] >> 10^{-10.33}$

i.e., as long as pH << 10.33

This is true in most natural waters

CO_2 Solubility, HCO_3^- and CO_3^{2-}

Another perspective

$CO_2 + H_2O \leftrightarrow H_2CO_3$

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ Net direction if pH >~ 6
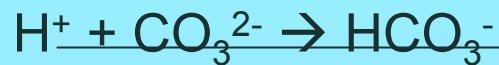
$H^+ + CO_3^{2-} \rightarrow HCO_3^-$ Net direction if pH <~ 10

$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$

Consider CO$_2$ Solubility (again)

P_{CO2} $= [H_2CO_3]/K_H$

$= [H^+][HCO_3^-]/(K_1K_H)$

$= (K_2[HCO_3^-]/[CO_3^{2-}])([HCO_3^-]/(K_1K_H))$

$= K_3[HCO_3^-]^2/[CO_3^{2-}]; \; (K_3 = K_2/(K_1K_H))$

So what?

pH of Natural Waters
Alkalinity

- Imagine we dissolve some $CaCO_3$ in the system

- Now: $2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

- In this case, $[H^+]$ is free to have lower values (pH > 7) as long as $[Ca^{2+}]$ is present

pH of Natural Waters
Alkalinity

Not all cation sources will work this way…

- Imagine we dissolve some NaCl into the system
- Now: $[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [Cl^-] + [OH^-]$

$$But: [Na^+] = [Cl^-], right?$$

- So, no effect on charge balance equation
- To cope: Distinguish between "conservative" and "nonconservative" ions…

pH of Natural Waters
Alkalinity

- **Conservative ions**: Ions whose concentrations are *not* affected by pH (or pressure or temperature; not important variables here)
  - Examples: Ca^{2+}, Na^+, NO_3^-, K^+, Cl^-, etc.

- **Nonconservative ions**: Ions whose concentrations are affected by pH
  - Examples: CO_3^{2-}, HCO_3^-, NH_4^+, $B(OH)_4^-$, H^+, OH^-

- **"Alkalinity"** $\equiv \Sigma n[i^{n+}] - \Sigma m[j^{m-}]$ where i and j are only conservative ions; alkalinity is what's left over after these are accounted for.
  - Units: equiv./liter

pH of Natural Waters
Alkalinity

- If we consider only HCO_3^-, CO_3^{2-}, OH^- and H^+ and conservative ions, then we may write:

- $\Sigma n[i^{n+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + \Sigma m[j^{m-}]$

- $\Sigma n[i^{n+}] - \Sigma m[j^{m-}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

- Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

- Typically, Alkalinity ~ $[HCO_3^-] + 2[CO_3^{2-}] \equiv Alk_{carb}$

- For seawater, Alkalinity ~ 2.3×10^{-3} equiv/liter

- Fresh waters , Alkalinity   0 to 5 meq/liter

pH of Natural Waters
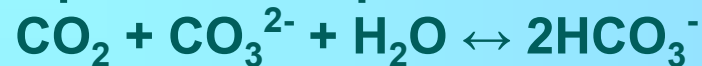## *Alkalinity*

- Alkalinity of seawater allows it to dissolve more CO_2

- Higher alkalinity leads to lower $[H^+]$ and higher pH

- Any reaction that introduces $[H^+]$ lowers alkalinity

  - *e.g.*, $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

- Any reaction that raises $[CO_3^{2-}]$ or $[HCO_3^-]$ raises alkalinity

  - – *e.g.*, $CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$

CO_2 Solubility, HCO_3^- and CO_3^{2-}

$$P_{CO2} = K_3[HCO_3^-]^2/[CO_3^{2-}]$$

This is the equilibrium expression for the reaction:
$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$$
i.e., solubility of CO_2 consumes CO_3^{2-}, produces HCO_3^-;

Note that addition of CO_2 itself does *not* affect Alkalinity (gain 2 moles HCO_3^- for every CO_3^{2-})

