Lecture 26 – Chapter 18, Section 5
Complexes

• Complexation
• Chelates
• Heavy metal poisons
Complexes

• Also called **coordination compounds**
• A combination of a metal with **ligands** that can be neutral or charged
• For instance \([\text{Ag(NH}_3\text{)}_2]^2+\) is a complex
  – The metal is \(\text{Ag}^{2+}\)
  – The ligands are \(\text{NH}_3\)
  – The equilibrium is
\[
\text{Ag}^{2+} + 2\text{NH}_3 \leftrightarrow [\text{Ag(NH}_3\text{)}_2]^2+
\]
Coordination

• The ligand is said to be coordinated to the metal
• The key characteristic of a complex/coordination compound is that the ligand donates a lone pair into empty orbitals on the metal
• For instance, in our \([\text{Ag(NH}_3)_2]^2+\) each N of NH\(_3\) are donating an electron pair to the Ag ion
• Understanding the stoichiometry of complexes is more complicated than we will deal with this year – I’ll always provide the stoichiometry to you.
Chelates

• One common class of ligands are **chelating agents**.
• Chelates are ligands that form multiple bonds to the metal.
  – Chelate comes from the greek *chele*, meaning claw
• For instance ethylenediamine (en) is a common chelate
  – It has two N atoms that donate lone pairs (bidentate)
Chelates bond strongly

- The metal-N bond in ethylene diamine is about the same strength as the metal-N bond in ammonia complexes
- But en binds much more strongly

\[
\begin{align*}
\text{Ni}^{2+} \ (\text{aq}) + 6 \text{NH}_3 \ (\text{aq}) & \leftrightarrow [\text{Ni(NH}_3)_6]^{2+} \ (\text{aq}) \quad K_f = 2.0 \times 10^8 \\
\text{Ni}^{2+} \ (\text{aq}) + 3 \text{en} \ (\text{aq}) & \leftrightarrow [\text{Ni(en)}_3]^{2+} \ (\text{aq}) \quad K_f = 4.1 \times 10^{17}
\end{align*}
\]

- This is called the chelate effect
- What causes this?
Chelate Effect

- In the ammonia complex, if one of the ligands falls off briefly, two things can happen
  - The ammonia can recombine
    - Called geminate recombination
  - The ammonia can leave and be replaced by water
    - Called ligand exchange

\[
[Ni(NH_3)_6]^{2+} \text{ (aq)} \leftrightarrow [Ni(NH_3)_5]^{2+} \text{ (aq)} + NH_3 \text{ (aq)}
\]

\[
[Ni(NH_3)_5]^{2+} \text{ (aq)} + H_2O \leftrightarrow [Ni(NH_3)_5(H_2O)]^{2+} \text{ (aq)}
\]
Chelate Effect (II)

- The same two things can happen when \( \text{en} \) is the ligand.
- But because the ligand is still attached even after one of the metal-N bonds breaks, the N can’t get very far away.
- Therefore, that same N is far more likely to bond to the metal than anything else.
Chelates in Medicine

• Chelates are also called sequestering agents
• They are used to deactivate or sequester heavy metal contaminants in blood.
• For instance ethylenediaminetetraacetate ion (EDTA\(^{4-}\)) is used to treat many kinds of metal poisoning, especially mercury and lead.
• One EDTA\(^{4-}\) ion contains 6 atoms that donate lone pairs
  – 2 Ns from the en
  – 4 O\(^-\) from the acetates
  – EDTA is hexadentate
• Consequently EDTA\(^{4-}\) forms very strong complexes with many metals
• Actually, EDTA\(^{4-}\) itself is a poison. Why?
Heavy Metal Poisoning

- EDTA$^{4-}$ binds very well to iron ions
  - Not good if you like your blood red
- Fortunately, calcium ions bind EDTA$^{4-}$ more strongly than iron, but less strongly than lead or mercury
- So, the calcium complex is the actual useful drug

[Ca(EDTA)]$^{2-}$
Complexation Equilibria

- These problems are no different than everything else we have been doing
- The $K_f$ are often very large
  - So, take the reaction to completion first
  - Then use equilibrium to allow reaction to drift back
If 1.000 L of 0.100 M AgNO₃ are mixed with 1.000 L of 0.250 M KBr, what are the final concentrations of Ag⁺ and Br⁻?

\[ \text{Ag}^+_{(aq)} + \text{Br}^-_{(aq)} \rightleftharpoons \text{AgBr}_{(s)} \quad K_{eq} = 1.87 \times 10^{12} \]

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<tr>
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<th>1. 0 M Ag⁺</th>
<th>0 M Br⁻</th>
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<tr>
<td>25%</td>
<td>2. 3.57 \times 10^{-13} M Ag⁺</td>
<td>0.075 M Br⁻</td>
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<tr>
<td>25%</td>
<td>3. 3.57 \times 10^{-13} M Ag⁺</td>
<td>0.150 M Br⁻</td>
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<tr>
<td>25%</td>
<td>4. 1.17 \times 10^{17} M Ag⁺</td>
<td>1.17 \times 10^{17} M Br⁻</td>
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How does adding acid affect the solubility of Aluminum hydroxide?

\[ \text{Al(OH)}_3 \rightarrow \text{Al}^{3+} + 3\text{OH}^- \]

33% 1. Increase

33% 2. Decrease

33% 3. Stay the same
How does cooling affect the solubility of calcium chloride?

\[ \text{CaCl}_2 (s) \rightarrow \text{Ca}^{2+} (aq) + 2 \text{Cl}^- (aq) \]
\[ \Delta H_{\text{rxn}} = +585 \text{ kJ/mol} \]

33% 1. Increase
33% 2. Decrease
33% 3. Stay the same
How does adding water affect the solubility of calcium chloride?

\[
\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{Cl}^-(aq)
\]

\[\Delta H_{\text{rxn}} = +585 \text{ kJ/mol}\]

33% 1. Increase
33% 2. Decrease
33% 3. Stay the same
How does adding EDTA\(^{4-}\) affect the solubility of calcium chloride?

\[
\text{CaCl}_2\,(s) \rightarrow \text{Ca}^{2+}\,(aq) + 2\,\text{Cl}^-\,(aq)
\]
\[
\Delta H_{\text{rxn}} = +585 \text{ kJ/mol}
\]

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Today

- Finish CAPA #16
- Seminar 2:15  Martha Miller Rotunda (Nigerian Professor)
- Seminar 4:00  Schaap 1000 (Spectroscopy of Halocarbenes)

Tomorrow

- Go Home! (or someplace better)

Monday (after break)

- Review with Dr. Silver

Wednesday

- Exam
  - NO cheat sheet.
  - Come with just pencils and a calculator