

## Buffers: Applications in Chemical Equilibrium

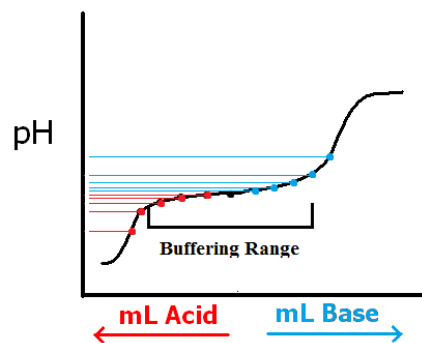
Minneapolis Community and Technical College

C1152: Principles of Chemistry 2

v.2.16

### I. Introduction

A buffer is a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid. The buffer's function is to neutralize additional acids ( $\text{H}_3\text{O}^+$  ions) or bases ( $\text{OH}^-$  ions) thus keeping the pH of the solution approximately constant. In many chemical and biological systems buffers are important. Blood plasma, a natural example in humans, is a bicarbonate buffer that keeps the pH of blood between 7.2 and 7.6. pH's outside of this range are fatal.



Of course, no buffer is perfect and slight changes in pH will be observed as the buffer operates within its buffering range (figure above). As an acid is added to the buffering system, the buffer's own base is consumed and the pH drops slightly. Similarly, when strong base is added to the buffer, the buffer's own acid is consumed and the pH rises slightly. Eventually, either the buffer's acid or base component is used up and the pH changes dramatically. At this point the buffer is no longer operating within its "buffering range" and we say the buffer is exhausted.

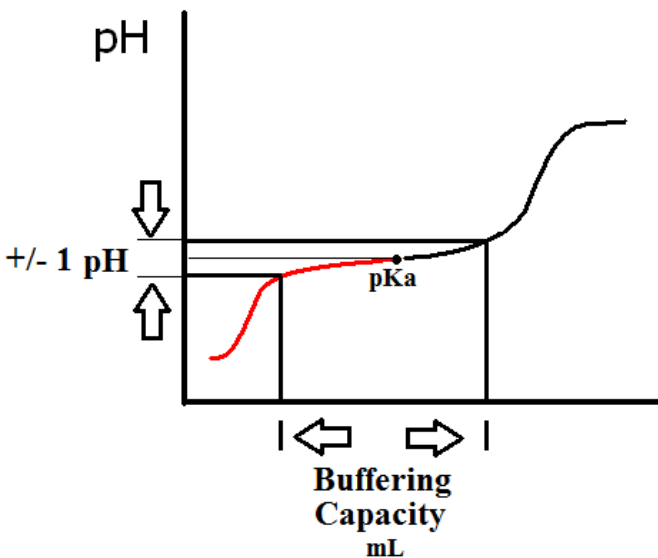
A buffer will have greater capacity if the concentrations of the conjugate acid and base are high. This is because there are more moles of buffer present to react with additional strong acid or base. The buffer capacity is also greatest when the concentrations of the conjugate acid and base are equal. In this case  $\text{pH}_{\text{buffer}} = \text{pK}_a$  and the buffer is positioned in the middle of its buffering range.

A buffer's operating range is said to be  $\pm 1$  pH unit on either side of the  $\text{pK}_a$  point. These limits define what's known as the Buffering Capacity.

The Buffering Capacity (figure at right) is loosely defined to be the total volume (mL) of acid ( $\text{H}^+$ ) and base ( $\text{OH}^-$ ) required to completely exhaust the buffer.

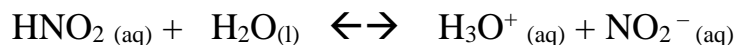
Determining the Buffering Capacity involves several steps:

1. Identify the point in the EXACT CENTER of the buffering range.
2. Determine the pH corresponding to the midpoint. This is the  $\text{pK}_a$  value.
3. Add/subtract "1" from this value to determine the buffer's pH limits
4. Draw horizontal lines corresponding to the  $\pm 1$  buffer limits.
5. Mark where the horizontal lines intersect the titration curve.
6. Draw vertical lines downward from these both points and determine their positions on the "x" axis.
7. Determine the buffer's capacity by calculating the total volume (mL) between the vertical lines.



