New Situation: The Common Ion Effect

CH₃COOH ⇌ H⁺(aq) + CH₃COO⁻(aq)

Consider the equilibrium involving the weak acid at 298K shown above. What will happen to the pH if some solid CH₃COONa is added while the temperature is held constant?

Prediction:
1. The pH will increase
2. The pH will decrease
3. The pH will not be effected.
4. There is not enough information to determine the effect on the pH.

Common Ion Effect

DEMO:

CH₃COOH ⇌ H⁺(aq) + CH₃COO⁻(aq)

pH =

Add CH₃COONa:
CH₃COONa → Na⁺ + CH₃COO⁻(aq)

pH =

What happened to [CH₃COO⁻]?

[CH₃COOH]?

[H⁺]?
**Addition of Acids or Bases to Common Ion Mixtures**

**Common Ion Mixtures are called Buffer Solutions**

A buffer is a solution that “resists” a change in pH

E.g. blood contains substances that keep its pH fixed at 7.3 - important for life functions

**Buffer solutions consist of either:**

- A weak acid + salt of its conjugate base
- A weak base + salt of its conjugate acid

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<table>
<thead>
<tr>
<th>pH</th>
<th>Acid Alone</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1M CH₃COOH(aq)</td>
<td>0.1M CH₃COOH 0.1M CH₃COONa</td>
</tr>
<tr>
<td>Initial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add NaOH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Calculate pH Quantitatively

Calculate the pH of a solution that is 0.1M CH₃COOH and 0.1M CH₃COONa. For acetic acid, $K_a = 1.8 \times 10^{-5}$.

pH of Buffers

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Henderson-Hasselbalch equation

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

Note: If $[HX] = [X^-]$, $pH = pK_a$

Buffers work best near $pH = pK_a$
FYI

HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)

\[ K_a = \frac{[H^+][X^-]}{[HX]} = \frac{[H^+]}{[HX]} \]

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

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

\[ pK_a = pH - \log \left( \frac{[X^-]}{[HX]} \right) \]

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

Henderson-Hasselbalch equation

If [HX] = [X^-], pH = pK_a

pH of Buffer Solutions

Calculate the pH of a solution that is 0.1M NH₃ and 0.2M NH₄Cl.  \( K_b \) (for NH₃) = 1.8 \times 10^{-5}. 
Mixtures of acids

A solution of HCl has a pH of 4.74.

\[ [\text{H}^+] = 1.8 \times 10^{-5} \text{ M} \]

Add 20 ml of 1.0 M HCl to 1 L of this solution.

What is the pH of the solution?

1. 4.74
2. 1.00
3. 7.00
4. 1.70
5. 3.04

Addition of Acid or Base to Buffer

\[ \text{CH}_3\text{COOH} \longrightarrow \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq}) \]

Start with same pH; 1 L solution,

\[ \text{pH} = \text{pK}_a = 4.74 \]

\[ [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] = 0.30 \text{ M} \]

Add a dropper (~20ml) of 1M HCl

Add a dropper (~20ml) of 1M NaOH

Addition of Acid or Base to a Buffer follows a 2 step process:

a) Neutralization (stoichiometry and ice table)

b) Acid dissociation (H-H equation)
CH₃COOH ⇌ H⁺(aq) + CH₃COO⁻(aq)

Strategy:
1) neutralize added A/B (ice)
2) equilibrium acid dissociation (H-H)

Buffer Capacity: How much Acid or Base can it absorb without a large pH change?

Buffer Mixture: CH₃COOH + CH₃COONa

<table>
<thead>
<tr>
<th>Solution</th>
<th>Molarity</th>
<th>Initial pH</th>
<th>pH after adding 1M HCl</th>
<th>pH after adding 1M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.1 M</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 M HCl changed pH from 4.74 to 1.70 upon addition of acid.
**Practical Limits of Buffer Use**

**Buffer Capacity:**

![Graph showing pH vs. mL NaOH]

**pH Range of a Buffer:**

If \([HX] = [X^-]\) then \(pH = ?\)

What if the concentration of one is greater than 10 times the other?

Since \(\log 10 = 1\), the usable range of a buffer is what?

**Addition of Strong Acids or Bases to Buffers**

Finding the pH is a Two Step Process:

1. **Stoichiometry Calculation**
   
   If you are within the buffer capacity, the added Acid or Base is used up completely. Use stoichiometry to find concentrations of HX and X^-.

2. **Equilibrium Calculation**
   
   Now you have a buffer equilibrium; use H-H equation to find pH.
Sample problem:
A buffer solution contains 0.10 mol of acetic acid and 0.13 mol of sodium acetate in 1.00 L. What is the pH of the buffer after the addition of 0.02 mol of HCl?

Calculation of pH during Acid-Base Titrations

Titration:

Finding the pH at any point in the titration is a two step process.

1. Neutralization
What exists in solution after neutralization?

2. Find the pH based on excess species leftover in solution
   A) strong acid/base
   B) weak/acid base
   Do an equilibrium calculation
   May be a buffer solution
Strong Acid-Strong Base TITRATION EXAMPLE

Titrate 50 mL of 0.1\textit{M} HCl with 0.2\textit{M} NaOH:

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

1) Calculate pH with 0 mL NaOH solution added:
\[
[\text{H}^+] = 0.1\textit{M} \quad \text{pH} =
\]
Moles of H\textit{+} = MV

2) Calculate pH with 20 mL NaOH solution added:
Step 1. Neutralize. What is left over?
\[
\text{Moles of OH}^+ \text{ added} = \text{MV} = \\
\text{Moles of H}^+ \text{ remaining} =
\]
Step 2. Find pH of what is left over.
\[
[\text{H}^+] =
\]
\[
\text{pH} =
\]

