Example 1 - Buffer Method 1

What is the pH of a buffer made by adding 4.68g of sodium benzoate (NaC\textsubscript{7}H\textsubscript{5}O\textsubscript{2}) to 250.0mL of 0.15M benzoic acid solution? \( K_a = 6.5 \times 10^{-5} \)

Need concentration of the conjugate base benzoate ion (C\textsubscript{7}H\textsubscript{5}O\textsuperscript{2-}):

\[
(4.68g \text{ NaC}_7\text{H}_5\text{O}_2) \left( \frac{1\text{mol NaC}_7\text{H}_5\text{O}_2}{144.1g \text{ NaC}_7\text{H}_5\text{O}_2} \right) \left( \frac{1\text{mol C}_7\text{H}_5\text{O}_2^-}{1\text{mol NaC}_7\text{H}_5\text{O}_2} \right) = 0.325\text{mol C}_7\text{H}_5\text{O}_2^-
\]

\[
\left[\text{C}_7\text{H}_5\text{O}_2^-\right] = \frac{0.0325\text{mol C}_7\text{H}_5\text{O}_2^-}{0.25L} = 0.13\text{ M C}_7\text{H}_5\text{O}_2^-
\]

\[
\begin{array}{c|c|c|c|c}
 & \text{HC}_7\text{H}_5\text{O}_2 & + & \text{H}_2\text{O} & \Leftrightarrow & \text{H}_3\text{O}^+ & + & \text{C}_7\text{H}_5\text{O}_2^- \\
I & & & & & 0 \\
C & & & & +x & & \\
E & & & & & x \\
\end{array}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]}
\]

CHECK: Henderson - Hasselbalch Equation

If assume x is small compared to initial concentrations of acid and conjugate base, one can use the initial values of the acid and conjugate base for equilibrium concentrations.

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

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

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

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

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

\[
\text{pH} =
\]
Example 2 - Buffer Method 2
What is the pH of a buffer made by adding 125mL of 0.14M HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2} solution with 165mL of 0.16M NaC\textsubscript{7}H\textsubscript{5}O\textsubscript{2} solution?  \( K_a = 6.5 \times 10^{-5} \)

Need concentrations of the conjugate acid and base in the mixture.

\[
\begin{array}{|c|c|c|}
\hline
& HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2} & + \ H_2O \\ \hline \hline
I & 0 \\ \hline
C & +x \\ \hline
E & x \\ \hline
\end{array}
\]

\[
K_a = \frac{[H_3O^+][C\textsubscript{7}H\textsubscript{5}O\textsubscript{2}^-]}{[HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2}]} \]

CHECK: \( pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \)

Example 3 – Buffer Range
At what pH does buffer work best?  Best buffer system when pH = pK\(_a\)
What is the range of a buffer?  Buffer works within ±1 of pK\(_a\) value so buffer pH = pK\(_a\) ± 1

What is the buffer range of benzoic acid/benzoate buffer?
\( pK_a = -\log(6.5 \times 10^{-5}) = 4.19 \)  Buffer range = 4.19 ± 1  so  3.19 to 5.19

What is the pH for best buffer capacity and what is the buffering range for each of the following?

<table>
<thead>
<tr>
<th>Buffer components</th>
<th>pH best buffering capacity</th>
<th>Buffer range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} / C\textsubscript{2}H\textsubscript{3}O\textsubscript{2}^-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HClO / ClO^-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO\textsubscript{3}^- / CO\textsubscript{3}^-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO\textsubscript{2} / CHO\textsubscript{2}^-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{4}^+ / NH\textsubscript{3}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example 4 – Addition of base to buffer
What is the new pH if 5.0 mL of 0.50M NaOH is added to 50.0mL of benzoic acid-benzoate buffer from problem 1?

\[ [\text{HC}_7\text{H}_5\text{O}_2] = 0.15 \text{M} \quad [\text{C}_7\text{H}_5\text{O}_2^-] = 0.13 \text{M} \]

First determine how much buffer reacts since NaOH is a strong base, NaOH will react 100% with the acid component of the buffer. MUST WORK STOICHIOMETRY IN MOLES.

\[
\begin{align*}
\text{HC}_7\text{H}_5\text{O}_2 & \quad + \quad \text{NaOH} \quad \rightarrow \quad \text{H}_2\text{O} \quad + \quad \text{NaC}_7\text{H}_5\text{O}_2 \\
(0.0500L \times 0.15M) & \quad + \quad (0.0050L \times 0.50M) & \quad \rightarrow \quad (0.0500L \times 0.13M)
\end{align*}
\]

Initial mol
Reaction
Final mol

Note: Must divide by the total volume before entering new values into ICE chart. Total volume = 50.0 mL + 5.0 mL = 55.0 mL or 0.0550L

\[ [\text{HC}_7\text{H}_5\text{O}_2] = \quad \quad \quad [\text{C}_7\text{H}_5\text{O}_2^-] = \]

\[
\begin{array}{c|cccc}
 & \text{HC}_7\text{H}_5\text{O}_2 & + & \text{H}_2\text{O} & \Leftrightarrow & \text{H}_3\text{O}^+ & + & \text{C}_7\text{H}_5\text{O}_2^- \\
\hline
I & 0 \\
C & +x \\
E & x
\end{array}
\]

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} \]

CHECK: \[ \text{pH} = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \]

Example 5 – Addition of acid to buffer
What is the new pH if 10.0 mL of 0.15M HCl was added to 50.0mL of benzoic acid-benzoate buffer from problem 1?

