CEE 680: Water Chemistry

Lecture #30

Coordination Chemistry: case studies

(Stumm & Morgan, Chapt.6: pg.305-319)

Benjamin; Chapter 8.1-8.6
Summary of a few general rules

- At the intersection of sequential alphas, $\alpha_i$ and $\alpha_{i+1}$:
  \[ \log[L] = pK_{i+1} \]

- At the peak of an intermediate alpha, $\alpha_i$, where $i \neq 0$, or the coordination number:
  \[ \log[L] = \frac{1}{2}(pK_i + pK_{i+1}) \]

- This peak is also usually near intersection of the previous and following alphas (i.e., $\alpha_{i-1}$ and $\alpha_{i+1}$), and its maximum height is estimated from:
## Cadmium Complexes

### Bisulfide Ligand

<table>
<thead>
<tr>
<th>Species</th>
<th>log K</th>
<th>Log Beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdL</td>
<td>Log $K_1 = 10.17$</td>
<td>Log $\beta_1 = 10.17$</td>
</tr>
<tr>
<td>CdL$_2$</td>
<td>Log $K_2 = 6.36$</td>
<td>Log $\beta_2 = 16.53$</td>
</tr>
<tr>
<td>CdL$_3$</td>
<td>Log $K_3 = 2.18$</td>
<td>Log $\beta_3 = 18.71$</td>
</tr>
<tr>
<td>CdL$_4$</td>
<td>Log $K_4 = 2.19$</td>
<td>Log $\beta_4 = 20.90$</td>
</tr>
</tbody>
</table>

### Cyanide Ligand

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<tbody>
<tr>
<td>CdL</td>
<td>Log $K_1 = 5.32$</td>
<td>Log $\beta_1 = 5.32$</td>
</tr>
<tr>
<td>CdL$_2$</td>
<td>Log $K_2 = 5.05$</td>
<td>Log $\beta_2 = 10.37$</td>
</tr>
<tr>
<td>CdL$_3$</td>
<td>Log $K_3 = 4.46$</td>
<td>Log $\beta_3 = 14.83$</td>
</tr>
<tr>
<td>CdL$_4$</td>
<td>Log $K_4 = 3.46$</td>
<td>Log $\beta_4 = 18.29$</td>
</tr>
</tbody>
</table>
Cd-HS system

$\alpha_0$, $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$
Cadmium Bisulfide

<table>
<thead>
<tr>
<th>Species</th>
<th>( \log K )</th>
<th>( \log \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdL</td>
<td>( \log K_1 = 10.17 )</td>
<td>( \log \beta_1 = 10.17 )</td>
</tr>
<tr>
<td>CdL(_2)</td>
<td>( \log K_2 = 6.36 )</td>
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<td>CdL(_4)</td>
<td>( \log K_4 = 2.19 )</td>
<td>( \log \beta_4 = 20.90 )</td>
</tr>
</tbody>
</table>

- **Specific Problem**
  - \( 5 \times 10^{-4} \) M Cd total
  - \( 10^{-3} \) M HS total
Cd-HS system

Alpha vs. Log [L] graph with labeled points \( \alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4 \).
$5 \times 10^{-4} \text{M} \text{Cd}_{\text{total}} + 10^{-3} \text{M} \text{HS}_{\text{total}}$

Graph showing the concentration of various species ($\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$) as a function of log concentration ($[L]$) with labels for mass balance and equilibrium (n-bar).
5x10^{-4} \text{M } \text{Cd}_{\text{Total}} + 2.5x10^{-4} \text{M } \text{Cu}_{\text{Total}} + 10^{-3} \text{M } \text{HS}_{\text{Total}}

\begin{align*}
\alpha_0 & \quad \alpha_1 & \quad \alpha_2 & \quad \alpha_3 & \quad \alpha_4 \\
\text{n-bar (mass balance)} & \quad \text{n-bar (equ)}
\end{align*}
Cadmium Cyanide

<table>
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<tr>
<th>Species</th>
<th>log K</th>
<th>Log Beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdL</td>
<td>log K₁ = 5.32</td>
<td>log β₁ = 5.32</td>
</tr>
<tr>
<td>CdL₂</td>
<td>log K₂ = 5.05</td>
<td>log β₂ = 10.37</td>
</tr>
<tr>
<td>CdL₃</td>
<td>log K₃ = 4.46</td>
<td>log β₃ = 14.83</td>
</tr>
<tr>
<td>CdL₄</td>
<td>log K₄ = 3.46</td>
<td>log β₄ = 18.29</td>
</tr>
</tbody>
</table>

- **Specific Problem**
  - \(10^{-5}\) M Cd total
  - \(2.5 \times 10^{-5}\) M CN total
$10^{-5} \text{M } \text{Cd}_{\text{Total}} + 2.5 \times 10^{-5} \text{M } \text{CN}_{\text{Total}}$
Zinc Cyanide