Calculation of pH at the EQUIVALENCE POINT
(Problem Continued)

The equivalence point is where:
Total Moles of base added =

3) Calculate pH with 25 mL NaOH solution added:
Step 1. Neutralize. What is left over?
Moles of OH\textit{+} added = MV =

Excess of moles of H\textit{+} =

Step 2. Find pH of what is left over.
\[
\text{pH} =
\]
\[
\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}
\]
Calculation of pH *PAST* the equivalence point

(Problem Continued)

4) Calculate pH with 30 mL NaOH solution added:
Step 1. Neutralize. What is left over?
Moles of OH⁻ added = MV =

Excess of moles of _______ =
Step 2. Find pH of what is left over.
[OH⁻] =
pOH =
pH = 14 – pOH =

HCl(aq) + NaOH(aq) → NaCl(aq) + H₂O(l)

---

**Strong Acid-Strong Base Titration Data**

50 mL of 0.1M HCl titrated with 0.2M NaOH:

<table>
<thead>
<tr>
<th>Added</th>
<th>mL OH⁻</th>
<th>Total</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume</td>
<td>H⁺ Left</td>
<td>[H⁺]</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
<td>5x10⁻³</td>
<td>0.1</td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>1x10⁻³</td>
<td>1.4x10⁻²</td>
</tr>
<tr>
<td>24.5</td>
<td>74.5</td>
<td>1.3x10⁻⁴</td>
<td>1.01x10⁻³</td>
</tr>
<tr>
<td>24.9</td>
<td>74.9</td>
<td>2x10⁻⁵</td>
<td>2.67x10⁻⁴</td>
</tr>
<tr>
<td>24.99</td>
<td>74.99</td>
<td>2x10⁻⁶</td>
<td>2.67x10⁻⁵</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>7.5x10⁻⁹</td>
<td>1x10⁻⁷</td>
</tr>
<tr>
<td>26</td>
<td>76</td>
<td>3.8x10⁻¹²</td>
<td>11.4</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>9.0x10⁻¹³</td>
<td>12.1</td>
</tr>
</tbody>
</table>

1. How is moles of H⁺ at equivalence calculated??

2. How is [H⁺] past equivalence calculated??
Titration of a **Strong Acid** with a **Strong Base**

- X axis is number of mL 0.100 M NaOH added to 50.0 mL 0.100 M HCl

Titration of a **Strong Base** with a **Strong Acid**

- pH 7
- Equivalence point
- mL acid
TITRATION OF A WEAK ACID

Buffer solutions are encountered during titrations

Titrate 0.1M CH₃COOH with 0.2M NaOH:

Start with 50 mL of CH₃COOH solution.
Moles of CH₃COOH = MV

Find pH with 0 mL NaOH solution added:

CH₃COOH(aq) ⇌ H⁺(aq) + CH₃COO⁻(aq)

A) Neutralization

CH₃COOH + OH⁻ → H₂O + CH₃COO⁻

At equilibrium:
[CH₃COO⁻] = [CH₃COOH] =

B) pH determination

CH₃COOH(aq) ⇌ H⁺(aq) + CH₃COO⁻(aq)

pH =
TITRATION OF A WEAK ACID

3) equivalence point:
With 25 mL NaOH solution added:
A) Neutralization

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

At equilibrium: [CH₃COO⁻] =

B) pH determination

\[
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- 
\]
Effect of Acid Strength on Titration Curve Shape

pH at the Equivalence Point

1) Titrating a **strong acid** with a **strong base** (OR strong base with a **strong acid**)  
   - pH at equivalence = 7

2) Titrating a **weak acid** with a **strong base**  
   - pH at equivalence > 7  
   - *the weaker the acid, the smaller the pH change at equivalence*

3) Titrating a **weak base** with a **strong acid**  
   - pH at equivalence < 7
INDICATORS

\[ \text{InH}^+ \rightleftharpoons \text{In} + \text{H}^+ \]

Common acid-base indicators

<table>
<thead>
<tr>
<th>Name</th>
<th>pH interval for color change</th>
<th>Acid color</th>
<th>Base color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>1 - 2</td>
<td>Yellow</td>
<td>Violet</td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>1.5 - 2.5</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>2.5 - 4.0</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.2 - 6.3</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromthymol blue</td>
<td>6.0 - 7.6</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>8.0 - 9.6</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.5 - 10</td>
<td>Colorless</td>
<td>Pink</td>
</tr>
<tr>
<td>Alizarin yellow G</td>
<td>10.1-12.0</td>
<td>Yellow</td>
<td>Red</td>
</tr>
</tbody>
</table>

Choice of Indicator:

Titration of a **weak base** with a **strong acid**
Titration of a Di- or Tri-protic Acid

\[
\begin{align*}
H_3X &= H^+ + H_2X^- \quad K_{a1} \\
H_2X^- &= H^+ + HX^{2-} \quad K_{a2} \\
HX^{2-} &= H^+ + X^{3-} \quad K_{a3}
\end{align*}
\]

\[K_{a1} \gg K_{a2} \gg K_{a3}\]

Practice Problem

A buffer solution is 0.20M in HPO\(_4^{2-}\) and 0.10M in H\(_2\)PO\(_4^-\). What is the [H\(^+\)] in this solution?

H\(_3\)PO\(_4\): \(K_{a1} = 7.5 \times 10^{-3}\)
\(K_{a2} = 6.2 \times 10^{-8}\)
\(K_{a3} = 1 \times 10^{-12}\)

A. \(3.7 \times 10^{-3}\) M
B. \(3.7 \times 10^{-4}\) M
C. \(3.1 \times 10^{-8}\) M
D. \(3.1 \times 10^{-9}\) M
E. \(5 \times 10^{-13}\) M
End of Exam 2 Material

(Begin Exam 3 Material with Solubility)