

EXPERIMENT 9 BUFFERS

PURPOSE:

To understand the properties of a buffer solution

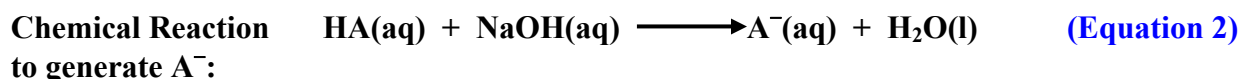
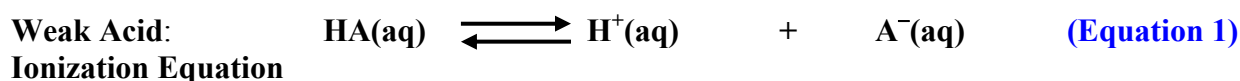
PRINCIPLES:

A buffered solution is an aqueous solution that resists changes in pH upon the addition of **small amounts** of acids and bases. In order for the solution to resist changes in pH, the **weak acid (HA)** and its **conjugate base (A⁻)**, which are the buffering species, must be within a factor of 10 of each other in concentration. This range assures that there is an appreciable amount of conjugate base (A⁻) to react with any added acid and that there is an appreciable amount of the weak acid (HA) to react with any added base (or the replenish any H⁺ that may have reacted with the added base).

The following summarizes information that is essential to understanding the properties of buffered solutions:

1. **A solution with both the weak acid (HA) and its conjugate base (A⁻) present** acts as a buffer; it does have buffer capacity. The HA present can react with small amounts of added base and the A⁻ present can react with small amounts of added acid. The HA and A⁻ “work” together to keep the pH relatively constant.
2. **A solution of the weak acid alone (HA)** does not act as a buffer; it does not have any buffer capacity. If acid is added, there is too little conjugate base, A⁻ present (from the partial ionization of the weak acid) to keep the pH constant.
3. **A solution of the conjugate base alone (A⁻)** does not act as a buffer; it does not have any buffer capacity. If base is added, there is too little weak acid, HA present (from the partial ionization of the conjugate base) to keep the pH constant

The pH of a buffer solution is determined by the ratio of the conjugate base to the weak acid. This can be understood by examining the following equations:



Acid Ionization Constant expression:
$$K_a = \frac{[\text{H}^{\text{+}}][\text{A}^{\text{-}}]}{[\text{HA}]}$$
 (Equation 3)

Solving Equation 3 for [H⁺] yields:
$$[\text{H}^{\text{+}}] = K_a \frac{[\text{HA}]}{[\text{A}^{\text{-}}]}$$
 (Equation 4)

Taking negative logarithms of both parts of Equation 4 yields:

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$$-\log [\text{H}^+] = -\log \left[\text{Ka} \times \frac{[\text{HA}]}{[\text{A}^-]} \right] = -\log \text{Ka} - \log \frac{[\text{HA}]}{[\text{A}^-]} = -\log \text{Ka} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Recall that:

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

$$-\log \text{Ka} = \text{pKa}$$

It follows that:

$\text{pH} = \text{pKa} + \log \frac{[\text{A}^-]}{[\text{HA}]}$	or	$\text{pH} = \text{pKa} + \log \frac{[\text{Base}]}{[\text{Acid}]}$	(Equation 5)
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Equation 5 is known as the **Henderson-Hasselbach Equation**. This equation shows that if a buffer with a specific pH is desired:

- A weak acid and its conjugate base must be found for which the pKa of the weak acid is close to the desired pH, and
- The concentration of the conjugate base, $[\text{A}^-]$ and of the weak acid $[\text{HA}]$ must be reasonably close to each other (must be within a factor of 10 of each other).

The closer the Ratio of $\frac{[\text{Base}]}{[\text{Acid}]}$ to 1, the better the Buffering Capacity of the Buffer

This implies that if in a buffer solution:

$$[\text{Base}] \approx [\text{Acid}],$$

the buffer is able to perform its “double duty” very well in maintaining its pH almost constant when either an acid or a base is added to the buffered solution

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PROCEDURE

PART I: Preparation of Solutions

1. Record the molarity of the sodium hydroxide solution provided
2. Record the molarity of the acetic acid solution provided.
3. Measure the volumes of sodium hydroxide solution, acetic acid solution and deionized water from the burets provided into six separate, 50 mL labeled beakers according to the table below.

(Note that the solutions in Table A and Table B are duplicates of the same solutions, but are labeled differently. A will represent acid addition in section III and B will represent base in section III.)

