Solubility of CO$_2$ and Carbonate Equilibrium

CO$_2$(g) ↔ CO$_2$(aq) ↔ H$_2$CO$_3$ ↔ HCO$_3^-$ ↔ CO$_3^{2-}$

CO$_2$(g) ↔ CO$_2$(aq) + H$_2$O ↔ H$_2$CO$_3$

H$_2$CO$_3$ ↔ HCO$_3^-$ + H$^+$

HCO$_3^-$ ↔ CO$_3^{2-}$ + H$^+$

H$_2$O ↔ H$^+$ + OH$^-$
Solubility of CO$_2$ and Carbonate Equilibrium

1. $K_H = \frac{[H_2CO_3]}{P_{CO_2}} = 3 \times 10^{-2}$ M atm$^{-1} = 10^{-1.5}$ M atm$^{-1}$
2. $K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 9 \times 10^{-7}$ M = $10^{-6.1}$ M
3. $K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 2.7 \times 10^{-10}$ 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...

KKC Box Fig. 8-2
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)
- $P_{CO_2} = 3.5 \times 10^{-4}$ 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*

\[
[H^+] = K_1 K_H P_{CO_2}/[H^+] + 2K_1 K_2 K_H P_{CO_2}/[H^+]^2 + K_w/[H^+]
\]

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

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

In this case:

\[
[H^+] = K_1 K_H P_{CO_2}/[H^+] + K_w/[H^+]
\]

or

\[
[H^+]^2 = K_1 K_H P_{CO_2} + K_w
\]

This is easily solved:

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

\[ \therefore [H^+] = 2.4 \times 10^{-6} \) M\]

\[ \text{pH} = 5.62 \]

\[ \therefore \text{“Acid rain” is a term applied to pH < 5} \]
pH of Natural Waters
Assess simplifying assumption…

Is it fair to assume $[\text{CO}_3^{2-}] << [\text{HCO}_3^-]$?

\[
K_2 = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-] = 10^{-10.33} \text{ (pure water, 25°C)}
\]
So: $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 10^{-10.33}/[\text{H}^+]$

Clearly, $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] << 1$ as long as $[\text{H}^+] >> 10^{-10.33}$

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

This is true in most natural waters
Another perspective

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \]

\[ \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{Net direction if pH} \gtrsim 6 \]

\[ \text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- \quad \text{Net direction if pH} \lesssim 10 \]

\[ \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- \]
Consider CO₂ Solubility (again)

\[ P_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{K_H} \]

\[ = \frac{[\text{H}^+][\text{HCO}_3^-]}{(K_1K_H)} \]

\[ = \frac{(K_2[\text{HCO}_3^-]/[\text{CO}_3^{2-}])([\text{HCO}_3^-]/(K_1K_H))}{[\text{CO}_3^{2-}]} \]

\[ = K_3[\text{HCO}_3^-]^2/[\text{CO}_3^{2-}]; \ (K_3 = K_2/(K_1K_H)) \]

So what?
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: $[\text{Na}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Cl}^-] + [\text{OH}^-]$
  
  But: $[\text{Na}^+] = [\text{Cl}^-]$, 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” ≡ Σ$n[i^{+}]$ - Σ$m[j^{-}]$ where i and j are only conservative ions; alkalinity is what’s left over after these are accounted for.
  - Units: equiv./liter
If we consider only $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, $\text{OH}^-$ and $\text{H}^+$ and conservative ions, then we may write:

$\Sigma n[i^{n+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + \Sigma m[j^{m-}]$

$\Sigma n[i^{n+}] - \Sigma m[j^{m-}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$

Alkalinity $= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$

Typically, Alkalinity $\sim [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \equiv \text{Alk}_{\text{carb}}$

For seawater, Alkalinity $\sim 2.3 \times 10^{-3}$ 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., $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$
- Any reaction that raises [CO$_3^{2-}$] or [HCO$_3^-$] raises alkalinity.
  - e.g., $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
CO₂ Solubility, HCO₃⁻ and CO₃²⁻

\[ P_{CO₂} = K₃[HCO₃⁻]^2/[CO₃²⁻] \]

This is the equilibrium expression for the reaction:
\[ CO₂ + CO₃²⁻ + H₂O \leftrightarrow 2HCO₃⁻ \]
i.e., solubility of CO₂ consumes CO₃²⁻, produces HCO₃⁻;