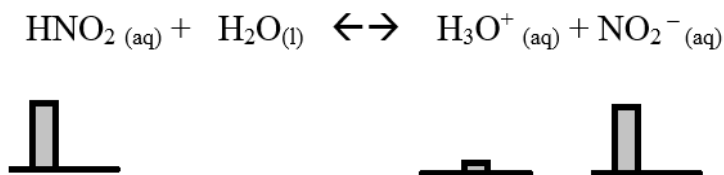
### Buffering Action

A buffer is an equilibrium system. Consider the weak acid (nitrous acid,  $\text{HNO}_2$ ) equilibrium below:

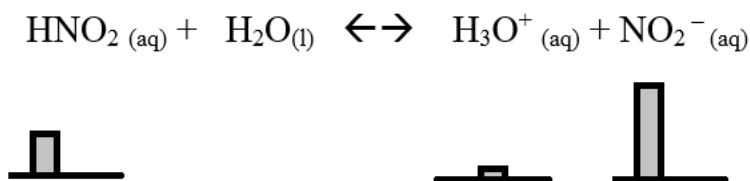


For the forward reaction,  $\text{HNO}_2$  is acting as a Lowry Bronsted acid (proton donor) and the  $\text{H}_2\text{O}$  molecule acts as the base (proton receiver). For the reverse reaction the  $\text{H}_3\text{O}^+$  ion acts as an acid and the  $\text{NO}_2^-$  acts as the base. To be a buffering system, the equilibrium must possess significant concentrations of both the weak acid ( $\text{HNO}_2$ ) and the conjugate base ( $\text{NO}_2^-$ ).

In the figure below, bar graphs are used to indicate the significant, non-zero equilibrium concentrations of weak acid and conjugate base. A much smaller equilibrium concentration of  $\text{H}_3\text{O}^+$  is what determines the pH of the buffer. As both buffer components are equal in concentration (same bar heights), the pH of the buffer equals the  $\text{pK}_a$ . For  $\text{HNO}_2$ , the  $\text{pK}_a = 4.60 \times 10^{-4}$ . Thus the pH of the buffer under these circumstances =  $-\log K_a = -\log (4.60 \times 10^{-4}) = 3.400$ .

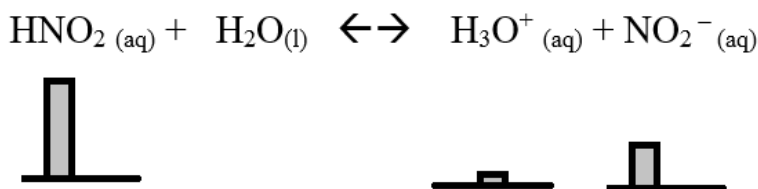


Now, consider the addition of a strong base (e.g.  $\text{NaOH}$ ) to the buffering system. The additional  $\text{OH}^-$  ions are immediately neutralized by the buffer's supply of  $\text{H}_3\text{O}^+$  hydronium ions to produce water. This decreases in  $\text{H}_3\text{O}^+$  concentration and causes the buffer to shift right. In doing so, the buffer's supply of weak acid ( $\text{HNO}_2$ ) decreases whilst the concentration of conjugate base ( $\text{NO}_2^-$ ) increases with this result:



The equilibrium's shift right replaces lost  $\text{H}_3\text{O}^+$  ions and keeps their concentration approximately constant. Since  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ , it too is kept approximately constant. However, in reality the  $[\text{H}_3\text{O}^+]$  does decrease a little bit as the buffering action isn't perfect. Thus the pH increases *slightly* until all weak acid is used up and the buffer is exhausted. At this point, the pH increases dramatically.

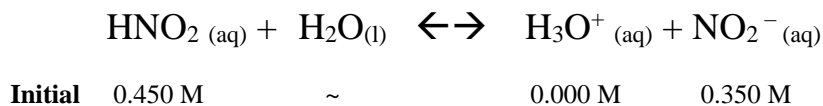
When adding a strong acid to a buffering system, all of the above arguments are reversed. The addition of a strong acid increases the  $\text{H}_3\text{O}^+$  concentration causing the buffer to shift left to bring those levels back down. Doing so, the buffer consumes the conjugate base ( $\text{NO}_2^-$ ) and produces more  $\text{HNO}_2$  (see figure below). This action continues until the supply of  $\text{NO}_2^-$  is gone at which point the buffer is exhausted.



## Buffers: Determining Initial pH

There are two ways to determine the initial pH of a buffering system: Conventional I.C.E. and the Henderson Hasselbalch equation.

To demonstrate both approaches, let's consider the following buffering system and initial concentrations.

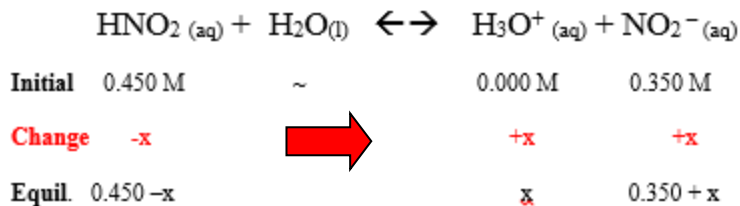


The initial concentrations are the result of dilution calculations using original bottle labels and volumes of both the weak acid and conjugate base solutions.