Note also that capacity for CO_2 uptake determined by $[CO_3^{2-}]$

CO_2 Solubility, HCO_3^- and CO_3^{2-}

$$Alk \sim [HCO_3^-] + 2[CO_3^{2-}]$$

$$\Sigma CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

$$\sim [HCO_3^-] + [CO_3^{2-}]$$

$$P_{CO2} = K_3[HCO_3^-]^2/[CO_3^{2-}]$$

Algebra…

$$[CO_3^{2-}] = Alk - \Sigma CO_2$$

$$[HCO_3^-] = 2\,\Sigma CO_2 - Alk$$

$$P_{CO2} = K_3(2\,\Sigma CO_2 - Alk)^2/(Alk - \Sigma CO_2)$$

i.e., P_{CO2} is controlled by Alk and ΣCO_2

Distribution of major species of dissolved inorganic carbon at 20°C
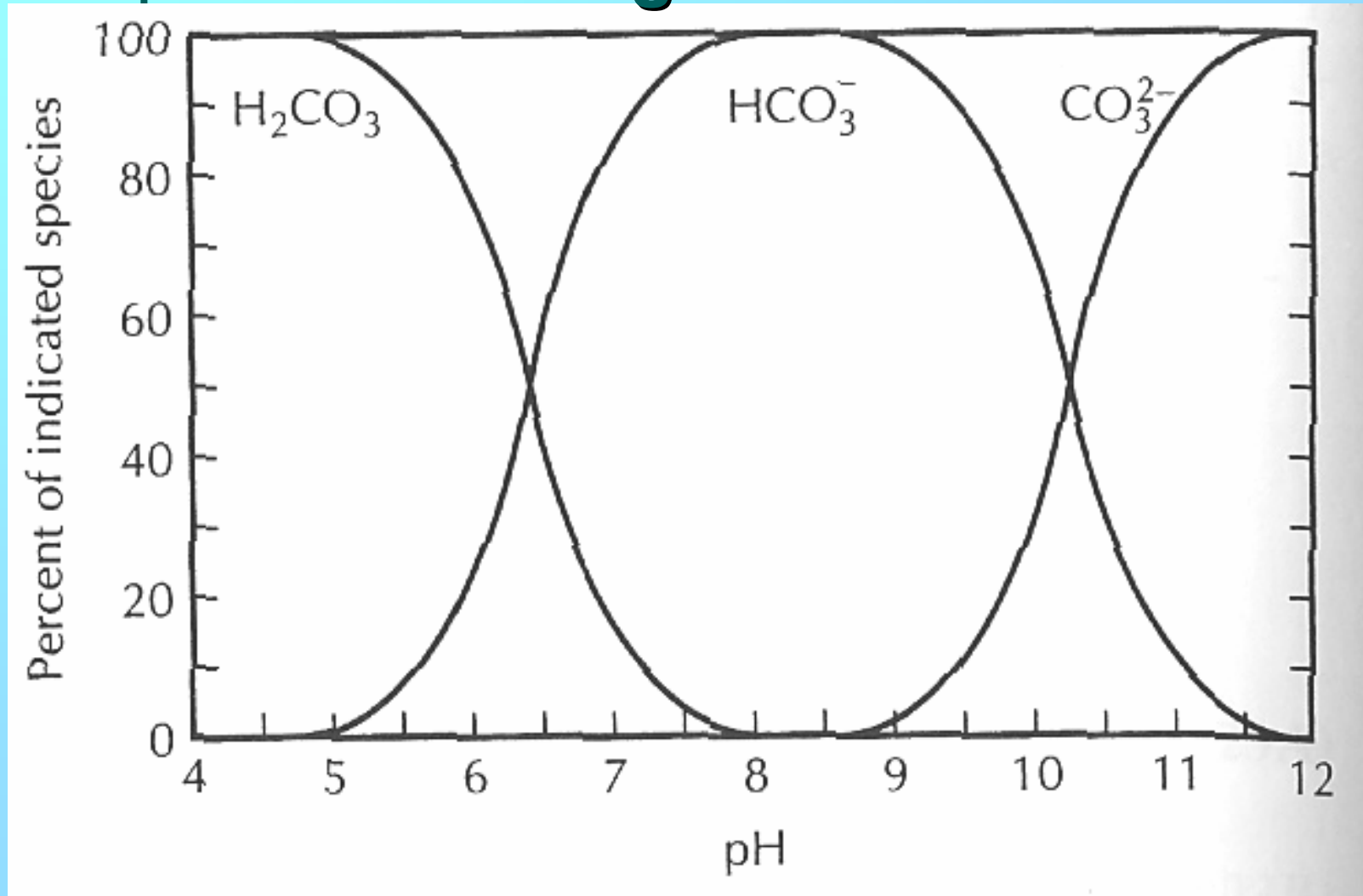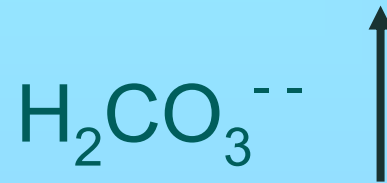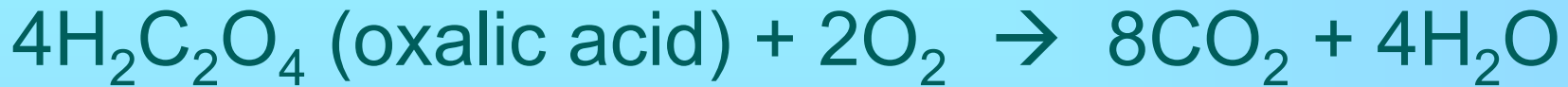

