The Henderson-Hasselbalch approximation allows us one method to approximate the pH of a buffer solution. The basic equation is as follows:

\[
\text{pH} \approx \text{pK}_a + \log_{10} \frac{[A^-]}{[HA]}
\]

We have straightforward calculations for strong acids and bases, but the computations behind buffers are rather complex and time consuming. By using the fact that weak acids and bases barely ionize, allowing us to approximate the pH of buffer solutions using initial concentrations. Though the approximation has a few restrictions, it simplifies a lengthy calculation into a simple equation derived from \(K\).

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878-1942) was a talented biochemist, among many other titles, who spent most of his career at Harvard. He was responsible for developing the components of the equation after studying equilibrium reactions that took place within blood as a result of respiration (specializing in "fatigue"). His equation was incomplete without the solid calculations into it provided by Hasselbalch.

Karl Albert Hasselbalch (1874-1962) was a chemist who studied pH closely. He also studied blood and reactions that took place with oxygen, to put in the simplest of terms. He eventually modified Henderson’s equation by putting mathematical logs into it creating a solid relationship.

**Derivation for Buffers from Weak Acids**

For a weak acid \( HA \) and its conjugate base \( A^- \):

\[(HA + H_2O \rightleftharpoons H^+ + A^-)\]

which has an acid ionization constant \(K_a\). The Henderson-Hasselbalch approximation is derived from this acid ionization constant.

\[
\begin{align}
\text{pH} &= \text{pK}_a + \log_{10} \frac{[A^-]}{[HA]} \\
\text{pK}_a &= -\log_{10} K_a \\
K_a &= \frac{[H^+][A^-]}{[HA]}
\end{align}
\]

Equation \ref{HH1} is formulated in terms of equilibrium concentrations in solution. Since \( HA \) is a weak acid and weakly dissociates and we can introduce two approximations

\[
[HA] \approx [HA]_i
\]

and

\[
[A^-] \approx [A^-]_i
\]

Hence, we can use the initial concentrations rather than equilibrium concentrations because
\[ pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \approx pK_a + \log_{10} \frac{[A^-]}{[HA]} = pH \]

Example \( \PageIndex{1} \): Nitrous acid buffer

Find \( [H^+] \) in a solution of 1.0 M \( HNO_2 \) and 0.225 M \( NaNO_2 \). The \( K_a \) for \( HNO_2 \) is \( 5.6 \times 10^{-4} \) (Table E1).

Solution

\[ pK_a = -\log_{10} K_a = -\log_{10} (7.4 \times 10^{-4}) = 3.14 \]
\[ pH = pK_a + \log_{10} \left( \frac{[NO_2^-]}{[HNO_2]} \right) \]
\[ pH = 3.14 + \log_{10} \left( \frac{1}{0.225} \right) \]
\[ pH = 3.14 + 0.648 = 3.788 \]
\[ [H^+] = 10^{-pH} = 10^{-3.788} = 1.6 \times 10^{-4} \]

Example \( \PageIndex{2} \): Acetic Acid buffer

What ratio \( \frac{[A^-]}{[HA]} \) will create an acetic acid buffer of pH 5.0? \( K_a \) acetic acid is \( 1.75 \times 10^{-5} \) (Table E1).

Solution

\[ pKa = -\log Ka = -\log(1.75 \times 10^{-5}) = 4.74 \]
\[ pH = pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]
\[ 5.0 = 4.74 + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]
\[ 0.26 = \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]
\[ 10^{0.26} = \frac{[A^-]}{[HA]} \]
\[ 1.8 = \frac{[A^-]}{[HA]} \]

Derivation for Buffers from Weak Bases

Similarly, for a weak base \( B \) and its conjugate acid \( HB^+ \):

\[ B + H_2O \rightleftharpoons OH^- + HB^+ \]

which has an base ionization constant \( K_b \). The Henderson-Hasselbalch approximation for basic buffers is derived from this base ionization constant.
\[ \begin{align*}
K_b &= \frac{[OH^-][HB^+]}{[B]} \\
-\log_{10} K_b &= -\log_{10} \frac{[OH^-][HB^+]}{[B]} \\
-\log_{10} K_b &= -\log_{10} [OH^-] - \log_{10} \frac{[HB^+]}{[B]} \\
pK_b &= pOH - \log_{10} \frac{[HB^+]}{[B]} \\
pOH &= pK_b + \log_{10} \frac{[HB^+]}{[B]}
\end{align*} \]

Note that (B) is a weak base and does not dissociate completely and we can say \([B] \approx [B]_i\) and \([HB^+] \approx [HB^+]_i\). Hence, we can use the initial concentrations because

\[ \begin{align*}
pK_b + \log_{10} \frac{[HB^+]_i}{[B]_i} &\approx pK_b + \log_{10} \frac{[HB^+]}{[B]} = pOH
\end{align*} \]

Example (PageIndex[3]): Ammonium Buffer

You prepare a buffer solution of 0.323 M \((NH_3)\) and \((NH_4)_2SO_4\). What molarity of \((NH_4)_2SO_4\) is necessary to have a pH of 8.6? The \(pK_b\) for \(NH_3\) is 4.74 (Table E2).

Solution

\[ \begin{align*}
pK_a + pK_b &= 14 \\
pK_a &= 14 - 4.74 = 9.26
\end{align*} \]

\[ \begin{align*}
pH &= pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \\
8.6 &= 9.26 + \log_{10} \left( \frac{0.323}{[NH_4^+]\right)} \\
-0.66 &= \log_{10} \left( \frac{0.323}{[NH_4^+]}\right) \\
[NH_4^+] &= 1.48 M
\end{align*} \]

Example (PageIndex[4]): Buffering Capability

What is the pH of a buffer 0.500 moles acetic acid and 0.500 moles acetate ion and the total volume is 5 L when you add 0.350 moles HCl? The \(K_a\) for acetic acid is \(1.75 \times 10^{-5}\) (Table E1).

Solution

\[ \begin{align*}
pK_a &= -\log_{10} \left( \frac{[A^-]}{[HA]} \right) = 4.756
\end{align*} \]

\[ \begin{align*}
pH &= pK_a + \log_{10} \left( \frac{\text{acetate}}{\text{acetic acid} + [HCl]} \right) \\
pH &= 4.756 + \log_{10} (0.588) \\
pH &= 4.756 - 0.230 = 4.52
\end{align*} \]

Example (PageIndex[5]): Effective Buffer Range

What is the range of an acetic acid buffer described in problem (PageIndex[4]) without the added \(\text{HCl}\)?
Solution

The effective buffer range is of magnitude 2 pH units with the $pK_a$ as the midpoint.

\[
pK_a = -\log_{10} K_a = -\log_{10} (1.75 \times 10^{-5}) = 4.756
\]

Hence, the buffer range would be 3.75 to 5.75.

Assumptions in the Henderson-Hasselbach Approximation

- $-1 < \log_{10} \left( \frac{[A^-]}{[HA]} \right) < 1$
- The molarity of the buffer(s) should be 100x that of the acid ionization constant, or $K_a$.
- This equation will give poor or inaccurate results if there are strong acids or bases. $pK_a$ values between 5 and 9 will give good approximations, but when we are out of this range there is a strong chance that the pH value will be incorrect.\(^J\) In other words near the end or the beginning of a titration where the "relative concentrations of the acid or base differ substantially[,]... approximate calculations break down."\(^J\)

References


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