Results from Monday's lecture

A buffer solution contains both members of an acid/base conjugate pair.

What is the pH of a solution that is 0.010 M in both acetic acid and sodium acetate?

\[ \text{NaC}_2\text{H}_3\text{O}_2 \rightarrow \text{Na}^+ + \text{C}_2\text{H}_3\text{O}_2^- \]

<table>
<thead>
<tr>
<th></th>
<th>[CH$_3$COOH]</th>
<th>[H$_3$O$^+$]</th>
<th>[CH$_3$COO$^-$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-1.8 \times 10^{-5}$</td>
<td>$+1.8 \times 10^{-5}$</td>
<td>$+1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.010</td>
<td>$1.8 \times 10^{-5}$</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Buffer solutions tend to maintain constant pH despite the addition of additional H$^+$ or OH$^-$. 
Demo

Water + Universal indicator
Before adding 1 drop 1 M HCl

After adding 1 drop 1 M HCl

Water + Universal indicator
Before adding 1 drop 1 M NaOH

After adding 1 drop 1 M NaOH

pH = 5 buffer + Universal indicator
Before adding 1 drop 1 M HCl

After adding 1 drop 1 M HCl

pH = 5 buffer + Universal indicator
Before adding 1 drop 1 M NaOH

After adding 1 drop 1 M NaOH

How does the buffer manage to resist changes in pH?

The H$_3$O$^+$ from HCl reacts with the acetate ion.

The OH$^-$ from NaOH reacts with the acetic acid.
The reaction between $\text{H}_3\text{O}^+$ and $\text{CH}_3\text{COO}^-$ goes to completion.

$$\text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{COOH}$$

$k_b \approx 10^{-10}$

Very strong acid
(1) \[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \quad K_1 = K_b \]

(2) \[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \frac{1}{2}\text{H}_2\text{O} \quad K_2 = \frac{1}{K_W} \]

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

\[
\begin{align*}
5.6 \times 10^{-4} & = K_3 = K_b \frac{1}{K_W}
\end{align*}
\]

Add square root:

\[
\begin{align*}
5.6 \times 10^{-10} & \approx \sqrt{3.9}
\end{align*}
\]
The reaction between OH\(^-\) and CH\(_3\)COOH goes to completion.

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

Strongest base inaq soln

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

\[K_a = 1.8 \times 10^{-5}\]
0. \[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \quad K_1 = K_a \]

2. \[ \text{HSO}_4^- + \text{OH}^- \rightarrow \frac{1}{2}\text{H}_2\text{O} \quad K_2 = \frac{1}{K_w} \]

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

\[ K_3 = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9 \]

\[ K_3 = \frac{1}{K_{1b}} \]

4a
What is the pH of our original buffer (0.010 M acetic acid and 0.010 M sodium acetate) after one drop (0.05 mL) of 1 M HCl is added to 10.0 mL of the buffer?

First, consider that the HCl is being diluted.

\[ M_c V_c = M_D V_D \]

\[ (1 \text{ M})(0.05 \text{ mL}) = M_D (10.0 \text{ mL}) \]

\[ M_D = 0.005 \text{ M} \]

\[ \text{ Added HCl} \]

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

\[
\begin{array}{ccc}
| & 0.005 \text{ M} & 0.010 \text{ M} & 0.010 \text{ M} \\
L & 0.005 & 0.010 & \\
C & -0.005 & -0.005 & +0.005 \\
\min & 0.005 & 0.015 & \\
\end{array}
\]

Set up a new i-c-e table reflecting these new concentrations of acetate ion and acetic acid.

<table>
<thead>
<tr>
<th></th>
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<th>[H$_3$O$^+$]</th>
<th>[CH$_3$COO$^-$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.005</td>
<td></td>
<td>0.005</td>
</tr>
<tr>
<td>Change</td>
<td>-y</td>
<td>y</td>
<td>y</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.015 -y</td>
<td>y</td>
<td>0.005 +y</td>
</tr>
</tbody>
</table>

After HCl was added
Again, we need just a slight adjustment to bring the system back to equilibrium.

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

\[ 1.8 \times 10^{-5} = y \left(0.005\text{M}\right) \]

\[ \frac{0.015}{y} = x \]

\[ y = \frac{0.015}{0.005} \left(1.8 \times 10^{-5}\right) = 5.4 \times 10^{-5} = [\text{H}_3\text{O}^+] \]

\[ \text{pH} = 4.27 \]

The new pH should be lower than the original pH

\[ \text{pH} = 4.74 \]

but not much lower.

\[ \text{pH} = 4.27 \]
\[ k_a = \frac{[\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COO}^-]} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COON}^-]} \]

\[ [\text{H}_3\text{O}^+] \text{ depends on } k_a \]

\[ \text{ratio} \]

\[ \frac{[\text{conj. base}]}{[\text{acid}]} \]

\[ 69 \]
You should be able to show that the pH will be raised, but only slightly, when 1 drop of 1M NaOH is added to 10.0 mL of the original buffer.

Original buffer

\[ [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] = 0.010 \]

\[ \text{pH} = 4.74 \]

After add OH

\[ \text{pH} \approx 5.20 \]
\[
CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O
\]

\[
\begin{align*}
0.010 \text{ m} & \quad 0.005 \text{ m} & \quad 0.010 \text{ m} \\
-0.005 & \quad -0.005 & \quad +0.005 \\
0.005 & \quad \sim 0 & \quad 0.015
\end{align*}
\]

\[
K_a = \frac{[CH_3COOH]}{[CH_3COO^-]} \cdot \frac{[H^+]^2}{[OH^-]}
\]

\[
1.8 \times 10^{-5} = \frac{[H_3O^+]}{[OH^-]} \frac{(0.015)}{(0.005)}
\]

\[
[H_3O^+] = 6.0 \times 10^{-6}
\]

\[
\text{pH} = 5.22
\]

Note: \(pOH = 8.78 \quad \text{and} \quad [OH^-] = 1.7 \times 10^{-9} \quad (\sim 0)\)
A buffer that is 1.0 M in acetic acid and 1.0 M in sodium acetate should also have a pH of 4.74 but it has a higher buffer capacity (ability to resist pH change).

\[
K_a = \frac{[H_3O^+][C_2H_3COO^-]}{[C_2H_3COOH]}
\]

\[1.8 \times 10^{-5} = \frac{[H_3O^+]}{\frac{1.0}{1.0}}\]

\[\text{pH} = 4.74\]

The best buffers are those for which \(pK_a\) is close to the pH desired for the buffer.
Can you make a buffer with pH = 9.0 from acetic acid/acetate in?

\[ K_a = \frac{[H_3O^+]}{[CH_3COO^-]} \]

\[ \frac{[CH_3COOH]}{[CH_3COO^-]} \]

\[ 1.8 \times 10^{-5} = 1 \times 10^{-9} \]

\[ [CH_3COO^-] \]

\[ \sqrt{8.9} \]

\[ pH = -\log [H_3O^+] \]

\[ [H_3O^+] = 10^{-pH} \]
\[
\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-9}} = 1.8 \times 10^4
\]

A solution 0.010 M in CH₃COOH

Then

\[
[\text{CH}_3\text{COO}^-] = 1.8 \times 10^4 \times 0.010
\]

\[
= 1.8 \times 10^2
\]

Buffer 0.010 M in acetic acid
180 M in sodium acetate