4. Weak, monoprotic acid + salt of the weak acid

- buffer solution: resists change in pH when small amounts of acid or base are added

It’s easy (relatively) to transform the $K_a$ expression to relate pH to the ratio of $A^-$ to $HA$:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$log K_a = log[H_3O^+] + log\frac{[A^-]}{[HA]}$$

$$K_a = [H_3O^+]\frac{[A^-]}{[HA]}$$

$$log K_a = log\left(\frac{[H_3O^+][A^-]}{[HA]}\right)$$

$$pK_a = pH - log\frac{[A^-]}{[HA]}$$

$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

---

$Henderson-Hasselbach\ Equation$

Add $OH^-$ to a buffer: some $H_3O^+$ reacts to consume it.

$[A^-] \uparrow$; $[HA] \downarrow$; $\frac{[A^-]}{[HA]}$ increases; pH increases slightly

Add $H_3O^+$ to a buffer: some $A^-$ reacts to consume it.

$[A^-] \downarrow$; $[HA] \uparrow$; $\frac{[A^-]}{[HA]}$ decreases; pH decreases slightly

Relative amounts of $HA$ and $A^-$ are important!!! Large amounts of $HA$ and $A^-$ will keep relative changes small when small amounts of acid or base are added.

buffer capacity: measure of the ability of a buffer to resist pH change—the amount of acid/base a buffer can “absorb” without “significant” change in pH—usually defined as ± 1 pH unit, “buffer range”

Optimal buffering occurs when $[A^-] = [HA]$.

- When $[A^-] = [HA]$, solution will buffer equally well against addition of acid or base.
- If not equal, the buffer will be better against either acid or base than the other.

$$pH = pK_a + log\frac{[A^-]}{[HA]},\ so\ if\ [A^-] = [HA], then \ pH = pK_a.$$ e.g., if you want a pH 4 buffer with $[A^-] = [HA]$, you need to find an acid with $pK_a = 4$, i.e., $K_a = 10^{-4}$.

A Buffer Prepared with a Base and its Conjugate Acid

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$pOH = pK_b + log\frac{[BH^+]}{[B]}$$

e.g., if you want a pH 10 buffer with $[BH^+] = [B]$, you need to find a base with $pK_b = 4$, i.e., $K_b = 10^{-4}$.

---

¡¡¡CAUTION!!!

It is NOT necessarily true that a “basic buffer” (a buffer solution with pH > 7) must be made with a weak base and its conjugate acid. For example, if you used equal concentrations of $HA$ and $A^-$ where $HA$ had $K_a = 1.0 \times 10^{-8}$, then the pH of that buffer would be 8.00.
Calculate the pH of a buffer prepared by mixing 0.21 mol HCOOH and 0.33 mol HCOONa in 2.0 L solution.

\[
\text{pH} = 3.74 + \log \frac{0.33}{0.21}
\]

\[
\text{pH} = 3.94
\]

\[
\begin{align*}
\text{pK}_a &= \log \frac{[A^-]}{[HA]} \\
\text{HC}O\text{OH} &\quad \text{formic acid} \\
\text{K}_a &= 1.8 \times 10^{-4} \\
\text{pK}_a &= 3.74 \\
* \frac{[A^-]}{[HA]} &= \frac{0.33\text{mol}}{2.0\text{L}} = \frac{0.21\text{mol}}{2.0\text{L}}
\end{align*}
\]

Strong acid/strong base titration:

\[
\text{pH} @ \text{eq. pt.} = 7.00
\]

\[
\text{HA} + \text{MOH} \rightarrow \text{MA} + \text{H}_2\text{O}
\]

\[
\begin{align*}
\text{e.g. HCl} &\quad \text{e.g. NaOH} &\quad \text{e.g. NaCl}
\end{align*}
\]

Weak base

\[
\begin{align*}
\text{e.g., NH}_3 \text{ with HCl}
\end{align*}
\]

\[
\begin{align*}
\text{pH} &\rightarrow \frac{1}{2} \text{eq. pt.} \rightarrow \text{at half titration, pH = pK}_a \text{ of NH}_4^+ \\
\text{(pOH} = \text{pK}_b \text{ of NH}_3^+)
\end{align*}
\]
**Titration Curves**
- **end point**: where the indicator changes color in a titration
- **equivalence point**: where exactly enough base (acid) has been added to react with the acid (base) originally present in a titration.

Ideally, the end point and equivalence point are reached at the same time in your titration.

**Weak Acid/Strong Base titration**

\[
\begin{align*}
\text{HA(aq) + H}_2\text{O(l)} & \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \\
\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) & \rightarrow \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \\
\text{HA(aq) + OH}^-(aq) & \rightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)
\end{align*}
\]

- **pH at equivalence point > 7.0**
  At equivalence point, solution contains water, the cation of the strong base, and the anion of the weak acid (its conjugate base). The anion of a weak acid is basic, so the pH at the equivalence point is > 7.

- **buffer region**
- **Half-equivalence point**
  at “half-titration” (i.e., \(V_{\text{BASE}} = \frac{1}{2}V_{\text{EP}}\)), half of the original acid has been converted to its conjugate base (i.e., \([\text{A}^-] = \frac{1}{2}[\text{HA}]_o\)). Thus \([\text{A}^-] = [\text{HA}]\) here, so at this point, \(\text{pH} = \text{pK}_a\) of the weak acid.

\[
\text{pH} = \text{pK}_a + \log \frac{\frac{1}{2}[\text{HA}]_o}{\frac{1}{2}[\text{HA}]_o}
\]

\[
\text{pK}_a = 4.89 \quad \text{K}_a = 10^{-4.89} = 1.3 \times 10^{-5}
\]

**Lewis Acid-Base Model**

**Big Question #3 Alert!**

- **Lewis acid**: a substance that accepts a pair of electrons.
- **Lewis base**: a substance that donates a pair of electrons.

All Arrhenius/Brønsted acids are Lewis acids (ditto for bases) (but not the other way around)

![Lewis Acid-Base Model](image)
Lewis acids: \(e^-\) deficient species (e.g. BF\(_3\))

\(\pi\)-bonded central atoms w/polar bonds (e.g. CO\(_2\))

highly-charged metal ions (e.g. Al\(^{3+}\))

\(\text{pH at equivalence point of } HPr \text{ titration above}
\]

0.00400 mol \(Pr^-\) in total of 80.00 mL solution at eq. pt.

\[\frac{0.00400 \text{ mol}}{0.0800 \text{ L}} = 0.050 \text{ M } Pr^-\]

0.050 M \(NaPr\)

\(\text{Ka} (HPr) = 1.3 \times 10^{-5}\)

\(\text{pH} = ?\)

Solved in usual table format

\[Pr^- + H_2O \rightleftharpoons HPr^- + OH^-\]

\[K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}\]

\[K_b = \frac{x^2}{0.05 - x} \approx \frac{x^2}{0.050} = 7.7 \times 10^{-10}\]

\[x = \sqrt{7.7 \times 10^{-10} (0.050)} = 6.2 \times 10^{-6} = [OH^-]\]

\[\text{pOH} = 5.20 \Rightarrow \text{from } 14\]

\[\text{pH} = 8.80\]