Chapter 8: Phenomena

Phenomena: Buffers are sometimes defined as: a solution that resists changes in pH when an acid or base is added to it. This definition can be a little misleading. Look at the four titration curves below. The circled regions are considered buffer regions while the boxed regions are not. What do all of the boxed regions have in common and why are they not considered buffers?

**Strong Acid Titrated with Strong Base**

- Initial conditions: 
  - $[\text{OH}^-] = 0.1 \text{ M}$
  - $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$

- Buffer conditions: 
  - $[\text{OH}^-] = 1 \text{ M}$
  - $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$

**Weak Acid Titrated with Strong Base**

- Initial conditions: 
  - $[\text{H}^+] = 1 \times 10^{-8} \text{ M}$
  - $[\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

- Buffer conditions: 
  - $[\text{OH}^-] = 1 \text{ M}$
  - $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$

**Strong Base Titrated with Strong Acid**

- Initial conditions: 
  - $[\text{H}^+] = 0.1 \text{ M}$
  - $[\text{OH}^-] = 1 \text{ M}$

- Buffer conditions: 
  - $[\text{OH}^-] = 1 \times 10^{-7} \text{ M}$
  - $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$

**Weak Base Titrated with Strong Acid**

- Initial conditions: 
  - $[\text{H}^+] = 1 \times 10^{-4} \text{ M}$
  - $[\text{OH}^-] = 1 \times 10^{-6} \text{ M}$

- Buffer conditions: 
  - $[\text{OH}^-] = 1 \times 10^{-6} \text{ M}$
  - $[\text{H}^+] = 1 \text{ M}$
Big Idea: Buffer systems maintain the pH value of a solution even when small amounts of acid or bases are added to the system. In order to have a buffer, a weak acid and its conjugate base or a weak base and its conjugate acid must be present.
Determine the major species in solution:

- Ca(OH)$_2$
  - Major Species:
- HC$_2$H$_3$O$_2$
  - Major Species:
- HClO$_4$
  - Major Species:
- NaCN
  - Major Species:
- CH$_3$NH$_3$Cl
  - Major Species:
**Buffer**

A solution that resists any change in pH when small amounts of acid or base are added.

**Buffers Consist of:**

- Weak Acid and its Conjugate Base
  - $(\text{HC}_2\text{H}_3\text{O}_2 / \text{NaC}_2\text{H}_3\text{O}_2)$
- Weak Base and its Conjugate Acid
  - $(\text{NH}_3 / \text{NH}_4\text{Cl})$
Buffer Solutions

- **Step 1:** Identify major species in solution.
- **Step 2(a):** Identify IF any reaction will go to completion (this happens if you have $\text{H}^+$ and a weak base or $\text{OH}^-$ and a weak acid in your major species). If no reaction goes to completion go to step 3.
- **Step 2(b):** If a reaction goes to completion, make an “IF” table to determine the major species in solution after the reaction goes to completion (products and excess reactants.) IF tables are in moles not molarity.
- **Step 3:** Examine major species to see if you have a buffer solution.
Buffer Solutions

Student Question

How many of the following can be mixed to form a buffer solution?

- KOH & HF
- RbOH & HBr
- NaC$_2$H$_3$O$_2$ & HCl
- H$_3$PO$_4$ & HBr
- NH$_3$ & NH$_4$Cl

a) 1  
b) 2  
c) 3  
d) 4  
e) 5

Chapter 8: Applications of Aqueous Equilibrium
Buffer Solutions

Buffer Problems

- Assume that [HA] is constant
- Assume that [A\(^-\)] is constant

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

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

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

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

\[
\log \left( \frac{K_a}{[H^+]} \right) = \log \left( \frac{[A^-]}{[HA]} \right)
\]

\[
\log(K_a) - \log([H^+]) = \log \left( \frac{[A^-]}{[HA]} \right)
\]

\[
-\log([H^+]) = -\log([K_a]) + \log \left( \frac{[A^-]}{[HA]} \right)
\]

\[
pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)
\]
Buffer Solutions

Identify Major Species

Find species after reactions goes to completion

- ONLY
  - Strong Acid
  - or
  - Strong Base
  - or
  - Strong Acid and a Weak Acid
  - or
  - Strong Base and a Weak Base

- ONLY
  - Weak Acid
  - or
  - Weak Base

- Weak Acid and its Conjugate Base
  - or
  - Weak Base and its Conjugate Acid

Chapter 8: Applications of Aqueous Equilibrium
Buffer Solutions

How to determine pH

Strong Acid or Strong Acid and a Weak Acid

Strong Base or Strong Base and a Weak Base

Weak Acid

Weak Acid and its Conjugate Base

Weak Base

Weak Base and its Conjugate Acid

The amount of $H^+$/OH$^-$ from the weak acid/base is negligible in comparison to the strong acid/base therefore just use the strong acid/base to calculate the pH.

