Introduction

A buffer solution consists of roughly equal concentrations of either a weak acid and its conjugate base or a weak base and its conjugate acid. In a buffer solution contained roughly equal concentrations of a weak acid and its conjugate base, the following acid ionization reaction is in equilibrium:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Le Châtelier's Principle applies to any reaction in equilibrium. A reaction in equilibrium will resist changes in concentration of both reactants and products. Because $H^+(aq)$ is a product, a buffer solution will resist changes in $[H^+]$. Because pH is dependent on $[H^+]$, a buffer solution will resist changes in pH. Buffer solutions are used in many biological systems to maintain the pH of the system to a very narrow range.

For a weak acid, the acid ionization reaction is governed by an acid ionization constant, K_a, which is defined as:

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

If you take the negative logarithm of both sides, the following equation may be obtained:

$$\begin{aligned} -\log K_a &= -\log\left(\frac{[H^+][A^-]}{[HA]}\right) \\ &= -\log[H^+] - \log\left(\frac{[A^-]}{[HA]}\right) \end{aligned}$$

Given that $pK_a = -\log K_a$ and $pH = -\log[H^+]$:

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

Solving this equation for pH will give the **Henderson-Hasselbach equation**:

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

The Henderson-Hasselbach equation can be used to determine the pH of buffer solutions. For example, consider a buffer solution that is 0.75 M in $HC_2H_3O_2$ (acetic acid) and 0.50 M in $NaC_2H_3O_2$ (sodium acetate). The K_a for $HC_2H_3O_2$ is given in your textbook as 1.8×10^{-5}. Therefore, the pK_a is equal to:

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

For a buffer solution, [HA] = $[HC_2H_3O_2]$ = 0.75 M and $[A^-] = [C_2H_3O_2^-] = [NaC_2H_3O_2]$ = 0.50 M. The pH of this buffer solution is equal to:

$$pH = 4.74 + \log\frac{0.50}{0.75} = 4.74 - 0.18 = 4.56$$

Buffer solutions will resist changes in pH as long as there are significant concentrations of the conjugate acid-base pair in solution. Addition of acid to a buffer solution converts the conjugate base to the weak acid. Conversely, addition of base to a buffer solution converts the weak acid to its conjugate base. For example, suppose 0.15 moles per liter of NaOH is added to the acetic acid-sodium acetate buffer described above. The addition of 0.15 moles per liter of NaOH will convert 0.15 moles per liter of the acetic acid to acetate ion. This will change the concentrations of $[HC_2H_3O_2]$ and $[C_2H_3O_2^-]$ as follows:

$$[HC_2H_3O_2] = 0.75 - 0.15 = 0.60\ M$$

$$[C_2H_3O_2^-] = 0.50 + 0.15 = 0.65\ M$$

The pH of the buffer solution can be calculated again using the Henderson-Hasselbach equation:

$$pH = 4.74 + \log\frac{0.65}{0.60} = 4.74 + 0.03 = 4.77$$

The pH change of 0.21 units is very small for the addition of 0.15 moles per liter of NaOH.

Buffer Capacity

It is possible to overwhelm a buffer solution by adding too much acid or base. If enough of acid or base is added to a buffer solution so that one of the members of the conjugate acid-base pair in the buffer is totally used up, then the solution will no longer act like a buffer solution. The **buffer capacity** of a buffer is the amount of acid or base that a buffer can neutralize before the pH begins to change appreciably. For example, if 0.50 moles per liter of HCl was added to the acetic acid-sodium acetate buffer described above, all of the sodium acetate would be converted to acetic acid. Since only acetic acid is present, the solution would no longer act like a buffer.

In this experiment, a number of solutions of varying amounts of acetic acid and sodium acetate will be prepared. Their pH will be measured and then their buffering abilities will be investigated. For the acetic acid/sodium acetate buffer system, the pH can be calculated using the Henderson-Hasselbach equation:

$$pH = 4.74 + \log\frac{[NaC_2H_3O_2]}{[HC_2H_3O_2]}$$

Procedure

Solution Preparation

1. Obtain 6 (six) 30 mL beakers.
2. There should be bottles of 0.50 M $HC_2H_3O_2$ and 0.50 M $NaC_2H_3O_2$ solution available in the lab. You will need about 75 mL of both solutions to perform this experiment.
3. Using your 10-mL graduated cylinder, make up the following solutions in the 6 beakers as shown in Table 1. Start by measuring out the volumes of 0.50 M $HC_2H_3O_2$ and pouring them into the beakers.
4. Then, rinse out the graduate cylinder and measure out the volumes of 0.50 M $NaC_2H_3O_2$ and pour them into the 6 beakers.
5. Swirl the solutions in each beaker to mix them.

