Chapter 17: Acid-Base Equilibria and Solubility Equilibria

Key topics:
- Common ion effect
- Buffers
- Acid-base equilibria
- Solubility equilibria; complex ion formation

The Common Ion Effect

If we have two solutes each containing the same ion, the equilibrium is affected. This is called the common ion effect.

Consider adding acetic acid (CH$_3$COOH) and sodium acetate (NaCH$_3$COO) to water. The acetate anion from sodium acetate will inhibit acetic acid from dissociating (Le Chatelier).

First consider the situation with only acetic acid, at 0.10 $M$

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$COOH</th>
<th>$\Leftrightarrow$</th>
<th>H$^+$ +</th>
<th>CH$_3$COO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \Rightarrow x = 1.34 \times 10^{-3} \]

which means the pH = 2.87 and the % ionization = 1.34%

Next, consider adding 0.050 moles of sodium acetate to 1.00 L of our acetic acid solution (assume volume does not change).
CH$_3$COOH $\rightleftharpoons$ H$^+$ + CH$_3$COO$^-$

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$COOH</th>
<th>H$^+$</th>
<th>CH$_3$COO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.09866</td>
<td>1.34 x 10$^{-3}$</td>
<td>5.134 x 10$^{-2}$</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>-x</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.09866 + x</td>
<td>1.34 x 10$^{-3}$ - x</td>
<td>5.134 x 10$^{-2}$ -x</td>
</tr>
</tbody>
</table>

(note: the equilibrium must shift to the left from Le Chatelier)

\[ K_a = 1.8 \times 10^{-5} = \frac{(0.00134 - x)(0.05134 - x)}{0.09866 + x} \Rightarrow x = 1.305 \times 10^{-3} \]

This gives [H$^+\] = 3.5 \times 10^{-5}$ (using the quadratic equation)

which means the pH = 4.46 and the % ionization = 0.035%

The common ion effect is significant!

**Comment:** The last calculation was hard because we had to use the quadratic equation. We can redo the last calculation by adding both of our solutes at the same time. This simplifies the math but does not affect the final equilibrium.

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<tr>
<th></th>
<th>CH$_3$COOH</th>
<th>H$^+$</th>
<th>CH$_3$COO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0</td>
<td>0.050</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 - x</td>
<td>x</td>
<td>0.050 + x</td>
</tr>
</tbody>
</table>

\[ K_a = 1.8 \times 10^{-5} \approx \frac{(x)(0.050 + x)}{0.10 - x} \Rightarrow x = 3.6 \times 10^{-5} \]

**Buffer Solutions**

A buffer is a solution that contains comparable amounts of a weak acid and its conjugate base, or a weak base and its conjugate acid.

Buffers resist changes in pH upon addition of acid or base.
Consider a buffer consisting of HA and A\(^-\) (weak acid/base)
If we add a strong acid: \(\text{H}^+ + \text{A}^- \rightarrow \text{HA}\)
The strong acid is converted to a weak acid: minimal pH shift
If we add a strong base: \(\text{OH}^- + \text{HA} \rightarrow \text{A}^- + \text{H}_2\text{O}\)
The strong base is converted to a weak base: minimal pH shift

We will use the acetate buffer to illustrate:
Suppose we have 1 L of a solution that is 1 \(M\) acetic acid and 1 \(M\) sodium acetate.

<table>
<thead>
<tr>
<th></th>
<th>CH(_3)COOH</th>
<th>H(^+) +</th>
<th>CH(_3)COO(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.0 – x</td>
<td>x</td>
<td>1.0 + x</td>
</tr>
</tbody>
</table>

\[K_a = 1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{1.0 - x} \approx x \implies x = 1.8 \times 10^{-5}\]
so the pH = 4.74

Now add 0.10 mol of HCl (neglect the volume change)
Note: Adding 0.10 mol of HCl to pure water gives pH = 1.00

Strategy: assume all the H\(^+\) is consumed, and then allow H\(^+\) to be regenerated by the buffer.

