Lecture 22 – Chapter 18, Section 4
Indicators, Solubility Products

• Choosing an indicator
• Quantifying solubility
• Common Ion Effect
• Effects of pH
Indicators

• Many titrations are carried out with pH meters
• But, it is often faster and easier to use an indicator
  – Titrations are still often done this way.

• Indicators are simply weak acids/bases that are strongly colored
  – AND color must change with protonation state
Indicators

• For the indicator to change color at the appropriate time in the titration – the stoichiometric point
  – This means $pK_a$ of indicator $\approx \text{pH at stoich. point}$

<table>
<thead>
<tr>
<th>Indicator</th>
<th>$pK_{in}$*</th>
<th>pH Range</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thymol blue**</td>
<td>1.75</td>
<td>1.2–2.8</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.40</td>
<td>3.1–4.4</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>4.68</td>
<td>4.0–5.6</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.95</td>
<td>4.4–6.2</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromocresol purple</td>
<td>6.3</td>
<td>5.2–6.8</td>
<td>Yellow</td>
<td>Purple</td>
</tr>
<tr>
<td>Phenol red</td>
<td>7.9</td>
<td>6.4–8.0</td>
<td>Yellow</td>
<td>Red</td>
</tr>
<tr>
<td>Thymol blue**</td>
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<tr>
<td>Phenolphthalein</td>
<td>9.4</td>
<td>8.0–10.0</td>
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<td>Red</td>
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<tr>
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* The acid dissociation constant of an indicator is designated $K_{in}$.

**Thymol blue has two acidic hydrogen atoms, so it can be used as an indicator for two different pH regions.
Example: What indicator is best for titrating carbonic acid in a solution that is approx. 0.010 M? (Ka = 4.5 × 10⁻⁷)

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Solubility Equilibria

- Memorized qualitative solubility rules before
- Now we’ll treat things more quantitatively

- Insoluble compounds: solubility is less than 0.01 mol of dissolved material per liter of solution, $K_{sp} \ll 1$ ($< 10^{-5}$)
  - Cu(OH)$_2$ $K_{sp} = 1.1 \times 10^{-15}$
- Slightly soluble: $10^{-5} < K_{sp} < 10^{-2}$
  - Ag$_2$SO$_4$ $K_{sp} = 1.2 \times 10^{-5}$
- Soluble: $K_{sp} > 10^{-2}$
  - NaCl $K_{sp} = 6.2$

- (Don’t memorize these boundaries – they are ‘rough’)
Common Ion Effect

• One manifestation of Le Chatelier’s Principle

• Suppose salt B has an ion ‘in common’ with salt A
  – Then concentration of B effects solubility of A

• For example
  \[
  \text{Cd(OH)}_2 \rightarrow \text{Cd}^{2+} + \text{OH}^{-}
  \]

  NaOH is a salt with an ion in common
Considering Le Chatelier’s Principle:
If we introduce lots of NaOH, how should the concentration of Cd$^{2+}$ change?

\[
\text{Cd(OH)}_2 \rightarrow \text{Cd}^{2+} + 2 \text{OH}^- 
\]

33% 1. Increase
33% 2. Decrease
33% 3. Stay the same
Common Ion Effect

• This is used to control amount of dissolved Cd²⁺ (and other heavy metal contaminants)
• If we have wastewater with lots of Cd²⁺
• We can reduce Cd²⁺ by introducing lots of strong base.

• Example: We have 100 L of $1.2 \times 10^{-5} \text{ M Cd}^2+$
• Add 1.0 L of 6.0 M NaOH
• What is new Cd²⁺ concentration?
Cd$^{2+}$ Solution

- OH$^-$ drives equilibrium far toward Cd(OH)$_2$
  \[ \text{Cd(OH)}_2 \rightarrow \text{Cd}^{2+} + 2 \text{OH}^- \]
- ‘Initial’ amounts
  - Cd(OH)$_2$ = (solid)
  - Cd$^{2+}$ = 0
  - OH$^-$ = 1L/100L * 6M = 0.06 M
- Amounts at equilibrium
  - Cd(OH)$_2$ = (solid)
  - Cd$^{2+}$ = +y
  - OH$^-$ = 0.06 + 2y
- $K_{sp} = y(0.06 + 2y)^2 \approx 0.0036y$
  \[ y = 2.0 \times 10^{-12} \ll 1.2 \times 10^{-5} \text{M} \]
pH often involved in common ion

- In last example the ‘common ion’ was hydroxide
- Obviously, pH has an effect on Cd$^{2+}$ concentration
- Said another way, pH effects Cd(OH)$_2$ solubility
  - Cd(OH)$_2$ solubility depends on pH because OH$^-$ is a base

- Book does nice example with CaCO$_3$
  - This depends on pH because CO$_3^{2-}$ is a base (conjugate base of carbonic acid H$_2$CO$_3$)
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
Exam

• Some easy $K_{eq}/K_{sp}/K_a$ questions (multiple choice?)
• Several Le Chatelier questions (multiple choice or short answer)
• Some question relating $\Delta G$ (or maybe $\Delta H$ and $\Delta S$) with $K_{eq}$
• Some difficult buffer, weak acid pH, polyprotic acid question
• Some common ion / $K_{sp}$ question
• Titration question – maybe indicators and/or something about titration plot/curve
• Acid strength chemical comparison (matching or short answer)
Today

• Finish CAPA #13
• Work lots of problems – don’t do it alone

Friday

• Seminar – student invited speaker
• Keep Reviewing! Study Groups! Practice Exams
• Quiz in class