**Learning goals and key skills:**
- Describe the common ion effect.
- Explain how a buffer functions.
- Calculate the pH of a buffer solution.
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base.
- Calculate the pH at any point in an acid-base titration of a strong acid and strong base.
- Understand the differences between titration curves for a strong-acid-strong base titration and those when either the acid or base is weak.
- Calculate the pH at any point in a titration of a weak acid with a strong base or a weak base with a strong acid.
- Calculate $K_{sp}$ from molar solubility and molar solubility from $K_{sp}$.
- Calculate the molar solubility in the presence of a common ion.
- Predict the effect of pH on solubility.
- Predict whether a precipitate will form when solutions are mixed by comparing $Q$ and $K_{sp}$.
- Calculate the ion concentrations required to begin precipitation.
- Explain the effect of complex ion formation on solubility.

**Chapter 17: Additional Aspects of Aqueous equilibria**

**Common-ion effect**

The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.

$$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$

Note: this is merely an application of Le Châtelier’s principle.

**Buffers:** solutions that resist changes in pH upon addition of small amounts of acids/bases.

- Usually prepared from solutions of a weak conjugate acid-base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.

**Common-ion effect**

$$\text{HA}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{A}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$$

Having a common ion (the conjugate base, $\text{A}^-$) will limit the ionization of the weak acid ($\text{HA}$).

$$\text{B}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{BH}^+_{(aq)} + \text{OH}^-_{(aq)}$$

Similarly, having a common ion (the conjugate acid, $\text{BH}^+$) will limit the ionization of the weak base ($\text{B}$).

**Example: common-ion effect**

A 0.10 M lactic acid solution ($K_a = 1.4 \times 10^{-4}$) has a pH of 2.43 and 3.7% ionization of the acid. Let’s calculate the pH and percent ionization of a 0.10 M lactic acid solution when 0.10 M sodium lactate is added.

$$\text{lactic acid}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{lactate ion}_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$$

(alternative equation)

$$\text{HLac}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Lac}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$$

**Buffers:** solutions that resist changes in pH upon addition of small amounts of acids/bases.

- Usually prepared from solutions of a weak conjugate acid-base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.
Henderson-Hasselbalch equation

Use only with valid assumptions!

\[
HA (aq) + H_2O (l) \rightleftharpoons A^- (aq) + H_3O^+ (aq)
\]

\[
K_a = \frac{[A^-][H_3O^+]}{[HA]}
\]

\[
-pH = -\log [H_3O^+] + \log \frac{[A^-]}{[HA]}
\]

Example: Buffer Calculation

What is the pH of a buffer that is 0.12 M in lactic acid, \( \text{CH}_3\text{CH(OH)COOH} \), and 0.10 M in sodium lactate? \( K_a \) for lactic acid is \( 1.4 \times 10^{-4} \).

Example: Buffer Calculation

Determine the pH of a solution that is 0.0500 M in benzoic acid, \( \text{HC}_7\text{H}_5\text{O}_2 \) (\( K_a = 6.50 \times 10^{-5} \)), and 0.150 M in sodium benzoate, \( \text{NaC}_7\text{H}_5\text{O}_2 \), at 25 °C.

Example: Buffer Calculation

Determine the pH of a solution that contains 0.119 M pyridine, \( \text{C}_5\text{H}_5\text{N} \) (\( pK_b = 8.77 \)) and 0.234 M pyridine hydrochloride at 25 °C.

Be careful! It’s a base!

\[
\text{pH} = (14-8.77) + \log \frac{0.119}{0.234} \text{ M}
\]

\[
\text{pH} = 4.94
\]
**Henderson-Hasselbalch equation**

The pH is very important in biological systems. It changes the charges – and thus both the structure and activity – of proteins.

![Images from http://www.virtuallaboratory.net/Biofundamentals/lectureNotes/Topic2-2_Water.htm](http://www.virtuallaboratory.net/Biofundamentals/lectureNotes/Topic2-2_Water.htm)

When Strong Acids or Bases Are Added to a Buffer...

...it is safe to assume that all of the strong acid or base is consumed in the reaction.

**Addition of Strong Acid or Base to a Buffer**

1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson-Hasselbalch equation to determine the new pH of the solution.

**Calculating pH Changes in Buffers**

A buffer is made by adding 0.300 mol HC$_2$H$_3$O$_2$ and 0.300 mol NaC$_2$H$_3$O$_2$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added.

Before reaction

<table>
<thead>
<tr>
<th>HC$_2$H$_3$O$_2$</th>
<th>C$_2$H$_3$O$_2$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.300 mol</td>
<td>0.300 mol</td>
<td>0.020 mol</td>
</tr>
</tbody>
</table>

**Example: pH changes to buffers**

In a previous example we found pH = 4.66 for a solution containing 0.0500 M benzoic acid, HC$_7$H$_5$O$_2$ ($K_a = 6.50 \times 10^{-5}$), and 0.150 M in sodium benzoate, NaC$_7$H$_5$O$_2$, at 25 °C. Now find the pH when 5.00 mL of 1.51 M HCl is added to 100.00 mL of this buffered solution.

Compare to the pH when 5.00 mL of 1.51 M HCl is added to 100.00 mL of pure H$_2$O.

**Buffer capacity**

The buffer capacity is the amount of acid or base that can be added to the buffer before the pH begins to change to an appreciable degree.

The buffer capacity depends on:

- the amount of acid
- the amount of base

The pH of the buffer depends on the above amounts and the $K_a$. 

![Images from http://www.virtuallaboratory.net/Biofundamentals/lectureNotes/Topic2-2_Water.htm](http://www.virtuallaboratory.net/Biofundamentals/lectureNotes/Topic2-2_Water.htm)
Buffer capacity
Buffers work best when the amount of acid is approximately equal to the amount of base.

\[ \text{pH} \approx \text{pK}_a \]

In practice, the buffering action is poor when one component has 10 times the concentration of the other component.

Thus, buffers usually have a usable range within ±1 pH unit of \( \text{pK}_a \).

Titration
In this technique a known concentration of base (or acid) is slowly added to a solution of acid (or base).

A pH meter or indicators are used to determine when the solution has reached the equivalence point, at which the stoichiometric amount of acid equals that of base.

Indicators
acidic form basic form
of methyl red \( (\text{pK}_a = 5.00) \)

Indicators

\[
\text{HInd}^{\text{(aq)}} + \text{H}_2\text{O}^{(l)} \xrightleftharpoons{} \text{H}_3\text{O}^{+}(\text{aq}) + \text{Ind}^- (\text{aq})
\]

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{Ind}^-]}{[\text{HInd}]}.
\]

Acid-base titration
(strong base added to a strong acid)
Consider the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH at 25.0 °C. Calculate the volume of base required to reach the equivalence point and the pH after the addition of 0.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0 and 50.0 mL NaOH.

Strategy:
1) The initial pH is just the pH from the strong acid solution.
2) Before the equivalence point, \( \text{H}_2\text{O}^{+} \) is in excess. Calculate the \( [\text{H}_2\text{O}^{+}] \) by subtracting the number of moles of added \( \text{OH}^- \) from the initial moles of \( \text{H}_2\text{O}^{+} \) and dividing by total volume.
3) At the equivalence point, neither reactant is in excess and the pH = 7.00.
4) Beyond the equivalence point, \( \text{OH}^- \) is in excess. Calculate the \( [\text{OH}^-] \) by subtracting the initial number of moles of \( \text{H}_2\text{O}^{+} \) from the number of moles of added \( \text{OH}^- \) and dividing by total volume.
Titration of a Weak Acid with a Strong Base

- Unlike in the previous case, the conjugate base of the acid affects the pH when it is formed.
- At the equivalence point the pH is >7.
- Phenolphthalein is commonly used as an indicator in these titrations.

Example Titration of a Weak Acid with a Strong Base

Determine the pH when the following quantities of 0.0500 M potassium hydroxide have been added to 50.0 mL of a 0.0250 M solution of benzoic acid, \( HC_7H_5O_2 \), \( K_a = 6.5 \times 10^{-5} \).

a. 0.00 mL
b. 20.0 mL
c. 25.0 mL
d. 30.0 mL

Example part a

Determine the pH when the following quantities of 0.0500 M potassium hydroxide have been added to 50.0 mL of a 0.0250 M solution of benzoic acid, \( HC_7H_5O_2 \), \( K_a = 6.5 \times 10^{-5} \).

a. 0.00 mL

Example part b

Determine the pH when the following quantities of 0.0500 M potassium hydroxide have been added to 50.0 mL of a 0.0250 M solution of benzoic acid, \( HC_7H_5O_2 \), \( K_a = 6.5 \times 10^{-5} \).

b. 20.0 mL

Example part c

Determine the pH when the following quantities of 0.0500 M potassium hydroxide have been added to 50.0 mL of a 0.0250 M solution of benzoic acid, \( HC_7H_5O_2 \), \( K_a = 6.5 \times 10^{-5} \).

c. 25.0 mL
Example part d

Determine the pH when the following quantities of 0.0500 M potassium hydroxide have been added to 50.0 mL of a 0.0250 M solution of benzoic acid, \( \text{HC}_7\text{H}_5\text{O}_2 \), \( K_a = 6.5 \times 10^{-5} \).

d. 30.0 mL

Titration of a Weak Acid with a Strong Base

With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.

Titration of a Weak Base with a Strong Acid

- The pH at the equivalence point in these titrations is < 7.
- Methyl red is the indicator of choice.

Good and poor indicators for titration of a weak acid with a strong base

When one titrates a polyprotic acid with a base there is an equivalence point for each dissociation.

Polyprotic acid titrations
We know from table 4.1 that barium sulfate is qualitatively "insoluble" but in reality a small amount of it does dissolve.

\[
\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)
\]

The equilibrium constant expression for this equilibrium is

\[
K_{sp} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]
\]

where the equilibrium constant, \(K_{sp}\), is called the solubility product.

**Example: \(K_{sp}\)**

Determine the molar solubility of calcium phosphate (\(K_{sp} \approx 2.07 \times 10^{-33}\)).
Factors that affect solubility

1. The common-ion effect
2. pH
3. Complex ion formation

These are again simply applications of Le Châtelier’s principle.

Example: common-ion effect and $K_{sp}$

Determine the molar solubility of calcium phosphate ($K_{sp} = 2.07 \times 10^{-33}$) in 0.20 M calcium chloride.

Factors that affect solubility

• The common-ion effect

The presence of a second solute that furnishes a common ion decreases the solubility of a slightly soluble salt. A common ion decreases the solubility.

Factors that affect solubility

• pH

The solubility of a basic compound increases with increasing acidity (i.e., decreasing pH).

• Complex ion formation

pH and solubility

Consider a salt

\[ \text{MA(s)} \rightleftharpoons \text{M}^{+}(\text{aq}) + \text{A}^{-}(\text{aq}) \quad K_{sp} = [\text{M}^{+}][\text{A}^{-}] \]

and the hydrolysis of the anion (conjugate base)

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

If a substance has a basic anion, it will be more soluble in an acidic solution.

• Common basic anions include $\text{OH}^{-}, \text{S}^{2-}, \text{CO}_3^{2-}$.
Complex ion formation

- The common-ion effect
- pH
- complex ion formation

The formation of a complex ion with the metal ion can affect the solubility of the metal salt.

Complex Ions

- The formation of these complex ions increases the solubility of these salts.

Precipitation reactions

Will a Precipitate Form?

Compare $Q_{sp}$ and $K_{sp}$

- $Q_{sp} < K_{sp}$ not saturated
- $Q_{sp} = K_{sp}$ saturated (at equilibrium)
- $Q_{sp} > K_{sp}$ supersaturated

Factors Affecting Solubility

- Amphotericism
  
  Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
  
  Examples of such cations are $\text{Al}^{3+}$, $\text{Zn}^{2+}$, $\text{Cr}^{3+}$, and $\text{Sn}^{2+}$.

Example: Precipitation rxns

Determine if gold (III) chloride ($K_{sp} = 3.2 \times 10^{-25}$) precipitates if 30.0 mL of $4.0 \times 10^{-3}$ M gold (III) nitrate is mixed with 20.0 mL of $2.0 \times 10^{-4}$ M sodium chloride.
**Selective precipitation**

If salts have a large difference in $K_{sp}$’s then one metal ion can be selectively precipitated over another.

The sulfide ion is often used because the $K_{sp}$’s of metal sulfides span a large range and depend greatly on the pH of the solution.

<table>
<thead>
<tr>
<th>Metal Sulfide</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS</td>
<td>$3 \times 10^{-20}$</td>
</tr>
<tr>
<td>CoS</td>
<td>$5 \times 10^{-22}$</td>
</tr>
<tr>
<td>ZnS</td>
<td>$2 \times 10^{-25}$</td>
</tr>
<tr>
<td>SnS</td>
<td>$1 \times 10^{-26}$</td>
</tr>
<tr>
<td>PbS</td>
<td>$3 \times 10^{-28}$</td>
</tr>
<tr>
<td>CdS</td>
<td>$8 \times 10^{-28}$</td>
</tr>
<tr>
<td>CuS</td>
<td>$6 \times 10^{-37}$</td>
</tr>
<tr>
<td>AgS</td>
<td>$6 \times 10^{-51}$</td>
</tr>
<tr>
<td>MnS</td>
<td>$2 \times 10^{-53}$</td>
</tr>
<tr>
<td>HgS</td>
<td>$2 \times 10^{-53}$</td>
</tr>
</tbody>
</table>