## pH Determination: I.C.E. Method

The figure at right demonstrates the I.C.E. problem solving approach for the buffering system above.

We assume no  $\text{H}_3\text{O}^+$  ions initially and this requires the equilibrium shift right to produce them. The “Change” reflects exactly that; weak acid is used up (-x) and both  $\text{H}_3\text{O}^+$  and  $\text{NO}_2^-$  are produced (+x) in a 1:1:1 mole ratio. The equilibrium levels are determined by applying the changes to the initial concentrations.



The Law of Mass Action for this reaction is written as.....

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

Substituting the equilibrium concentrations into the Law of Mass Action ...

$$K_a = \frac{x(0.350 + x)}{(0.450 - x)} = 4.60 \times 10^{-4}$$

Using the  $x \sim 0$  \* assumption simplifies the algebra .....  
*Verify that  $x \sim 0$  is valid via the 5% rule.*

$$K_a = \frac{x(0.350)}{(0.450)} = 4.60 \times 10^{-4}$$

Solving for “x” and the hydronium concentration .....

$$x = [\text{H}_3\text{O}^+] = 5.914 \times 10^{-4} \text{ M}$$

Finally, the **pH** can be determined as 3.228.....

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log (5.914 \times 10^{-4} \text{ M}) = 3.23$$

## Henderson Hasselbalch Equation

The Henderson Hasselbalch (H.H.) equation at right can also be used to determine the pH of a buffering system. It relies on the  $x \sim 0$  assumption and so should only be used when it's known that “x” is very small. After using the H.H. equation, check the result with the 5% rule to be sure that the  $x \sim 0$  assumption is valid.

Henderson Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

We can use the H.H. equation to determine the pH of the buffering system above by substituting known values for  $\text{p}K_a$  and the concentrations of weak acid and its conjugate base. Since  $K_a = 4.60 \times 10^{-4}$  for  $\text{HNO}_2$ , we determine  $\text{p}K_a$  as follows:

$$\text{p}K_a = -\log K_a = -\log (4.60 \times 10^{-4}) = 3.33724$$

Substituting this value for  $\text{p}K_a$  and the known concentrations of  $\text{HNO}_2$  and  $\text{NO}_2^-$  we have the following:

$$\text{pH} = 3.33724 + \log \frac{0.350}{0.450} = 3.22_{809} = 3.23$$

which is in agreement with the result determined via the I.C.E. method above. You should practice doing the above calculation with your calculator to be sure you are performing log calculations correctly.

**II. PRE-LAB EXERCISE** *Clearly answer these questions in INK in your lab notebook before coming to lab.*

1. Consider the following four buffers made from the weak acid HA and its conjugate base NaA. ( $K_a = 3.84 \times 10^{-9}$ )

	[HA]	[A <sup>-</sup> ]	pH
A.	0.25 M	0.75 M	
B.	0.50 M	0.50 M	
C.	0.75 M	0.25 M	
D.	0.025 M	0.075 M	

- Use the Henderson-Hasselbalch equation to determine pH of each buffer
  - Recall which buffer components are consumed when strong acids and bases are added to buffering systems. Which of the buffers above is best prepared to maintain constant pH when a strong acid is added?
  - Why is buffer "B" equally able to defend against strong acid OR strong base additions?
  - The starting pH's of buffers A and D are the same. Which buffer has greater capacity and why?
2. In this experiment, you'll be constructing a NaCH<sub>3</sub>COO/CH<sub>3</sub>COOH buffer with a specific pH. To do this, you'll add a mass of solid NaCH<sub>3</sub>COO (g) to 100mL of 0.100 M acetic acid (CH<sub>3</sub>COOH) to achieve an assigned target pH.

Determining the necessary mass of NaCH<sub>3</sub>COO in grams requires a mathematical rearrangement of the H.H. equation.

Mathematically rearrange the H.H. equation and solve for the base/acid ratio.

$$\frac{[\text{base}]}{[\text{acid}]} = ?$$

3. Use the Henderson-Hasselbalch equation you derived above to calculate the concentration, moles and mass of NaCH<sub>3</sub>COO required to construct two buffers with target pH's of 4.90 and 3.80.

Assume you're starting with 100mL of 0.100 M acetic acid (CH<sub>3</sub>COOH) and use 82.0339 g/mol as the molar mass of NaCH<sub>3</sub>COO.

