Lecture #20

Dissolved Carbon Dioxide: Closed Systems II & Alkalinity

(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 5.4 & 7
Alkalinity

- **Alkalinity**: ability of a water to neutralize strong acids
  - a form of Acid Neutralizing Capacity (ANC)
  - Interpretation in most natural waters:
    - $\text{Alk}_{\text{tot}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$
      - Net deficiency of protons with respect to CO$_2$
      - Alk = 0 for a pure solution of carbon dioxide; therefore, CO$_2$ does not add alkalinity: $\text{CO}_2(aq) + \text{OH}^- = \text{HCO}_3^-$
    - $\text{Alk}_{\text{tot}} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$
  - Measurement by titration with a strong acid back to the pH of a pure CO$_2$ solution (about 4.5)
Acidity

- Acidity: ability of a water to neutralize strong bases
  - a form of Base Neutralizing Capacity (BNC)
- Interpretation in most natural waters
  - \( \text{Acy}_{\text{tot}} = 2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-] \)
    - Net excess of protons with respect to \( CO_3^{2-} \)
    - \( \text{Acy} = 0 \) for a pure solution of carbonate; therefore, \( Na_2CO_2 \) does not add acidity: \( Na_2CO_2 + H^+ = HCO_3^- + 2Na^+ \)
  - \( \text{Acy}_{\text{tot}} = (2\alpha_0 + \alpha_1)C_T + [H^+] - [OH^-] \)
- Measurement by titration with a strong base back to the pH of a pure \( CO_3^{2-} \) solution (about 10.7)
Acidity & Alkalinity (cont.)

• Summation
  - \( \text{Alk}_{\text{tot}} + \text{Acy}_{\text{tot}} \)
    - \( = ([\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]) + (2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-]) \)
    - \( = 2[\text{H}_2\text{CO}_3] + 2[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \)
    - \( = 2C_T \)
  - therefore, you can determine \( C_T \) from the two titrations

• Since Alkalinity is not affected by addition of \( \text{CO}_2 \) it is considered a conservative substance in “open systems”
  - e.g., loss of \( \text{CO}_2 \) to the atmosphere does not affect alkalinity either
Other Alkalinity Species

- In sea water we use:
  - \( \text{Alk}_{\text{tot}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{HPO}_4^{2-}] + [\text{H}_3\text{SiO}_4] + [\text{MgOH}^-] + [\text{OH}^-] - [\text{H}^+] \)

<table>
<thead>
<tr>
<th>Species</th>
<th>pKa</th>
<th>Average Conc. (M)</th>
<th>Equilibria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td>10.3/6.4</td>
<td>1x10^{-3}</td>
<td>( \text{CO}_3^{2-} + 2\text{H}^+ = \text{HCO}_3^- + \text{H}^+ = \text{H}_2\text{CO}_3 )</td>
</tr>
<tr>
<td>Silicates</td>
<td>9.8</td>
<td>2x10^{-4}</td>
<td>( \text{H}_3\text{SiO}_4 + \text{H}^+ = \text{H}_4\text{SiO}_4 )</td>
</tr>
<tr>
<td>Organics</td>
<td>3 to 10</td>
<td>1x10^{-4}</td>
<td>( \text{R-COO}^- + \text{H}^+ = \text{R-COOOH} )</td>
</tr>
<tr>
<td>Borates</td>
<td>9.2</td>
<td>1x10^{-6}</td>
<td>( \text{B(OH)}_4^- + \text{H}^+ = \text{B(OH)}_3 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Ammonia</td>
<td>9.2</td>
<td>2x10^{-6}</td>
<td>( \text{NH}_4\text{OH} + \text{H}^+ = \text{NH}_4^+ + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Iron</td>
<td>6.0/4.6</td>
<td>2x10^{-6}</td>
<td>( \text{Fe(OH)}_4^- + 3\text{H}^+ = \text{Fe(OH)}_2^+ + \text{H}^+ = \text{Fe(OH)}^+ + 2\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>8.0/5.7</td>
<td>2x10^{-6}</td>
<td>( \text{Al(OH)}_4^- + 2\text{H}^+ = \text{Al(OH)}_3 + \text{H}^+ = \text{Al(OH)}_2^+ )</td>
</tr>
<tr>
<td></td>
<td>4.3/5.0</td>
<td></td>
<td>( \text{Al(OH)}_2^+ + 2\text{H}^+ = \text{Al(OH)}^+ + \text{H}^+ = \text{Al}^+ + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Phosphates</td>
<td>7.2</td>
<td>7x10^{-7}</td>
<td>( \text{HPO}_4^{2-} + \text{H}^+ = \text{H}_2\text{PO}_4^- )</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>14.0</td>
<td>2x10^{-7}</td>
<td>( \text{OH}^- + \text{H}^+ = \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Copper</td>
<td>9.8/7.3</td>
<td>1x10^{-7}</td>
<td>( \text{Cu(OH)}_3^- + 3\text{H}^+ = \text{Cu(OH)}^+ + \text{H}^+ = \text{Cu}^+ + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Nickel</td>
<td>6.9</td>
<td>2x10^{-8}</td>
<td>( \text{Ni(OH)}_2 + \text{H}^+ = \text{NiOH}^+ )</td>
</tr>
<tr>
<td>Cadmium</td>
<td>7.6</td>
<td>1x10^{-8}</td>
<td>( \text{Cd(OH)}^+ + \text{H}^+ = \text{Cd}^+ + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Lead</td>
<td>6.2</td>
<td>1x10^{-8}</td>
<td>( \text{Pb(OH)}^+ + \text{H}^+ = \text{Pb}^+ + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Sulfides</td>
<td>7.0</td>
<td>variable</td>
<td>( \text{HS}^- + \text{H}^+ = \text{H}_2\text{S} )</td>
</tr>
<tr>
<td>Zinc</td>
<td>6.1/9.0</td>
<td>variable</td>
<td>( \text{Zn(OH)}_2^+ + 2\text{H}^+ = \text{Zn(OH)}^+ + \text{H}_3\text{O}^+ = \text{Zn}^+ + 2\text{H}_2\text{O} )</td>
</tr>
</tbody>
</table>