- **Specific Problem**
  - $10^{-4}$ M Zn total
  - $5 \times 10^{-4}$ M CN total

<table>
<thead>
<tr>
<th>Species</th>
<th>Betas</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnL</td>
<td>Log $\beta_1 = 5.7$</td>
</tr>
<tr>
<td>ZnL$_2$</td>
<td>Log $\beta_2 = 11.1$</td>
</tr>
<tr>
<td>ZnL$_3$</td>
<td>Log $\beta_3 = 16.1$</td>
</tr>
<tr>
<td>ZnL$_4$</td>
<td>Log $\beta_4 = 19.6$</td>
</tr>
</tbody>
</table>
$10^{-4} \text{M Zn}_{\text{Total}} + 5 \times 10^{-4} \text{M CN}_{\text{Total}}$
Complexation

\(10^{-4} \text{M } \text{Zn}_{\text{Total}} + 5 \times 10^{-4} \text{M } \text{CN}_{\text{Total}}\)

\[
\begin{align*}
\alpha_0 & \quad \text{n-bar (mass balance)} \\
\alpha_1 & \\
\alpha_2 & \\
\alpha_3 & \\
\alpha_4 & \quad \text{n-bar (equ)}
\end{align*}
\]
Complexation

$10^{-2} \text{M Hg}_{\text{Total}} + 3 \times 10^{-2} \text{M Cl}_{\text{Total}}$

**Graphical Representation**

- $\alpha_0$
- $\alpha_1$
- $\alpha_2$
- $\alpha_3$
- $\alpha_4$

**Axes**

- **Log [L]**
- **Alpha**

**Legend**

- $\alpha_0$, $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$
Complexation

\[10^{-2}\text{M Ag}_{\text{Total}} + 10^{-2}\text{M Br}_{\text{Total}}\]
Aluminum Fluoride system

- Significance
  - Aluminum in natural waters
  - Aluminum in coagulation

- Thermodynamic Values: Smith & Martel (Benjamin)
  - Log $K_1 = 6.16$ (7.01)
  - Log $K_2 = 5.05$ (5.74)
  - Log $K_3 = 3.91$ (4.27)
  - Log $K_4 = 2.71$ (2.70)
  - Log $K_5 = 1.46$ (1.08)
  - Log $K_6 = 0$ (-0.3)

- Now calculate alpha’s

$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \Lambda + \beta_n[L]^n\right)^{-1}$$

$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n[L]^n$$
Aluminum Fluoride

Log [L]

-9 -8 -7 -6 -5 -4 -3 -2 -1 0 1

Alpha

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2

n-bar

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

$\alpha_0$ $\alpha_1$ $\alpha_2$ $\alpha_3$ $\alpha_4$ $\alpha_5$ $\alpha_6$

Log [L]
The figure shows a graph with the x-axis labeled as \( \text{Log} \ [L] \) and the y-axis labeled as \( \alpha \). The graph includes several peaks labeled as \( \alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6 \). The \( \text{n-bar (equ)} \) curve is also plotted. The pK's are indicated by arrows pointing to the x-axis at the values 6.16, 5.05, 3.91, 2.71, 1.46, and 0.
Natural Fluoride

10^{-5.5} \quad \longleftrightarrow \quad 10^{-3.8}

Figure 15.1, pg. 873 in Stumm & Morgan, 1996

Figure 1.4, pg. 9 in Benjamin, 2015
Fluoride addition

- Balance between Dental Caries and Fluorosis
- Recommended dose
  - 0.7 to 1.2 mg/L, Based on temperature

Fig. 15.3 from Water Quality & Treatment, 1999 (5th edition)

http://fluoride-math-tutorial.blogspot.com/
Al-F Problems & Discussion

- **Typical WT Situation**
  - Alum dose = 33 mg/L
  - Total Fluoride = 1.9 mg/L
- **High Fluoride pulse & high alum dose**
  - Alum dose = 660 mg/L
  - Total Fluoride = 190 mg/L
- **Impacts of OH complexation?**
Log \[ L \]

\[ -8 -6 -4 -2 0 \]

Alpha

\[ 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 \]

\[ n-bar \]

\[ 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 \]

\[ n-bar (equ) \]

\[ \alpha_0 \]

\[ \alpha_1 \]

\[ \alpha_2 \]

\[ \alpha_3 \]

\[ \alpha_4 \]

\[ \alpha_5 \]

\[ \alpha_6 \]

10^{-5.5} 10^{-3.8}

\[ AlF^+2 \]

\[ AlF_2^+ \]

\[ AlF_3^- \]
Iron Thiocyanate system

- **Significance**
  - Metal plating wastewaters
  - Used in colorimetric analysis of iron

- **Thermodynamic Values**
  - \( \log K_1 = 2.11 \)
  - \( \log K_2 = 1.19 \)
  - \( \log K_3 = 0 \)
  - \( \log K_4 = 0 \)
  - \( \log K_5 = -0.1 \)
  - \( \log K_6 = -0.9 \)

