CHAPTER 16. ACID-BASE EQUILIBRIA

16.2 COMMON ION EFFECT

common ion effect: The shift in equilibrium caused by the addition of a substance having an ion in common with the equilibrium mixture. Addition of the common ion causes the equilibrium to shift left; this suppresses the ionization of a weak acid or a weak base.

- The source of the common ion is typically provided by adding a strong acid, a strong base or a soluble salt to the equilibrium reaction mixture.

E.g. Given this reaction: \( \text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \). What happens to the pH of the acetic acid solution if we add (a) \( \text{HCl} \)? (b) \( \text{Na}_2\text{C}_2\text{H}_3\text{O}_2 \)?

Common Ion Problems:
1. Include the initial concentration of the common ion in the ICE table.
2. Use the approximation method to solve the equilibrium constant expression.

16.3 BUFFER SOLUTIONS

Buffer: A solution that resists changes in pH when a small amount of acid or base is added.

The best buffer systems consist of either
- a weak acid and a salt containing its conjugate base (e.g. \( \text{HC}_2\text{H}_3\text{O}_2 \) and \( \text{Na}_2\text{C}_2\text{H}_3\text{O}_2 \));
- a weak base and a salt containing its conjugate acid (e.g. \( \text{NH}_3 \) and \( \text{NH}_4\text{Cl} \)).

For these buffer systems:
1. The acid component of the buffer can neutralize added base and the base component of the buffer can neutralize added acid.
2. Since they are a conjugate acid-base pair, the acid and base in the buffer don't react with one another.

Buffer capacity is the amount of acid or base the buffer can neutralize before there is a significant change in pH. The buffer capacity is a measure of the effectiveness of a buffer.

- Buffer capacity is greater when larger amounts of \( \text{HA} \) and \( \text{A}^- \) are present.
- pH will stay relatively constant as long as \( [\text{HA}] \) and \( [\text{A}^-] \) are greater than the amount of acid or base added.
- Buffers work best when \( [\text{HA}] \) and \( [\text{A}^-] \) are approximately equal. For buffers to be effective, the ratio of Base:Acid should be between 1:10 to 10:1.

Consider the following weak acid buffer reaction: \( \text{HA}^{(aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-{(aq)} \)

The ionization constant, \( K_a \), is given by \( K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \)

Rearrange: \[ [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \]

Taking - log both sides: \[ -\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \]

\[ \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{Henderson-Hasselbalch equation} \]
In solving common ion and buffer problems, assume $[HA]_{eq}$ and $[A^-]_{eq}$ are equal to their initial concentrations. (That is, the approximation method is valid for these problems.)

A special situation occurs when $[HA] = [A^-]$:

By substitution, the $K_a$ expression becomes: $[H^+] = K_a$.

Thus, $pH = pK_a$.

We can use the Henderson-Hasselbalch relationship to prepare a buffer solution with a certain pH - select an acid with a $pK_a$ close to the pH you want ($pK_a \pm 1$), and adjust the [base]/[acid] ratio to obtain the desired pH.

**Buffer Problems Involving Addition of Acid or Base**

1) Stoichiometric calculation for the acid-base neutralization reaction; assume the neutralization reaction goes to completion:

   If a strong acid is added, $H^+$ reacts with the conjugate base: $A^- + H^+ \rightarrow HA$

   If a strong base is added, $OH^-$ reacts with the weak acid: $HA + OH^- \rightarrow A^- + H_2O$

2) Equilibrium calculation – plug $[HA]$ and $[A^-]$ into the $K_a$ expression for the acid ionization:

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

Since buffers contain a weak acid/base pair, you can set up the problem using either a weak acid ionization reaction and $K_a$ or a weak base ionization reaction and $K_b$.

If you start with the weak base reaction, set up the $K_b$ expression and solve for $x$, where $x = [OH^-]$.

**16.4 ACID-BASE TITRATIONS**

**Acid-base titration curve**: plot of pH vs. volume added during a titration; 4 important regions.

**Equivalence point**: the point at which the acid and base are present in equal stoichiometric amounts.

**Titration of a Strong Acid by a Strong Base**

![Titration Curve for SA/SB](image)

**Calculations for finding pH during Strong Acid – Strong Base Titration**

Net-ionic neutralization reaction for SA/SB titration: $H^+ + OH^- \rightarrow H_2O$

1) **Initial pH**: depends on the concentration of the strong acid.