$pH = -\log[H^+]$

$pOH = -\log[OH^-]$

$pH = 14 - pOH$

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

Ice Table
**Buffer Solutions**

**Situation #1:**

<table>
<thead>
<tr>
<th>Solution #1 (1L)</th>
<th>Add</th>
<th>Solution #2 (1L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1 drop HCl</td>
<td>0.010 M HCl</td>
</tr>
<tr>
<td>([H^+]) =</td>
<td></td>
<td>([H^+]) =</td>
</tr>
<tr>
<td>pH =</td>
<td></td>
<td>pH =</td>
</tr>
</tbody>
</table>
### Situation #2:

<table>
<thead>
<tr>
<th>Solution #1 (1L)</th>
<th>Add</th>
<th>Solution #2 (1L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 M $\text{HC}_2\text{H}_3\text{O}_2$</td>
<td>1 drop HCl</td>
<td>0.010 M HCl</td>
</tr>
<tr>
<td>0.50 M $\text{NaC}_2\text{H}_3\text{O}_2$</td>
<td></td>
<td>0.50 M $\text{HC}_2\text{H}_3\text{O}_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50 M $\text{NaC}_2\text{H}_3\text{O}_2$</td>
</tr>
</tbody>
</table>

$[\text{H}^+]=1.8\times10^{-5}$ M

pH = 4.74

[H+] = 

pH =
Buffer Solutions

**Student Question**

A buffer solution contains 0.0200 M acetic acid and 0.0200 M sodium acetate. What is the pH after 2.0 mmol of NaOH are added to 1.00L of this buffer?

*Helpful Information: pK$_a$ = 4.75 for acetic acid*

a) 4.75  
b) 4.70  
c) 4.80  
d) 4.84  
e) None of the above
Buffer Solutions

Buffer Capacity: An indication of the amount of acid or base that can be added before a buffer loses its ability to resist the change in pH

- A buffer has the greatest buffer capacity when:
  - there are equal amounts of [HA] and [A-]
  - there are large quantities of [HA] and [A-]

Note: When choosing a buffer, pick a buffer that has a pK_a closest to what you want the pH to be.
 Equivalence Point: The stage of a titration when exactly the right volume of solution needed to complete the reaction has been added.

Note: The equivalence point is sometimes called the stoichiometric point.
Titration Curves

- **Weak Base/ Strong Acid (NH₃/HCl)**
  - Calculate the pH at the following four points of a titration curve in which 0.50 M HCl is added to 50. mL of 1.0 M NH₃ ($K_b=1.8\times10^{-5}$).

  - **Case #1**: No acid added (50. mL of 1.0 M NH₃)
  - **Case #2**: 50. mL of HCl added (50. mL of 1.0 M NH₃ and 50. mL of 0.50 M HCl)
  - **Case #3**: 100. mL of HCl added (50. mL of 1.0 M NH₃ and 100. mL of 0.50 M HCl)
  - **Case #4**: 150. mL of HCl added (50. mL of 1.0 M NH₃ and 150. mL of 0.50 M HCl)
Mark these points on your titration curve

a. The equivalence point
b. The region with maximum buffering
c. \( \text{pH} = \text{pK}_a \)
d. \( \text{pH} \) depends only on \([A^-]\) (weak base only present)
e. \( \text{pH} \) depends only on \([HA]\) (weak acid only present)
f. The \( \text{pH} \) only depends on the amount of strong acid or base added
Buffer Solutions

Chapter 8: Applications of Aqueous Equilibrium

Identify Major Species

Find species after reactions goes to completion

ONLY
Strong Acid
or
Strong Base
or
Strong Acid and a Weak Acid
or
Strong Base and a Weak Base

ONLY
Weak Acid
or
Weak Base

Weak Acid and its Conjugate Base
or
Weak Base and its Conjugate Acid

Identify Major Species

Find species after reactions goes to completion

ONLY
Strong Acid
or
Strong Base
or
Strong Acid and a Weak Acid
or
Strong Base and a Weak Base

ONLY
Weak Acid
or
Weak Base

Weak Acid and its Conjugate Base
or
Weak Base and its Conjugate Acid
Buffer Solutions

What method would you use to calculate the pH at each of the points?

