Using equations, explain how a buffer functions.

Buffers consist of a solution of a weak acid, $\text{HA}$, and its conjugate base, $\text{A}^-$, at high concentrations. They resist changes in pH because any added $\text{H}_3\text{O}^+$ or $\text{OH}^-$ is consumed as follows:

$$\text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \rightarrow \text{HA}(aq)$$

$$\text{HA}(aq) + \text{OH}^-(aq) \rightarrow \text{A}^-(aq) + \text{H}_2\text{O}(l)$$

Thus, as long as the concentrations of $\text{HA}(aq)$ and $\text{A}^-(aq)$ are not consumed, the pH change is minimal compared to addition to a non-buffer solution.

Why is the buffer most effective when pH = p$K_a$?

The pH of a buffer solution is given by the Henderson-Hasselbalch equation:

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

Buffers are most effective when $[\text{acid}] = [\text{base}]$ at which point pH = p$K_a$.

This is because the change in the value of the log function, $\log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$, is smallest when around $\log_{10}(1)$ which occurs when $[\text{base}] = [\text{acid}]$.

Why is it not possible to make a buffer using a strong acid and its conjugate base?

Adding $\text{H}_3\text{O}^+(aq)$ results in a large change in $[\text{H}_3\text{O}^+(aq)]$ as the conjugate base of a strong acid will not react with it to form $\text{HA}(aq)$ – the latter will dissociate completely.

Adding $\text{OH}^-(aq)$ results in reaction with the $\text{H}_3\text{O}^+(aq)$ present from dissociation of the strong acid. A large change in $[\text{H}_3\text{O}^+(aq)]$ results.

In both cases, the large change in $[\text{H}_3\text{O}^+(aq)]$ leads to a large change in the pH.

ANSWER CONTINUES ON THE NEXT PAGE
What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 5.00? The pKₐ of acetic acid is 4.76.

Using the Henderson-Hasselbalch equation:

\[ \text{pH} = \text{pK}_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \]

\[ 5.00 = 4.76 + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \text{ or } \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 0.24 \]

Hence,

\[ \frac{[\text{base}]}{[\text{acid}]} = 10^{0.24} = 1.74 \text{ or } \frac{[\text{acid}]}{[\text{base}]} = 0.58 \]

ANSWER: 0.58
Solution A consists of a 0.15 M aqueous solution of nitrous acid (HNO₂) at 25 °C. Calculate the pH of Solution A. The pKₐ of HNO₂ is 3.15.

Nitrous acid is a weak acid so [H₃O⁺] must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>HNO₂</th>
<th>H₂O</th>
<th>H₃O⁺</th>
<th>NO₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.15</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.15 – x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:

$$K_\text{a} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.15 - x}$$

As $K_\text{a} = 10^{-3.15}$ is very small, $0.15 - x \sim 0.15$ and hence:

$$x^2 = 0.15 \times 10^{-3.15} \quad \text{or} \quad x = 1.03 \times 10^{-2} \text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+(aq)] = -\log_{10}(1.03 \times 10^{-2}) = 1.99$$

PH = 1.99
At 25 °C, 1.00 L of Solution B consists of 13.8 g of sodium nitrite (NaNO\textsubscript{2}) dissolved in water. Calculate the pH of Solution B.

The formula mass of NaNO\textsubscript{2} is (22.99 (Na) + 14.01 (N) + 2 × 16.00 (O)) = 69. Therefore, 13.8 g corresponds to:

\[
\text{number of moles of NaNO}_2 = \frac{\text{mass}}{\text{formula mass}} = \frac{13.8}{69.0} = 0.200 \text{ mol}
\]

As this is dissolved in 1.00 L, the concentration is 0.200 M.

NO\textsubscript{2}\textsuperscript{-} is a weak base so [OH\textsuperscript{-}(aq)] must be calculated from the equilibrium:

\[
\begin{array}{c|cc|cc}
& \text{NO}_2^- & \text{H}_2\text{O} & \leftrightarrow & \text{OH}^- & \text{HNO}_2 \\
\hline
\text{initial} & 0.200 & \text{large} & & 0 & 0 \\
\text{change} & -y & \text{negligible} & +y & +y & \\
\text{final} & 0.200 - y & \text{large} & y & y & \\
\end{array}
\]

The equilibrium constant \(K_b\) is given by:

\[
K_b = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{y^2}{0.2 - y}
\]

For an acid and its conjugate base, \(pK_a + pK_b = 14.00\) so:

\[pK_b = 14.00 - 3.15 = 10.85\]

As \(pK_b = 10.85\), \(K_b = 10^{-10.85}\). \(K_b\) is very small so \(0.200 - y \approx 0.200\) and hence:

\[y^2 = 0.200 \times 10^{-9.24} \quad \text{or} \quad y = 1.68 \times 10^{-6} \text{ M} = [\text{OH}^-(aq)]\]

Hence, the pOH is given by pOH = −log\textsubscript{10}([OH\textsuperscript{-}(aq)]) = −log\textsubscript{10}(1.68 × 10\textsuperscript{-6}) = 5.77

Finally, pH + pOH = 14 so pH = (14.00 − 5.77) = 8.23

\[
\text{pH} = 8.23
\]

ANSWER CONTINUES ON THE NEXT PAGE
Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C. Calculate the pH of the final solution.