H\(^+\) added: 0.1 mol 1.0 mol 1.0 mol
\[\text{H}^+ + \text{CH}_3\text{COO}^- \leftrightarrow \text{CH}_3\text{COOH}\]
H\(^+\) consumed: 0 mol 0.9 mol 1.1 mol

<table>
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<th>CH(_3)COOH</th>
<th>H(^+) +</th>
<th>CH(_3)COO(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.1</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.1 – x</td>
<td>x</td>
<td>0.9 + x</td>
</tr>
</tbody>
</table>
\[ K_a = 1.8 \times 10^{-5} = \frac{(x)(0.9 + x)}{1.1 - x} \approx \frac{(x)(0.9)}{1.1} \Rightarrow x = 2.2 \times 10^{-5} \]

so the pH is 4.66  (a change of 0.08 pH units)

**We can derive a simple equation for buffer calculations:**

For \( HA \rightleftharpoons H^+ + A^- \) we have

\[ K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow [H^+] = \frac{K_a[HA]}{[A^-]} \]

\[ \Rightarrow \log[H^+] = \log K_a + \log \frac{[HA]}{[A^-]} \]

\[ \Rightarrow \text{pH} = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \]

This is called the *Henderson – Hasselbalch equation*.

**Important points:**

1. “x” is small, so we can use the initial [ ] for HA and A⁻
2. since you have a ratio, you can use \( M \) or moles
3. dilution won’t change \([A^-]/[HA]\), so pH won’t change

**For a weak base / conjugate acid buffer it reads:**

\[ \text{pOH} = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]} \]

e.g., How much HCl must be added to a liter of buffer that is 1.5 \( M \) in acetic acid and 0.75 \( M \) in sodium acetate to give a buffer pH of 4.10?  (pKₐ = 1.8 x 10⁻⁵)

**Solution:**
Adding \( x \) moles of HCl gives (0.75 - x) moles sodium acetate and (1.5 + x) moles acetic acid. Thus
\[
\text{pH} = pK_a + \log \left( \frac{0.75 - x}{1.5 + x} \right)
\]

\[
4.10 = 4.74 + \log \left( \frac{0.75 - x}{1.5 + x} \right)
\]

\[
10^{-0.64} = \left( \frac{0.75 - x}{1.5 + x} \right) \quad \Rightarrow \quad x = 0.33
\]

**Buffer Capacity:** how much acid or base can be adsorbed before the buffer is spent.

**Buffer Range:**
Buffers are most effective (maximum buffering capacity) when \([HA] = [A^-]\). When \([HA] \) and \([A^-]\) differ by more than a factor of 10, the buffer has lost its ability to absorb acid / base.

\[
10 \geq \frac{\text{conjugate base}}{\text{weak acid}} \geq 0.1 \quad \Rightarrow \quad \text{pH} = pK_a \pm 1
\]

### Preparing a buffer solution with a specific pH:

**e.g.,** Prepare a pH = 9.50 buffer using phenol.

**Solution:**

We have

\[
9.50 = 9.89 + \log \left( \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \right) \quad \Rightarrow \quad \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} = 10^{-0.39} = 0.41
\]

We could therefore dissolve 0.41 moles of NaC\(_6\)H\(_5\)O and 1.00 mol of C\(_6\)H\(_5\)OH in 1 L of water.
**Acid-Base Titrations**

**Titration:** reaction of an acid with a base (neutralization)

Specifically, the addition of a solution of accurately known concentration (*e.g.* acid) to a solution of unknown concentration (*e.g.* base) until the reaction is complete.

From the known concentration, the concentration of the other species can be calculated from the stoichiometry.

**Definitions:**
- **Standard solution:** one of known concentration.
- **Equivalence point:** point when stochiometrically equivalent amounts of acid and base are present.
- **Endpoint:** the point in the laboratory when the titration is stopped (often around the equivalence point); typically signaled by the color change of an indicator.
- **Titrant** = the solution that is placed in the buret (typically the one of known concentration)
- **Titration Curve:** pH vs. volume (or moles) of titrant added

**Types of titration systems that will be considered:**
- strong acid – strong base
- weak acid – strong base
- strong acid – weak base

**Items to keep track of during a titration:**
- reaction taking place (what is in the beaker)
- moles of acid or base in the beaker
- moles of base or acid added from the buret
- total volume
Different places to do a pH calculation in a titration:

1. beginning
2. between the beginning and the equivalence point
3. equivalence point
4. after the equivalence point
5. $\frac{1}{2}$ equivalence point
**Titration of Strong Acid with Strong Base:**

- reaction:
  
  \[
  \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \quad \text{(molecular eq)}
  \]
  
  \[
  \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \text{(net ionic eq)}
  \]