Figure 9.1 Fetter, *Applied Hydrogeology 4th Edition*

Organic acids (e.g.. Oxalic acid)

- * O Organic material breaks down and releases acids (pH ~ 5). These natural acids play an important role in weathering in absence of human activity; behaves very much like carbonic acid

$$4H_2C_2O_4 \text{ (oxalic acid)} + 2O_2 \rightarrow 8CO_2 + 4H_2O$$

$$H_2CO_3^{--}$$

CO$_2$ in three forms in ocean (H_2CO_3, HCO_3-, $CO_3=$):

- CO$_2$ (aq)(H$_2$CO$_3$) = 10-5 M

$$= kPCO_2 = 10^{-1.5} \text{ x } 10^{-3.5}$$

- **HCO$_3$-** = $10^{-2.8}$ M Dominant pH 6.3 - 10.3
- CO$_3^=$ = $10^{-3.8}$ M

CO$_2$ is in equilibrium at the surface of the ocean

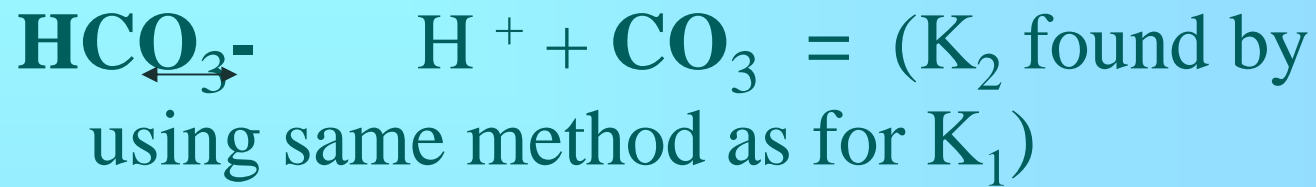$$[CO_2] = k\mathbf{P_{CO2}} \qquad pH = 8.4$$

$$[H^+] = 10^{-8.4}$$

- $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$K_1 = \dfrac{[HCO_3^-][H^+]}{[H2CO_3]} = 10^{-6.3} \ , \ pK_1 = 6.3$
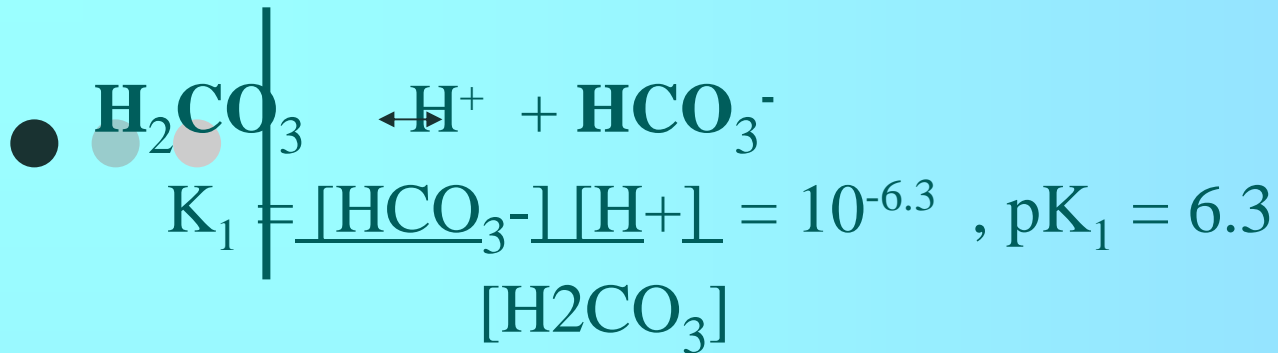
(When $A + B \rightarrow C + D$, $K = $ products/reactants $= $ [C][D]/[A][B]).

