Lecture 25 – 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 their color changes with protonation state
Indicators

- The indicator must change color at the appropriate time in the titration – the stoichiometric point
  - This means $pK_a$ of indicator $\approx$ pH at stoich. point

<table>
<thead>
<tr>
<th>Indicator</th>
<th>$pK_{ln}$</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>
<td>8.9</td>
<td>8.0–9.6</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>9.4</td>
<td>8.0–10.0</td>
<td>Colorless</td>
<td>Red</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>10.0</td>
<td>9.4–10.6</td>
<td>Colorless</td>
<td>Blue</td>
</tr>
</tbody>
</table>

* The acid dissociation constant of an indicator is designated $K_{ln}$.
**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 \times 10^{-7})

1. Bromocresol green
2. Methyl Red
3. Phenol Red
4. Phenolphthalein

* 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.
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, $K_{sp} \ll 1$ ($< 10^{-5}$)
  - $\text{Cu(OH)}_2$ $K_{sp} = 1.1 \times 10^{-15}$
- **Slightly soluble**: $10^{-5} < K_{sp} < 10^{-2}$
  - $\text{Ag}_2\text{SO}_4$ $K_{sp} = 1.2 \times 10^{-5}$
- **Soluble**: $K_{sp} > 10^{-2}$
  - $\text{NaCl}$ $K_{sp} = 6.2$

- (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 Cd$^{2+}$ (and other heavy metal contaminants)
- If we have wastewater with lots of Cd$^{2+}$
- We can reduce Cd$^{2+}$ by introducing lots of strong base.

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

- OH$^-$ drives equilibrium far toward Cd(OH)$_2$
  \[ \text{Cd(OH)}_2 \rightarrow \text{Cd}^{2+} + 2 \text{OH}^- \]
- So, we start with all Cd in Cd(OH)$_2$ form. ‘Initial’ amounts
  - Cd(OH)$_2$ = (solid) $\equiv$ 1
  - Cd$^{2+}$ = 0
  - OH$^-$ = 1L/101L * 6M $\approx$ 1L/100L * 6M = 0.06 M
- Amounts at equilibrium
  - Cd(OH)$_2$ = (solid) $\equiv$ 1
  - Cd$^{2+}$ = $+y$
  - OH$^-$ = 0.06 + 2$y$
- $K_{sp} = 7.2 \times 10^{-15} = y(0.06 + 2y)^2 \approx 0.0036y$
  $y = 2.0 \times 10^{-12} \ll 1.2 \times 10^{-5} \text{M}$
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
Today

• Finish CAPA #15
• Registration information session 4:00pm  Schaap 1000
• Work lots of problems – don’t do it alone

Wednesday

• We’ll finish Chapt 18
• Seminar – usual time and place (4:00 right here)
• Finish CAPA #16
• Keep Reviewing!  Study Groups!  Practice Exams