\[ [\text{HC}_7\text{H}_5\text{O}_2] = 0.15 \text{M} \quad [\text{C}_7\text{H}_5\text{O}_2^-] = 0.13 \text{M} \]

First determine how much buffer reacts since HCl is a strong acid, HCl will react 100% with the base component of the buffer. MUST WORK STOICHIOMETRY IN MOLES.

\[
\begin{align*}
\text{NaC}_7\text{H}_5\text{O}_2 & \quad + \quad \text{HCl} \quad \rightarrow \quad \text{HC}_7\text{H}_5\text{O}_2 \quad + \quad \text{NaCl} \\
(0.0500L \times 0.13M) & \quad + \quad (0.010L \times 0.15M) & \quad \rightarrow \quad (0.0500L \times 0.15M)
\end{align*}
\]

Initial mol
Reaction
Final mol
Note: Must divide by the total volume before entering new values into ICE chart.

Total volume =

<table>
<thead>
<tr>
<th></th>
<th>HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2}</th>
<th>+</th>
<th>H\textsubscript{2}O</th>
<th>⇌</th>
<th>H\textsubscript{3}O\textsuperscript{+}</th>
<th>+</th>
<th>C\textsubscript{7}H\textsubscript{5}O\textsubscript{2}\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>+x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} \]

CHECK: \[ \text{pH} = \text{p}K_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \]

Example 6 – Depleting buffer

How much of the 0.15M HCl would have to be added to 50.0 mL of the benzoic acid/benzoate buffer to deplete it completely?

\[ [HC_7H_5O_2] = 0.15\text{M} \quad [C_7H_5O_2^-] = 0.13\text{M} \]

Since an acid added to a buffer will act with the conjugate base, determine how much acid will be required to react with 50.0 mL of 0.13M C\textsubscript{7}H\textsubscript{5}O\textsubscript{2}\textsuperscript{-}.

\[
\begin{array}{ccc}
\text{NaC}_7\text{H}_5\text{O}_2 & + & \text{HCl} \\
(0.0500L \times 0.13M) & & (\text{? L} \times 0.15M)
\end{array}
\Rightarrow
\begin{array}{ccc}
\text{HC}_7\text{H}_5\text{O}_2 & + & \text{NaCl} \\
(0.0500L \times 0.15M) & & 
\end{array}
\]

<table>
<thead>
<tr>
<th></th>
<th>NaC\textsubscript{7}H\textsubscript{5}O\textsubscript{2}</th>
<th>+</th>
<th>HCl</th>
<th>→</th>
<th>HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2}</th>
<th>+</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial mol</td>
<td>0.0065 mol</td>
<td></td>
<td>0.0065 mol</td>
<td></td>
<td>0.0075 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>- 0.0065 mol</td>
<td>- 0.0065 mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final mol</td>
<td>0 mol</td>
<td>0 mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Buffer would be depleted when _______ mL of 0.15M HCl has been added.
At this point only acid HC\textsubscript{7}H\textsubscript{5}O\textsubscript{2} remains. Note: can NOT use Henderson-Hasselbalch equation since NO longer a buffer.

\[
[\text{HC}_7\text{H}_5\text{O}_2] = \frac{\text{mol}}{L} = \]

Volume = 50. mL + _____ mL =
Likewise, similar calculation can be done for depletion of acid component of buffer.

Example 7 – Determining acid/base ratio needed for buffer pH

When need to know either
(A) how much of one of the buffer components to add to produce a certain pH or
(B) what ratio of conjugate base to acid is needed to produce a certain pH,
use Henderson-Hasselbalch equation.

How many grams of sodium benzoate (NaC₇H₅O₂) must be added to 100. mL of 0.13M benzoic acid (HC₇H₅O₂) to produce a buffer with a pH of 4.30?

Kₐ = \frac{[H_3O^+][C_7H_5O_3^-]}{[HC_7H_5O_2]}

pKₐ = -\log Kₐ = -\log(6.5 \times 10^{-5}) = 4.19

pH = pKₐ + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{Calculate concentration of base needed to produce pH of 4.30.}

Then what mass of base NaC₇H₅O₂ is needed to produce desired concentration in 100. mL volume?

To prepare 100. mL of buffer at pH 4.30, measure out ______ g NaC₇H₅O₂ and add 0.13M acid HC₇H₅O₂ to total volume of 100. mL.
Blood Buffer System

\[
\text{H}_2\text{CO}_3 \quad \text{conjugate acid} \quad (\text{formed when blood gas CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3)
\]
\[
\text{Na}^+ \text{ HCO}_3^- \quad \text{conjugate base}
\]

If add base:
\[
\text{H}_2\text{CO}_3 + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{Na}^+ \text{ HCO}_3^-
\]
If add acid:
\[
\text{Na}^+ \text{ HCO}_3^- + \text{HCl} \rightarrow \text{H}_2\text{CO}_3 + \text{Na}^+ \text{Cl}^-
\]

Cell Buffer System

\[
\text{H}_2\text{PO}_4^- \quad \text{conjugate acid}
\]
\[
\text{HPO}_4^{2-} \quad \text{conjugate base}
\]

If add base:
\[
\text{H}_2\text{PO}_4^- + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{Na}^+ \text{ HPO}_4^{2-}
\]
If add acid:
\[
\text{HPO}_4^{2-} + \text{HCl} \rightarrow \text{H}_2\text{PO}_4^- + \text{Cl}^-
\]