CEE 680: Water Chemistry

Lecture #34

Precipitation and Dissolution: Basics and metal solubility

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Topics

- Hydrolysis
  - Aquo metal ion gives rise to hydroxo complexes
  - Magnesium and Iron Hydroxide solubility
Precipitation and Dissolution

- Environmental Significance
  - Engineered systems
    - coagulation, softening, removal of heavy metals
  - Natural systems
    - composition of natural waters
    - formation and composition of aquatic sediments
    - global cycling of elements

- Composition of natural waters
  - S&M, 3rd ed., figure 15.1 (pg. 873)
  - Benjamin, 2nd ed., figure 1.1

Concentration of inorganics in fresh water

From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1

Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)
Solubility Products

- General Equilibrium
  - $A_mB_n(s) \leftrightarrow mA^{+n} + nB^{-m}$
  
- Solubility Product Equation
  - $K_{so} = [A^{+n}]^m[B^{-m}]^n$
  - also sometimes written: $K_{sp}$

Example

- Calcium Carbonate
  - sources: Smith & Martell; S&M, table 7.1 (pg.362-364)

$K_{so}$ and Q

- Reaction Quotient (Q)
  - computed value from actual measurements
  - may not be at thermodynamic equilibrium
  - comparison with $K_{sp}$ will tell you about tendency toward dissolution or precipitation
    - $Q>K_{so}$, then water will precipitate solid phase
    - $Q<K_{so}$, then water will dissolve solid phase

Example: Calcium Carbonate solubility

- $Ca^{+2} = 40 \text{ mg/L}$ and $CO_3^{-2} = 100 \text{ mg/L}$ as $CaCO_3$
  - what is Q?
  - if $K_{so}$ is $10^{-8.34}$, what does this tell us?
Solubility of some simple salts

- Barium sulfate
  - \( \text{BaSO}_4 = \text{Ba}^{+2} + \text{SO}_4^{-2} \)
  - \( K_{\text{so}} = 10^{-9.96} = [\text{Ba}^{+2}][\text{SO}_4^{-2}] \)
  - How much will dissolve, and what will the barium and sulfate concentrations be?
  - How much will dissolve in a 1mM solution of \( \text{Na}_2\text{SO}_4 \)?

\[
10^{-9.96} = x^2 \\
x = 10^{-4.98}
\]

\[
10^{-9.96} = x(10^{-3} + x) \\
= x^2 + 10^{-3}x \\
x = \frac{-10^{-3} \pm \sqrt{10^{-6} - 4 \times 10^{-9.96}}}{2} \\
= 1.097 \times 10^{-7} = 10^{-6.96}
\]

Solubility of “simple” salts

Stumm & Morgan, 1996, Figure 7.1, pg. 354
Solubility of oxides & hydroxides

- Does not consider the hydroxometal complexes

Stumm & Morgan, 1996, Figure 7.3, pg. 365

Solubility of metal hydroxides

- Adds complexity
  - hydroxide concentration is controlled by pH and therefore affected by buffering
  - many “hydrolyzing” metals have soluble hydroxide species too
- Example: Magnesium Hydroxide
  - Weakly hydrolyzes
  - Only one soluble hydroxide species
  - Practical: we remove Mg by precipitative softening
Surfactants

- Anionics
  - 65%
- Cationics
  - 7%
- Nonionics
  - 28%

From: Schwarzenbach et al., 1993, pg. 38

**Magnesium Hydroxide**

- Thermodynamics
  - \( \text{Mg(OH)}_2 (s) = \text{Mg}^{+2} + 2\text{OH}^- \quad K_{\text{SO}} = 10^{-11.16} \)
  - \( \text{Mg}^{+2} + \text{OH}^- = \text{MgOH}^+ \quad K_1 = 10^{2.6} \)
- Mass Balance
  - \( \text{Mg}_T = [\text{Mg}^{+2}] + [\text{MgOH}^+] \)
  - Total soluble concentration (does not include precipitated Mg)

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**Table 2.6 Examples of Commercially Important Surfactants**

