Applications of Aqueous Equilibria
log fun with $K_a$:

**Henderson-Hasselbalch Equation**

$$
HA (aq) \rightleftharpoons H^+(aq) + A^- (aq)
$$

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

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

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

$$
pH = pK_a + \log \frac{[A^-]}{[HA]}
$$

$$
pH = pK_a + \log \frac{[\text{conj.base}]}{[\text{acid}]}
$$
Buffer Solutions

• resist changes in pH upon the addition of small amounts of either acid or base

• contain a weak acid (or base) and its conjugate in a salt form.
Example

Which of the following are buffer systems?

(a) KF / HF
   yes; HF is a weak acid and F\(^{-}\) is its conjugate base

(b) KBr/ HBr
   no; HBr is a strong acid

(c) Na\(_2\)CO\(_3\)/ NaHCO\(_3\)
   yes; HCO\(_3\)^{-} is a weak acid and CO\(_3^{2-}\) is its conjugate base

(d) 0.5 mol HCl added to 1 mol KF solution
   yes
   \[ \text{H}^+ + \text{F}^- \rightarrow \text{HF} \]

\[
\begin{array}{c|ccc}
\text{I} & 0 & 0.5 & 1 \\
\text{E} & 0 & 0.5 & 0.5 \\
\end{array}
\]
How a sodium acetate/ acetic acid buffer buffers

The chemistry

Weak acid

H − OAc

Buffers have ~equal amounts of these to start with

Its conjugate base in salt form

AcO−

OH− add base

AcO−

H+ add acid

H − OAc
How a sodium acetate/ acetic acid buffer buffers

the mathematics

\[ K_a = \frac{[H^+] [AcO^-]}{[HOAc]} = 1.8 \times 10^{-5} \]

Rewriting in the form of Henderson-Hasselbalch equation

\[ pH = pK_a + \log \frac{[AcO^-]}{[HOAc]} \]

What pH’s do you get for this buffer when \([AcO^-]/[HOAc] = 1:1, 2:1, 3:1, 4:1, 5:1, 1:2, 1:3, 1:4?\]

Group # 1 2 3 4 5 6 7 8
UNBUFFERED SOLUTIONS

Calculate the pH of two 1.00-L beakers of water after adding a) 0.100 mol HCl to one and b) 0.100 mol NaOH to the other. (both are strong so use stoichy!)

\[
\text{HCl} \rightarrow \text{H}^+ (aq) + \text{Cl}^- (aq)
\]

\[
\begin{array}{c|c|c|c}
\text{I} & \text{0.100 M} & 0 & 0 \\
\text{E} & 0 & 0.100 \text{ M} & 0.100 \text{ M} \\
\end{array}
\]

\[
pH = -\log[H^+] = -\log(0.100)
\]

\[\text{a) } pH = 1\]

\[
\text{NaOH} \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)
\]

\[
\begin{array}{c|c|c|c}
\text{I} & \text{0.100 M} & 0 & 0 \\
\text{E} & 0 & 0.100 \text{ M} & 0.100 \text{ M} \\
\end{array}
\]

\[
pOH = -\log[OH^-] = -\log(0.100)
\]

\[\text{pOH} = 1\]

\[
pH + pOH = 14
\]

\[\text{b) } pH = 13\]
3 Scenarios to contrast with our unbuffered examples:

1. HOAc/OAc- buffer alone

2. #1 with 0.10 mol HCl added

3. #1 with 0.10 mol NaOH added
BUFFERED SOLUTIONS

Calculate the pH of a buffer containing $1.0 \, M$ acetic acid and $1.0 \, M$ sodium acetate.

\[ \text{H} - \text{OAc} \, (\text{aq}) \rightleftharpoons \text{H}^+ \, (\text{aq}) + \text{AcO}^- \, (\text{aq}) \]

\[
\begin{array}{c|c|c}
\text{I} & 1.0 \, \text{M} & 0 \\
\text{E} & 1.0 \, \text{M} - x & +x \\
\end{array}
\]

\[
1.8 \times 10^{-5} = K_a = \frac{[\text{H}^+] \, [\text{AcO}^-]}{[\text{HOAc}]}.
\]

\[
\text{pH} = pK_a + \log \frac{[\text{conj.base}]}{[\text{acid}]}.
\]

\[
\text{pH} = -\log(1.8 \times 10^{-5}) + \log \frac{(1.0 \, \text{M} + x)}{(1.0 \, \text{M} - x)}.
\]

\[
\text{pH} = 4.74
\]
Calculate the pH of a buffer containing 1.0 M acetic acid and 1.0 M sodium acetate.

\[ \text{pH} = 4.74 \]

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

Key 1st step: Strong acid + weak base (OAc\(^{-}\)) goes to completion. Use stoichiometry with acid/base neutralization reaction.

\[
\begin{align*}
\text{H}^{+} (aq) + \text{AcO}^{-} (aq) & \rightarrow \text{H} \equiv \text{OAc} (aq)
\end{align*}
\]

\[
\begin{array}{ccc}
\text{I} & 0.1 \text{ mol} & 1.0 \text{ mol} & 1.0 \text{ mol} \\
\downarrow & & & \\
\text{E} & \approx 0.0 \text{ mol} & 0.9 \text{ mol} & 1.1 \text{ mol}
\end{array}
\]
\[
\text{H}^+ \text{(aq)} + \text{AcO}^- \text{(aq)} \Leftrightarrow \text{H}^- \text{OAc} \text{(aq)}
\]

\[E \equiv 0.0 \text{ mol} \quad 0.9 \text{ mol} \quad 1.1 \text{ mol}\]

Key 2nd step: Now let system reach equilibrium using these as initial conditions in the acid dissociation \((K_a)\) reaction.

\[
\text{H}^- \text{OAc} \text{(aq)} \Leftrightarrow \text{AcO}^- \text{(aq)} + \text{H}^+ \text{(aq)}
\]

\[
\begin{align*}
\text{I} & \quad \frac{1.1 \text{ mol}}{1 \text{L}} & \quad \frac{0.9 \text{ mol}}{1 \text{L}} & \quad 0 \text{ M} \\
\text{E} & \quad 1.1 \text{ M} - x & \quad 0.9 \text{ M} + x & \quad +x
\end{align*}
\]

\[
K_a = \frac{[\text{H}^+][\text{AcO}^-]}{[\text{HOAc}]} = 1.8 \times 10^{-5} = \frac{x (0.9 + x)}{(1.1 - x)}
\]

\[x = [\text{H}^+] = 2.2 \times 10^{-5} \text{ M}\]

\[\text{pH} = 4.66\]
Same calculation using the Henderson-Hasselbalch equation

\[
\begin{align*}
H - OAc (aq) & \quad \iff \quad AcO^- (aq) + H^+ (aq) \\
E & \quad 1.1 \text{ mol} - x \quad \quad \quad \quad 0.9 \text{ mol} + x \quad +x
\end{align*}
\]

\[
\begin{align*}
\text{pH} & = \text{p}K_a + \log \left[ \frac{\text{c.base}}{\text{acid}} \right] \\
\text{pH} & = - \log K_a + \log \left( \frac{0.9 + x}{1.1 - x} \right)
\end{align*}
\]

\[
\text{pH} = 4.74 - 0.09 = 4.65
\]
Calculate the pH of a buffer containing 1.0 \( M \) acetic acid and 1.0 \( M \) sodium acetate.