- titration of 25.00 mL 0.100 \( M \) HCl (beaker) with 0.100 \( M \) NaOH (in buret)

1. initial pH: \[ [\text{HCl}] = [\text{H}^+] = 0.100 \ M \]

\[
\text{pH} = 1.00
\]

\[
(0.100 \ M) (0.02500 \ L) = 2.50 \times 10^{-3} \text{ mol } \text{H}^+ \text{ in beaker}
\]
2. add 10.00 mL of 0.100 M NaOH (total):

\[ 2.50 \times 10^{-3} \text{ mol H}^+ \text{ in beaker} \]

\[ (0.100 \text{ M}) (0.01000 \text{ L}) = 1.00 \times 10^{-3} \text{ mol OH}^- \text{ added} \]

--- how do you know where you are in titration??

= compare moles H\(^+\) in beaker to moles OH\(^-\) added

\[ \rightarrow \text{ if mol H}^+ > \text{ mol OH}^- \rightarrow \text{ before equiv. pt.} \]
\[ \rightarrow \text{ if mol H}^+ < \text{ mol OH}^- \rightarrow \text{ after equiv. pt.} \]
\[ \rightarrow \text{ if mol H}^+ = \text{ mol OH}^- \rightarrow \text{ at equiv pt.} \]

- mol H\(^+\) excess = \( (2.50 \times 10^{-3}) - (1.00 \times 10^{-3}) \)
  \[ = 1.50 \times 10^{-3} \text{ mol H}^+ \]

- total volume = 25.00 + 10.00 mL = 35.00 mL

- \([H^+] = (1.50 \times 10^{-3} \text{ mol}) / (0.03500 \text{ L}) = 0.0429 \text{ M} \]

- pH = 1.364
3. add 25.00 mL of 0.100 M NaOH (total):

\[ 2.50 \times 10^{-3} \text{ mol H}^+ \text{ in beaker initially} \]

\[ (0.100 \text{ M}) (0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol OH}^- \text{ added} \]

\[ \Rightarrow \text{ mol H}^+ = \text{ mol OH}^- \Rightarrow \text{ at equivalence point} \]

• when at the equivalence point, look at what’s left in solution

\[ \text{HCl} + \text{NaOH} \rightarrow \boxed{\text{NaCl}} + \text{H}_2\text{O} \quad \text{(molecular eq)} \]

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]

\[ \Rightarrow \text{ neither affect pH } \Rightarrow \text{ neutral} \]

\[ \Rightarrow \text{ pH} = 7.00 \]

for ANY strong acid/strong base titration, pH at equiv. pt. = 7.00
4. add 35.00 mL of 0.100 \( M \) NaOH (total):

\[
2.50 \times 10^{-3} \text{ mol H}^+ \text{ in beaker initially}
\]

\[
(0.100 \text{ M})(0.03500 \text{ L}) = 3.50 \times 10^{-3} \text{ mol OH}^- \text{ added}
\]

\[\Rightarrow \text{ mol H}^+ < \text{ mol OH}^- \Rightarrow \text{ after equivalence point}\]

= excess OH\(^-\) in solution \(\Rightarrow\) basic solution

- \( \text{mol OH}^- \text{ excess} = (3.50 \times 10^{-3}) - (2.50 \times 10^{-3}) \)
  \[= 1.00 \times 10^{-3} \text{ mol OH}^- \]

- total volume = 25.00 + 35.00 mL = 60.00 mL

- \([\text{OH}^-] = (1.00 \times 10^{-3} \text{ mol}) / (0.06000 \text{ L}) = 0.0167 \text{ M}\]

- \(\text{pOH} = 1.778\)

\[\text{pH} = 12.22\]

- Variations:
  -- strong base titrated with strong acid:
    = handled same way \(\Rightarrow\) titration curve is just inverted
  -- \(\text{H}_2\text{SO}_4\) vs \(\text{HCl}\) or \(\text{Ba(OH)}_2\) vs NaOH
  -- different concentrations of acid and base
**Titration of Weak Acid with Strong Base:**

- more complex due to equilibrium
- reaction:
  \[
  \text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH} \rightarrow \text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \quad \text{(molecular eq)}
  \]
  \[
  \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \leftrightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \quad \text{(net ionic eq)}
  \]

