

Experiment 32A

BUFFERS (One-Day Version)¹

MATERIALS: Small plastic vials (12), 10 mL pipets (2), pipet bulbs (2), 50 mL buret, 50 mL volumetric flask, stirring rods (2), plastic beakers (10), plastic droppers (6), weighing boats (2), straw, pH meter.

PURPOSE: The purpose of this experiment is to study the properties of buffers.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

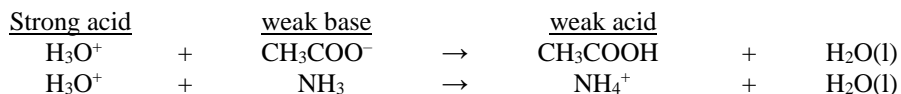
1. Distinguish between strong acid and weak acid systems.
2. Define a buffer and explain how a buffer works.
3. Explain how an acid-base indicator is used in the laboratory.
4. Qualitatively describe the important regions of a titration curve.
5. Prepare a buffer at a specified pH.

NOTE: During the lab period, you will need to reuse your glassware. Don't contaminate your solutions. Acids will be neutralized by even trace amounts of base. **Rinse glassware thoroughly with distilled water before each use.**

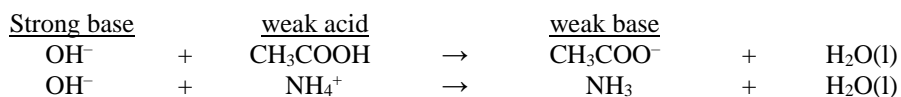
DISCUSSION:

Solutions that contain *significant amounts* of both members of a weak conjugate acid/base pair (e.g. $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ or $\text{NH}_4^+/\text{NH}_3$) are known as **buffers** (in the following discussion, the acid/base conjugates that comprise the buffer will be referred to as the "buffer components"). A useful characteristic property of a buffer solution is that it **resists changes in pH** upon addition of limited amounts of strong acid or strong base. The impact of buffers on solution pH in natural systems is of vital importance in biochemistry and environmental science, and buffers are commonly added to provide pH control during chemical synthesis and analytical procedures as well.

The buffer reacts with and absorbs added strong acid (H_3O^+) via a neutralization reaction involving the weak base component; this effectively converts the added strong acid into an equivalent amount of weak acid. For example:

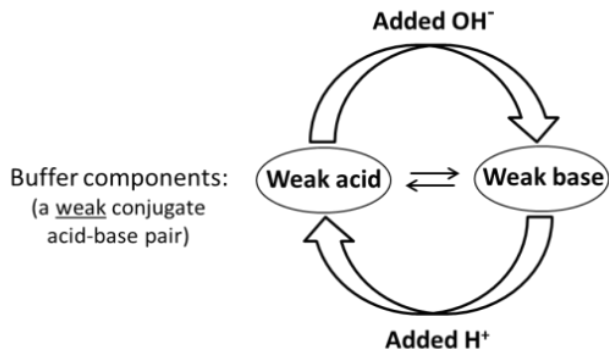


Likewise, upon addition of a strong base, the buffer effectively converts it into an equivalent amount of weak base via the corresponding neutralization reaction with the weak acid component:



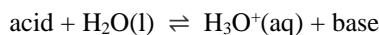
In each case, one buffer component is converted into its conjugate by the neutralization reaction with added strong acid or base; this is summarized in the figure at right.

The key feature to focus on here is that addition of strong acid or strong base to a buffer alters the relative amounts of the buffer components that are present in the equilibrium mixture, and this in turn induces a relatively modest change in the solution pH. Provided that the **buffer capacity** (see below) is not exceeded, the pH change of the buffer solution will be far smaller than the corresponding pH change that would occur were the same amount of strong acid or base to be added to an equivalent volume of pure water (or any unbuffered solution).



¹Partially adapted from "Working with Chemistry, A Laboratory Inquiry Program" by D.J. Wink, S.F. Gislason, and J.E. Kuehn, W.H. Freeman and Company, 2000.

To understand the origin of the buffering effect, we now consider the reaction equilibrium that links the weak acid and conjugate base components together (represented by the double arrow in the figure above). In the following reaction equation, “acid” and “base” represent the conjugate pair that defines the buffer:



You should recognize that this is just the acid ionization equilibrium, the K_a expression for which is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]}$$

Solving this equation for $[\text{H}_3\text{O}^+]$, taking the negative base-10 logarithm of both sides and rearranging yields the extremely useful relationship known as the “**Henderson-Hasselbalch equation**”:

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

This equation shows that **the pH range of effective buffering is determined by the $\text{p}K_a$ value** of the weak acid component. To make a buffer that is able to maintain the solution pH in an acidic range (such as the mixtures studied in this lab), it is necessary to use a weak acid component with $K_a > 1 \times 10^{-7}$ ($\text{p}K_a < 7.0$). Conversely, use of a weak acid having $K_a < 1 \times 10^{-7}$ ($\text{p}K_a > 7.0$) will produce a basic buffer ($\text{pH} > 7.0$).