Note that addition of CO₂ itself does not affect Alkalinity
(gain 2 moles HCO₃⁻ for every CO₃²⁻)

Note also that capacity for CO₂ uptake determined by [CO₃²⁻]
CO₂ Solubility, HCO₃⁻ and CO₃²⁻

\[
\begin{align*}
\text{Alk} & \quad \sim [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \\
\Sigma \text{CO}_2 & \quad = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\
& \quad \sim [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\
P_{\text{CO}_2} & \quad = K_3[\text{HCO}_3^-]^2/[\text{CO}_3^{2-}] \\
\end{align*}
\]

Algebra...

\[
\begin{align*}
[\text{CO}_3^{2-}] & \quad = \text{Alk} - \Sigma \text{CO}_2 \\
[\text{HCO}_3^-] & \quad = 2 \Sigma \text{CO}_2 - \text{Alk} \\
P_{\text{CO}_2} & \quad = K_3(2 \Sigma \text{CO}_2 - \text{Alk})^2/(\text{Alk} - \Sigma \text{CO}_2) \\
\end{align*}
\]

i.e., \( P_{\text{CO}_2} \) is controlled by Alk and \( \Sigma \text{CO}_2 \)
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)

* 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

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

\[ H_2CO_3 \rightarrow \]
CO$_2$ in three forms in ocean (H$_2$CO$_3$, HCO$_3^-$, CO$_3^{2-}$):

- CO$_2$ (aq)(H$_2$CO$_3$) = $10^{-5}$ M
  - $= k$PCO$_2 = 10^{-1.5} \times 10^{-3.5}$
- HCO$_3^-$ = $10^{-2.8}$ M Dominant pH 6.3 - 10.3
- CO$_3^{2-}$ = $10^{-3.8}$ M

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

$$[CO_2] = kP_{CO_2} \quad \text{pH} = 8.4$$

$$[H^+] = 10^{-8.4}$$
\( H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \)

\[
K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 10^{-6.3}, \quad pK_1 = 6.3
\]

(When \( A + B \rightarrow C + D \), \( K = \frac{\text{products}}{\text{reactants}} = \frac{[C][D]}{[A][B]} \)).

When \( [HCO_3^-] = [H_2CO_3] \)

then \( \frac{[HCO_3^-]}{[H_2CO_3]} = 1 \)

and \( H^+ = 10^{-6.3} \) and \( \text{pH} = 6.3 \)
pK$_2$ = 10.3

$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^-$ = (K$_2$ found by using same method as for K$_1$)

This balance is controlled by H$^+$, pK$_1$, pK$_2$, charge balance
**Surface Ocean**

\[ Ca^{++} + CO_3^- \rightarrow CaCO_3 (s) \] (a percentage sinks and redissolves)

**CO₂ Removal**

\[ CO_2 + H_2O \rightarrow CH_2O + O_2 \]

\[ H_2CO_3 + CO_3^- \rightarrow 2HCO_3^- \]

**Photosynthesis**

More CO₂ will dissolve from atmosphere

\[ [CO_2] = kPCO_2 \]

**Deep Water \rightarrow Respiration**

\[ CH_2O + O_2 \rightarrow CO_2 + H_2O \]

\[ H_2CO_3 + CO_3^- \rightarrow 2 HCO_3^- \]

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:

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

Acid:

$$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{Ac}^- \quad K_{eq} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{H}_2\text{CO}_3]} = 10^{-7.3}$$

$$[\text{H}_2\text{CO}_3] = k_T P_{\text{CO}_2} \quad \text{at } P_{\text{CO}_2} = 10^{-3.45} \quad [\text{H}_2\text{CO}_3] = 10^{-5} \text{ M}$$

$$\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad k = 10^{-1.55}$$

$$pK_1 = +5.7 \quad \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad k_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$10^{-9.2} = 10^{-10.7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{HCO}_3^-] = [\text{H}^+] = 10^{-5.4} \rightarrow \text{pH} = 5.4 \quad k_1 = 10^{-5.7}$$

Soil $P_{\text{CO}_2} \sim 10,000 \text{ ppm} \rightarrow 10^{-2} \rightarrow \text{pH} \sim 4.6$