Solution A, HNO\textsubscript{2}(aq), is 0.15 M. When 1.00 L of A is added to 1.00 L of B, a 2.00 L solution is formed. This dilution halves the concentration to 0.075 M. Similarly, solution B, KNO\textsubscript{2}(aq), which is initially 0.200 M is diluted to 0.100 M by the addition of solution A.

The combined solution contains a mixture of a weak acid (HNO\textsubscript{2}) and its conjugate base (NO\textsubscript{2}\textsuperscript{-}) so acts as a buffer and the Henderson-Hasselbalch equation can be used:

\[
\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{with} \quad [\text{base}] = [\text{NO}_2^-(aq)] \quad \text{and} \quad [\text{acid}] = [\text{HNO}_2(aq)].
\]

As \( pK_a \) for \( \text{HNO}_2 \) = 3.15, \([\text{NO}_2^-(aq)] = 0.100 \) M and \([\text{HNO}_2(aq)] = 0.075 \) M:

\[
\text{pH} = 3.15 + \log_{10} \left( \frac{0.100}{0.075} \right) = 3.27
\]

If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

\text{acid (HNO}_2)
Describe the difference between a strong and a weak acid.

A strong acid dissociates completely in water:

\[
\text{HA(aq) + H}_2\text{O(l) } \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

As dissociation is complete, the \([\text{H}_3\text{O}^+(aq)]\) is equal to the initial concentration of HA and so the pH is given by:

\[
\text{pH} = -\log(\text{H}_3\text{O}^+(aq)) = -\log([\text{HA(aq)}]_{\text{initial}})
\]

A weak acid does not dissociate 100% in water:

\[
\text{HA(aq) + H}_2\text{O(l) } \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

The position of the equilibrium and hence \([\text{H}_3\text{O}^+(aq)]\) are determined by the acid dissociation constant, \(K_a\):

\[
K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{A}^-(aq)]}{[\text{HA(aq)}]}
\]

Describe in qualitative terms how the percentage ionisation of a weak acid changes when an aqueous solution of the weak acid is diluted.

Dilution increases the percentage dissocation.

Which chemical principle can be used to explain the change in percentage ionisation of a weak acid on dilution and how?

Le Chatelier’s principle can be used to rationalize this effect. Increasing the amount of water shifts the equilibrium to the right.

\[
\text{HA(aq) + H}_2\text{O(l) } \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

Dilution decreases \([\text{H}_3\text{O}^+(aq)]\) and \([\text{A}^-(aq)]\) by an equal amount and decreases \([\text{HA(aq)}]\). As \(K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{A}^-(aq)]}{[\text{HA(aq)}]}\) is a constant, the decrease in \([\text{H}_3\text{O}^+(aq)]\) and \([\text{A}^-(aq)]\) must be smaller than that of \([\text{HA(aq)}]\) and so the percentage dissociation increases.
What is the pH of a 0.010 M solution of \( \text{Ca(OH)}_2 \)?

\( \text{Ca(OH)}_2 \) is a strong base and dissociates completely according to the equation:

\[
\text{Ca(OH)}_2(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})
\]

A 0.010 M solution therefore has \([\text{OH}^{-}(\text{aq})] = 0.020 \text{ M}\) and

\[
\text{pOH} = -\log_{10}([\text{OH}^{-}(\text{aq})]) = -\log_{10}(0.020) = 1.70
\]

As \( \text{pH} + \text{pOH} = 14.00 \), \( \text{pH} = (14.00 - 1.70) = 12.30 \)

\[
\text{pH} = 12.30
\]

What is the pH of a 0.010 M solution of \( \text{HNO}_2 \)? The \( \text{pK}_a \) of \( \text{HNO}_2 \) is 3.15.

Nitrous acid is a weak acid so \([\text{H}_3\text{O}^+]\) must again be calculated:

<table>
<thead>
<tr>
<th></th>
<th>( \text{HNO}_2(\text{aq}) )</th>
<th>( \text{H}_2\text{O(l)} )</th>
<th>( \rightarrow )</th>
<th>( \text{H}_3\text{O}^+(\text{aq}) )</th>
<th>( \text{NO}_2^- ) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
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<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
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<td>negligible</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
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<td>0.010 − x</td>
<td>large</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \( \text{K}_a \) is given by:

\[
\text{K}_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{0.010 − x}
\]

As \( \text{K}_a = 10^{-3.15} \) is very small, \( 0.010 − x \sim 0.010 \) and hence:

\[
x^2 = 0.010 \times 10^{-3.15} \quad \text{or} \quad x = 2.66 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+(\text{aq})]
\]

Hence, the pH is given by:

\[
\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})] = -\log_{10}(2.66 \times 10^{-3}) = 2.58
\]

\[
\text{pH} = 2.58
\]
What is the pH of a solution that is 0.020 M in CH$_3$COOH and 0.010 M in CH$_3$CO$_2$–? The $K_a$ of CH$_3$COOH is $1.8 \times 10^{-5}$ M.

The solution contains a mixture of a weak acid (CH$_3$COOH) and its conjugate base (CH$_3$COO–) so acts as a buffer and the Henderson-Hasselbalch equation can be used:

$$\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

with $[\text{base}] = [\text{CH}_3\text{COO}^-(aq)]$ and $[\text{acid}] = [\text{CH}_3\text{COOH}(aq)]$.

As $K_a = 1.8 \times 10^{-5}$, $pK_a = -\log_{10} K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$.

Hence:

$$\text{pH} = 4.74 + \log_{10} \left( \frac{0.010}{0.020} \right) = 4.44$$

$pH = 4.44$