- titration of 25.00 mL 0.100 \(M\) \(\text{HC}_2\text{H}_3\text{O}_2\) (beaker) with 0.100 \(M\) \(\text{NaOH}\) (in buret)

1. **initial pH:** weak acid equilibrium \(K_a = 1.8 \times 10^{-5}\)

   \[
   \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)
   \]

   Initial concentration \((M)\):
   \[
   \begin{array}{c|c|c}
   & 0.10 & 0 \\
   \hline
   \text{Change in concentration (}M\text{)}: & -x & +x \\
   \hline
   \text{Equilibrium concentration (}M\text{)}: & 0.10-x & x & x
   \end{array}
   \]

   \[
   K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.10-x} \approx \frac{x^2}{0.10} = 1.8 \times 10^{-5}
   \]

   \[
   [\text{H}^+] = 1.34 \times 10^{-3}
   \]

   \[
   \text{pH} = -\log(1.34 \times 10^{-3}) = 2.87
   \]
2. add 10.00 mL of 0.100 M NaOH (total):

~~ 2.50x10^{-3} \text{ mol } \text{HC}_2\text{H}_3\text{O}_2 \text{ in beaker} \n
(0.100 \text{ M}) (0.01000 \text{ L}) = 1.00x10^{-3} \text{ mol OH}^- \text{ added} \\
\Rightarrow \text{ mol } \text{HC}_2\text{H}_3\text{O}_2 > \text{ mol OH}^- \Rightarrow \text{ before equiv. pt.} \\
\text{HC}_2\text{H}_3\text{O}_2 + \text{ OH}^- \rightarrow \text{ C}_2\text{H}_3\text{O}_2^- + \text{ H}_2\text{O} \\
2.50x10^{-3} \quad 1.00x10^{-3} \quad 0 \\
-1.00x10^{-3} \quad -1.00x10^{-3} \quad +1.00x10^{-3} \\
1.50x10^{-3} \quad 0 \quad 1.00x10^{-3} \quad \text{BUFFER!!} \\

- \text{ total volume } = 25.00 + 10.00 \text{ mL } = 35.00 \text{ mL} \\
\text{pH} = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{pH} = 4.74 - \log(1.00x10^{-5}/1.50x10^{-5}) \\

- \text{ pH } = 4.56
3. add 25.00 mL of 0.100 M NaOH (total):

\[ \sim 2.50 \times 10^{-3} \text{ mol HC}_2\text{H}_3\text{O}_2 \text{ in beaker} \]

\[(0.100 \text{ M}) (0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol OH}^- \text{ added} \]

\[ \Rightarrow \text{ mol } \text{HC}_2\text{H}_3\text{O}_2 = \text{ mol OH}^- \Rightarrow \text{ at equivalence point} \]

• when at the equivalence point, look at what’s left in solution

\[
\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH} \rightarrow \boxed{\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}}
\]

\[
\text{NaC}_2\text{H}_3\text{O}_2 \rightarrow \text{Na}^+ + \text{C}_2\text{H}_3\text{O}_2^- \Rightarrow \text{C}_2\text{H}_3\text{O}_2^- \text{ is weak base} \Rightarrow \text{ basic} \]

\[ \Rightarrow \text{ pH } > 7.00 \]

• weak base calculation:

\[
K_b = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \]

\[
[\text{CH}_3\text{COO}^-] = \frac{2.50 \text{ mmol}}{50.0 \text{ mL}} = 0.050 \text{ M}
\]

\[
\begin{align*}
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{OH}^- (aq) + \text{CH}_3\text{COOH(aq)} \\
\text{Initial concentration (M)}: &\quad 0.050 \quad 0 \quad 0 \\
\text{Change in concentration (M)}: &\quad -x \quad +x \quad +x \\
\text{Equilibrium concentration (M)}: &\quad 0.050 - x \quad x \quad x \\
\end{align*}
\]

\[
K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} = 5.6 \times 10^{-10}
\]

\[
[\text{OH}^-] = 5.3 \times 10^{-6} \text{ M} \quad \text{pOH} = 5.28
\]

\[
\text{pH} = 14.00 - 5.28 = 8.72
\]
for ANY weak acid/strong base titration, pH at equiv. pt. > 7.00