- **Strong Acid or Strong Acid and a Weak Acid**
- **Strong Base or Strong Base and a Weak Base**
- **Weak Acid**
- **Weak Base**
- **Weak Acid and its Conjugate Base**
- **Weak Base and its Conjugate Acid**

The amount of $H^+/OH^-$ from the weak acid/base is negligible in comparison to the strong acid/base therefore just use the strong acid/base to calculate the pH.

\[
pH = -\log[H^+] \\
pOH = -\log[OH^-] \\
pH = 14 - pOH
\]

\[
pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)
\]

Chapter 8: Applications of Aqueous Equilibrium
Mark these points on your titration curve

a. The equivalence point
b. The region with maximum buffering
c. pH = pK_a
d. pH depends only on [A^-] (weak base only present)
e. pH depends only on [HA] (weak acid only present)
f. The pH only depends on the amount of strong acid or base added
## Solubility

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_{sp}(25^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium sulfate</td>
<td>BaSO$_4$</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO$_3$</td>
<td>$8.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>Calcium fluoride</td>
<td>CaF$_2$</td>
<td>$4.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)$_2$</td>
<td>$1.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO$_4$</td>
<td>$6.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Copper(II) sulfide</td>
<td>CuS</td>
<td>$8.5 \times 10^{-45}$</td>
</tr>
<tr>
<td>Iron(II) carbonate</td>
<td>FeCO$_3$</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Iron(II) hydroxide</td>
<td>Fe(OH)$_2$</td>
<td>$1.8 \times 10^{-15}$</td>
</tr>
<tr>
<td>Lead(II) chloride</td>
<td>PbCl$_2$</td>
<td>$1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Lead(II) sulfate</td>
<td>PbSO$_4$</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>Lead(II) sulfide</td>
<td>PbS</td>
<td>$7 \times 10^{-29}$</td>
</tr>
<tr>
<td>Magnesium carbonate</td>
<td>MgCO$_3$</td>
<td>$1 \times 10^{-15}$</td>
</tr>
<tr>
<td>Magnesium hydroxide</td>
<td>Mg(OH)$_2$</td>
<td>$8.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>Silver chloride</td>
<td>AgCl</td>
<td>$1.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>Silver chromate</td>
<td>Ag$_2$CrO$_4$</td>
<td>$9.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>Silver iodide</td>
<td>AgI</td>
<td>$1.5 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

Select values from table 8.5 in book.
Student Question

What is the molar solubility of CaF₂?

K_{sp} = 4.0 \times 10^{-11}

a) 2.1 \times 10^{-4} \text{ M}

b) 3.4 \times 10^{-4} \text{ M}

c) 4.3 \times 10^{-4} \text{ M}

d) 6.3 \times 10^{-6} \text{ M}

e) None of the above
Big Idea: Buffer systems maintain the pH value of a solution even when small amounts of acid or bases are added to the system. In order to have a buffer, a weak acid and its conjugate base must be present or a weak base and its conjugate acid.

Buffer Solution

- Be able to identity buffer solutions. (15,46,47)
  - Weak acid/conjugate base
  - Weak base/conjugate acid
- Be able to calculate the pH of a buffer solution (21,22,23,27,29,35,37,39,40,42,43,44,48,49)
  - Henderson-Hasselbalch Equation
    - \[ pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]
Take Away From Chapter 8

- **Buffer Solution** (Continued)
  - Know when a solution has the greatest buffer capacity. (16)
    - When there is ample amounts of both [A⁻] and [HA]
    - When [A⁻]=[HA]

- **Titration Curves**
  - Be able to calculate the pH at any point in a titration curve. (63, 64, 65, 66)
  - Be able to draw titration curves for: (54, 55, 56, 57, 61)
    - Strong acid/strong base
    - Strong base/strong acid
    - Weak acid/strong base
    - Weak base/strong acid

Numbers correspond to end of chapter questions.
Take Away From Chapter 8

- **Solubility**
  - Be able to calculate the molar solubility of a solid given the $K_{sp}$. (98)
  - Be able to calculate/know the effect on the molar solubility when a common ion is present in solution. (106, 107)

Numbers correspond to end of chapter questions.