G. C. 2 - 9: THE EFFECT OF A BUFFER SOLUTION

OBJECTIVES

By the end of this experiment you should be able to:

- ✓ evaluating the pH effect of adding acids and bases to a buffer solution compared to water
- ✓ utilizing the Henderson-Hasselbalch equation to determine the expected pH of a buffer solution.
- ✓ understanding the equilibrium of a buffer system

REFERENCES

- ✓ Read Chapter 17.1-17.9 and 18.1-18.3 in your textbook.

BACKGROUND

Buffering systems resist change of pH. The best known buffer is human blood. Like many delicate systems, the human body is extremely sensitive to pH changes. The hydronium ion concentration, $[H_3O^+]$, in the blood can be affected easily if it was not protected by buffer systems. The normal pH range of human blood is 7.35 – 7.45. If the buffer does not function and the pH rises above 7.45, the result is a condition called alkalosis. If the pH falls below 7.35, the result is acidosis and can lead to coma and even to death.

Buffer systems are discussed more in detail in Chapter 18.2 in your textbook. A buffer consists of either a solution of a weak acid and the salt of its conjugate base, or a solution of a weak base and the salt of its conjugate acid. For example, we can look at a buffer system made from acetic acid (CH_3COOH) and its sodium salt, sodium acetate ($Na^+CH_3COO^-$). The dissociation of acetic acid is shown below:

$$\mathbf{CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + CH_3COO^-_{(aq)}} \qquad \text{Eq.1}$$

or

$$\mathbf{HAc \leftrightarrows H^+ + Ac^-} \qquad \text{Eq. 2}$$

Where HAc = acetic acid and Ac^- = acetate ion.

The system above will reach equilibrium as indicated by the double arrows in Equation 1. From the equation we can determine the equilibrium constant expression, which in the case of an acid/base reaction is referred to as the acid equilibrium constant (K_a) or base

equilibrium constant expression (K_b). In the case above it will be the acid equilibrium constant expression as seen in Equation 3.

The equilibrium constant for acetic acid is expressed as

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \quad \text{or} \quad [H^+] = \frac{K_a \times [HAc]}{[Ac^-]} \qquad \text{Eq. 3}$$

Understanding what happens in a buffer system is crucial to understanding how to calculate a solution's pH at any time during a titration. In order to understand this concept, think of each species in terms of how it dissociates:

- The weak acid, CH_3COOH will dissociate to **some** extent (not much, remember that extent is dependent upon the acid's K_a) into CH_3COO^- and H^+.
- The sodium acetate will dissociate into CH_3COO^- and Na^+ ions, but the important species to consider is the CH_3COO^-.

We can calculate the pH of a buffer system by utilizing the Henderson Hasselbach equation:

$$pH = pKa + \log \frac{[acetate]}{[acetic\ acid]} \qquad \text{Eq. 4}$$

Additions of Acids and Bases

What happens when a strong acid such as HCl or a strong base such as NaOH is added to the buffer? Each mole of HCl added will be free to react with each **available** mole of CH_3COO^- in solution. We will therefore get the following reaction:

$$H^+ \text{ (from HCl)} + CH_3COO^- \rightarrow CH_3COOH + H_2O \qquad \text{Eq. 5}$$

The H^+ from HCl reacts with the acetate ions forming additional acetic acid. We get a decrease in acetate ions (since they reacted with the strong acid) and an increase in acetic acid molecules being formed. Note: this reaction can only happen as **long as there are acetate ions still available** in the solution.

Now let us assume that we added 10.0 mL of 1.0M HCl to the original buffer solution. Since HCl is a strong acid, it dissociates completely. Thus, we can calculate the number of moles of H^+, knowing that there is one mole of H^+ in one mole of dissociated HCl. 1.0M × 0.010L = 0.010 moles of HCl = 0.010 moles of H^+ .

A similar thing happens if we add base to this buffer solution. The sodium hydroxide would react with the acetic acid, thus its amount would decrease, while more acetate ions would form.