\[
\text{pH} = 4.74
\]

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

\[
\text{pH} = 4.66
\]

What happens when 0.10 mol of solid NaOH is added to 1.0 L of this solution?
add 0.10 mol of NaOH(s) to 1.0 L of a solution that is 1.0 M in NaOAc and HOAc

Key 1st Step: Strong base + weak acid goes to completion. Use stoichiometry with acid/base neutralization reaction.

\[
\text{OH}^- + \text{H}^-\text{OAc} \rightarrow \text{H}_2\text{O} + \text{AcO}^-
\]

\[
\begin{array}{ccc}
0.1 \text{ mol} & 1.0 \text{ mol} & 1.0 \text{ mol} \\
\downarrow & \downarrow & \downarrow \\
0.0 \text{ mol} & 0.9 \text{ mol} & 1.1 \text{ mol}
\end{array}
\]
\[
\text{OH}^- + \text{H}^+ - \text{OAc}^- \rightleftharpoons \text{H}_2\text{O} + \text{AcO}^- \\
\cong 0.0 \text{ mol} \quad 0.9 \text{ mol} \quad 1.1 \text{ mol}
\]

Key 2nd step: Now let system reach equilibrium using these as initial conditions for the acid dissociation (K_a) reaction.

\[
\begin{align*}
\text{E} & \quad \frac{0.9 \text{ mol}}{1 \text{L}} - x \\
\text{H}^- - \text{OAc}^- & \rightleftharpoons \text{H}^+ + \text{AcO}^- \\
& \quad \frac{1.1 \text{ mol}}{1 \text{L}} + x
\end{align*}
\]

\[
K_a = \frac{[\text{H}^+][\text{AcO}^-]}{[\text{HOAc}]} = 1.8 \times 10^{-5} = \frac{[\text{H}^+](1.1 + x)}{(0.9 - x)}
\]

\[
[\text{H}^+] = 1.47 \times 10^{-5} \text{ M} \quad \text{pH} = 4.83
\]
Same calculation using the Henderson-Hasselbalch equation

\[
\text{H} - \text{OAc} \quad \Longleftrightarrow \quad \text{H}^+ \quad + \quad \text{AcO}^- \\
E \quad 0.9 \text{ mol - } x \quad +x \quad 1.1 \text{ mol } + x
\]

\[
pH = pK_a + \log \left( \frac{[\text{c.base}]}{[\text{acid}]} \right)
\]

\[
pH = - \log (1.8 \times 10^{-5}) + \log \left( \frac{1.1 + x}{0.9 - x} \right)
\]

\[
pH = 4.74 + 0.09 = 4.83
\]
Calculate the pH of a buffer containing 1.0 M acetic acid and 1.0 M sodium acetate.

\[ \text{pH} = 4.74 \]

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

\[ \text{pH} = 4.66 \]

What happens when 0.10 mol of solid NaOH is added to 1.0 L of this solution?

\[ \text{pH} = 4.83 \]

Compare to pH = 1 and pH = 13 for unbuffered solution!
Distribution Curves

Show the fraction of each species present as a function of pH

acid and conjugate base

base and conjugate acid
distribution curves for acetic acid and acetate ion as a function of pH

pH = \( pK_a = 4.74 \)
Buffer range = \( pK_a \pm 1.00 \)
The bicarbonate/carbonate acid buffer is more complicated because carbonic acid is a diprotic acid.

It is important because it contributes to controlling the pH of blood at 7.4.
distribution curves for carbonic acid and bicarbonate ion as a function of pH

\[ pK_a = 6.83 \]

\[ pK_a = 10.32 \]
Preparing a Buffer Solution with a Specific pH

\[ \text{pH} = pK_a + \log \frac{[\text{c.base}]}{[\text{acid}]} \]

- center of buffer range: \([\text{acid}] = [\text{conj. base}]\)

What’s true about pH then? \( \text{pH} = pK_a \)

- choose a weak acid/conjugate base combination where the \( pK_a \) of the acid corresponds to the pH at which you want the solution buffered
How would you prepare a liter of “carbonate buffer” at a pH of 10.10?

you have available:

$\text{H}_2\text{CO}_3$  \hspace{1cm} $pK_a$ 6.38

NaHCO$_3$  \hspace{1cm} $pK_a$ 10.32

Na$_2$CO$_3$

Pick NaHCO$_3$ and its conjugate base.
How would you prepare a liter of “carbonate buffer” at a pH of 10.10?

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{c.base}]}{[\text{acid}]}
\]

\[
10.10 = 10.32 + \log \frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]}
\]

\[
\frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]} = 10^{-0.22} = 0.60
\]
Acid-Base Titrations
Titration

a solution of known concentration, called a standard solution is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete

equivalence point

• the exact number of moles required for the reaction

• detected by a color change in an acid-base indicator or electronically
Acid-Base Titrations

How does the pH change during the course of the following kinds of titration?

- strong acid-strong base
- weak acid-strong base
- weak base-strong acid
Titrations Involving a Strong Acid and a Strong Base
Titrations Involving a Strong Acid and a
Strong Base

titratenote: 25.0 mL of 0.100 M HCl with 0.100 M NaOH

Note: \( \text{mmol/mL} \) and \( \text{mol/L} \)

are equivalent

And for strong w/ strong, simply use stoichy! No \( K_{eq} \).
What is the pH after the addition of 10.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl?

\[
\text{HCl (aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O (l)} + \text{NaCl (aq)}
\]

\[
10\text{ml} \times \frac{0.1\text{mmol NaOH}}{\text{mL}} = 1.0\text{mmol OH}^-
\]

\[
25\text{ml} \times \frac{0.1\text{mmol HCl}}{\text{mL}} = 2.5\text{mmol H}^+
\]

\[
\text{H}^+ (aq) + \text{OH}^- (aq) \leftrightarrow \text{H}_2\text{O (l)}
\]

I

| 2.5mmol H^+ | 1.0mmol | 0 |

E

| 1.5mmol H^+ | 0 | 1.0mmol |
What is the pH after the addition of 10.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl?

\[
\begin{align*}
H^+ (aq) + OH^- (aq) & \rightleftharpoons H_2O (l) \\
[\text{H}^+] &= \frac{1.5 \text{ mmol H}^+}{35.0 \text{ mL (solution)}} = 4.28 \times 10^{-2} \text{ M} \\
\text{pH} &= 1.37
\end{align*}
\]
What is the pH after the addition of 25.0 mL of 0.100 \( M \) NaOH to 25.0 mL of 0.100 \( M \) HCl?

\[
\begin{align*}
25 \text{ mL} & \times \frac{0.1 \text{ mmol NaOH}}{\text{mL}} = 2.5 \text{ mmol OH}^- \\
25 \text{ mL} & \times \frac{0.1 \text{ mmol HCl}}{\text{mL}} = 2.5 \text{ mmol H}^+
\end{align*}
\]

\[\text{H}^+ (aq) + \text{OH}^- (aq) \rightleftharpoons \text{H}_2\text{O} (l)\]