4. add 35.00 mL of 0.100 M NaOH (total):
   - after equivalence point identical to strong acid/strong base titration ➔ OH⁻ in solution
   - \([\text{OH}^-] = (1.00 \times 10^{-3} \text{ mol}) / (0.06000 \text{ L}) = 0.0167 \text{ M}\)
   - pOH = 1.778
   - pH = 12.22
5. add 12.50 mL of 0.100 M NaOH (total):

\[ \sim 2.50 \times 10^{-3} \text{ mol HC}_2\text{H}_3\text{O}_2 \text{ in beaker} \]

\[(0.100 \text{ M})(0.01250 \text{ L}) = 1.25 \times 10^{-3} \text{ mol OH}^- \text{ added} \]

\[ \Rightarrow \text{ mol HC}_2\text{H}_3\text{O}_2 = 2 (\text{mol OH}^-) \Rightarrow \frac{1}{2} \text{ equivalence point} \]

\[
\begin{array}{ccc}
\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- & \rightarrow & \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \\
2.50 \times 10^{-3} & 1.25 \times 10^{-3} & 0 \\
-1.25 \times 10^{-3} & -1.25 \times 10^{-3} & +1.25 \times 10^{-3} \\
1.25 \times 10^{-3} & 0 & 1.25 \times 10^{-3} \\
\end{array}
\]

\[
pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{pH} = 4.74 - \log(1.25 \times 10^{-5}/1.25 \times 10^{-5}) = 4.74 - \log(1)
\]

- pH = pKa = 4.74

for ANY weak acid/strong base titration, pH at 1/2 equiv. pt. = pKa
**Titration of Weak Base with Strong Acid:**
- similar to weak acid/strong base
- reaction:
  \[ \text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \quad \text{(molecular eq)} \]
  \[ \text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \quad \text{(net ionic eq)} \]
- titration of 25.00 mL 0.100 M NH\(_3\) (beaker) with 0.100 M HCl (in buret)

1. **initial pH:** weak base equilibrium

   Initial concentration (M):
   \[
   \begin{array}{ccc}
   \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{NH}_4^+(\text{aq}) + \text{OH}^- (\text{aq}) \\
   \hline
   \text{0.10} & \text{0} & \text{0} \\
   \text{\text{-}x} & \text{+x} & \text{+x} \\
   \text{0.10} - x & x & x
   \end{array}
   \]

   \[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \approx \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 1.8 \times 10^{-5} \]

   \[ [\text{OH}^-] = 1.34 \times 10^{-3} \text{ M} \]
   \[ \text{pOH} = 2.87 \]
   \[ \text{pH} = 14.00 - 2.87 = 11.13 \]
2. add 10.00 mL of 0.100 M HCl (total):

\[ \sim 2.50 \times 10^{-3} \text{ mol NH}_3 \text{ in beaker} \]

\[(0.100 \ M) (0.01000 \ L) = 1.00 \times 10^{-3} \text{ mol H}^+ \text{ added} \]

\[ \Rightarrow \text{ mol NH}_3 > \text{ mol H}^+ \Rightarrow \text{ before equiv. pt.} \]

\[
\begin{array}{ccc}
\text{NH}_3 & + & \text{H}^+ & \rightleftharpoons & \text{NH}_4^+ \\
2.50 \times 10^{-3} & 1.00 \times 10^{-3} & 0 \\
-1.00 \times 10^{-3} & -1.00 \times 10^{-3} & +1.00 \times 10^{-3} \\
1.50 \times 10^{-3} & 0 & 1.00 \times 10^{-3}
\end{array}
\]

**BUFFER!!**

- total volume = 25.00 + 10.00 mL = 35.00 mL

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
K_b = 1.8 \times 10^{-5} = [\text{OH}^-](1.00 \times 10^{-5} \text{ mol}) / (1.50 \times 10^{-5} \text{ mol})
\]

\[ [\text{OH}^-] = 2.7 \times 10^{-5} \ M \]

\[ \text{pOH} = 4.56 \]

\[ \text{pH} = 9.43 \]
3. add 25.00 mL of 0.100 M HCl (total):

\[ \approx 2.50 \times 10^{-3} \text{ mol NH}_3 \text{ in beaker} \]

\[ (0.100 \text{ M}) (0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol H}^+ \text{ added} \]

\[ \Rightarrow \text{ mol NH}_3 = \text{ mol H}^+ \Rightarrow \text{ at equivalence point} \]