<table>
<thead>
<tr>
<th>Common Name of Surfactant</th>
<th>General Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anionic Surfactants</strong></td>
<td></td>
</tr>
<tr>
<td>Soaps</td>
<td>( R-\text{CH}<em>2-\text{COO}^\text{Na}^+ ), ( R = \text{C}</em>{12-18} )</td>
</tr>
<tr>
<td>Linear alkylbenzene sulfonates (LAS)</td>
<td>( R-\text{O}-\text{CH}=(\text{C}<em>2\text{H}<em>4)\text{SO}</em>{2}\text{H}^+ ), ( R = \text{C}</em>{10-13} )</td>
</tr>
<tr>
<td>Secondary alkyl sulfonates (SAS)</td>
<td>( R_2-\text{CH}-\text{CH}<em>2-\text{SO}</em>{2}\text{H}^+ ), ( R_1, R_2 = \text{C}_{11-17} )</td>
</tr>
<tr>
<td>Fatty alcohol sulfates (Alkyl sulfates, FAS)</td>
<td>( R-\text{OH} = \text{O}-\text{CH}=(\text{C}<em>2\text{H}<em>4)\text{SO}</em>{2}\text{H}^+ ), ( R = \text{C}</em>{11-17} )</td>
</tr>
<tr>
<td><strong>Cationic Surfactants</strong></td>
<td></td>
</tr>
<tr>
<td>Quaternary ammonium chloride (QAC)</td>
<td>( \left[ R_1-\text{CH}=(\text{C}<em>2\text{H}<em>4)\text{CH}</em>{2}\text{CH}</em>{2}\text{CH}=(\text{C}_2\text{H}<em>4)\text{H}\right]^{+} ), ( R_1 = \text{C}</em>{12-16} )</td>
</tr>
<tr>
<td><strong>Nonionic Surfactants</strong></td>
<td></td>
</tr>
<tr>
<td>Alkylphenol polyethylene glycol ethers (APEO)</td>
<td>( R-\text{O}-\text{CH}=(\text{C}<em>2\text{H}<em>4)\text{CH}</em>{2}\text{CH}</em>{2}\text{OH} ), ( n = 5-12 )</td>
</tr>
<tr>
<td>Fatty alcohol polyethylene glycol ethers (AEO)</td>
<td>( R-\text{CH}=(\text{C}_2\text{H}<em>4)\text{CH}</em>{2}\text{CH}=(\text{C}_2\text{H}_4)\text{OH} ), ( n = 3-15 )</td>
</tr>
</tbody>
</table>

*From Pier (1987).*
Magnesium Hydroxide

- Tableau
  - $[Mg^{2+}] = 10^{16.84}[H^+]^2$

<table>
<thead>
<tr>
<th>Components</th>
<th>Reactants</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgOH$_2$ (Brucite)</td>
<td>1</td>
<td>16.84</td>
</tr>
<tr>
<td>MgOH$^+$</td>
<td>1</td>
<td>5.42</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Magnesium Hydroxide II

- From the $K_{so}$ and $K_w$ develop an equation for the free metal in terms of $H^+$
  - $K_{so} = [Mg^{2+}][OH^-]^2$
  - $[Mg^{2+}] = K_{so}/[OH^-]^2$
  - $[Mg^{2+}] = K_{so}/K_w[H^+]^2$
  - $[Mg^{2+}] = 10^{16.84}[H^+]^2$
  - $Log[Mg^{2+}] = 16.84 - 2pH$

- Then use the $K_i$ to get an equation for the soluble hydroxide species
  - $K_i = \frac{[MgOH^+]}{[Mg^{2+}][OH^-]}$
  - $[MgOH^+] = K_i[Mg^{2+}][OH^-]$
  - $= K_i[Mg^{2+}]K_w/[H^+]$
  - $= 10^{2.6}[H^+]^{[10^{16.84}[H^+]^2} [10^{16.84}[H^+]^2] / [H^+]$
  - $= 10^{5.44}[H^+]$
  - $Log[MgOH^+] = 5.44 - pH$
Magnesium Hydroxide III

- **Total Magnesium**
  - $M_{t} = [Mg^{2+}] + [MgOH^{+}]$
  - Follows upper line where lines are well separated
  - Falls 0.3 log units above intersection of any two major species

- **Applications**
  - Mg is a hardness cation
  - Solubility is controlled by hydroxide precipitate
  - Easily removed by softening at high pH
• To next lecture