Table 1 Composition of Solutions in Beakers

Beaker #	Volume of 0.50 *M* $HC_2H_3O_2$ (mL)	Volume of 0.50 *M* $NaC_2H_3O_2$ (mL)
1	10.00	0.00
2	8.00	2.00
3	6.00	4.00
4	4.00	6.00
5	2.00	8.00
6	0.00	10.00

6. Obtain a pH meter. Then, measure and record the pH of the solutions in each of the beakers.

Addition of Strong Acid to Buffered and Unbuffered Solutions

7. There should be dropper bottles of 3 M HCl and 3 M NaOH available on the lab desks. Add 5 drops of 3 M HCl to each beaker and stir the solutions.
8. Measure and record the pH of each solution. If the pH of a solution changes by more than 0.5 units, then that solution no longer acts as a buffer because its acid buffer capacity has been exceeded. The solutions in these beakers can be discarded.
9. Add another 5 drops of 3 M HCl to the buffer solutions in the remaining beakers and stir the solutions. Measure and record the pH of each solution. Again, if the

pH of a solution changes from the last reading by more than 0.5 units, then that solution will no longer act as a buffer and you may discard that solution.

10. Keep repeating adding 5 drops of 3 M HCl to the remaining beakers and recording the pH until the acid buffer capacities of all the solutions have been exceeded (the pH drops by more than 0.5 units after an addition).
11. Rinse out all of the beakers and mix up the buffer solutions as described in Table 5 again. Measure each solution's pH with the pH meter and record.

Addition of Strong Base to Buffered and Unbuffered Solutions

12. Add 5 drops of 3 M NaOH to each beaker and stir.
13. Measure and record the pH of each solution. If the pH of a solution changes by more than 0.5 pH units, then that solution's base buffer capacity has been exceeded and the solution may be discarded.
14. Repeat this procedure with 5 drop portions of 3 M NaOH and measuring the pH until all of the solutions' base buffer capacities has been exceeded.

Calculations

Calculate the concentration of $HC_2H_3O_2$ and $C_2H_3O_2^-$ in each buffer solution by using the volumes of each solution added to the beaker and the dilution formula:

$$[HC_2H_3O_2]_{buffer} = \frac{(\text{volume of } 0.50\ M\ HC_2H_3O_2 \text{ used})(0.50\ M)}{10.00 \text{ mL}}$$

$$[C_2H_3O_2^-]_{buffer} = \frac{(\text{volume of } 0.50\ M\ NaC_2H_3O_2 \text{ used})(0.50\ M)}{10.00 \text{ mL}}$$

For the solutions in beakers 1 and 6, since undiluted acid and base solution are used, the concentration of acid and base are the concentrations of the acid and base solution respectively. Calculate a theoretical pH for the solution in beaker 1 by performing a weak acid problem to calculate the pH of 0.50 *M* $HC_2H_3O_2$. Calculate a theoretical pH for the solution in beaker 6 by performing a weak base problem to calculate the pH of 0.50 *M* $NaC_2H_3O_2$. Use the Henderson-Hasselbach equation to calculate what the pH of the buffer solutions in the remaining beakers should be theoretically:

$$pH_{\text{calculated}} = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Compare your experimental pHs of the buffer solution to the calculated pHs.

Buffer Capacity

In this experiment, we will define the buffer capacity of a buffer as the number of drops of either 3.0 *M* HCl or 3.0 *M* NaOH needed before the pH of the solution changes by more than 0.5 pH units. For example, if the pH of a buffer solution changes by more than 0.5 pH units during the second 5 drop addition of 3 *M* HCl, then that buffer solution's acid buffer capacity will be "5 drops." Or, if the pH of a buffer solution changes by more than 0.5 pH units during the 1st 5 drop addition of 3 *M* NaOH, then that buffer solution's base buffer capacity is "0 drops."

Write the acid and base buffer capacities for the solutions in each beaker on the data sheet. Compare the acid and base buffer capacities to the concentrations of acid and base in the buffer solutions. Can you denote a pattern between the buffer capacities and the concentrations? Please write your observations on the data sheet.

