Choosing buffers based on $pK_a$

In many experiments, we need a buffer that maintains the solution at a specific pH.

We may need an acidic or a basic buffer, depending on the experiment.

The Henderson-Hasselbalch equation can help us choose a buffer that has the pH we want.

$$\text{pH} = pK_a + \log([\text{conj. base}]/[\text{conj. acid}])$$

With equal amounts of conjugate acid and base (preferred so buffers can resist base and acid equally), then …

$$\text{pH} = pK_a + \log(1) = pK_a + 0 = pK_a$$

So choose conjugates with a $pK_a$ closest to our target pH.
Example: You need a buffer with pH of 7.80. Which conjugate acid-base pair should you use, and what is the molar ratio of its components?
Practice: Choose the best conjugate acid-base pair for preparing a buffer with pH 5.00. What is the molar ratio of the buffer components?
buffer capacity: the amount of strong acid or strong base that can be added to a buffer without changing its pH by more than 1 unit; essentially the number of moles of strong acid or strong base that uses up all of the buffer’s conjugate base or conjugate acid.

Example: What is the capacity of the buffer solution prepared with 0.15 mol lactic acid CH₃CHOHCOOH (HA, Kₐ = 1.0 x 10⁻⁴) and 0.20 mol sodium lactate NaCH₃CHOHCOO (NaA) and enough water to make 1.00 L of solution? (from previous lecture notes)
Review of equivalence point

equivalence point: moles of $H^+$ = moles of $OH^-$
(moles of acid = moles of base, only when the acid has only one acidic proton and the base has only one hydroxide ion).

What is the pH at the equivalence point* for a strong acid-strong base titration?

\[
\text{HNO}_3 + \text{KOH} \rightarrow \text{H}_2\text{O(l)} + \text{KNO}_3(\text{aq})
\]

I 0.100 moles each
*(sample $H^+ = OH^-$ in titrant)

End

No products are acidic or basic enough to affect the pH of the solution, so the pH is 7 at the equivalence point. Fig. 16.5, p. 589.

Note that $\text{KNO}_3(\text{aq}) = \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$.

$\text{K}^+ + \text{H}_2\text{O(l)}$

$\text{NO}_3^- + \text{H}_2\text{O(l)}$
What is the pH at the equivalence point* for a weak acid-strong base titration?
(Note: CH$_3$COOH = HA, and CH$_3$COO$^-$ = A$^-$.)

\[
\text{HA} + \text{NaOH} \rightarrow \text{H}_2\text{O}(l) + \text{NaA}(aq)
\]

I 0.100 moles each

*(sample H$^+$ = OH$^-$ in titrant)

End

Note: NaCH$_3$COO(aq) = Na$^+(aq) + $CH$_3$COO$^-(aq)$

\[
\text{Na}^+ + \text{H}_2\text{O}(l)
\]

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

I

C

Eq

Equilibrium process (Chapter 15 calculations) results in pH > 7 (basic). Fig. 16.6, p. 59.
What is the pH at the equivalence point* for a weak base-strong acid titration?

\[
\text{NH}_3 + \text{HCl} \quad \text{H}_2\text{O(l)} + \text{NH}_4\text{Cl(aq)}
\]

I 0.100 moles each
*(sample OH\(^-\) = \text{H}^+ \text{ in titrant)*

C

End

Note: \(\text{NH}_4\text{Cl(aq)} = \text{NH}_4^+(aq) + \text{Cl}^-(aq)\)

\[
\text{Cl}^- + \text{H}_2\text{O(l)}
\]

\[
\text{NH}_4^+ + \text{H}_2\text{O(l)} \quad \text{NH}_3 + \text{H}_3\text{O}^+
\]

I

C

Eq

Equilibrium process (Chapter 15 calculations) results in pH < 7 (acidic). Fig. 16.7, p. 593.
**pH before equivalence point**

Before the equivalence point in a titration, the stoichiometric reaction neutralizes only a portion of the sample.

**Example: Strong acid – strong base titration**

\[
\begin{align*}
\text{HNO}_3 & + \text{KOH} & \text{H}_2\text{O(l)} & + \text{KNO}_3(\text{aq}) \\
\text{I} & \quad 0.100 & 0.020 \\
\end{align*}
\]

C

End

Calculate remaining (unreacted) \( \text{HNO}_3 \Rightarrow \text{H}_3\text{O}^+ \). (Chapter 4 and 5 calculations = stoichiometric)

\[
M = \frac{\text{mol}}{\text{L}} \quad \text{Volume? HNO}_3? \text{ KOH?}
\]

\[
\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{(Chapter 15 calculation)}
\]
Example: Weak acid - strong base titration

\[
\begin{align*}
\text{HA} & + \text{OH}^- & \text{H}_2\text{O(l)} & + \text{A}^- \\
\text{I} & & 0.100 & 0.010 \\
\end{align*}
\]

End

The strong base is converting the weak acid into a weak base (its conjugate base). The sample and titrant are essentially creating a buffer solution that contains unreacted weak acid (HA) and newly formed conjugate base (A\textsuperscript{-}). See buffer region, Fig. 16.6, p. 591.

To find the pH, do the equilibrium calculation with some initial amount of conjugate base:

\[
\begin{align*}
\text{CH}_3\text{COOH} & + \text{H}_2\text{O(l)} & \text{CH}_3\text{COO}^- & + \text{H}_3\text{O}^+ \\
\text{I} & & & \\
\end{align*}
\]
Example: 50.0 mL of 0.100 M acetic acid is titrated with 0.100 M NaOH solution. Calculate the pH after 25.0 mL of titrant has been added.
The half-equivalence point is a special case prior to reaching the equivalence point.

At the half-equivalence point, the strong base has converted half of the weak acid into its conjugate base. We now have a buffer solution that contains equal amounts of conjugate acid and base.

\[ \text{pH} = \text{pK}_a + \log([\text{conj. base}]/[\text{conj. acid}]) \]

\[ \text{pH} = \text{pK}_a \]

Again, the H-H equation is useful when dealing with buffer calculations.

Titrations for weak base-strong acid work similarly, except the strong acid converts the weak base into its conjugate acid.

Next time: pH after equivalence point.