- when at the equivalence point, look at what’s left in solution

\[ \text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \]

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

\[ \Rightarrow \text{NH}_4^+ \text{ is weak acid } \Rightarrow \text{ acidic} \]

\[ \Rightarrow \text{ pH } < 7.00 \]

- weak acid calculation:

\[ K_a = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \]

\[ [\text{NH}_4^+] = \frac{2.50 \text{ mmol}}{50.0 \text{ mL}} = 0.050 \text{ M} \]

\[
\begin{array}{c|c|c|c}
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{NH}_3(aq) + \text{H}_3\text{O}(aq) \\
0.0500 & 0 & 0 \\
-x & +x & +x \\
0.0500 - x & x & x \\
\end{array}
\]

\[ K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} = 5.6 \times 10^{-10} \]

\[ [\text{H}^+] = 5.29 \times 10^{-6} \text{ M} \]

\[ \text{pH} = 5.28 \]
for ANY weak base/strong acid titration, pH at equiv. pt. < 7.00

4. add 35.00 mL of 0.100 M HCl (total):

- after equivalence point identical to strong base/strong acid titration ➞ $\text{H}^+$ in solution
- $[\text{H}^+] = \frac{(1.00 \times 10^{-3} \text{ mol})}{(0.06000 \text{ L})} = 0.0167 \text{ M}$
- pH = 1.778
5. add 12.50 mL of 0.100 M HCl (total):

\[ \sim 2.50 \times 10^{-3} \text{ mol NH}_3 \text{ in beaker} \]

\[ (0.100 \text{ M}) (0.01250 \text{ L}) = 1.25 \times 10^{-3} \text{ mol H}^+ \text{ added} \]

\[ \Rightarrow \text{ mol NH}_3 = 2(\text{mol H}^+) \Rightarrow 1/2 \text{ equiv. pt.} \]

\[ \text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \]

\[
\begin{array}{ccc}
2.50 \times 10^{-3} & 1.25 \times 10^{-3} & 0 \\
-1.25 \times 10^{-3} & -1.25 \times 10^{-3} & +1.25 \times 10^{-3} \\
1.25 \times 10^{-3} & 0 & 1.25 \times 10^{-3} \quad \text{BUFFER!!} \\
\end{array}
\]

- \[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

\[ \text{K}_b = 1.8 \times 10^{-5} = [\text{OH}^-](1.25 \times 10^{-5} \text{ mol}) / (1.25 \times 10^{-5} \text{ mol}) \]

\[ [\text{OH}^-] = \text{K}_b \]

\[ \text{pOH} = 4.74 \]

\[ \text{pH} = 9.26 \]
**Acid-base indicator:**
is a weak organic acid or base for which the ionized and un-ionized forms (i.e. weak acid and conjugate base, or weak base and conjugate acid) are different colors.

The pH range over which the indicator changes color depends on the value of its $K_a$ or $K_b$.

The color change is used to signal endpoints during a titration. Therefore want this to occur at the steepest part of the titration (need $pK_{\text{indicator}}$ to be within ± 1 pH units of equiv. point).

The pH at the equivalence point of the titration must be within the pH range where the indicator changes color.

**TABLE 17.3** Some Common Acid-Base Indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>In Acid</th>
<th>In Base</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thymol blue</td>
<td>Red</td>
<td>Yellow</td>
<td>1.2–2.8</td>
</tr>
<tr>
<td>Bromophenol blue</td>
<td>Yellow</td>
<td>Bluish purple</td>
<td>3.0–4.6</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Orange</td>
<td>Yellow</td>
<td>3.1–4.4</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red</td>
<td>Yellow</td>
<td>4.2–6.3</td>
</tr>
<tr>
<td>Chlorophenol blue</td>
<td>Yellow</td>
<td>Red</td>
<td>4.8–6.4</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow</td>
<td>Blue</td>
<td>6.0–7.6</td>
</tr>
<tr>
<td>Cresol red</td>
<td>Yellow</td>
<td>Red</td>
<td>7.2–8.8</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
<td>Reddish pink</td>
<td>8.3–10.0</td>
</tr>
</tbody>
</table>

Phenolphthalein can be used for both strong acid – strong base (blue curve) and for weak acid – strong base (red curve). But methyl red is not appropriate for the weak acid – strong base case because its color change is not on the steepest part of the curve.
Solubility Equilibria

