Pre-Health Post-Baccalaureate Program Study Guide and Practice Problems

Course: CHM2046

Textbook Chapter: 19.1-19.2
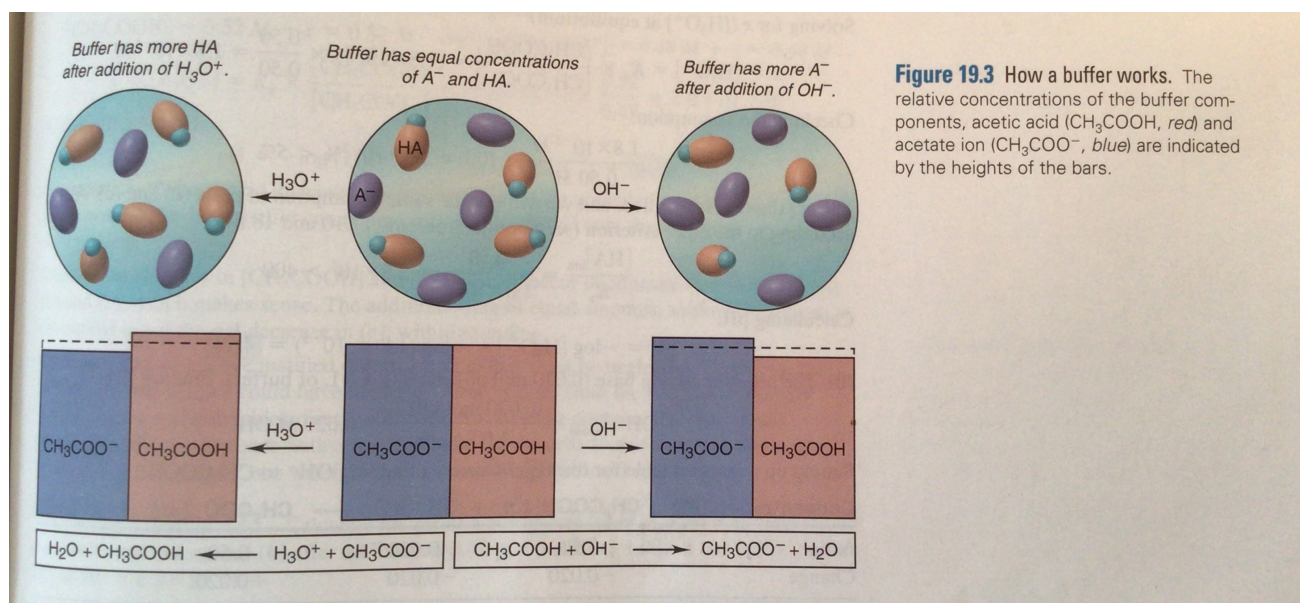
Topics Covered: Titrations and Buffers

Created by Isaac Loy

1. What is a buffer and how does it work?

If we add even a small amount of strong acid or base to a neutral solution, we will see huge and immediate jumps in overall solution pH. As your textbook says, an acid-base buffer, "lessens the impact on pH from the addition of acid or base."

In order for our buffer solution to lessen the impact of either acid or base that is added, the buffer must contain an acid and a base. The acid and base in the buffer cannot neutralize each other, or the solution could not function as a buffer, so conjugate acid-base pairs (such as acetic acid and sodium acetate) are used to create buffers solutions.

If our buffer contains equal concentrations of acid and conjugate base, then the addition of an "outside" acid to our beaker will cause a proton transfer from the "outside" acid to the conjugate base from our buffer solution, creating more of the acid that was found in the buffer solution. See the image below, from the textbook, for a visual:

Buffer has more HA after addition of H_3O^+.

Buffer has equal concentrations of A^- and HA.

Buffer has more A^- after addition of OH^-.

Figure 19.3 How a buffer works. The relative concentrations of the buffer components, acetic acid (CH_3COOH, *red*) and acetate ion (CH_3COO^-, *blue*) are indicated by the heights of the bars.