Chemical species which may contribute to alkalinity

See also, Table IX in Faust & Aly, 1981
Methyl Orange

- used as a colorimetric indicator of the final alkalinity titration endpoint
  - changes color at about pH 4.5
  - where all carbonates are as $\text{H}_2\text{CO}_3$
  - $f=2$
Phenolphthalein

- used as a colorimetric indicator of alkalinity and acidity first endpoint
  - changes color at about pH 8.3
  - pH signifies loss of OH\(^-\) and where all carbonates are as HCO\(_3^-\)
  - at f=1, and g=1
Alkalinity procedures (cont.)

- calculations
  - $E_{qu_t} = E_{qu_s}$
  - $V_tN_t = V_sN_s$
  - $N_s = \frac{V_tN_t}{V_s}$

- Sliding endpoint depending on concentration

<table>
<thead>
<tr>
<th>Alkalinity (mg/L)</th>
<th>Potentiometric (pH)</th>
<th>Colorimetric (from greenish blue to)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.9</td>
<td>light blue &amp; lavender</td>
</tr>
<tr>
<td>150</td>
<td>4.6</td>
<td>light pink</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>red</td>
</tr>
</tbody>
</table>
Alkalinity: Chemical Interpretation

- At the phenolphthalein endpoint ($\text{Alk}_{\text{ph}}$), the following has occurred:
  - $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
  - $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$
- Then at the methyl orange endpoint ($\text{Alk}_{\text{mo}}$):
  - $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$
- Units:
  - equ/L
  - or more commonly, mg/L as CaCO$_3$
    - 1 equ/L = 50,000 mg/L as CaCO$_3$
Types of Alkalinity

- Speciation based on carbonate system
  - $\text{Alk}_{\text{OH}} = 50,000[\text{OH}^-] = 50,000(10^{\text{pHi}-14})$
  - $\text{Alk}_{\text{HCO}_3} = 50,000[\text{HCO}_3^-]$
  - $\text{Alk}_{\text{CO}_3} = 100,000[\text{CO}_3^{-2}]$
Scheme for Alk determination

- If $\text{Alk}_{ph} > 0.5 \times \text{Alk}_{mo}$
  - $\text{Alk}_{OH} = 2 \times \text{Alk}_{ph} - \text{Alk}_{mo}$
  - $\text{Alk}_{CO3} = 2(\text{Alk}_{mo} - \text{Alk}_{ph})$
  - $\text{Alk}_{HCO3} = 0$

- If $\text{Alk}_{ph} \leq 0.5 \times \text{Alk}_{mo}$
  - $\text{Alk}_{OH} = 0$
  - $\text{Alk}_{CO3} = 2 \times \text{Alk}_{ph}$
  - $\text{Alk}_{HCO3} = \text{Alk}_{mo} - 2 \times \text{Alk}_{ph}$

Where:
- $\text{Alk}_{ph} = 50,000 \times V_{ph} N_t / V_s$
- $\text{Alk}_{mo} = 50,000 \times V_{mo} N_t / V_s$
Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity

\[ H^+ + OH^- = H_2O \]

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

\[ H^+ + HCO_3^- = H_2CO_3 \]

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

\[ H^+ + OH^- = H_2O \]
Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity

![Graph showing pH vs. Titrant Volume]
Alkalinity & titrations (cont.)

- Relationship between chemistry, titration and buffer intensity
  - See Stumm & Morgan, Figure 4.1 (pg. 154)

- Impact of $C_T$ on titration endpoints
  - Refer to Benjamin, Figure 5.10
    - Also: Stumm & Morgan, Figure 4.3 (pg.157) and Pankow’s Figure 9.2 (pg. 169)

- Conservation of Alkalinity
  - Stumm & Morgan, Figures 4.7 and 4.10 (pgs. 167 and 177)
Pure $\text{H}_2\text{CO}_3$: $f=0$
Pure $\text{HCO}_3^- : f=1$
Pure $\text{CO}_3^{2-}$: $f=2$
Stumm & Morgan
Figure 4.3; pg. 157
To next lecture