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

then $\dfrac{[HCO_3^-]}{[H_2CO_3]} = 1$

and $H^+ = 10^{-6.3}$ and pH = 6.3

$pK_2 = 10.3$

$HCO_3^- \longleftrightarrow H^+ + CO_3^= $ (K_2 found by using same method as for K_1)

This balance is controlled by H^+, pK_1, pK_2, charge balance

<u>Surface Ocean</u> $Ca^{++} + CO_3^= \rightarrow$ **$CaCO_3$ (s)** (a percentage sinks and redissolves)

<u>CO_2 Removal</u> $CO_2 + H_2O \rightarrow CH_2O + O_2$

$H_2CO_3 + CO_3^= \rightarrow 2HCO_3-$
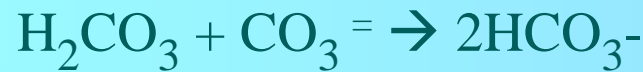
<u>Photosynthesis</u> More CO_2 will dissolve from atmosphere

$[CO_2] = kPCO_2$

<u>Deep Water</u> $\rightarrow$ <u>Respiration</u> $CH_2O + O_2 \rightarrow CO_2 + H_2O$

$H_2CO_3 + CO_3^= \rightarrow 2\ HCO_3-$
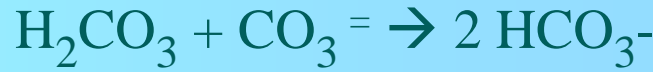
Shifts pH down, increases [H+]

Higher **H_2CO_3** or (PCO_2) $\rightarrow$ **3 - 5 times**

Lower pH, **$CO_3^=$** pH decreases, 8.4 at **surface**

7.8 deep water
(Pacific)

○ 1. Lack of $CaCO_3$

● 2. Thin or no soil = high surface flow into lakes

3. Thick soil: large exchangeable pool of Ca^{2+}

Review of Equilibrium:

$xA + yB \rightarrow zC + wD$ $\qquad K_{eq} = \dfrac{[C]^z[D]^w}{[A]^x[B]^y}$ $\qquad = 10^{-5.6} \rightarrow pK = 5.6$

Acid : $\quad HaC \leftrightarrow H^+ + Ac^-$ $\qquad K_{eq} = \dfrac{[H^+][Ac^-]}{[Hac]}$ $\qquad [Ac^-] = 10^{-7.3}$

$[H_2CO_3] = k_T P_{CO2}$ $\qquad$ at $P_{CO2} = 10^{-3.45}$ $\qquad [H_2CO_3] = 10^{-5}$ M

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ $\quad k = 10^{-1.55}$

$pk_1 = +5.7$ $\qquad H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ $\qquad k_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$
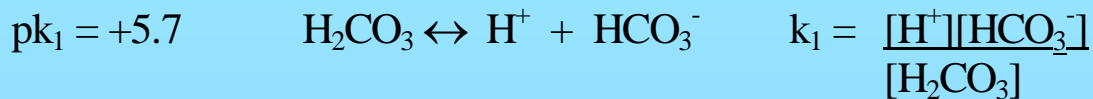
$10^{-9.2} = 10^{-10.7} = [H^+][HCO_3^-]$

$[HCO_3^-] = [H^+] = 10^{-5.4} \rightarrow pH = 5.4$ $\qquad k_1 = 10^{-5.7}$

Soil $P_{CO2} \sim 10,000$ ppm $\quad \rightarrow 10^{-2} \rightarrow pH{\sim}4.6$