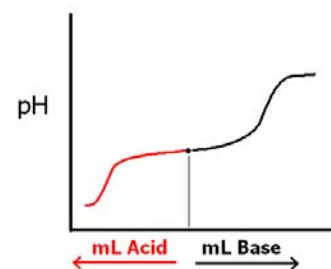
### III. Word Processed Report

#### Page 1: Graphs

**Upper right corner:** Your names, lab section number & Date of exp.

#### GRAPH 1: CH<sub>3</sub>COOH/NaCH<sub>3</sub>COO buffer titration graph

- Appropriate graph title. Indicate your assigned pH
- Y axis: pH
- X axis: leftward mL of HCl (acid) and rightward mL of NaOH (base)  
Excel: Right Click on graph, Select Data, Add  
Use negative HCl volumes to flip the HCl data.
- Labeled pK<sub>a</sub> point in the exact center of the buffering range.
- Graph title and axis labels
- Horizontal +/- 1 pH lines (refer to Introduction section)
- Vertical buffer capacity lines (refer to Introduction section)



#### GRAPH 2: NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> Buffer titration graph (see figure at right)

- Appropriate graph title: Include your buffer assignment (A or B).
- Y axis: pH
- X axis: leftward mL of HCl (acid) and rightward mL of NaOH (base)  
Excel: R Click on graph, Select Data, Add  
Use negative HCl volumes to flip the HCl data
- Labeled pK<sub>a</sub> point in the exact center of the buffering range.
- Graph title and axis labels
- Horizontal +/- 1 pH lines (refer to Introduction section)
- Vertical buffer capacity lines (refer to Introduction section)

#### Page 2: Questions

1. What is the total capacity in mL for the CH<sub>3</sub>COOH/NaCH<sub>3</sub>COO buffer? (Use your graph and round to nearest 0.1 mL)
2. What is the total capacity in mL for your NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> buffer? (Use your graph and round to nearest 0.1 mL)
3. Based on your experimental titration curves, compare and contrast the two buffers above in chemical terms.
4. 350.0 mL of buffer is known to contain 0.325 M CH<sub>3</sub>COOH and 0.630 M NaCH<sub>3</sub>COO.
  - a. Determine the initial pH of this buffer
  - b. Determine the volume (mL) of 0.150 M HCl required to neutralize the buffer.
  - c. Determine the volume (mL) of 0.150 M NaOH required to neutralize the buffer.



## IV. PROCEDURE

### A. pH Probe Calibration

Calibrate your pH probe using pH = 2 and pH = 12 buffer solutions provided in capped vials. Remember to keep the pH probe immersed in clean distilled water when not being used.

### B. Buffer preparation and adjustment

You will be assigned a buffer pH when you come to class. At that time you and your partner will be asked to calculate the mass of solid  $\text{NaCH}_3\text{COO}$  (82.034 g/mol) you will need to combine with 100.0 mL of the 0.100 M acetic acid for your assigned pH.

When you have completed your calculation show it to the lab instructor who will check it for correctness.

Next, use a top loading balance to weigh out the sodium acetate in a tared 150 mL beaker. Dissolve the solid in 100.0 mL of the 0.100 M acetic acid solution.

Measure the pH of the buffer solution with your calibrated pH probe and record the pH in your notebook.

### C: $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ Buffer titrations


Set up two burets using a single buret clamp. Rinse and fill one buret with 0.50 M NaOH solution and the other with 0.50 M HCl solution.

Adjust each buret to read exactly zero.

#### *NaOH titration*

Use a graduated cylinder to measure out 10.0 mL of your buffer solution into a 150 mL beaker and add 15.0 mL of distilled water. Place the beaker on a magnetic stirrer and adjust the positions of the buret and pH probe and magnetic stirrer.

Record the initial buret reading (zero) and corresponding pH. Now carefully add 0.500 M NaOH solution to the buffer in 0.2 mL increments.



After each addition, monitor the pH for 5 seconds before recording the burette reading in your notebook.

Continue adding NaOH incrementally and recording the pH until you have at least 12 points at high pH. If in doubt, make more measurements.

#### *HCl Titration*

Adjust each burette to read exactly zero.

Use a graduated cylinder to measure out 10.0 mL of your buffer solution into a 150 mL beaker and add 15.0 mL of distilled water. Place the beaker on a magnetic stirrer and adjust the positions of the buret and pH probe and magnetic stirrer.

Record the initial burette reading (zero) and corresponding pH. Now carefully add 0.500 M HCl solution to the buffer in 0.2 mL increments.

After each addition, monitor the pH for 5 seconds before recording the burette reading in your notebook.

Continue adding HCl incrementally and recording the pH until you have at least 12 points at very low pH. If in doubt, make more measurements.

Dispose of the used buffer solutions in the sink.

### D: $\text{NH}_4^+/\text{NH}_3$ Buffer titrations

Your instructor will assign your team one of two different  $\text{NH}_4^+/\text{NH}_3$  buffer solutions (A or B) to analyze.

Repeat the HCl and NaOH titration procedures above for the  $\text{NH}_4^+/\text{NH}_3$  buffering system you've been assigned. Don't forget to dilute the 10 mL of buffer with 15 mL of distilled water before beginning.