Initial: 2.5 mmol H\(^+\)  \hspace{1cm} 2.5 mmol \hspace{1cm} 0

Final: 0 \hspace{1cm} 0 \hspace{1cm} 2.5 mmol
What is the pH after the addition of 25.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl?

\[
\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

\[
[H^+] = 1.0 \times 10^{-7} \text{ M}
\]

\[
\text{pH} = 7.0
\]
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<th>volume (NaOH)</th>
<th>volume (total)</th>
<th>mmol (HCl)</th>
<th>$[\text{H}^+]_M$</th>
<th>pH</th>
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<td>2.5</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td>10.0 ml</td>
<td>35.0 ml</td>
<td>1.5</td>
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<td>1.37</td>
</tr>
<tr>
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<td>45.0 ml</td>
<td>0.5</td>
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<td>1.95</td>
</tr>
<tr>
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<td>49.0 ml</td>
<td>0.1</td>
<td>0.002</td>
<td>2.69</td>
</tr>
<tr>
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<td>0.05</td>
<td>0.001</td>
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</tr>
<tr>
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<td>50.0 ml</td>
<td>0</td>
<td>$10^{-7}$</td>
<td>7.00</td>
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</table>
Titration of 25.00 ml of 0.100 M HCl with 0.100 M NaOH.

The pH is 7.0 at the equivalence point.
What is the pH after the addition of 35.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl?

\[
\begin{align*}
35\text{ml} \times \frac{0.1\text{mmol NaOH}}{\text{mL}} &= 3.5\text{mmol OH}^- \\
25\text{ml} \times \frac{0.1\text{mmol HCl}}{\text{mL}} &= 2.5\text{mmol H}^+
\end{align*}
\]

\[\text{H}^+ (aq) + \text{OH}^- (aq) \rightleftharpoons \text{H}_2\text{O} (l)\]

\[
\begin{array}{c|c|c|c}
\text{start} & 2.5 \text{ mmol} & 3.5 \text{ mmol} & 0 \\
\text{end} & 0 & 1.0 \text{ mmol} & 2.5 \text{ mmol}
\end{array}
\]
What is the pH after the addition of 35.0 mL of 0.100 \( M \) NaOH to 25.0 mL of 0.100 \( M \) HCl?

\[
\text{H}^+ (aq) + \text{OH}^- (aq) \rightleftharpoons \text{H}_2\text{O} (l)
\]

\[
[\text{OH}^-] = \frac{1.0 \text{ mmol OH}^-}{60.0 \text{ mL (solution)}} = 1.66 \times 10^{-2} \text{ M}
\]

\[
\text{pOH} = 1.78
\]

\[
\text{pH} = 12.22
\]
<table>
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<tr>
<th>volume (NaOH)</th>
<th>volume (total)</th>
<th>mmol (HCl)</th>
<th>$[\text{H}^+]_M$</th>
<th>pH</th>
</tr>
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<tbody>
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<td>50.0 ml</td>
<td>0</td>
<td>$10^{-7}$</td>
<td>7.00</td>
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<td>0.001</td>
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<td>0.10</td>
<td>0.002</td>
<td>11.29</td>
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<td>55.0 ml</td>
<td>0.50</td>
<td>0.009</td>
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<td>1.50</td>
<td>0.023</td>
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</tr>
<tr>
<td>50.0 ml</td>
<td>75.0 ml</td>
<td>2.50</td>
<td>0.033</td>
<td>12.52</td>
</tr>
</tbody>
</table>
Titration of 25.00 ml of 0.100 M HCl with 0.100 M NaOH at 7.0 at equivalence point.
Sketch the titration curve if strong base is in the beaker and strong acid is in the buret.

Titration of 25.00 ml of 0.100 M HCl with 0.100 M NaOH
Titrations Involving a weak Acid and a Strong Base
Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding
(a) 10.0 mL of 0.100 M NaOH
(b) 25.0 mL of 0.100 M NaOH
(c) 35.0 mL of 0.100 M NaOH

Molecular Eqn
\[ \text{CH}_3\text{COOH} \ + \ \text{NaOH} \quad \rightleftharpoons \quad \text{CH}_3\text{COONa} \ + \ \text{H}_2\text{O} \]

Net Ionic Eqn
\[ \text{CH}_3\text{COOH} \ + \ \text{OH}^- \quad \rightleftharpoons \quad \text{CH}_3\text{COO}^- \ + \ \text{H}_2\text{O} \]
Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding (a) 10.00 mL of 0.100 M NaOH.

Key 1st step: Strong base (sodium hydroxide) + weak acid (acetic) goes to completion. Use stoichiometry with neutralization reaction.

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

### Initial Conditions
- **I**: 2.5 mmol \(\text{CH}_3\text{COOH}\), 1.0 mmol \(\text{OH}^-\), 0 mmol \(\text{CH}_3\text{COO}^-\), 0 mmol \(\text{H}_2\text{O}\)
- **E**: 1.5 mmol \(\text{CH}_3\text{COOH}\), 0 mmol \(\text{OH}^-\), 1.0 mmol \(\text{CH}_3\text{COO}^-\), 1.0 mmol \(\text{H}_2\text{O}\)

Key 2nd step: Now let system reach equilibrium using these as initial conditions for the acid dissociation \((K_a)\) reaction.

\[ K_a = 1.8 \times 10^{-5} \]

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

- **E**: 1.5 mmol \(\text{CH}_3\text{COOH}\) - x, 1.0 mmol \(\text{CH}_3\text{COO}^-\) + x, \(\text{H}^+\) + x
Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding (a) 10.00 mL of 0.100 M NaOH.

\[ K_a = 1.8 \times 10^{-5} \]

\[ \text{CH}_3\text{COOH} \quad \rightleftharpoons \quad \text{CH}_3\text{COO}^- \quad + \quad \text{H}^+ \]

Plan: Assume x is small since \( K_a \) is small and turn mmol into \( M \).

\[
\begin{align*}
\frac{1.5 \text{mmol}}{35.0 \text{mL}} & = 0.0043 \text{ M} \\
\frac{1.0 \text{mmol}}{35.0 \text{mL}} & = 0.0028 \text{ M}
\end{align*}
\]

\[
\text{pH} = - \log (1.8 \times 10^{-5}) + \log \left( \frac{0.0028 + x}{0.0043 - x} \right)
\]

\[
\text{pH} = 4.57
\]
Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding (b) 25.0 mL of 0.100 M NaOH.

Key 1st step: Strong base (sodium hydroxide) + weak acid (acetic) goes to completion. Use stoichiometry with neutralization reaction.