   A strong acid is 100 % ionized: $HA_{(aq)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$

   The reaction is complete; thus, $[H^+] = [HA]$.

2) **pH after initial but before equivalence point**: depends on the amount of excess acid remaining after neutralization.
\[ [H^+] = \frac{\text{moles acid initial} - \text{moles base added}}{\text{volume solution}} \]

where moles acid = \( L_{\text{acid}} \times M_{\text{acid}} \) and moles base = \( L_{\text{base}} \times M_{\text{base}} \)

volume solution = volume (acid + base)

3) \textbf{pH at equivalence point}: pH = 7 only for SA/SB (or SB/SA) titrations because a neutral salt water solution is present.

⇒ The acid has been completely neutralized by the base, leaving a neutral salt solution. Recall that the cation of a strong base (e.g. \( \text{Na}^+ \)) and the anion of a strong acid (e.g. \( \text{Cl}^- \)) are neutral ions, so they do not react with water.

4) \textbf{pH after equivalence pt}: depends on the amount of excess base remaining after the neutralization reaction.

\[ [\text{OH}^-] = \frac{\text{moles base added} - \text{moles acid initial}}{\text{volume solution}} \]

\[ pOH = - \log [\text{OH}^-]; \; \text{pH} = 14.00 - pOH \]

\textbf{Titration of a Weak Acid by a Strong Base}

\[ \text{Titration curve for WA/SB} \]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{titration_curve.png}
\end{figure}

\textbf{Calculations for finding pH during Weak Acid-Strong Base Titration}

1) \textbf{Initial pH}: A weak acid does not completely ionize; so \([H^+] \neq [\text{HA}]\).

To find \([H^+]\) for a weak acid, set up the ICE table and \(K_a\) expression, then solve for \(x\).

\text{RXN (1) } \text{HA}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{A}^-_{(aq)}

\[ K_a = \frac{[H^+][A^-]}{[\text{HA}]} = \frac{x^2}{[\text{HA}]} \Rightarrow x = [H^+] = \sqrt{K_a[HA]} \]

2) \textbf{pH after initial but before equivalence point}: a buffer solution (HA/A^-) is present.

A. Calculate the amount of A^- formed & HA remaining after the neutralization reaction:

\text{RXN (2) } \text{Neutralization Reaction: } \text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}

moles HA remaining = initial moles acid - moles base added
moles A^- formed = moles base added

B. Convert moles to M, then plug [HA] and [A^-] into the \(K_a\) expression for RXN (1).

\text{solve } K_a \text{ for } [H^+]; \quad [H^+] = K_a \frac{[\text{HA}]}{[A^-]} \]

3) \textbf{pH at equivalence point}: pH \textbf{DOES NOT} = 7 due to hydrolysis of the conjugate base, A^-.

⇒ At the equivalence point all of the strong base and weak acid have been consumed in RXN (2), leaving the conjugate base, A^-, in solution. A^- is a weak base – it reacts with \( \text{H}_2\text{O} \) to produce \( \text{OH}^- \) ions:

\text{RXN (3) } \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-
\[ K_b = \frac{[HA][OH^-]}{[A^-]} \]

where \( K_b = \frac{K_w}{K_a} \) and \( [A^-] = \frac{\text{initial moles acid}}{\text{total volume of solution}} \)

From the ICE table: \( K_b = \frac{x^2}{[A^-]} \)

Thus, the \([OH^-]\) is found by solving for \( x \):

\[ x = \sqrt{K_b[A^-]} \]

4) **pH after equivalence pt**: depends on the amount of excess base present (same as SA/SB). Excess strong base is the primary source of \( OH^- \). Hydrolysis of the conjugate base, \( A^- \), also produces \( OH^- \), but this amount is much smaller than the \( OH^- \) obtained from the strong base, so we can neglect the \( OH^- \) formed by the conjugate base hydrolysis.

**Shape of Strong Acid - Strong Base Curve vs. Weak Acid - Strong Base Curve**

- The initial pH of a strong acid is lower than that of a weak acid of similar concentration due to the complete ionization of the strong acid; thus, the initial \([H^+]\) is higher for a strong acid.
- Region 2 for the weak acid curve: initially, the pH rises abruptly as base is added due to suppression of the acid ionization, but then the pH levels off as the HA/A^- buffer mixture is formed.
- At the half-neutralization point of the weak acid, the moles of acid remaining = moles of conjugate base formed, so \([HA] = [A^-]\). Thus, \( pH = pK_a \) at the half equivalence point.
- At the equivalence point: pH = 7 for a SA/SB titration since a neutral salt water solution is present; pH > 7 for a WA/SB titration because the salt contains the conjugate base, \( A^- \), which reacts with water to produce \( OH^- \) ions.
- Near the equivalence pt: pH rises very sharply for the strong acid titration from about pH 3 to pH 11; whereas, the pH rises less for a weak acid titration from about pH 7 to pH 11.
- After the equivalence point: the shape of the curves is the same because pH is determined by the excess \( OH^- \) ions provided by the strong base.