H_3O^+ A^- OH^-

CH_3COO^- | CH_3COOH CH_3COO^- | CH_3COOH CH_3COO^- | CH_3COOH

H_3O^+ OH^-

$H_2O + CH_3COOH \longleftarrow H_3O^+ + CH_3COO^-$ $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$

As you can see in the image, we can create reaction equations which show the reactions happening between the buffer acid and base, and the added aqueous acid or base. If working with an added aqueous strong acid or base, we can represent the acid as just H_3O^+ and the base as HO^-.

If strong acid is added to a buffer solution:

initial   final
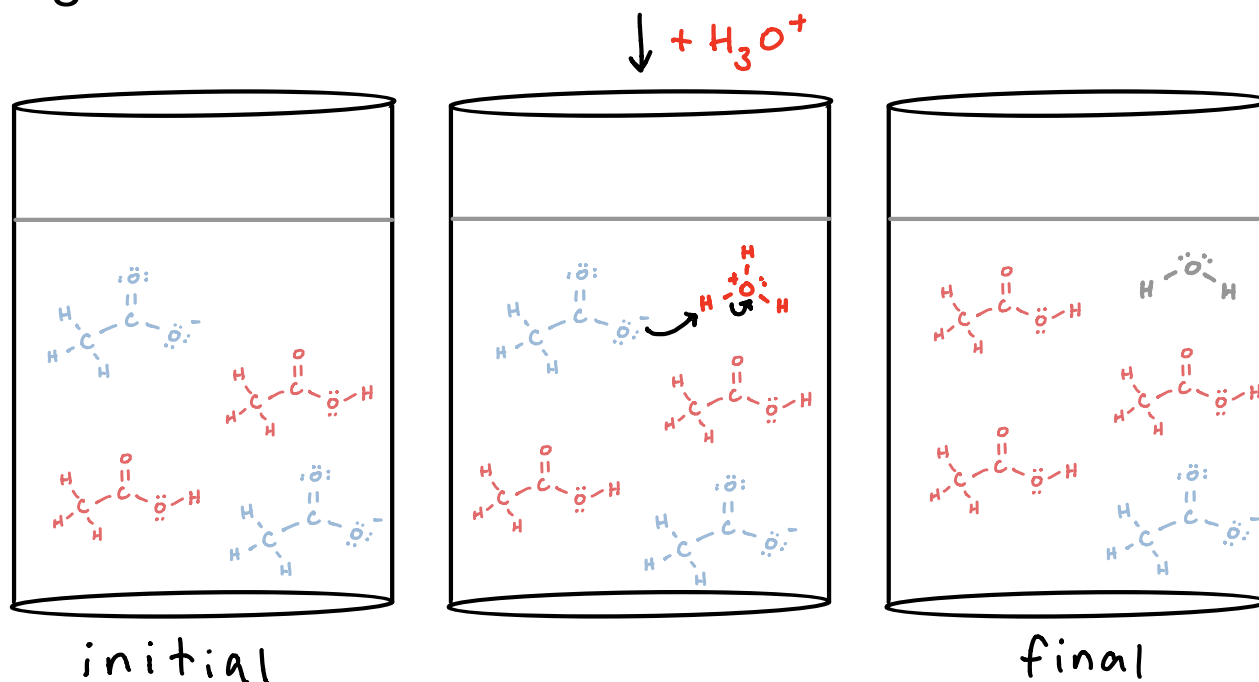
If strong base is added to a buffer solution:

initial   final
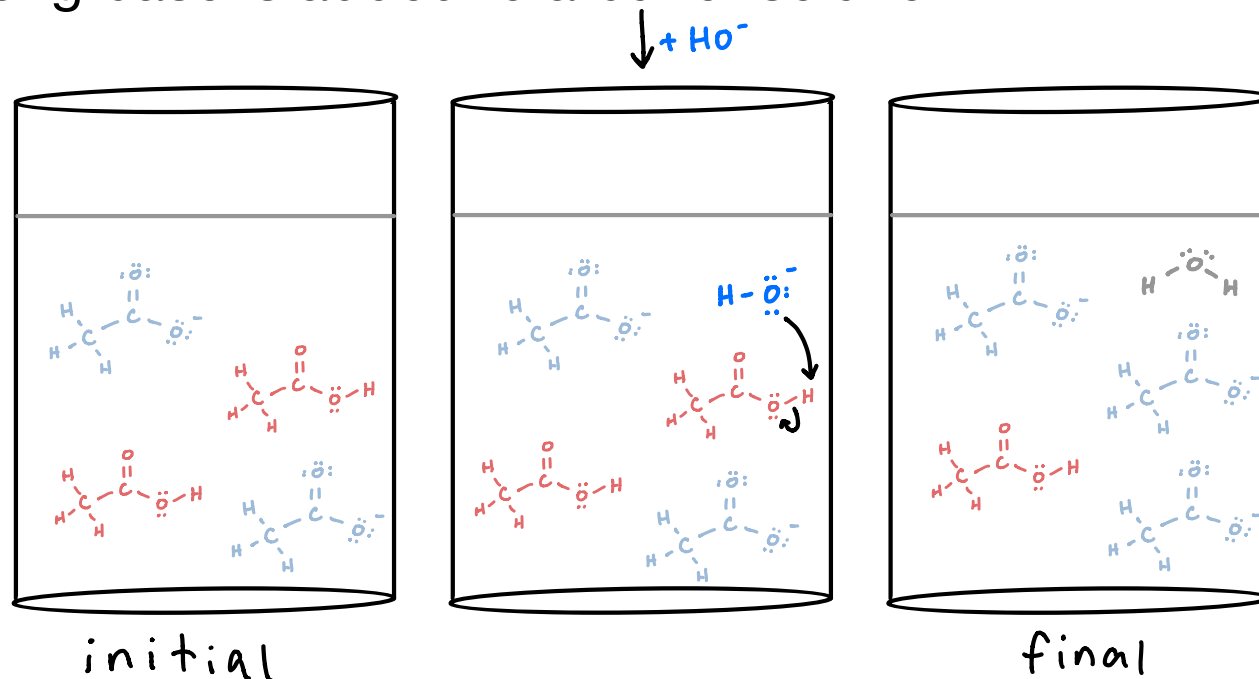
If we know the concentrations of the ions involved in the A-B reaction, then we can determine the [hydronium] using the K_a equation:

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

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

K is a constant, meaning we can predict changes to the [hydronium] just by looking at changes to the [buffer acid] and the [buffer conjugate base]. We can build off of this and previous chemistry knowledge to derive the Henderson-Hasselbalch Equation, which allows us to solve directly for pH rather than first determining [hydronium].

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

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

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

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

2. Buffer Capacity and Range

Think of buffer capacity as its ability to "stand its ground" in the presence of an added strong acid or base. A buffer has a high capacity if the acid and conjugate base that make it up each exist in high concentrations that are close to one another.

The buffer range gives us the pH range over which the buffer can work. Buffer range is also determined by how close the concentrations of acid and conjugate base are in the buffer. Buffers work within 1 pH unit (+/-) of the pKa of the acidic component.

3. Titrations

In the lab, we use bright indicators that, as an acid, have a different color from their conjugate base. A change in color queues us into the reality of a chemical change.

Titrations are usually displayed on a graph, which displays pH level on the Y-axis and the volume of titrant added on the X-axis.

The equivalence point is the position on our curve where the number of moles of acid equals the number of moles of base.

We can determine the concentration of an unknown acid titrand, for example, by noting the volume of acid that we start with and the molarity and volume of basic titrant used to reach the equivalence point. This will tell us how many moles of base were required, which also equals the number of moles of acid present in the original mixture. Using the number of moles present and the original volume, concentration can be determined.

Watch the video below for a lab demonstration of an A-B titration:

https://youtu.be/HVjvFydMOc8

Strong acid-strong base titration:

pH starts very low, increases slowly until around pH 6, increases very quickly from pH 6-8, and then flattens off and increases slowly. Equivalence point is at pH 7.
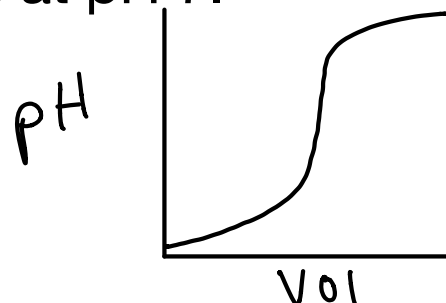
Weak acid-strong base titration:

pH starts moderately low, increases slowly until around pH 6, increases very quickly from pH 6-12, and then flattens off and increases slowly. Equivalence point is slightly basic.
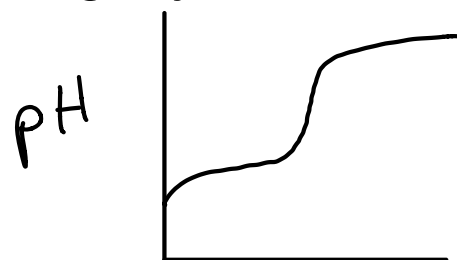
Weak base-strong acid titration:

pH starts moderately high, decreases slowly until around pH 8, decreases very quickly from pH 8-2, and then flattens off and decreases slowly. Equivalence point is slightly basic.
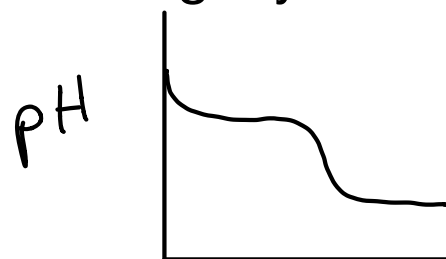
Polyprotic acid titration:

As its name suggests, Polyprotic acids have multiple acidic protons. Because of this, these curves are more complex, with multiple equivalence points.
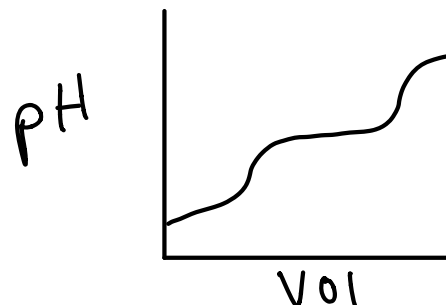
Problems:

1a. Calculate the pH of a buffer solution consisting of 0.50M CH_3COOH and 0.50M CH_3COONa. K_a CH_3COOH $= 1.8 \times 10^{-5}$

1b. Calculate the pH after adding 0.020 mol of solid NaOH to 1L of buffer solution from problem #1.

1a. Calculate the pH of a buffer solution consisting of 0.50M CH_3COOH and 0.50M CH_3COONa.

ICE table

$$[H_3O^+] = x = K_a \frac{[CH_3COOH]_{eq}}{[CH_3COO^-]_{eq}} \approx 1.8\times10^{-5}\left(\frac{0.5}{0.5}\right)$$

$$pH = -\log[H_3O^+] = -\log(1.8\times10^{-5}) = 4.74$$

H-H eqn.

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

$$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = 4.74 + 0 = 4.74$$

1b. Calculate the pH after adding 0.020 mol of solid NaOH to 1L of buffer solution from part a.

	CH_3COOH +	HO^- ⇌	CH_3COO^- +	H_2O
I	0.5	0.02	0.5	—
C	−0.02	−0.02	+0.02	—
E	0.48	0	0.52	—

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = -\log K_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{0.52}{0.48}\right)$$