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

\[
\begin{array}{c|cc|c|c|c|c}
 & \text{CH}_3\text{COOH} & \text{OH}^- & \rightarrow & \text{CH}_3\text{COO}^- & + & \text{H}_2\text{O} \\
\hline
\text{I} & 2.5 \text{mmol} & 2.5 \text{mmol} & & 0 & & 0 \\
\text{E} & 0 & 0 & & 2.5 \text{mmol} & & 2.5 \text{mmol} \\
\end{array}
\]

Key 2nd step: Now let system reach equilibrium using these as initial conditions for the base dissociation (\(K_b\)) reaction.

\[ K_b = 5.6 \times 10^{-10} \]

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

\[
\frac{2.5 \text{mmol}}{50.0 \text{ mL}} = 5.0 \times 10^{-2} \text{ M}
\]
Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding (b) 25.0 mL of 0.100 M NaOH.

\[
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \\
5.0 \times 10^{-2} \text{ M} \cdot x \quad x 
x
\]

\[
5.6 \times 10^{-10} = \frac{x^2}{(5.0 \times 10^{-2} - x)}
\]

\[
[\text{OH}^-] = x = 5.29 \times 10^{-6}
\]

pOH = 5.27

pH = 8.72
Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH after adding (c) 35.0 mL of 0.100 M NaOH.

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad + \quad \text{OH}^- & \quad \text{H}_2\text{O} \\
\text{I} & \quad 2.5\text{mmol} & \quad 3.5\text{mmol} \\
\text{E} & \quad 0 & \quad 1.0\text{mmol} & \quad 2.5\text{mmol} & \quad 2.5\text{mmol}
\end{align*}
\]

Strong base dominates, so we can ignore weak base and directly determine pH.

\[
\begin{align*}
1.0\text{mmol} \quad \text{OH}^- \\
60.0 \text{ mL (solution)} &= 1.67 \times 10^{-2} \text{ M}
\end{align*}
\]

\[
p\text{OH} = 1.78 \\
p\text{H} = 12.22
\]
<table>
<thead>
<tr>
<th>volume (NaOH)</th>
<th>volume (total)</th>
<th>mmol (HOAc)</th>
<th>mmol (NaOAc)</th>
<th>$[\text{H}^+]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ml</td>
<td>25.0 ml</td>
<td>2.5</td>
<td>0</td>
<td>$1.3 \times 10^{-3}$</td>
<td>2.87</td>
</tr>
<tr>
<td>10.0 ml</td>
<td>35.5 ml</td>
<td>1.5</td>
<td>1</td>
<td>$2.7 \times 10^{-5}$</td>
<td>4.57</td>
</tr>
<tr>
<td>25.0 ml</td>
<td>50.0 ml</td>
<td>0</td>
<td>2.5</td>
<td>$1.9 \times 10^{-9}$</td>
<td>8.72</td>
</tr>
<tr>
<td>35.0 ml</td>
<td>60.0 ml</td>
<td>0</td>
<td>1</td>
<td>$1.7 \times 10^{-2}$</td>
<td>12.22</td>
</tr>
</tbody>
</table>
Titration of 25.0 ml of 0.10 M acetic acid with 0.10 M NaOH

Maximum buffer

Why?

Why?

15 -
12.5 -
10 -
7.5 -
5 -
2.5 -

pH

0  25  50

volume  (0.10 M NaOH)

$4.75$

$8.72$ Why?
Titrations Involving a Strong Acid and a Weak Base
Calculate the pH in the titration of 25.0 mL of 0.100 M HCl with 0.100 M NH₃ after adding
(a) 10.0 mL of 0.100 M NH₃
(b) 25.0 mL of 0.100 M NH₃
(c) 35.0 mL of 0.100 M NH₃

\[
\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-
\]

\[
\text{H}^+ + \text{NH}_3 \rightleftharpoons \text{NH}_4^+
\]
Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 M HCl with 0.100 M NH₃ after adding (a) 10.00 mL of 0.100 M NH₃.

Key 1st step: Strong acid (HCl) + weak base (ammonia) goes to completion. Use stoichiometry with neutralization reaction.

\[
\begin{array}{c}
\text{H}^+ + \text{NH}_3 \leftrightarrow \text{NH}_4^+
\end{array}
\]

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>2.5mmol</th>
<th>1.0mmol</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>1.5mmol</td>
<td>0</td>
<td>1.0mmol</td>
<td></td>
</tr>
</tbody>
</table>

Strong acid dominates, so we can ignore weak acid NH₄⁺ and directly determine pH.

\[
[H^+] = \frac{1.5 \text{ mmol H}^+}{35.0 \text{ mL}} = 4.29 \times 10^{-2} M
\]

\[\text{pH} = 1.37\]
Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 \( M \) HCl with 0.100 \( M \) NH\(_3\) after adding (b) 25.0 mL of 0.100 \( M \) NH\(_3\).

**Key 1st step:** Strong acid (HCl) + weak base (ammonia) goes to completion. Use stoichiometry with neutralization reaction.

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

<table>
<thead>
<tr>
<th></th>
<th>2.5 mmol</th>
<th>2.5 mmol</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>2.5 mmol</td>
</tr>
</tbody>
</table>

**Key 2nd step:** Now let system reach equilibrium using these as initial conditions for the acid dissociation (\( K_a \)) reaction.

\[
K_a = 5.6 \times 10^{-10}
\]

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

\[
\frac{2.5 \text{mmol}}{50.0 \text{mL}} = 5.0 \times 10^{-2} \text{M}
\]
Calculate the pH in the titration of 25.0 mL of 0.100 M HCl with 0.100 M NH₃ after adding (b) 25.0 mL of 0.100 M NH₃.

**Titrations Involving a Strong Acid and a Weak Base**

\[ K_a = 5.6 \times 10^{-10} \]

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

\[ E \quad 2.5 \text{mmol} - x \quad +x \quad +x \]

\[ 5.6 \times 10^{-10} = \frac{x^2}{(5.0 \times 10^{-2} - x)} \]

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

\[ \text{pH} = 5.28 \]
Calculate the pH in the titration of 25.0 mL of 0.100 M HCl with 0.100 M NH₃ after adding (c) 35.0mL of 0.100 M NH₃.

\[
\begin{align*}
\text{H}^+ & \quad + \quad \text{NH}_3 \quad \rightleftharpoons \quad \text{NH}_4^+ \\
2.5 \text{ mmol} & \quad 3.5 \text{ mmol} \quad 0 \\
0 & \quad 1.0 \text{ mmol} \quad 2.5 \text{ mmol} \\
K_a & = 5.6 \times 10^{-10}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_4^+ & \quad \rightleftharpoons \quad \text{NH}_3 \quad + \quad \text{H}^+ \\
2.5 \text{ mmol} & \quad 1.0 \text{ mmol} \quad 2.5 \text{ mmol} \\
\frac{2.5 \text{ mmol}}{60.0 \text{ mL}} & = 4.1 \times 10^{-2} \text{M} \quad \frac{1.0 \text{ mmol}}{60.0 \text{ mL}} & = 1.66 \times 10^{-2} \text{M}
\end{align*}
\]
Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 M HCl with 0.100 M NH₃ after adding (c) 35.0 mL of 0.100 M NH₃.