Name: ____ Section: _________

Partner: ____ Date: ___/___/___

Report Sheet: Buffer Solutions

Buffer solutions: pH after addition of 3.0 *M* HCl

Beaker #	Initial pH	pH after addition of 5 drops HCl	pH after 10 drops	pH after 15 drops	pH after 20 drops	pH after 25 drops
1						
2						
3						
4						
5						
6						

Buffer solutions: pH after addition of 3.0 *M* NaOH

Test tube #	Initial pH	pH after addition of 5 drops NaOH	pH after 10 drops	pH after 15 drops	pH after 20 drops	pH after 25 drops
1						
2						
3						
4						
5						
6						

Concentrations of [$HC_2H_3O_2$] and [$C_2H_3O_2^-$] in each beaker:

	[$HC_2H_3O_2$]	[$C_2H_3O_2^-$]
Beaker # 1	______________	______________

Calculations:

Beaker # 2	______________	______________

Calculations:

Beaker # 3	______________	______________

Calculations:

Beaker # 4	______________	______________

Calculations:

Beaker # 5 _______________ _______________

Calculations:

Beaker # 6 _______________ _______________

Calculations:

Comparison of experimental and theoretical pH's

	Measured pH	**Calculated pH**	**ΔpH**
Beaker # 1	____________	____________	____________

Calculations:

Beaker # 2	____________	____________	____________

Calculations:

Beaker # 3 ____________ ____________ ____________

Calculations:

Beaker # 4 ____________ ____________ ____________

Calculations:

Beaker # 5 ____________ ____________ ____________

Calculations:

Beaker # 6 ____________ ____________ ____________

Calculations:

Buffer capacities for each solution:

	Acid buffer capacity	Base buffer capacity
Beaker # 1	______________	______________

Beaker # 2 ________________ ________________

Beaker # 3 ________________ ________________

Beaker # 4 ________________ ________________

Beaker # 5 ________________ ________________

Beaker # 6 ________________ ________________

Observations about any patterns between buffer capacities and the concentration of acid or base in each buffer solution:

Name: ________________________________ Section: ____________

Partner: ____ Date: ___/___/___

Experiment Buffer Solutions: Pre-Lab Exercise

Following instructions in the Lab Manual, you have prepared six different solutions in six different beakers by placing appropriate volumes of 0.50 *M* acetic acid and 0.50 *M* sodium acetate in them as shown below.

Composition of Solutions in Beakers

Beaker #	Volume of 0.50 *M* $HC_2H_3O_2$	Volume of 0.50 *M* $NaC_2H_3O_2$
1	10.00 mL	0.00 mL
2	8.00 mL	2.00 mL
3	6.00 mL	4.00 mL
4	4.00 mL	6.00 mL
5	2.00 mL	8.00 mL
6	0.00 mL	10.00 mL

Calculate the concentration of $HC_2H_3O_2$ and $C_2H_3O_2^-$ in each buffer solution by using the volumes of each solution added to the beaker and the dilution formula:

$$[HC_2H_3O_2]_{buffer} = \frac{(\text{volume of } 0.50\ M\ HC_2H_3O_2\ \text{used})(0.50\ M)}{10.00\ \text{mL}}$$

$$[C_2H_3O_2^-]_{buffer} = \frac{(\text{volume of } 0.50\ M\ NaC_2H_3O_2\ \text{used})(0.50\ M)}{10.00\ \text{mL}}$$

Use these values to fill in the table on the following pages and **show your calculations.**

Concentrations of [$HC_2H_3O_2$] and [$C_2H_3O_2^-$] in each beaker:

	[$HC_2H_3O_2$]	[$C_2H_3O_2^-$]
Beaker # 1	______________	______________

Calculations:

	[$HC_2H_3O_2$]	[$C_2H_3O_2^-$]
Beaker # 2	______________	______________

Calculations:

	[$HC_2H_3O_2$]	[$C_2H_3O_2^-$]
Beaker # 3	______________	______________

Calculations:

	[$HC_2H_3O_2$]	[$C_2H_3O_2^-$]
Beaker # 4	______________	______________

Calculations:

Beaker # 5 ________________ ________________

Calculations:

Beaker # 6 ________________ ________________

Calculations: