Chapter 17: Additional Aspects of Aqueous equilibria

Learning goals and key skills:
- Describe the common ion effect.
- Explain how a buffer functions.
- Calculate the pH of a buffer.
- 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.
- 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.
- Understand the differences between titration curves for a strong-acid-strong base titration and those when either the acid or base is weak.
- 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.

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.

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

Sodium acetate, a strong electrolyte, fully dissociates

$$\text{NaCH}_3\text{COO}(aq) \rightarrow \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

In a solution containing acetic acid and sodium acetate, the acetate ion shifts the equilibrium of the acetic acid to the left.

Addition of $\text{CH}_3\text{COO}^-$ shifts equilibrium concentrations, lowering $[\text{H}^+]$

This is an application of Le Châtelier’s principle.
Common-ion effect

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

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

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

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

The Common-Ion Effect

Calculate the fluoride ion concentration and percent ionization of solutions that are:

a) 0.200 \( M \) in HF
b) 0.200 \( M \) in HF and 0.100 \( M \) in HCl.

The \( K_a \) for HF is 6.8 \( \times 10^{-4} \).

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

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.80 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>[ \text{[HF], M} ]</th>
<th>[ \text{[H}_3\text{O}^+, M} ]</th>
<th>[ \text{[F}^-, M} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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. Calculate the pH and percent ionization of a 0.10 M lactic acid solution when 0.10 M sodium lactate is added.

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

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

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.
- Contain about $10^{-3}$ M of both the acid and base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.
A buffer resists changes in pH because it contains both an acid to neutralize OH\(^-\) ions and a base to neutralize H\(^+\) ions.

**Henderson-Hasselbalch equation**

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

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

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

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

Presence of HF counteracts addition of base; pH increase is small.

Presence of F\(^-\) counteracts addition of acid; pH decrease is small.
Example: Buffer Calculation
What is the pH of a buffer that is 0.12 \( M \) in lactic acid, \( \text{CH}_3\text{CH(OH)}\text{COOH} \), 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, C₅H₅N, (pKₐ = 8.77) and 0.234 M pyridine hydrochloride at 25 °C.

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) \]

Be careful! It’s a base!

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

\[ \text{pH} = 4.94 \]

Henderson-Hasselbalch equation

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) \]

at pH > pKₐ \quad [A^-] > [HA]

at pH = pKₐ \quad [A^-] = [HA]

at pH < pKₐ \quad [A^-] < [HA]
The Henderson-Hasselbalch equation

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

\[ \text{at pH } < \text{pK}_a \quad [A^{-}] < [HA] \]
\[ \text{at pH } > \text{pK}_a \quad [A^{-}] > [HA] \]

pictures from http://www.virtualaboratory.net/Biofundamentals/lectureNotes/Topic2-2_Water.htm

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 \( K_a \).

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 \( \text{pK}_a \).
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.

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

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

Acid-base titration
(strong base added to a strong acid)
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, H₃O⁺ is in excess. Calculate the [H₃O⁺] by subtracting the number of moles of added OH⁻ from the initial moles of H₃O⁺ 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, OH⁻ is in excess. Calculate the [OH⁻] by subtracting the initial number of moles of H₃O⁺ from the number of moles of added 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.
Titration of a Weak Acid with a Strong Base

At each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular time.

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$_7$H$_5$O$_2$, $K_a = 6.5 \times 10^{-5}$.

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, $\text{HC}_7\text{H}_5\text{O}_2$, $K_a = 6.5 \times 10^{-5}$.

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, $\text{HC}_7\text{H}_5\text{O}_2$, $K_a = 6.5 \times 10^{-5}$.

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, \( \text{HC}_7\text{H}_5\text{O}_2 \), \( K_a = 6.5 \times 10^{-5} \).

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

\[ \text{Indicators} \]

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

\[ \text{pH} = pK_a + \log \frac{[\text{Ind}^-]}{[\text{HInd}]} \]
Each indicator has a specific pH range over which it changes color.

An indicator can be used to find the equivalence point in a titration, if it changes color in a small volume change region where the pH rapidly changes.
Good and poor indicators for titration of a weak base with a strong acid

Polyprotic acid titrations

When one titrates a polyprotic acid with a base there is an equivalence point for each dissociation.
The concept of soluble and insoluble is a simplification.

**Solubility-product constant**

We know from solubility rules that barium sulfate is qualitatively “insoluble” but in reality a small amount of it dissolves.

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

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**.
Solubility vs. solubility-product constant

- **Solubility**: the quantity that dissolves to form a saturated solution. Solubility is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/100 mL) of solution, or in mol/L (M).
- **Molar solubility**: moles of solute that dissolve in forming a liter of saturated solution of the solute.
- **Solubility-product constant**: $K_{sp}$ is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution.

**Example: $K_{sp}$**

Determine the molar solubility of calcium phosphate at 25 °C. The $K_{sp} = 2.07 \times 10^{-33}$ at 25 °C.
## Solubility

Compare the solubility (g/L) of the following silver halide salts.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>$1.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>AgBr</td>
<td>$5.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>AgI</td>
<td>$8.5 \times 10^{-17}$</td>
</tr>
</tbody>
</table>

## Solubility

Compare the solubility (g/L) of the following silver salts.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>$1.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{Ag}_2\text{CrO}_4$</td>
<td>$1.1 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
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.

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.

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

Addition of Ca\(^{2+}\) or F\(^-\) shifts equilibrium concentrations, reducing solubility.
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

- pH

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

- complex ion formation
Consider a salt

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

and the hydrolysis of the anion (conjugate base)

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

If a substance has a basic anion (anion of a weak acid), it will be more soluble in an acidic solution.

- Common basic anions include OH\(^-\), S\(^{2-}\), CO\(_3^{2-}\).

**pH:** If a substance has a basic anion (anion of a weak acid), it will be more soluble in an acidic solution.
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: metal ions (Lewis acids) can form complex ions with Lewis bases in the solvent.

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>$K_f$</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(NH$_3$)$_2^+$</td>
<td>$1.7 \times 10^7$</td>
<td>Ag$^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)</td>
</tr>
<tr>
<td>Ag(CN)$_2^-$</td>
<td>$1 \times 10^{21}$</td>
<td>Ag$^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag(CN)}_2^-(aq)</td>
</tr>
<tr>
<td>Ag(S$_2$O$_3$)$_2^-$</td>
<td>$2.9 \times 10^{13}$</td>
<td>Ag$^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{2-}(aq)</td>
</tr>
<tr>
<td>Al(OH)$_4^-$</td>
<td>$1.1 \times 10^{-35}$</td>
<td>Al$^{3+}(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Al(OH)}_4^-(aq)</td>
</tr>
<tr>
<td>CdBr$_2^{2-}$</td>
<td>$5 \times 10^3$</td>
<td>Cd$^2+(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_2^{2-}(aq)</td>
</tr>
<tr>
<td>Cr(OH)$_4^-$</td>
<td>$8 \times 10^{-29}$</td>
<td>Cr$^{3+}(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Cr(OH)}_4^-(aq)</td>
</tr>
<tr>
<td>Co(SCN)$_2^{2-}$</td>
<td>$1 \times 10^{-3}$</td>
<td>Co$^{2+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co(SCN)}_2^{2-}(aq)</td>
</tr>
<tr>
<td>Cu(NH$_3$)$_2^+$</td>
<td>$5 \times 10^{12}$</td>
<td>Cu$^2+(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu(NH}_3)_2^+(aq)</td>
</tr>
<tr>
<td>Cu(CN)$_4^{2-}$</td>
<td>$1 \times 10^{-25}$</td>
<td>Cu$^2+(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu(CN)}_4^{2-}(aq)</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_6^{2+}$</td>
<td>$1.2 \times 10^8$</td>
<td>Ni$^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_6^{2+}(aq)</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td>$1 \times 10^{-15}$</td>
<td>Fe$^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_6^{3-}(aq)</td>
</tr>
<tr>
<td>Fe(CN)$_6^{4-}$</td>
<td>$1 \times 10^{-42}$</td>
<td>Fe$^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_6^{4-}(aq)</td>
</tr>
<tr>
<td>Zn(OH)$_2^2-$</td>
<td>$4.6 \times 10^{-17}$</td>
<td>Zn$^{2+}(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}_2^{2-}(aq)</td>
</tr>
</tbody>
</table>
The formation of these complex ions increases the solubility of these salts.

**Amphoterism**
- 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 $\text{Sn}^{2+}$.
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

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</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>Ag$_2$S</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>

![Diagram of selective precipitation](image-url)
Equilibrium constants

$K, K_{eq}$ or $K_c$  equilibrium constant
$K_p$  equilibrium constant (using partial pressures)
$K_a$  acid-dissociation constant
$K_b$  base-dissociation constant
$K_w$  ion-product constant of water
$K_{sp}$  solubility product constant
$K_f$  formation constant
$K_d$  dissociation constant

... and there are reaction quotients, Q’s, too!