\[ K_a = 5.6 \times 10^{-10} \]

\[ \begin{align*}
\text{NH}_4^+ & \quad \text{NH}_3 \quad + \quad \text{H}^+ \\
4.16 \times 10^{-2} & \quad 1.66 \times 10^{-2}
\end{align*} \]

\[ \begin{align*}
[H^+] &= \frac{[\text{NH}_4^+] \cdot K_a}{[\text{NH}_3]} \\
&= \frac{(4.16 \times 10^{-2})(5.6 \times 10^{-10})}{1.66 \times 10^{-2}} \\
&= 1.4 \times 10^{-9}
\end{align*} \]

\[ \text{pH} = 8.85 \]
<table>
<thead>
<tr>
<th>volume (NH₃)</th>
<th>volume (total)</th>
<th>mmol (HCl)</th>
<th>[H⁺]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ml</td>
<td>25.0 ml</td>
<td>2.5</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>10.0 ml</td>
<td>35.0 ml</td>
<td>1.5</td>
<td>0.0429</td>
<td>1.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mmol (NH₄⁺)</th>
<th>mmol (NH₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0 ml</td>
<td>50.0 ml</td>
</tr>
<tr>
<td>35.0 ml</td>
<td>60.0 ml</td>
</tr>
</tbody>
</table>
Titration of 25.0 ml of 0.10 M HCl acid with 0.10 M NH₃.

5.36 at equivalence point
Titration of 25.0 ml of 0.10 M HCl acid with 0.10 M NH₃

When [NH₃] = [NH₄⁺]

pH

9.25 when [NH₃] = [NH₄⁺]

volume (0.10 M NH₃)
Solubility Equilibria

Applies the principles of equilibrium to ionic solids of low solubility in water
• Milk of Magnesia demo
Solubility product ($K_{sp}$)

in a saturated solution, the species in solution is in equilibrium with undissolved material

is characterized by an equilibrium constant $K_{sp}$ called the solubility product
Examples:

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

\[K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.6 \times 10^{-10}\]

\[\text{Ag}_2\text{CO}_3 (s) \rightleftharpoons 2\text{Ag}^+ (aq) + \text{CO}_3^{2-} (aq)\]

\[K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = 8.1 \times 10^{-12}\]

\[\text{Ca}_3(\text{PO}_4)_2 (s) \rightleftharpoons 3\text{Ca}^{2+} (aq) + 2\text{PO}_4^{3-} (aq)\]

\[K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 1.2 \times 10^{-26}\]
<table>
<thead>
<tr>
<th>Ionic Solid</th>
<th>(K_{sp}) (at 25°C)</th>
<th>Ionic Solid</th>
<th>(K_{sp}) (at 25°C)</th>
<th>Ionic Solid</th>
<th>(K_{sp}) (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaF₂</td>
<td>(2.4 \times 10^{-5})</td>
<td>MgF₂</td>
<td>(6.4 \times 10^{-9})</td>
<td>PbF₂</td>
<td>(4 \times 10^{-8})</td>
</tr>
<tr>
<td>SrF₂</td>
<td>(7.9 \times 10^{-10})</td>
<td>CaF₂</td>
<td>(4.0 \times 10^{-11})</td>
<td>Hg₂CrO₄*</td>
<td>(2 \times 10^{-9})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbCl₂</td>
<td>(1.6 \times 10^{-5})</td>
<td>AgCl</td>
<td>(1.6 \times 10^{-10})</td>
<td>Hg₂Cl₂*</td>
<td>(1.1 \times 10^{-18})</td>
</tr>
<tr>
<td>AgCl</td>
<td>(1.6 \times 10^{-10})</td>
<td>SrCl₂</td>
<td>(7 \times 10^{-10})</td>
<td>NiCO₃</td>
<td>(1.4 \times 10^{-7})</td>
</tr>
<tr>
<td>Hg₂Cl₂*</td>
<td>(1.1 \times 10^{-18})</td>
<td></td>
<td></td>
<td>CaCO₃</td>
<td>(8.7 \times 10^{-9})</td>
</tr>
<tr>
<td>Bromides</td>
<td></td>
<td></td>
<td></td>
<td>CaCO₃</td>
<td>(8.7 \times 10^{-9})</td>
</tr>
<tr>
<td>PbBr₂</td>
<td>(4.6 \times 10^{-6})</td>
<td>Ag₂Br₂</td>
<td>(5.0 \times 10^{-13})</td>
<td>FeCO₃</td>
<td>(2.1 \times 10^{-11})</td>
</tr>
<tr>
<td>AgBr</td>
<td>(5.0 \times 10^{-13})</td>
<td>Ag₂CO₃</td>
<td>(8.1 \times 10^{-12})</td>
<td>ZnCO₃</td>
<td>(2 \times 10^{-10})</td>
</tr>
<tr>
<td>Hg₂Br₂*</td>
<td>(1.3 \times 10^{-22})</td>
<td>CdCO₃</td>
<td>(5.2 \times 10^{-12})</td>
<td>NiSO₄</td>
<td>(3 \times 10^{-21})</td>
</tr>
<tr>
<td>Iodides</td>
<td></td>
<td></td>
<td></td>
<td>CoS</td>
<td>(5 \times 10^{-22})</td>
</tr>
<tr>
<td>PbI₂</td>
<td>(1.4 \times 10^{-8})</td>
<td>Hg₂CO₃*</td>
<td>(9.0 \times 10^{-15})</td>
<td>ZnS</td>
<td>(2.5 \times 10^{-22})</td>
</tr>
<tr>
<td>AgI</td>
<td>(1.5 \times 10^{-16})</td>
<td>MgCO₃</td>
<td>(6.8 \times 10^{-6})</td>
<td>SnS</td>
<td>(1 \times 10^{-26})</td>
</tr>
<tr>
<td>Hg₂I₂*</td>
<td>(4.5 \times 10^{-29})</td>
<td></td>
<td></td>
<td>CdS</td>
<td>(1.0 \times 10^{-28})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PbS</td>
<td>(7 \times 10^{-29})</td>
</tr>
<tr>
<td>Sulfates</td>
<td></td>
<td></td>
<td></td>
<td>CuS</td>
<td>(8.5 \times 10^{-45})</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>(6.1 \times 10^{-5})</td>
<td>Ag₄O₄</td>
<td>(1.4 \times 10^{-8})</td>
<td>Ag₂S</td>
<td>(1.6 \times 10^{-49})</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>(3.2 \times 10^{-7})</td>
<td>Ba₃(OH)₄</td>
<td>(5.0 \times 10^{-3})</td>
<td>HgS</td>
<td>(1.6 \times 10^{-54})</td>
</tr>
<tr>
<td>PbSO₄</td>
<td>(1.3 \times 10^{-8})</td>
<td>Sr₃(OH)₆</td>
<td>(1 \times 10^{-31})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaSO₄</td>
<td>(1.5 \times 10^{-9})</td>
<td>Ca₃(OH)₆</td>
<td>(1.3 \times 10^{-32})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCrO₄</td>
<td>(3.6 \times 10^{-5})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Carbonates
* Sulfides
* Hydroxides
* Phosphates
The amount of excess solid present has no effect on the position of solubility equilibrium.