The **limit of the effective buffer range is usually considered to be ± 1 pH unit** around the central value defined by $\text{pH} = \text{p}K_a$. Within this range, the exact buffer pH is determined by the ratio of the concentrations of the acid and base buffer components. Because the second term in the equation involves the ratio of two concentrations, the units cancel; thus, we can simplify a problem by expressing the relative amounts of buffer components using moles (rather than molarity) when calculating the value of this ratio. Note also that because the second term is a base-10 logarithm, **the value of the base/acid ratio must change by a factor of ten in order to change the buffer pH value by one unit.**

If strong acid is added to the buffer, the neutralization reaction decreases the value of the numerator (moles of base) and increases the value of the denominator (moles of acid) by the same amount. Similarly, adding strong base increases the numerator and decreases the denominator. When solving problems involving adjusting buffer pH (as in Day 2 of this lab) it is vital to remember that **both the numerator and denominator of this ratio change** when the buffer reacts with added acid or base!!

Finally, the total concentration (or moles) of the buffer components is also an important factor that determines the **buffer capacity**. The more concentrated a buffer is, the greater the amounts of buffer components that will be available in the solution, and a larger the quantity of added strong acid or base will be required in order to change the solution pH by a given amount. If the quantity of strong acid (or base) that is added is sufficient to *completely* neutralize one or the other of the buffer components, then the buffer capacity is exceeded, and the pH will no longer be regulated by that buffer equilibrium.

PROCEDURE

Work with a partner:

1. From your instructor, learn the proper procedures for calibrating the pH meter and obtaining a pH measurement. Record the procedure for future reference.

Procedure for calibrating the pH meter:

2. Obtain a sample of distilled, degassed water from your instructor. Write down the expected pH of the water. Measure the pH. The pH may not completely stabilize so report the value after waiting 1-2 minutes. Is the pH what you expected? Using a clean straw, blow into the water for a few minutes and observe the pH (keep the pH electrode in the water). Explain what happened.

Distilled, degassed water: Expected pH at 25°C: _____ Measured pH: _____

Effect of bubbling into the water:

Explanation for pH change:

As you carry out the following steps of the procedure, be sure to **use good laboratory technique to avoid cross-contamination of solutions**. Specifically, be sure to:

- remember to pre-rinse the pipet with a small amount of the solution to be transferred *before* the transfer.
 - carefully rinse stirring rod with distilled water and dry with a paper towel before putting it into any solution.
3. Fill a clean 50 mL buret with distilled water. Make sure no air bubbles are trapped in the tip of the buret. **Whenever you need to add 10 mL of distilled water, use this buret to deliver the specified amount.**
 4. a. With a clean pipet, carefully transfer 10 mL of 0.20 M HCl into a clean plastic beaker. From your buret, add 10 mL of distilled water to the beaker. Mix the solution. What is the concentration of H⁺ in this diluted solution? Calculate the expected pH of this solution. Add 3 drops of universal indicator to the solution, mix, and note the color. Measure the pH using a pH meter. Record your data in the table below.

b. Repeat the procedure as described in part 4a, except this time using 0.20 M NaOH (instead of 0.20 M HCl). Remember to rinse your pipet and stirring rod.

c. Carefully pipet 10 mL of 0.20 M HCl and 10 mL of 0.20 M NaOH into a beaker and mix. Rinse the pipet between solutions. What is the expected pH of this solution? Add 3 drops of universal indicator, mix, and note the color. Measure the pH, then separate the solution equally into 2 vials (10 mL each). Use the graduations on the beaker and the levels of the liquids in the vials to ensure equal volumes in each vial. Add 2 drops of 6.0 M HCl to one vial, mix, note the color, and measure the pH. Add 2 drops of 6.0 M NaOH to the other vial, mix, note the color, and measure the pH. Record your data in the table on the next page.