**Titration of a Strong Base by a Strong Acid**

**Titration Curve for SB/SA**

**Titration of a Weak Base by a Strong Acid**

**Titration Curve for WB/SA**
16.5 ACID-BASE INDICATORS

End point - an experimentally observed point at which the indicator changes color.

Indicator - substance that changes color over a specific pH range; an indicator can exist in either its acid or base form and it changes color when proton gain/loss occurs.

\[ \text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^- \]

Acid form               Base form

- When \([\text{HIn}]/[\text{In}^-] \geq 10\), mostly HIn exists and the acid color prevails.
- When \([\text{HIn}]/[\text{In}^-] \leq 0.1\), mostly In\(^-\) exists and the base color prevails.
- When 0.1 < \([\text{HIn}]/[\text{In}^-] < 10\), the color is a mixture of acid and base colors.

E.g. methyl red: pH range is 4.2-6 (red in acid form, yellow in base form)

phenolphthalein: pH range 8.2-10 (clear in acid form, pink in base form)

For a given acid-base titration, a suitable indicator changes color over a pH range that coincides with the portion of the curve where the pH rises sharply.

<table>
<thead>
<tr>
<th>Titration Type</th>
<th>Equivalence Point</th>
<th>pH Range Near Equivalence Point</th>
<th>Suitable Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA by SB</td>
<td>7</td>
<td>3-11</td>
<td>phenolphthalein, methyl red</td>
</tr>
<tr>
<td>SB by SA</td>
<td>7</td>
<td>3-11</td>
<td>phenolphthalein, methyl red</td>
</tr>
<tr>
<td>WA by SB</td>
<td>&gt; 7</td>
<td>7-11</td>
<td>phenolphthalein</td>
</tr>
<tr>
<td>WB by SA</td>
<td>&lt; 7</td>
<td>3-7</td>
<td>methyl red</td>
</tr>
</tbody>
</table>

16.6 SOLUBILITY EQUILIBRIA

Important biological examples:
- tooth decay - tooth enamel dissolves in acidic solutions
- formation of kidney stones - salts precipitate in kidney

Many salts are only slightly soluble in water and form solid precipitates in aqueous solutions.

(Recall solubility rules from Section 4.2.)

These “insoluble” salts dissolve to a small extent and form a saturated solution.

The undissolved solid and the dissociated ions in solution establish an equilibrium system.

An example of this is the dissolution of AgBr: \[ \text{AgBr}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Br}^-(aq) \]

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

\( K_{sp} \) is called the solubility product constant; it is the equilibrium constant for insoluble salts.

It is a measure of how soluble a salt is in water - the smaller the \( K_{sp} \), the less soluble the salt.

- Values for \( K_{sp} \) are found in Table 16.2 (p 702).

E.g. Write the solubility equilibrium reaction and the \( K_{sp} \) expression for MgF\(_2\).

\[ \text{E.g. Which salt is less soluble?} \]

(A) CdS, \( K_{sp} = 8.0 \times 10^{-28} \)  (B) PbS, \( K_{sp} = 3.4 \times 10^{-28} \)  (C) CoS, \( K_{sp} = 4.0 \times 10^{-21} \)  (D) FeS, \( K_{sp} = 6.0 \times 10^{-19} \)
Relationship between $K_{sp}$ & salt solubility:

**Solubility** - the maximum amount of salt that will dissolve in a given quantity of solvent; units can be or g/L or mol/L. (For molar solubility, the units are mol/L.)

- Molar Solubility = concentration of the dissolved salt; ion concentrations are related to the solubility of the salt by their coefficients.

$$\text{For MgS, } \text{MgS}_1(s) \rightleftharpoons Mg^{2+}(aq) + S^{2-}(aq)$$

Solubility of MgS = $[\text{MgS}]$ ⇒ This is the concentration of the salt that dissolved in solution.

From the balanced equation, for each mole of MgS that dissolves, one mole of magnesium ions and one mole of sulfide ions form.