• solubility rules introduced in chapter 9:

<table>
<thead>
<tr>
<th>Water-Soluble Compounds</th>
<th>Insoluble Exceptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds containing an alkali metal cation (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) or the ammonium ion (NH₄⁺)</td>
<td>Compounds containing the nitrate ion (NO₃⁻), acetate ion (C₂H₃O₂⁻), or chlorate ion (ClO₃⁻)</td>
</tr>
<tr>
<td>Compounds containing the chloride ion (Cl⁻), bromide ion (Br⁻), or iodide ion (I⁻)</td>
<td>Compounds containing Ag⁺, Hg₂²⁺, or Pb²⁺</td>
</tr>
<tr>
<td>Compounds containing the sulfate ion (SO₄²⁻)</td>
<td>Compounds containing Ag⁺, Hg₂²⁺, Pb²⁺, Ca²⁺, Sr²⁺, or Ba²⁺</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water-Insoluble Compounds</th>
<th>Soluble Exceptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds containing the carbonate ion (CO₃²⁻), phosphate ion (PO₄³⁻), chromate ion (CrO₄²⁻), or sulfide ion (S²⁻)</td>
<td>Compounds containing Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or NH₄⁺</td>
</tr>
<tr>
<td>Compounds containing the hydroxide ion (OH⁻)</td>
<td>Compounds containing Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or Ba²⁺</td>
</tr>
</tbody>
</table>

• view presented in chapter 9 a little too simplistic
  -- the *most soluble compounds* can be made *insoluble* if you put *enough* solute in
  -- the *most insoluble compounds* can be made *soluble* if you put *little enough* solute in

• better view: gradient of solubilities

![Gradient of Solubilities](image)

• use concept of equilibrium to get the gradient
Solubility product = $K_{sp}$

Consider the equilibrium between undissolved silver chloride and a saturated silver chloride solution:

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
\]

Since this is a heterogeneous equilibrium, the equilibrium constant is

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-]
\]

- always write the $K_{sp}$ expression with the solid on the left
- Molar solubility: moles of solute in 1L of saturated solution
- Solubility: grams of solute in 1 L of saturated solution

e.g., Calculate the molar solubility and the solubility of PbF$_2$, given that $K_{sp} = 4.0 \times 10^{-8}$

Solution:

<table>
<thead>
<tr>
<th>PbF$_2$(s)</th>
<th>Pb$^{2+}$</th>
<th>2F$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>lots</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>x</td>
<td>2x</td>
</tr>
</tbody>
</table>

This gives $K_{sp} = (x)(2x)^2 = 4x^3 \Rightarrow x = 2.15 \times 10^{-3}$ M

This is the molar solubility. For the solubility we multiply by the molar mass of 207.2 + 2(19.00) = 245.2 to give 0.527 g/L.
e.g., Given that the solubility of Ag$_2$SO$_3$ is $4.6 \times 10^{-3}$ g/L, what is the solubility product constant $K_{sp}$?

Solution:

We first convert to molar solubility:

\[
(4.6 \times 10^{-3} \text{ g/L}) \div (295.87 \text{ g/mol}) = 1.55 \times 10^{-5} \text{ M}
\]

<table>
<thead>
<tr>
<th></th>
<th>Ag$_2$SO$_3$</th>
<th>2Ag$^+$</th>
<th>SO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>lots</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+2x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>2x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

We know that $x = 1.55 \times 10^{-5}$ M. Thus $K_{sp} = 4x^3 = 1.5 \times 10^{-14}$

e.g., What is the maximum mass (in grams) of (NH$_4$)$_2$SO$_4$ that can be added to 150 mL of 0.050 M BaCl$_2$ without causing a precipitate to form?

Solution:
First, we have to examine a $K_{sp}$ table (e.g., Table 17.4 in the textbook). We can find that the $K_{sp}$ for BaSO$_4$ is $1.1 \times 10^{-10}$

This means that if [Ba$^{2+}$][SO$_4^{2-}$] > $K_{sp}$, we get a precipitate. Since [Ba$^{2+}$] = 0.050 M, we can have at most [SO$_4^{2-}$] = $K_{sp}/0.050 = 2.2 \times 10^{-9}$ M.