When ions in solution reform solid they do so on the surface of the solid.
Doubling the surface area of the solid doubles both the rate of reforming and dissolving. 

position of equilibrium unchanged
Molar solubility: the number of moles solute in one liter of a saturated solution \((mol/L)\)

Solubility: the number of grams of solute in one liter of a solution \((g/L)\)

Depending on the text being used
Solubility v.s. Solubility Product

- **solubility product** is an equilibrium constant and thus has only one value at a certain temperature.

- **solubility** is an equilibrium position and has an infinite number of possible values at a given temperature depending on the conditions. 

  *i.e.: the common ion effect*
given $K_{sp}$ you should be able to calculate

molar solubility

concentration of anion in a saturated solution

concentration of cation in a saturated solution

molar solubilities when common-ion effect comes into play
Practice Exercise

The solubility of PbCrO$_4$ is $4.5 \times 10^{-5}$ g/L. What is its solubility product?

First convert to mol/L

\[
PbCrO_4 (s) \rightleftharpoons Pb^{2+} (aq) + CrO_4^{2-} (aq)
\]

\[
4.5 \times 10^{-5} \frac{g}{L} \times \frac{1 \text{ mol}}{323.2 \text{ g}} = 1.4 \times 10^{-7} \text{ mol/L}
\]
The solubility of PbCrO₄ is 4.5 x 10⁻⁵ g/L. What is its solubility product?

\[
PbCrO_4 (s) \rightleftharpoons Pb^{2+} (aq) + CrO_4^{2-} (aq)
\]

\[
K_{sp} = [Pb^{2+}][CrO_4^{2-}]
\]

\[
K_{sp} = (1.4 \times 10^{-7})(1.4 \times 10^{-7})
\]

\[
K_{sp} = 1.9 \times 10^{-14}
\]
Calculate the molar solubility of PbCO$_3$. 
($K_{sp} = 3.3 \times 10^{-14}$)

PbCO$_3$ (s) $\rightleftharpoons$ Pb$^{2+}$ (aq) + CO$_3^{2-}$ (aq)

$I$ $0.00 \ M$ $0.00 \ M$

$E$ $+x$ $+x$

$K_{sp} = [\text{Pb}^{2+}][\text{CO}_3^{2-}]$

$x = 1.8 \times 10^{-7} \text{mol/L}$

$K_{sp} = (x)(x) = (x)^2 = 3.3 \times 10^{-14}$
The $K_{sp}$ value for Cu(OH)$_2 = 2.2 \times 10^{-20}$ at 25°C. Calculate its solubility in g/L.

$$\text{Cu(OH)}_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq)$$

$I$ $E$

$0.00 \ M$ $0.00 \ M$

$+x$ $+2x$

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = (x)(2x)^2 = (x)(4x^2) = 4x^3 = 2.2 \times 10^{-20}$$
\[ 4x^3 = 2.2 \times 10^{-20} \]

\[ x = \left( \frac{2.2 \times 10^{-20}}{4} \right)^{1/3} \]

\[ x = 1.77 \times 10^{-7} \text{ mol/L} \times \frac{97.55 \text{ g}}{1 \text{ mol}} \]

\[ x = 1.72 \times 10^{-5} \text{ g/L} \]
Relative Solubilities

<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>$8.3 \times 10^{-17}$</td>
</tr>
<tr>
<td>CuI</td>
<td>$5.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>$6.1 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

All $K_{sp}$ expressions are of the form

$$K_{sp} = [X][Y]$$

Therefore, solubility decreases in the order

$$\text{CaSO}_4 > \text{CuI} > \text{AgCl}$$
Relative Solubilities

<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>$8.3 \times 10^{-45}$</td>
</tr>
<tr>
<td>Ag$_2$S</td>
<td>$1.6 \times 10^{-49}$</td>
</tr>
<tr>
<td>Bi$_2$S$_3$</td>
<td>$1.1 \times 10^{-73}$</td>
</tr>
</tbody>
</table>

$K_{sp}$ expressions are of the form

$[Cu^{2+}][S^{2-}]$, $[Ag^+]^2[S^{2-}]$, $[Bi^{3+}]^2[S^{2-}]^3$

Therefore, need to do a calculation
Relative Solubilities

\[
\begin{align*}
\text{CuS} & \rightleftharpoons \text{Cu}^{2+} \text{ (aq)} + \text{S}^{2-} \text{ (aq)} \\
8.3 \times 10^{-45} & = [\text{Cu}^{2+}] [\text{S}^{2-}] = x^2
\end{align*}
\]

\[
\begin{align*}
\text{Ag}_2\text{S} & \rightleftharpoons 2\text{Ag}^+ \text{ (aq)} + \text{S}^{2-} \text{ (aq)} \\
1.6 \times 10^{-49} & = [\text{Ag}^+]^2 [\text{S}^{2-}] = 4x^3
\end{align*}
\]

\[
\begin{align*}
\text{Bi}_2\text{S}_3 & \rightleftharpoons 2\text{Bi}^{3+} \text{ (aq)} + 3\text{S}^{2-} \text{ (aq)} \\
1.1 \times 10^{-73} & = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3 = 108x^5
\end{align*}
\]
<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
<th>Molar solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>$8.3 \times 10^{-45}$</td>
<td>$9.2 \times 10^{-23}$</td>
</tr>
<tr>
<td>Ag$_2$S</td>
<td>$1.6 \times 10^{-49}$</td>
<td>$3.4 \times 10^{-17}$</td>
</tr>
<tr>
<td>Bi$_2$S$_3$</td>
<td>$1.1 \times 10^{-73}$</td>
<td>$1.0 \times 10^{-15}$</td>
</tr>
</tbody>
</table>
Predicting Precipitation Reactions
Ion Product

\[ Q = \frac{[\text{products}]}{[\text{reactants}]} \]

- analogous to reaction quotient
- tells us whether a precipitate will form under a given set of reaction conditions

\[ Q_c > K_{sp}: \text{precipitate will form} \]
\[ Q_c = K_{sp}: \text{saturated solution} \]
\[ Q_c < K_{sp}: \text{no precipitate will form; substance dissolves} \]
If 2.00 ml of 0.200 M NaOH are added to 1.0 L of 0.100 M CaCl$_2$, will a precipitate form?
If 2.00 ml of 0.200 M NaOH are added to 1.0 L of 0.100 M CaCl₂, will a precipitate form?

\[ K_{sp} = 8.0 \times 10^{-6} \]

\[ \text{Ca(OH)}_2 (s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^- (aq) \]
\[
\text{Ca(OH)}_2 (s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^- (aq)
\]

\[
\begin{align*}
\text{Ca}^{2+} &= 1.0 \text{ L} \times \frac{0.10 \text{ mol}}{\text{L}} = 0.10 \text{ mol} \\
\text{OH}^- &= 2.0 \times 10^{-3} \text{ L} \times \frac{0.20 \text{ mol}}{\text{L}} = 4.0 \times 10^{-4} \text{ mol}
\end{align*}
\]

\[
\begin{align*}
\frac{0.1 \text{ mol}}{1.002 \text{ L}} &= 0.100 \text{ M} \\
\frac{4.0 \times 10^{-4} \text{ mol}}{1.002 \text{ L}} &= 0.0004 \text{ M}
\end{align*}
\]

\[\boxed{[\text{Ca}^{2+}] = 0.100 \text{ M}} \quad \boxed{[\text{OH}^-] = 0.0004 \text{ M}}\]
Ca(OH)₂ (s) ⇌ Ca²⁺(aq) + 2OH⁻(aq)

\[ Q = [\text{Ca}^{2+}][\text{OH}^-]^2 \]

\[ Q = (0.100)(0.0004)^2 \]

\[ Q = 1.6 \times 10^{-8} \]

\[ K_{sp} = 8.0 \times 10^{-6} \]

\[ Q < K_{sp} \quad ; \text{precipitate will not form} \]
Separation of Ions by Fractional Precipitation

When a solution contains several ions can one be removed by precipitation, leaving all the others in solution?
Practice Exercise

Calculate the concentration of $\text{Ag}^+$ necessary to cause precipitation of

(a) $\text{AgCl}$ \hspace{1cm} (K$_{sp}$ = 1.6 x 10$^{-10}$)

(b) $\text{Ag}_3\text{PO}_4$ \hspace{1cm} (K$_{sp}$ = 1.8 x 10$^{-18}$)

from a solution in which Cl$^-$ and PO$_4^{3-}$ are each present at a concentration of 0.10 M.
Practice Exercise

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

\[ [\text{Cl}^-] = 0.1 \text{ M} ; \quad K_{sp} = 1.6 \times 10^{-10} \]

\[
\text{Ag}_3\text{PO}_4 (s) \rightleftharpoons 3\text{Ag}^+ (aq) + \text{PO}_4^{3-} (aq)
\]

\[ [\text{PO}_4^{3-}] = 0.1 \text{ M} ; \quad K_{sp} = 1.8 \times 10^{-18} \]
calculate the concentration of Ag\(^+\) at which AgCl begins to precipitate

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

\[
[\text{Cl}^-] = 0.1 \ M; \quad K_{sp} = 1.6 \times 10^{-10}
\]

\[
1.6 \times 10^{-10} = [\text{Cl}^-] [\text{Ag}^+]
\]

\[
1.6 \times 10^{-10} = (0.1) [\text{Ag}^+]
\]

\[
[\text{Ag}^+] = 1.6 \times 10^{-9}
\]
Practice Exercise

calculate the concentration of Ag\(^+\) at which Ag\(_3\)PO\(_4\) begins to precipitate

\[
\text{Ag}_3\text{PO}_4 (s) \rightleftharpoons 3\text{Ag}^+ (aq) + \text{PO}_4^{3-} (aq)
\]

\[
[\text{PO}_4^{3-}] = 0.1 \ M; \quad K_{sp} = 1.8 \times 10^{-18}
\]

\[
1.8 \times 10^{-18} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]
\]

\[
1.8 \times 10^{-18} = (0.10) [\text{Ag}^+]^3
\]

\[
[\text{Ag}^+]^3 = 1.8 \times 10^{-17}
\]

\[
[\text{Ag}^+] = 2.6 \times 10^{-6}
\]
Practice Exercise

\[ [\text{Ag}^+] \text{ to begin precipitation of:} \]

\[ [\text{Cl}^-] = 1.6 \times 10^{-9} \, M \]

\[ [\text{PO}_4^{3-}] = 2.6 \times 10^{-6} \, M \]

Who precipitates first?

AgCl precipitates before Ag\(_3\)PO\(_4\)
Practice Exercise

What is $[\text{Cl}^-]$ when $\text{Ag}_3\text{PO}_4$ begin precipitate?

$\text{PO}_4^{3-}$ begins to precipitate when $[\text{Ag}^+]$ reaches $2.6 \times 10^{-6} \ M$.

$$K_{sp} = 1.6 \times 10^{-10} = [\text{Ag}^+] [\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (2.6 \times 10^{-6}) [\text{Cl}^-]$$

$$[\text{Cl}^-] = 6.2 \times 10^{-5}$$
The Common Ion Effect and Solubility

A common ion suppresses the solubility of an ionic substance
Calculate the solubility of AgBr in g/L in:
\[ K_{sp} = 7.7 \times 10^{-13} \]

(a) pure water
(b) 0.0010 M NaBr

\[ \text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \]
Practice Exercise

Calculate the solubility of AgBr in g/L in:
\[ K_{sp} = 7.7 \times 10^{-13} \]

(a) pure water
(b) 0.0010 M NaBr

\[ \text{AgBr (s) } \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \]

Le Chatelier’s principle: by adding NaBr, the equilibrium should shift to the **left** and the solubility of AgBr is **less**.
Practice Exercise

Calculate the solubility of AgBr in g/L in:
\[ K_{sp} = 7.7 \times 10^{-13} \]

(a) pure water

\[ \text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \]

\[ K_{sp} = [\text{Ag}^+][\text{Br}^-] = 7.7 \times 10^{-13} \]

\[ x^2 = 7.7 \times 10^{-13} \]

\[ x = 8.8 \times 10^{-7} \text{ M} = 1.7 \times 10^{-4} \text{ g/L} \]

solubility of AgBr
Practice Exercise

Calculate the solubility of AgBr in g/L in:
\[ K_{sp} = 7.7 \times 10^{-13} \]

(b) 0.0010 \( M \) NaBr

\[ \text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \]

\[ K_{sp} = [\text{Ag}^+] [\text{Br}^-] = 7.7 \times 10^{-13} \]

\[ [\text{Ag}^+] (0.0010) = 7.7 \times 10^{-13} \]

\[ [\text{Ag}^+] = 7.7 \times 10^{-10} \ M = 1.4 \times 10^{-7} \ g/L \]

solubility of AgBr
pH and Solubility
consider Mg(OH)$_2$

$$K_{sp} = 1.2 \times 10^{-11} = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

Mg(OH)$_2$ $\rightleftharpoons$ Mg$^{2+}$ + 2OH$^-$

solubility decreases in basic solution because increase in $[\text{HO}^-]$ requires decrease in $[\text{Mg}^{2+}]$
pH and Solubility

consider Mg(OH)$_2$

$$K_{sp} = 1.2 \times 10^{-11} = [Mg^{2+}] \ [HO^-]^2$$

Mg(OH)$_2$ $\rightleftharpoons$ Mg$^{2+}$ + 2 HO$^-$

solubility increases in acidic solution because [HO$^-$] is decreased
Practice Exercise

Calculate its molar solubility of Cr(OH)$_3$ (K$_{sp}$ = 3.0 x 10$^{-29}$) in a pH 10 buffer.

pOH = 4

Cr(OH)$_3$ (s) ⇌ Cr$^{3+}$ (aq) + 3OH$^-$ (aq)

$K_{sp} = 3.0 \times 10^{-29} = [Cr^{3+}] [OH^-]^3$

3.0 x 10$^{-29}$ = [Cr$^{3+}$] [10$^{-4}$]$^3$

[Cr$^{3+}$] = 3 x 10$^{-17}$ mol/L
In General

salts of weak acids will be more soluble in acid solution than in pure water because the anion of a weak acid (conjugate base) is basic
BaF$_2$ is a salt of a weak acid; its anion (F$^-$) is basic. 