OH^- (from NaOH) + $CH_3COOH \rightarrow CH_3COO^- + H_2O$ Eq. 6

Here are some sample calculations and guidelines to help you along during this experiment. Follow these guidelines until buffer capacity has been reached.

Method:

1. Identify the reaction that occurs between the HCl or NaOH added and the appropriate species in the buffer solution.
2. Assume this reaction goes to completion
3. Calculate the **amount of moles** of each species before any equilibrium and after each new addition.
4. Calculate the **concentration** of each species before any equilibrium and after each new addition.
5. Apply the equilibrium calculations to determine the pH or use the Henderson-Hasselbalch equation .

Example: 0.50L of a buffer solution consisting of a 0.1M solution of acetic acid and a 0.15M solution of sodium acetate. Using the Henderson Hasselbach equation, we can determine the pH of the original buffer. $pH = pKa + \log(0.15M/0.10M) = -\log(1.8 \times 10^{-5}) + \log(0.15M/0.10M)$. **The pH of the original buffer is 4.92.**

To this buffer solution we are adding 0.01L of 1.0M HCl. We can utilize the 5 steps above to solve.

Step 1: Identify the first reaction:

H^+ (from HCl) + $CH_3COO^- \rightarrow CH_3COOH + H_2O$

Step 2: Assume it goes to completion **(note: the following is NOT and ICE table)**

	H^+ (from HCl)	**+ CH_3COO^- →**	**CH_3COOH**	**+ H_2O**
Initial # moles:	(0.01L) (1.0M) =0.01 moles	(0.500L)(0.15M) = 0.075 moles	(0.500L)(0.1M) =0.05 moles	
Change	-0.01 moles	- 0.01moles	+0.01moles	
Step 3: Final # moles	0 moles	0.065 moles	0.060 moles	
Step 4: Final Conc.	0 M	(0.065mol/ 0.510 L) 0.127M	(0.060mol/0.510L) 0.118M	

Step 5: Apply the equilibrium calculations (see next step, or use the Henderson-Hasselbalch equation) . **For the equilibrium calculations**, use the equilibrium equation of the weak acid dissociation, and work an ICE table:

	CH_3COOH	+ H_2O →	H^+	+ CH_3COO^-
Initial	0.118M		0	0.127M
Change	-x		+x	+x
Equilibrium	0.118 – x		x	0.127 + x

If we apply the equilibrium calculations, utilizing the modified version of Eq. 3 we are able to solve for K_a . Note: <u>The concentration values included are those at equilibrium.</u>

$$Ka = \frac{x\,(0.127+x)}{(0.118-x)} = 1.74 \times 10^{-5}$$

Utilizing the equation above, we can solve for x as the concentration of H^+ or $[H^+]$, and then solve for pH. An alternative approach would be to apply the Henderson-Hasselbalch equation.

$$pH = pKa + \log \frac{[\text{acetate}]}{[\text{acetic acid}]} = 4.74 + \log (0.127/0.118) = 4.77$$

As you can see, the change in the pH is minor from 4.92 to 4.77. If you compare the addition of the same amount of HCl to water, which is essentially a dilution of the strong acid into water, the pH would change from 7 to 1.7.

Similar calculations can be performed for a base.

Step 1: Identify the reaction: OH^- (from NaOH) + $CH_3COOH \rightarrow CH_3COO^- + H_2O$

Step 2: Assume it goes to completion

	OH^- (from NaOH)	**+ CH_3COOH →**	**CH_3COO^-**	**+ H_2O**
Initial # moles:	(0.01L) (1.0M) =0.01 moles	0.500L)(0.10M) = 0.050 moles	(0.500L)(0.15M) =0.075 moles	
Change	-0.01 moles	- 0.01moles	+0.01moles	
Step 3: Final # moles	0 moles	0.04 moles	0.085 moles	
Step 4: Final concentrations	0 M	(0.040 mol/0.510L) = 0.078M	(0.085mol/0.510L) = 0.167M	

Step 5: Apply the equilibrium calculations or apply the Henderson-Hasselbalch equation. We apply the equation

$$pH = pKa + \log \frac{[\text{acetate}]}{[\text{acetic acid}]} = 4.74 + \log (0.167/0.078) = 5.07$$

The pH of the new solution is 5.07. As we have shown, a buffer is capable of maintaining a steady pH range of a system even after adding a substantial amount of acid or base. However, it cannot handle large amounts of addition. At some point a buffer will not be able to counteract the increased acid or base concentration. This is when the buffer reaches its "buffer capacity." (See pg. 858 of textbook).

