Lecture #26

Coordination Chemistry: Hydrolysis

(Stumm & Morgan, Chapt.6: pg.260-271)

Benjamin; Chapter 8.1-8.6
Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity

From Lecture #20
Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity

From Lecture #20

[Diagram with pH on the y-axis and Titrant Volume (mL) on the x-axis. The curve shows two equivalence points labeled as 1st and 2nd Equivalence Points. The equations involving Y[CO₃²⁻] + Z[HCO₃⁻], (Y + Z)[HCO₃⁻], and (Y + Z)[H₂CO₃] are also indicated.]
**Buffer Intensity**

- Amount of strong acid or base required to cause a specific small shift in pH

\[ \beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \]

From Lecture #17

- Starting Point: pH 3.35
- Mid-point: pH 4.7
- End Point: pH 8.35

Slope = \( 1/\beta \)
Base titration of an acid

- For a monoprotic
  - Lecture #16
  - \( C_B \equiv [\text{Na}^+] = [A^-] + [\text{OH}^-] - [H^+] \)

\[
f = \frac{V_B N_B}{V_s M_s} = \frac{\text{equ}_B}{\text{mole}_s} = \frac{C_B}{C_T}
= \frac{[A^-] + [\text{OH}^-] - [H^+]}{C_T}
= \alpha_1 + \frac{[\text{OH}^-] - [H^+]}{C_T}
\]

\[
\frac{1}{[H^+] + \frac{1}{K_a}}
\]

- For a diprotic
  - Using the same ENE approach

\[
f = \frac{2[A^{-2}] + [HA^-] + [OH^-] + [H^+]}{C_T}
= 2\alpha_2 + \alpha_1 + \frac{[OH^-] + [H^+]}{C_T}
\]

\[
\frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}
\]

\[
\frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}
\]
Example Titration

- **Base titration**
  - $V_s = 1000$ mL
  - $M_s = 0.001$ M
  - $N_B = 0.1$ M

- **Starting acids**
  - Pure water
  - $1$ mM HAc
  - $1$ mM $H_2CO_3$

\[
f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s}
\]

\[
pH_i = 3.85 \quad pK_a = ?? \quad pK_{as} = ??
\]
Titration of Humics

- Model for aquatic humic substances
  - Acetic acid + phenol

From Lecture #18

![Graph showing titration of humic substances with pH and mol base/mol functional groups axes.]

End point phenol
End point acetic acid
Titration of phenol–OH groups
Titration of carboxylic groups

(Acetic acid + phenol)
Humic acid
Protons & Metals Ions

- Why??

Fig 6.2
pg.259
David Reckhow
Hydroxide complexation?

No

Yes, a bit

Yes, quite a bit
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)
Intro: Chemical Reactions

- **Driving force**
  - Reactants strive to improve the stability of their electron configurations (i.e., lower $\Delta G$)

- **Types**
  - **Redox reactions**: change in oxidation state
  - **Coordinative reactions**: change in coordinative relationships
Intro: Coordinative Reactions

- Definition: where the coordination number or coordination partner changes

- Types
  - Acid/base reactions
    \[
    \text{HClO} = \text{H}^+ + \text{ClO}^-
    \]
  - Precipitation reactions
    \[
    \text{Mg}^{2+} + 2\text{OH}^- = \text{Mg(OH)}_2(\text{s})
    \]
  - Complexation reactions
    \[
    \text{Cu}^{2+} + 4\text{NH}_3 = \text{Cu(NH}_3)_4^{+2}
    \]

\[
\text{HClO} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{ClO}^-
\]
\[
\text{Mg(H}_2\text{O})_2^{+2} + 2\text{OH}^- = \text{Mg(OH)}_2(\text{s}) + 2\text{H}_2\text{O}
\]
\[
\text{Cu(H}_2\text{O})_4^{+2} + 4\text{NH}_3 = \text{Cu(NH}_3)_4^{+2} + 4\text{H}_2\text{O}
\]
Coordination Chemistry: References

- **Benjamin**, 2002: Chapt. 8
  - Appendix A4
- **Stumm & Morgan**, 1996: Chapt. 6
- **Butler**, 1998: Chapt. 7 & 8
- **Pankow**, 1991: Chapt. 18
- **Langmuir**, 1997: Chapt. 3
- **Snoeyink & Jenkins**, 1980: Chapt. 5
- **Morel & Hering**, 1993: Chapt. 6
  - **Morel**, 1983: Chapt. 6
- **Buffle**, 1988: Chapt. 5 & 6
Coordination