\[ K_{sp} = 1.7 \times 10^{-6} = [\text{Ba}^{2+}] [\text{F}^-]^2 \]

\[
\text{BaF}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{F}^- 
\]

Solubility increases in acid because F$^-$ concentration is decreased.
Solution of Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Hg$^{2+}$

Add H$_2$S (acidic, pH ≈ 2)

Precipitate of CuS, HgS

Solution of Mn$^{2+}$, Ni$^{2+}$

Add OH$^-$ to bring pH to 8

Precipitate of MnS, NiS
Solution of $\text{Hg}_2^{2+}$, $\text{Ag}^+$, $\text{Pb}^{2+}$, $\text{Hg}^{2+}$, $\text{Cd}^{2+}$, $\text{Bi}^{3+}$, $\text{Cu}^{2+}$, $\text{Sn}^{4+}$, $\text{Co}^{2+}$, $\text{Zn}^{2+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$, $\text{Fe}^{2+}$, $\text{Cr}^{3+}$, $\text{Al}^{3+}$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, $\text{Mg}^{2+}$, $\text{NH}_4^+$, $\text{Na}^+$, $\text{K}^+$

Add $\text{HCl (aq)}$

Precipitate of $\text{Hg}_2\text{Cl}_2$, $\text{AgCl}$, $\text{PbCl}_2$ (Group I)

Solution of Groups II–IV

Add $\text{H}_2\text{S (aq)}$

Precipitate of $\text{HgS}$, $\text{CdS}$, $\text{Bi}_2\text{S}_3$, $\text{CuS}$, $\text{SnS}_2$ (Group II)

Solution of Groups III–V

Add $\text{NaOH (aq)}$

Precipitate of $\text{CoS}$, $\text{ZnS}$, $\text{MnS}$, $\text{NiS}$, $\text{FeS}$, $\text{Cr(OH)}_3$, $\text{Al(OH)}_3$ (Group III)

Solution of Groups IV, V

Add $\text{Na}_2\text{CO}_3 (aq)$

Precipitate of $\text{CaCO}_3$, $\text{BaCO}_3$, $\text{MgCO}_3$ (Group IV)

Solution of Group V
Solution of Ag⁺, Hg₂²⁺, Pb²⁺

Add cold HCl (aq)

Precipitate of AgCl(s), Hg₂Cl₂(s), PbCl₂(s)

Heat

Solution of Pb²⁺

Add CrO₄²⁻

Precipitate of PbCrO₄(s) (yellow)

Precipitate of AgCl(s) (white)

Precipitate of Hg(l) (black), HgNH₂Cl(s) (white)

Solution of Ag(NH₃)₂⁺, Cl⁻

Add H⁺
Complex Ion Equilibria and Solubility

“A complex ion is an ion containing a central metal cation bonded to one or more molecules or ions.”

demos - write the equilibria for each step

\[
\begin{align*}
\text{CuCl}_2 + \text{NH}_3 + \text{HCl} & \\
\text{AgNO}_3 + \text{NaCl} + \text{NH}_3 + \text{HCl} & \\
\end{align*}
\]

Formation constant \( K_f = \frac{[\text{metal cation}][\text{neutral or anion ligand}]}{[\text{complex ion}]} \)

kind of like \( K_{sp} \) except.... the product is a dissolved ion complex, not a solid precipitate
\[
K_f = \frac{[\text{Cu(NH}_3\text{)}_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5.0 \times 10^{13}
\]
• a complex ion is formed by Lewis acid-Lewis base reaction;
  metal ion is the Lewis acid
  the neutral molecule or ion that acts as the Lewis base is called a Ligand

• the number of ligands attached to the metal ion is called the coordination number

• the bond between the Lewis acid and Lewis base is covalent

• a complex ion is characterized by the formation constant \((K^f)\)
### Some typical complex ions

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>complex ion</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ag</strong>$^+$</td>
<td>+</td>
<td>2NH$_3$</td>
<td>$\rightleftharpoons$</td>
<td>Ag(NH$_3$)$_2^+$</td>
</tr>
<tr>
<td><strong>Cu</strong>$^{2+}$</td>
<td>+</td>
<td>4CN$^-$</td>
<td>$\rightleftharpoons$</td>
<td>Cu(CN)$_4^{2-}$</td>
</tr>
<tr>
<td><strong>Co</strong>$^{3+}$</td>
<td>+</td>
<td>6NH$_3$</td>
<td>$\rightleftharpoons$</td>
<td>Co(NH$_3$)$_6^{3+}$</td>
</tr>
</tbody>
</table>
The effect of complex ion formation generally is to increase the solubility of a substance.
$K_f = \frac{[\text{Ag(NH}_3\text{)}_2^+]\ agitation\[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}^+][\text{NH}_3]^2} = 1.5 \times 10^7$
What is the molar solubility of AgBr in a 1.0 M solution of NH$_3$?

\[
\text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq)
\]

\[
\text{K}_{sp} = 7.7 \times 10^{-13}
\]

\[
\text{Ag}^+ (aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq)
\]

\[
\text{K}_f = 1.5 \times 10^7
\]

\[
\text{AgBr (s)} + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) + \text{Br}^- (aq)
\]

\[
\text{K}_f \text{K}_{sp} = \text{K}
\]
What is the molar solubility of AgBr in a 1.0 M solution of NH$_3$?

$$\text{AgBr (s) + 2NH}_3\text{(aq) } \rightleftharpoons \text{Ag(NH}_3)_2^+\text{(aq) + Br}^-\text{(aq)}$$

$$K_f K_{sp} = K = 12.3 \times 10^{-6}$$

$$12.3 \times 10^{-6} = \frac{x^2}{1.0}$$

$$x = 0.0035 \text{ M}$$

The solubility of AgBr in pure water is 9 x 10$^{-7}$ M.
## Some typical coordination numbers

<table>
<thead>
<tr>
<th>Coordination numbers</th>
<th>Coordination numbers</th>
<th>Coordination numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>2</td>
<td>Mn²⁺</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>2,4</td>
<td>Fe²⁺</td>
</tr>
<tr>
<td>Au⁺</td>
<td>2,4</td>
<td>Co²⁺</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td></td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co³⁺</td>
<td></td>
<td>Cr³⁺</td>
</tr>
<tr>
<td>Au³⁺</td>
<td></td>
<td>Sc³⁺</td>
</tr>
</tbody>
</table>
Some common ligands

- $\text{H}_2\text{O}$
- CO
- NO
- $\text{NH}_3$
- $\text{CH}_3\text{NH}_2$
- SCN$^-$
- CN$^-$
- I$^-$
- F$^-$
- Cl$^-$
- Br$^-$
Indicators
(Colorless acid form, HIn)

(Pink base form, In\(^-\))
The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.
<table>
<thead>
<tr>
<th>NaOH Added (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.99</td>
<td>5.3</td>
</tr>
<tr>
<td>100.00</td>
<td>7.0</td>
</tr>
<tr>
<td>100.01</td>
<td>8.7</td>
</tr>
</tbody>
</table>