In determining the pH of a buffer solution and the pH after addition of a strong acid or base, it is important to understand that the Henderson-Hasselbalch equation will **only** be used in the context of a weak acid dissociation. Once buffer capacity has been reached the Henderson-Hasselbalch equation will no longer be used.

At buffer capacity

At buffer capacity, the moles of Ac^- are equal to the moles of H^+, resulting in **all** the Ac^- ions being consumed. We can also utilize the 5 steps above to solve, however for Step 5, the equilibrium calculations will have to be used, since the Henderson Hasselbalch equation can only be used for buffer systems. For this step, we can substitute $[H^+]$ for $[Ac^-]$, and then solve for $[H^+]$ to determine the pH at buffer capacity as seen in Equation 7.

$$\mathbf{K_a = \frac{[H^+] \times [H^+]}{[HAc]}} \qquad \textbf{Or} \qquad \mathbf{[H^+]^2 = K_a \times [HAc]} \qquad \text{Eq. 7}$$

The buffer capacity can also be reached by addition of a base. The base will react with all of the acetic acid, and the acetic acid concentration will be zero. Here the solution contains only contains acetate ions-a weak base (anions that are conjugate bases of weak acids act themselves as weak bases in aqueous solutions), where the [HAc] will be equal to $[OH^-]$. The pH can be determined using the equilibrium expression for a weak base in Eq. 9. We have to keep in mind that we cannot use K_a, because it is the equilibrium constant of an acid system. The use of K_b becomes necessary, and Equation 10 indicates the relationship we need to utilize.

$$\mathbf{K_w = K_a \times K_b} \qquad \text{Eq. 9}$$

$$\mathbf{K_b = \frac{[OH^-] \times [OH^-]}{[Ac^-]}} \qquad \textbf{Or} \qquad \mathbf{[OH^-]^2 = K_b \times [Ac^-]} \qquad \text{Eq. 8}$$

After buffer capacity

Once the system exceeds buffer capacity, addition of extra acid or base will change the pH significantly, since there are no more acetate ions to buffer the strength of the strong acid. The system will act as a strong acid or base system, where the acid or base has been diluted. The acid concentration will be equal to $[H^+]$ or in case of a base addition, the base

concentration will be equal to [OH^-] once the dilution is taken into consideration. Thus, the pH of the system can be calculated using the simple pH equation:

$$\mathbf{pH = - \log [H^+]} \qquad \text{Eq. 10}$$

In today's experiment, you will use a series of indicators and compare the effects of adding HCl and NaOH solutions on the pH of distilled water and on the pH of a buffer using the Virtual Lab software. The disadvantage of using a single indicator is that we can only determine an estimated range of the pH and not an accurate measurement. For more precise determinations a pH meter is used.

For an easier data comparison, you will draw a graph of pH vs. the volume of HCl or NaOH added, for both your distilled water and buffer solutions. An example for this graph is shown in Figure 1.