$$pH = 4.74 + 0.03 = 4.77$$

Circle I: HA, A, A, A, HA, A, HA, A, HA

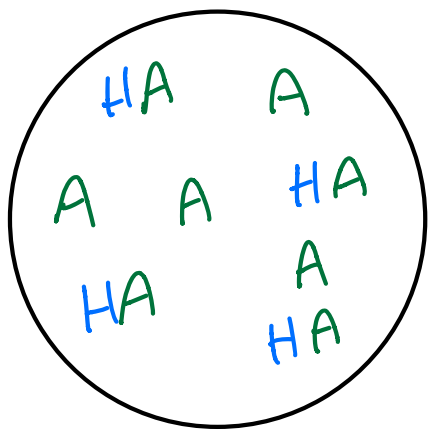Circle II: HA, HA, HA, HA, A
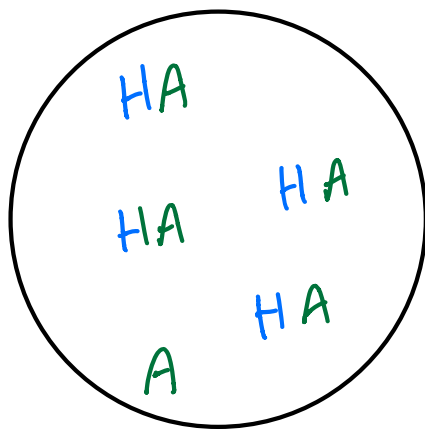
Circle III: HA, A, A, A, HA, A
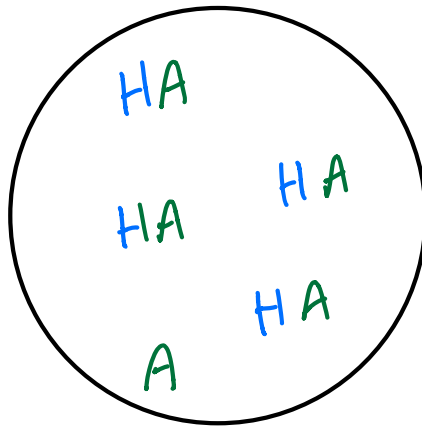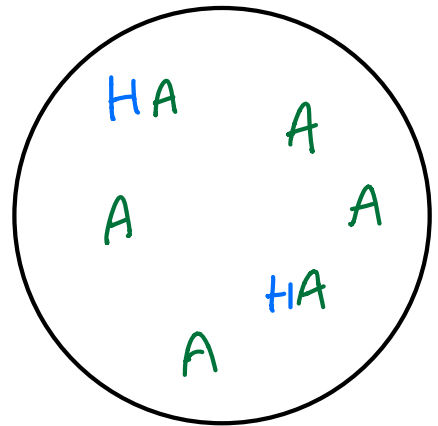
2a. Which of the above buffers has the highest pH?
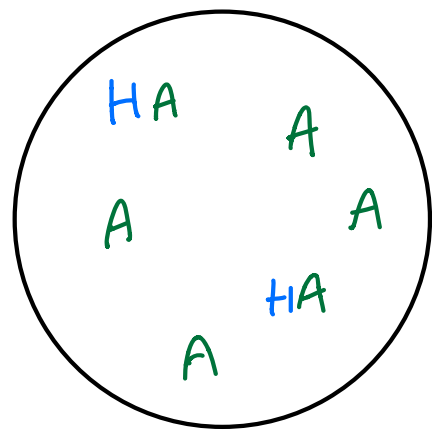
2b. Which of the above buffers has the greatest capacity?

I   II   III

2a. Which of the above buffers has the highest pH?

III

2b. Which of the above buffers has the greatest capacity?

I

3. Calculate the pH during the titration of 40.00mL of 0.1000M propanoic acid after the addition of 30.00mL of 0.1000M sodium hydroxide. $K_{a \; HPr} = 1.3 \times 10^{-5}$

3. Calculate the pH during the titration of 40.00mL of 0.1000M propanoic acid after the addition of 30.00mL of 0.1000M sodium hydroxide.

mols	HP_r +	HO^- ⇌	Pr^- +	H_2O
I	$(.04L \times 0.1m)$ = .004 mol	$(.03L \times 0.1m)$ = .003 mol	0	—
C	– .003	–.003	+.003	—
E	.001	0	.003	—

$$pH = pk_a + log\left(\frac{[Pr^-]}{[HPr]}\right)$$

$$pH = -log(1.3 \times 10^{-5}) + log(3)$$

$$pH = 4.89 + 0.48 = 5.37$$