Then we multiply by the volume and the molar mass:

\[
(2.2 \times 10^{-9} \text{ mol/L}) \times (0.150 \text{ L}) \times (132.154 \text{ g/mol}) = 4.4 \times 10^{-8} \text{ g}
\]
Factors Affecting Solubility

The common ion effect

Consider the solubility of AgCl:
\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \]
in a solution that already has dissolved AgNO\textsubscript{3} in it.

From Le Chatelier's Principle we know that AgCl will be significantly less soluble in 0.10 \textit{M} AgNO\textsubscript{3} than in pure water.

Work out the numbers:

Since \( K_{sp} \) for AgCl is \( 1.6 \times 10^{-10} \),
the molar solubility is just the square root of this: \( 1.3 \times 10^{-5} \).

Now consider the solubility of AgCl in 0.10 \textit{M} AgNO\textsubscript{3}

<table>
<thead>
<tr>
<th></th>
<th>AgCl ⇌</th>
<th>Ag\textsuperscript{+}</th>
<th>Cl\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>lots</td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td>0.10 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_{sp} = 1.6 \times 10^{-10} = (x)(0.10 + x) \approx (x)(0.10) \Rightarrow x = 1.6 \times 10^{-9} \]

\( pH \)

The solubility of a substance can depend on pH.

For example, consider \( \text{Mg(OH)}_{2}(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^{-}(aq) \)

At equilibrium, if we add OH\textsuperscript{-} ions (increase the pH) the equilibrium will shift to the left, decreasing the solubility of Mg(OH)\textsubscript{2}. 
If we add $\text{H}^+$ ions (decrease the pH), $\text{Mg(OH)}_2$ will become more soluble. This is why insoluble bases tend to dissolve in acidic solutions.

Adding $\text{H}^+$ results in the reaction $\text{2H}^+ + 2 \text{OH}^- \rightleftharpoons 2\text{H}_2\text{O}(l)$ which gives the net reaction

$$\text{Mg(OH)}_2(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l)$$

Another example: consider $\text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+} + 2\text{F}^-$

Since $\text{F}^-$ has acid/base properties, this equilibrium is also affected by pH. Specifically, at low pH, we can write

$$2\text{H}^+ + 2\text{F}^- \rightleftharpoons 2\text{HF}$$

which gives the net reaction

$$\text{BaF}_2(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{HF}(aq)$$

**Separation of Ions using Differences in Solubility**

*Fractional precipitation*

If we have two or more ions in solution we can separate them by using a compound that can form a precipitate with each of them (with different $K_{sp}$ values).

E.g., we can separate $\text{Cl}^-(aq)$ and $\text{Br}^-(aq)$ by using $\text{AgNO}_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AgCl}$</td>
<td>$1.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{AgBr}$</td>
<td>$7.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>$\text{AgI}$</td>
<td>$8.3 \times 10^{-17}$</td>
</tr>
</tbody>
</table>
Silver nitrate is added to a solution containing 0.020 $M$ $Cl^-$ and 0.020 $M$ $Br^-$. Calculate the concentration of $Ag^+$ ions needed to initiate precipitation of $AgBr$ without precipitating $AgCl$. Also, when the more soluble species begins to precipitate, what is $[Br^-]$?

Solution:

$AgBr$ will precipitate first because its $K_{sp}$ is smaller than $AgCl$.

From the expression $[Ag^+][Br^-] = K_{sp} = 7.7 \times 10^{-13}$
We get $[Ag^+] = 7.7 \times 10^{-13} / 0.020 = 3.9 \times 10^{-11} \ M$.
Any higher value for $[Ag^+]$ will cause $AgBr$ to precipitate.

From the expression $[Ag^+][Cl^-] = K_{sp} = 1.6 \times 10^{-10}$
We get $[Ag^+] = 1.6 \times 10^{-10} / 0.020 = 8.0 \times 10^{-9} \ M$.
Any higher value for $[Ag^+]$ will cause $AgCl$ to precipitate.

Therefore we can precipitate the maximum amount of $AgBr$ without causing any $AgCl$ to precipitate if we use $[Ag^+] = 8.0 \times 10^{-9} \ M$

At this point, what is $[Br^-]$?

It is $7.7 \times 10^{-13} / 8.0 \times 10^{-9} = 9.6 \times 10^{-5} \ M$.

This is less than 0.5 % of the original $[Br^-]$ so we are able to effectively separate $Cl^-$ and $Br^-$ (by filtration to remove $AgBr$).