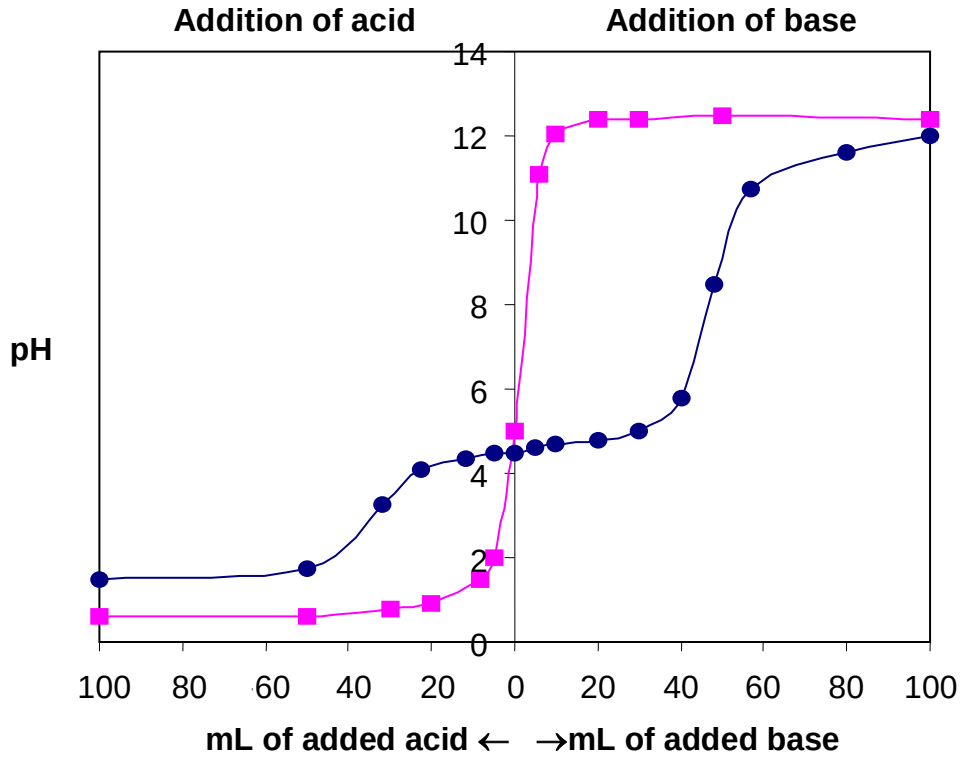


Figure 1. pH versus volume of added acid or base to distilled water (■) and to a buffer solution (●)

CHEMICALS AND SPECIAL EQUIPMENT

Virtual Lab© software developed by Carnegie Mellon University

(www.chemcollective.org/buffers)

PROCEDURE

Part I. Effects of HCl additions

The link for the virtual lab:

http://www.chemcollective.org/chem/fau/gc29n.html

Choose the appropriate glassware from the drop down menu of the glassware icon on the left sidebar on the workbench. You will need one 100mL volumetric flask and two 250mL Erlenmeyer flasks, one for the buffer and one for the DI water. You will also need two burets, one for the HCl and one for the NaOH.

Prepare 100.0 mL of the buffer by mixing 10.00mL of 1.0 M $NaC_2H_3O_2$ (Ac^-) with 10.00 mL 1.0 M $HC_2H_3O_2$ (HAc) and then fill up the flask with DI water to the 100mL mark. Using a graduated cylinder, transfer **50.00mL** of the buffer into one of the Erlenmeyer flasks, and 50.00mL DI water into the other one. Name the flasks appropriately to avoid confusion, by right clicking on them and selecting the rename option. (Note: volume transferred for dilution calculations). There no indicators will be used in this lab, please do not observe color change.

Fill up a buret with 0.1 M HCl solution. From the pH meter at the lower left corner of the screen record the pH value of the buffer and of the water before the first and after each addition of the acid.

Using the buret, transfer 5.00 mL of 0.1 M HCl (there is no 0.1 M solution in the stockroom, you have to dilute 1.0 M HCl to 0.1 M HCl using $M_1.V_1=M_2.V_2$ formula) into the buffer flask and record the pH of the solution. Continue by adding the following amounts of 0.1M HCl to the buffer solution as seen in your data table: 5.00 mL, 10.00 mL, 10.00 mL, 20.00 mL, 50.00 mL, while recording the pH and color of the solution.

Using the buret, transfer 5.00 mL of 0.1M HCl into the water flask by transferring 5.00 mL of 0.1M HCl into the water flask and record the pH of the solution. Continue by adding the following amounts of 0.1M HCl to the water solution as seen in your data table: 5.00 mL, 10.00 mL, 10.00 mL, 20.00 mL, 50.00 mL added into the water flask, while recording the pH of the solution.

Part II. Effects of NaOH additions

Using a graduated cylinder, transfer **50.00mL** of the buffer into one of the Erlenmeyer flasks, and 50.00mL DI water into the another flask. Again, name the flasks appropriately to avoid confusion, by right clicking on them and selecting the rename option. Fill up a buret with 0.10M NaOH solution (there is no 0.1 M solution in the stockroom, you have to dilute 1.0 M HCl to 0.1 M HCl using $M_1.V_1=M_2.V_2$). From the pH meter at the lower left corner of the screen record the pH value of the buffer and of the water before the first and after each addition of the base.

Using the buret, transfer 5.00 mL of 0.1 M NaOH into the buffer flask and record the pH. Continue by adding the following amounts of 0.1M NaOH to the buffer solution as seen in your data table: 5.00 mL, 10.00 mL, 10.00 mL, 20.00 mL, 50.00 mL, while recording the pH of the solution.

Using the buret, transfer 5.00 mL of 0.1M NaOH into the water flask by transferring 5.00 mL of 0.1M NaOH into the water flask and record the pH of the solution. Continue by adding the following amounts of 0.1M NaOH to the water solution as seen in your data table: 5.00 mL, 10.00 mL, 10.00 mL, 20.00 mL, 50.00 mL added into the water flask, while recording the pH of the solution. Dispose of your used buffer, water and sodium hydroxide solutions.

CALCULATIONS CONVERSIONS AND VALUES

1. Calculate the experimentally determined $[H^+]$ (M) from the pH data obtained by using the pH meter.
2. Calculate the expected pH (what are you expecting to obtain based on the concentrations of the components in each solution) for each addition, for both the buffer solution and the water when adding acid or base. Use the equations in the reading.
3. Draw a “pH vs. the volume of added **acid** to distilled water and buffer” graph.
4. Draw a “pH vs. the volume of added **base** to distilled water and buffer” graph.

On chem collective, the initial concentrations of the solutions do not match what is in your lab manual. Nor does the program have the right concentrations of HCl and NaOH.
Here is what we do:

To make 100mL buffer:
1. Put 10.0mL of 1.0M sodium acetate (NaCH3COO) in a glassware (I prefer 100.0mL volumetric flask)
2. Add 10.0mL of 1.0M acetic acid (CH3COOH) to the same glassware
3. Add 80.0mL of Water (H2O) to bring it up to 100.0mL of buffer
4. Follow directions from here on - use 50.0mL buffer for each part of the experiment

Calculation of concentration for components of the buffer:
C1V1=C2V2 --> (1.0M)(10mL)= (xM)(100mL)

To make 0.10M HCl:
1. Put 10.0mL of 1.0M HCl in a glassware (I prefer 100.0mL volumetric flask)
2. Add 90.0mL of water (H2O) to bring the final volume to 100.0mL
3. This will give you 0.10M of HCl. Use this for your lab part 1

To make 0.10M NaOH:
1. Put 10.0mL of 1.0M NaOH in a glassware (I prefer 100.0mL volumetric flask)
2. Add 90.0mL of water (H2O) to bring the final volume to 100.0mL
3. This will give you 0.10M of NaOH. Use this for your lab part 2

G. C. 2 - 9: LABORATORY REPORT

CONSIDERATIONS FOR DISCUSSION AND CONCLUSIONS SECTION:

As you write your discussion and conclusions paragraphs in your lab notebook, here are some tips and questions you should be answering. (This is in addition to the “Guidelines for a good discussion and conclusion” handout provided to you at your first lab class.

- Briefly explain/discuss all the concepts involved in the experiment (HINT: there are at least three).
- Discuss the methods used to solve for the pH.
- Compare the pH response of adding HCl and NaOH to the two systems tested using the graphs drawn.