- Definition
  - Any combining of cations with molecules or anions containing free pairs of electrons

\[ \text{Cu}^{+2} + 4\text{NH}_3 = \text{Cu(NH}_3)_4^{+2} \]

Complex or Coordination Compound

Central atom

Ligand

Ligand atom
Ligand types

- Constituent Ligand atoms
  - Nitrogen
  - Oxygen
  - Others: halides

- Numbers of active ligand atoms per ligand
  - One: monodentate (e.g., ammonia)
  - Two: bidentate (e.g., oxalate)
  - Three: tridentate (e.g., citrate)
  - Six: hexadentate (e.g., EDTA)

Multidentate

Resulting complexes are called chelates
Coordination Basics

• Importance
  • Affects solubility of metals
    • e.g., Al(OH)$_3$ solubility
  • Used in Analytical chemistry
    • Determination of hardness
  • Metals act as buffers in natural waters

• Coordination Number
  • 1 for Hydrogen
  • 2, 4, or 6 for most metals
Ion Pairs & Complexes

- Two types of complex species
  - Ion Pairs
    - Ions of opposite charge that form an association of lesser charge
    - Ion pairs are separated by at least one water molecule
      - These are called “outer-sphere” complexes
  - Complexes
    - Metal ion and neutral or anionic ligand
    - Direct bond formed with no water molecule between
      - These are called “inner-sphere” complexes
Ion pair stability

- Determined based on simple coulombic interactions

<table>
<thead>
<tr>
<th>Ion Charge</th>
<th>Log K (I=0)</th>
<th>Log K (seawater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 to 1</td>
<td>-0.5 to 0.5</td>
</tr>
<tr>
<td>2</td>
<td>1.5 to 2.4</td>
<td>0.1 to 1.2</td>
</tr>
<tr>
<td>3</td>
<td>2.8 to 4.0</td>
<td></td>
</tr>
</tbody>
</table>
Natural Particle as Ligands

- Natural Particles
  - High surface area
  - Usually coated with oxygen-containing surface groups which can donate electrons to metals (i.e., act as ligands)
# Chemical Speciation

<table>
<thead>
<tr>
<th>Free metal ion</th>
<th>Inorganic complexes</th>
<th>Organic complexes</th>
<th>Colloids</th>
<th>Surface bound</th>
<th>Solid bulk phase, lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–aq²⁺</td>
<td>CuCO₃</td>
<td>FC°</td>
<td>Inorganic Organic</td>
<td>Fe–OCu</td>
<td>CuO Cu₂(OH)₂CO₃ Solid solution</td>
</tr>
<tr>
<td></td>
<td>CuOH⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu(CO₃)₂</td>
<td>Fulvate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu(OH)₂</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

**Fig 6.1, pg. 258**

- **True solution**
- **Dissolved**
- **Particular**
- **Dialysis, gel filtration, membrane filtration**
Protons & Metals Ions

- All “free” metals and protons are actually hydrated in water
- Both can bind with hydroxide
Fig 6.3
Pg.259

The diagram illustrates the relationship between the concentration of ammonium ions (NH₄⁺) and the pH of a solution, along with the concentration of copper ions (Cu²⁺) and the complexation with trien ligands. The following key points are highlighted:

- **NH₃** and **NH₄⁺** concentrations are shown on the x-axis, with the pH on the y-axis.
- The concentration of Cu(NH₃)ₓ is represented by a curve that indicates the stability of the complex at different pH values.
- The concentration of Cu²⁺ is shown on another graph, with the pCu on the y-axis.
- The concentration of the trien ligand complex is shown on yet another graph, with the pTRIEN on the y-axis.

The graphs demonstrate how the concentrations of these species change with varying pH and mole percentages, providing insights into the chemical behavior of copper and ammonium ions in solution.
Brønsted & Lewis Acidity

- **Definition of Acids**
  - Brønsted: proton donors
    - Species with excess H⁺
  - Lewis: electron acceptors
    - H⁺, metal ions, others

- **Strength**
  - Tendency to accept electrons (or donate protons)
    - Measured by equilibrium constant
Complexes: Coordination #

- Me(Ligand)$_x$
  - Fe(H$_2$O)$_6^{+3}$
  - Fe(H$_2$O)$_4$(OH)$_2^{+1}$
  - PtCl$_6^{-2}$
  - Cu(NH$_3$)$_4^{+2}$
  - Si(OH)$_4$
  - HgS$_2^{-2}$
  - HOH

Coordination Number
- 6
- 4
- 2

Coordination # Depends on:
1. Size of central Atom
2. Charge of central Atom
3. Size of Ligand
• To next lecture