HCl/NaOH Solutions		calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
1	10 mL of 0.20 M HCl + 10 mL H ₂ O (buret)					
2	10 mL of 0.20 M NaOH + 10 mL H ₂ O					
3	10 mL 0.20 M HCl + 10 mL 0.20 M NaOH					

5. Similar to the procedures used for the HCl/NaOH system (summary given below), **work with another group** and study the following systems. One group will study the acetic acid system while the other group will study the maleic acid system. Both groups will share data so record results and observations carefully. Make sure you and your group can answer the post-lab questions based on your data.

Read the labels on the reagent bottles carefully! Rinse all glassware between solutions.

Test the following solutions using this procedure:

- Prepare the solution below. Read the reagent bottles carefully.
- Add 3 drops of universal indicator to the solution. Mix. Record the color of the solution.
- Measure the pH of the solution.
- Place 10 mL each into 2 separate vials.
- Add 2 drops 6.0 M HCl to one vial, mix, note the color, and measure the pH.
- Add 2 drops 6.0 M NaOH to the other vial, mix, note the color, and measure the pH.
- Calculate the expected pH of the solution (do this later or during free moments in lab) and compare to the measured pH.

Acetic Acid Solutions	<u>GROUP 1</u>	calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
4	Pipet 10 mL of 0.20 M CH ₃ COOH + 10 mL H ₂ O (buret)					
5	10 mL of 0.20 M CH ₃ COONa + 10 mL H ₂ O					
6	10 mL 0.20 M CH ₃ COOH + 10 mL 0.20 M CH ₃ COONa					
7	10 mL 0.0020 M CH ₃ COOH + 10 mL 0.0020 M CH ₃ COONa					

Maleic Acid Solutions	<u>GROUP 2</u>	calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
8	Pipet 10 mL of 0.20 M NaC ₄ H ₃ O ₄ + 10 mL H ₂ O (buret)	4.10				
9	10 mL of 0.20 M Na ₂ C ₄ H ₂ O ₄ + 10 mL H ₂ O	9.65				
10	10 mL 0.20 M NaC ₄ H ₃ O ₄ + 10 mL 0.20 M Na ₂ C ₄ H ₂ O ₄					

Acetic Acid, CH₃COOH:
 $K_a = 1.75 \times 10^{-5}$ $pK_a = 4.76$

Maleic Acid, C₄H₄O₄:
 $K_{a1} = 1.26 \times 10^{-2}$ $pK_1 = 1.90$
 $K_{a2} = 5.01 \times 10^{-7}$ $pK_2 = 6.30$

6. Make sure you have collected a range of pH values (pH ≈ 1–14) and their associated colors to answer Question #4 of the post-lab exercises. Show your results to your instructor and redo any solutions with inconsistent/faulty pH values.

Name(s) _____

Section _____

POST-LAB EXERCISES

Experiment 32A

1. Based on your observations in step 2 of the procedure, write down a chemical reaction that explains the pH change. What is produced as a result of blowing into a container of water? How would this affect the pH of the solution?

2. a. What is a buffer? Give a concise definition for a buffer:

In lab, you prepared 10 different solutions. Based on the *definition of a buffer* (not your experimental results), which solutions were considered buffers (list the solution numbers)?

Buffer Solutions = _____

- b. Was solution #3 a buffer solution? Explain why or why not.
 - c. Based on your experimental results, which solution was the best at resisting pH change upon addition of small amounts of H^+ or OH^- (i.e., which had the largest buffer capacity)? How did you know this? Use your data to support your answer.
 - d. Explain how a buffer works to resist large pH changes. Provide enough information to indicate your understanding of buffers.
3. Solutions #6 and #7 were prepared from CH_3COOH (acetic acid) and CH_3COONa (sodium acetate, the conjugate base of acetic acid). Which solution was a better buffer and why?

Do buffers have limits as to how much they can resist pH changes? Use data to support your answer.

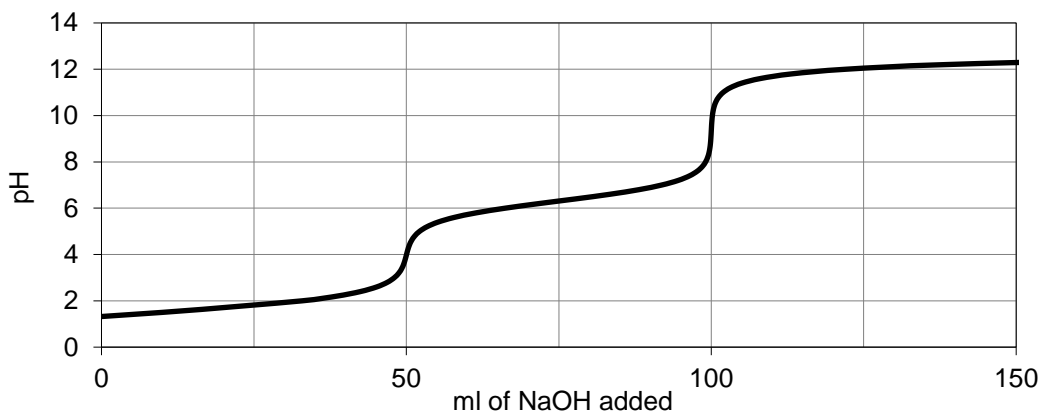
4. Universal indicator is an acid-base indicator which changes color with pH. Using your data as a guide, map out the color transitions, then answer the question below. You may need to estimate colors for some pH values.

Universal Indicator				
pH	observed color		pH	observed color
1			8	
2			9	
3			10	
4			11	
5			12	
6			13	
7			14	

Can an acid-base indicator, such as universal indicator, be used in place of a pH meter? Explain why or why not and any limitations.

5. Maleic acid, $C_4H_4O_4$, is a diprotic acid. Examine the titration curve for maleic acid below.
- a. On the titration curve, label the two equivalence points and two pK_a regions.

Titration Curve of
50 mL 0.10 M Maleic Acid with 0.10 M NaOH



- b. If universal indicator was added to the titration solution above, what color would the solution be at the *first equivalence point*? _____
- What color would the solution be at the *second equivalence point* in the titration? _____
- c. On the titration curve, circle the 2 buffer regions.
- d. How does your calculated pH and measured pH for solution #10 compare to each other?

What region of the titration curve were you in when you studied the mixture of 0.10 M $NaC_4H_3O_4$ and 0.10 M $Na_2C_4H_2O_4$ (solution #10)? Which pK_a value dominates the equilibrium in this region and why?

6. a. How would you prepare 50.0 mL of a $\text{NaC}_4\text{H}_3\text{O}_4/\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ buffer with $\text{pH} = 6.35$ (give specific masses of each component)? Assume that you want the total buffer concentration (i.e., [weak acid] + [conjugate base]) to be **0.100 M**. Make sure to select the appropriate K_a value for this buffer system. Show your work below.

Maleic Acid: $\text{pK}_1 = 1.90$ $\text{pK}_2 = 6.30$ ($\text{pK}_a = -\log K_a$)

For this buffer: [weak acid] + [conjugate base] = 0.100 M

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

MW ($\text{NaC}_4\text{H}_3\text{O}_4$) = 138.05 g/mol

MW ($\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$) = 160.04 g/mol

Mass of $\text{NaC}_4\text{H}_3\text{O}_4$ needed =

Mass of $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ needed =

- b. If 0.0010 moles of NaOH are added to the buffer in part a, what would happen to the pH (increase a little, decrease a little, or stay the same)? Explain your answer (no calculation is required here but drawing a picture or writing chemical reactions might be helpful).

Calculate the pH of the solution in part b.

***** INTENTIONALLY LEFT BLANK *****

Name _____

Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 32A

Read the experiment and complete this assignment **before** coming to lab.

1. Predict the pH of the following solutions that you will prepare in this experiment. Assume 25°C.

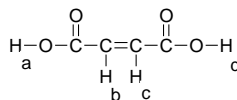
- | | | | |
|--|-----------|-----------|-----------|
| a. 0.10 M HCl | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| b. 0.10 M NaOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| c. 0.10 M CH ₃ COOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| d. 0.10 M CH ₃ COONa | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| e. 0.10 M Na ₂ C ₄ H ₂ O ₄ | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| f. 10 mL 0.20 M HCl mixed with 10 mL 0.20 M NaOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| g. 10 mL 0.20 M CH ₃ COOH mixed with 10 mL 0.20 M CH ₃ COONa | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| h. distilled water that has been exposed to the atmosphere. | a. pH < 7 | b. pH = 7 | c. pH > 7 |

2. a. Calculate the pH of a 0.20 M HCl solution

b. Calculate the pH of the solution prepared by mixing 10.0 mL of 0.20 M HCl and 10.0 mL of distilled water.

3. a. Calculate the pH of a 0.31 M CH₃COOH solution. K_a of CH₃COOH = 1.76×10^{-5} .

b. Calculate the pH of a 0.23 M CH₃COONa solution. (Think about whether this is an acidic or basic solution.)



4. The structure for maleic acid (C₄H₄O₄) is:

Which are the acidic hydrogens that are removed during deprotonization of this acid? (See labels on figure.) Select **ALL** that apply.

- a. H_a b. H_b c. H_c d. H_d