- Now calculate alpha’s

\[
\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \Lambda + \beta_n[L]^n\right)^{-1}
\]

\[
\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n[L]^n
\]
Specific problem

- **Total concentrations**
  - \( C_M = 0.1 \) M
  - \( C_L = 0.1 \) M

- **Mass based equation**
  - \( N \text{-bar} = 1 - 10[SCN^-] \)

- **Solution:** \( n \text{-bar} = 0.85 \)
  - \([Fe^{+3}] = 0.028\) M
  - \([FeSCN^{+2}] = 0.057\) M
  - \([Fe(SCN)_{2}^{+}] = 0.014\) M
Fe-S problem

- Below are the equilibria for the Fe\(^{+2}\) – HS system as listed in Benjamin’s book. Note that there are no equilibria for FeL, as this species is never significant. Prepare a graph of alpha values (vs \(\log[\text{HS}^-]\)) for the this system. Using this graph determine the complete ferrous-iron speciation in groundwater where the total sulfide concentration is 0.2 mM and total ferrous iron is 0.1 mM. Assume the pH of the groundwater is about 8.

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<tr>
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<th>Ligand</th>
<th>Log β values</th>
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<tbody>
<tr>
<td>FeL(_2)</td>
<td>HS(^-)</td>
<td>8.95</td>
</tr>
<tr>
<td>FeL(_3)</td>
<td>PO(_4)(^{-3})</td>
<td>10.99</td>
</tr>
<tr>
<td>FeH(_2)L</td>
<td>PO(_4)(^{-3})</td>
<td>22.25</td>
</tr>
</tbody>
</table>

Log β values (From Table 8.3 ; pg 374)
Thorium Concentrations

Surface concentration

Thorium (ppm)

NAD27/*DNAG
Thorium example I

- In pure water
  - $C_{Th} = 0.01 \mu g/L$
  - Temp = 25°C

From: Langmuir, 1997; Fig. 3.12a,
44(11)1753-1766
Thorium example II

- In pure water with sulfate
  - $C_{SO_4} = 100 \text{ mg/L}$
  - $C_{Th} = 0.01 \mu g/L$
  - Temp = $25^\circ C$

From: Langmuir, 1997, Fig. 3.12b

David Reckhow
Model groundwater without organics

- $C_{Th} = 0.01 \mu g/L$ & Temp $= 25^\circ C$

Groundwater composition

- Total fluoride $= 0.3$ mg/L
- Total chloride $= 10$ mg/L
- Total phosphate $= 0.1$ mg/L
- Total sulfate $= 100$ mg/L

From: Langmuir, 1997; Fig. 3.13a,
44(11)1753-1766
Thorium example IV

- Model groundwater with organics
- Same inorganic groundwater composition
- With organics
  - Total oxalate = 1.0 mg/L
  - Total EDTA = 0.1 mg/L

From: Langmuir, 1997; Fig. 3.13b,
44(11)1753-1766
End

• To next lecture
Fe-S problem

- Below are the equilibria for the Fe$^{+2}$ – HS system as listed in Benjamin’s book. Note that there are no equilibria for FeL, as this species is never significant. Prepare a graph of alpha values (vs log[HS-]) for the this system. Using this graph determine the complete ferrous-iron speciation in groundwater where the total sulfide concentration is 0.2 mM and total ferrous iron is 0.1 mM. Assume the pH of the groundwater is about 8.

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<th>Log $\beta$ values</th>
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<td>FeL$_2$</td>
<td>HS-</td>
<td>8.95</td>
</tr>
<tr>
<td>FeL$_3$</td>
<td>PO$_4^{3-}$</td>
<td>10.99</td>
</tr>
<tr>
<td>FeH$_2$L</td>
<td></td>
<td>22.25</td>
</tr>
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Log $\beta$ values (From Table 8.3; pg 374)
Calculations

- calculations

\[ \beta_2 = 10^{8.95} = \frac{[FeL_2]}{[Fe] [L^2]} \]

\[ \beta_3 = 10^{10.99} = \frac{[FeL_3]}{[Fe] [L^3]} \]

Log $\beta$ values (From Table 8.3; pg 374)

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<th>Species</th>
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<tbody>
<tr>
<td>HS-</td>
<td>PO$_4^{-3}$</td>
</tr>
<tr>
<td>Species</td>
<td>Conc (M)</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------</td>
</tr>
<tr>
<td>HS⁻</td>
<td>5.37E-05</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>2.70E-05</td>
</tr>
<tr>
<td>Fe(HS)₂⁺⁻</td>
<td>7.30E-05</td>
</tr>
<tr>
<td>Fe(HS)₃⁻</td>
<td>0</td>
</tr>
<tr>
<td>H⁺</td>
<td>1.00E-08</td>
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<tr>
<td>OH⁻</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>H₂S</td>
<td>5.75E-06</td>
</tr>
<tr>
<td>S²⁻</td>
<td>5.37E-11</td>
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