Thus, $[\text{MgS}] = [\text{Mg}^{2+}] = [\text{S}^{2-}]$

E.g. (a) Calculate $K_{sp}$ for Ag$_2$S if $[\text{Ag}^+] = 5.8 \times 10^{-17}$ M. (b) What is the solubility of Ag$_2$S?

Predicting Precipitation Reactions - Does a precipitate form?

We can modify the solubility of salts to dissolve minerals and ores, to precipitate ions from solution, and to separate and purify ions.

From calculating the reaction quotient, we can determine if dissolution or precipitation will occur. For solubility problems, Q is called the ion product.

3 Possibilities

1) If $Q < K_{sp}$, an unsaturated solution is present ⇒ precipitation does not occur. The ion concentrations are not high enough to form a solid.

2) If $Q = K_{sp}$, the system is at equilibrium so dissolution and precipitation occur at equal rates; a saturated solution exists in which the ion [ ]’s are just high enough for precipitation to occur.

3) If $Q > K_{sp}$, precipitation occurs as the reaction shifts left. There are excess ions in solution that will precipitate out to form a solid.

Types of problems

⇒ Calculate Q based on the [ ]’s of the ions in the salt and compare to $K_{sp}$ to determine whether or not the salt will precipitate.

⇒ Predict whether or not a precipitate will form when two solutions are mixed.

16.7 SEPARATION OF IONS BY FRACTIONAL PRECIPITATION

Often we have a mixture of ions present in solution; we can separate the ions by the method of fractional precipitation.

Fractional precipitation: add a reagent that enables you to separate the ions according to differences in their solubility.
16.8 THE COMMON ION EFFECT AND SOLUBILITY

Common ion effect: solubility is decreased when a common ion is added.

E.g. \( \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \)

If we add NaCl, \( [\text{Cl}^-] \uparrow \), which causes the reaction to shift left. Some AgCl precipitates out of solution; thus, adding the common ion (Cl\(^-\)) decreases the solubility of AgCl\((s)\).

Calculations for Common Ion problems
a) Include concentration of the common ion in the ICE table.
b) Use the approximation method ([common ion] >> x).
c) Solve \( K_{sp} \) for x, where x = solubility of salt.

16.9 pH AND SOLUBILITY

Addition of an acid can increase the solubility of an insoluble salt if the salt contains a basic anion.

E.g. \( \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq) \)

Adding a strong acid (e.g. HCl) provides H\(^+\) ions: \( \text{H}^+ + \text{F}^- \rightleftharpoons \text{HF} \)

Overall: \( 2\text{H}^+ + \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HF}(aq) \)

\( \Rightarrow \) Addition of H\(^+\) causes \([\text{F}^-]\) to decrease (i.e. F\(^-\) is removed); so the equilibrium shifts right to form more \( \text{F}^- \), thus the solubility of the salt increases as the salt dissolves.

E.g. For the following salts, predict whether the salt will dissolve in an acidic solution.

A. AgBr _____________ B. CdCO\(_3\) _____________
C. PbCl\(_2\) _____________ D. BaS _____________

16.10 COMPLEX ION EQUILIBRIA AND SOLUBILITY (p 713-715 only)

⇒ Formation of complex ions can increase the solubility of an insoluble salt.

Complex ion: ion containing a central metal cation bonded to one or more molecules or ions. The molecules or ions act as Lewis bases (E.g. NH\(_3\), H\(_2\)O, OH\(^-\)).

Complex ion formation is another type of equilibrium process.

E.g. \( \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_{\text{formation}} = 1.5 \times 10^7 \)

The equilibrium constant for the formation of a complex ion is called \( K_{\text{formation}} \) or \( K_f \).

E.g. Addition of NH\(_3\) to AgCl solution increases the solubility of AgCl:

(1) \( \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad K_1 = 1.6 \times 10^{-10} \)

(2) \( \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_2 = 1.5 \times 10^7 \)

Overall: (3) \( \text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad + \text{Cl}^-(aq) \quad K_{\text{net}} = K_1 \times K_2 = 2.4 \times 10^{-3} \)

• Forming a complex ion with NH\(_3\) removes Ag\(^+\) from solution, causing reaction (1) to shift right.
• Application: can use ammonia to dissolve a AgCl precipitate.

Example. Which of the following solutions could dissolve a AgCl precipitate?

A. NH\(_3\) B. KCl C. HNO\(_3\) D. AgNO\(_3\) E. all of these