TABLE A

Solution #	HC ₂ H ₃ O ₂ (mL)	NaOH (mL)	H ₂ O (mL)
1A	10.00	0.00	10.00
2A	10.00	5.00	5.00
3A	10.00	7.50	2.50

TABLE B

Solution #	HC ₂ H ₃ O ₂ (mL)	NaOH (mL)	H ₂ O (mL)
1B	10.00	0.00	10.00
2B	10.00	5.00	5.00
3B	10.00	7.50	2.50

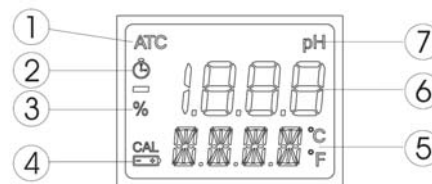
4. Mix the contents of each beaker prior to measuring the pH.

PART II: Measurement of pH

1. Rinse the electrode and wipe off the excess water with a Kimwipe.

DO NOT TOUCH THE ELECTRODE WITH YOUR FINGERS

2. From normal measuring mode, press and hold the /MODE button until OFF on the LCD, ⑤, is replaced by CAL. Release the button. The LCD enters the calibration mode displaying “pH 7.01 USE”. After 1 second the meter activates the automatic buffer recognition feature. If a valid buffer is detected then its value is shown on the LCD, ⑥, and REC appears on the LCD, ⑦. If no valid buffer is detected, the meter keeps the USE indication active for 12 seconds, and then it replaces it with WRNG, indicating the sample being measured is not a valid buffer.
3. Place the electrode in pH 7.01 buffer.
4. After the first calibration point has been accepted, the “pH 4.01 USE” message appears. (about 1 – 2 minutes)
5. Place the electrode in pH 4.01 buffer.
6. When the buffer is accepted, the LCD shows the accepted value with the “OK 2” message, and then the meter returns to the normal measuring mode. (about 1 – 2 minutes)
7. Measure the pH of each of your six solutions (1A, 2A, 3A, 1B, 2B & 3B) from Part I. Remember to repeat Steps 3 and 4 every time you change solutions. Record these pH measurements and calculate the average pH for each solution (1, 2 & 3)



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PART III: Measurement of Buffering Capacity

1. Add 2.00×10^{-4} moles of hydrochloric acid to each of the following solutions: 1A, 2A, and 3A. The exact volume that needs to be added from the buret depends on the molarity of the hydrochloric acid solution available in the lab (you need to calculate this volume). Mix well the solutions as before. Read and record the pH of the solutions to which hydrochloric acid has been added.
2. Add 2.00×10^{-4} moles of sodium hydroxide to each of the following solutions: 1B, 2B, and 3B. The exact volume that needs to be added from the buret depends on the molarity of the sodium hydroxide solution available in the lab (you need to calculate this volume). Mix well the solutions as before. Read and record the pH of the solutions to which hydrochloric acid has been added

When you are finished with your measurements, rinse the electrode and wipe off the excess water with a Kimwipe. Place the cap on the electrode and return the pH meter to your instructor in its original container.

CALCULATIONS

PART I & PART II

1. Calculate the Ratio $\frac{[\text{Base}]}{[\text{Acid}]}$ for solutions 1, 2 & 3

HINTS:

- Recall that solutions 1A and 1B, 2A and 2B, 3A and 3B respectively are initially identical
- Calculate the average pH obtained from two measurements for each solution
- For solution 1, the calculation of the Base/Acid Ratio is based on the measured pH
- For solutions 2 & 3 the calculation of the Base/Acid Ratio is based on stoichiometry

PART III: Buffering Capacity

1. Determine the change in pH for solutions 1A, 2A, and 3A, when 2.00×10^{-4} moles of hydrochloric acid is added ($\Delta\text{pH}_{\text{acid}}$)
2. Determine the change in pH for solutions 1B, 2B, and 3B, when 2.00×10^{-4} moles of sodium hydroxide is added ($\Delta\text{pH}_{\text{base}}$)
3. Average ($\Delta\text{pH}_{\text{acid}}$) and ($\Delta\text{pH}_{\text{base}}$) for solutions 1A, 1B and 2A, 2B and 3A, 3B respectively.
4. Determine which solution(s) can act as a buffer.
5. If more than one solution can act as a buffer, indicate which solution has a higher buffering capacity and why.

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REPORT FORM

NAME: _____

PARTNER: _____

Part I & Part II: Preparation of Solutions and Measurement of Solutions

Average pH of solutions

Solution	1A	1B	2A	2B	3A	3B
Measured pH						
Average pH						

Part III: Measurement of Buffering Capacity

1. Calculate the volume of hydrochloric acid to be added to solution 1A, 2A and 3A:

Molarity of Hydrochloric Acid: _____ M

Number of moles of Hydrochloric Acid to be added: _____ moles

Volume of Hydrochloric Acid to be added _____ mL
(Show calculations below)

pH after addition of hydrochloric acid:

Solution 1A: _____ Solution 2A: _____ Solution 3A: _____

2. Calculate the volume of sodium hydroxide to be added to solution 1B, 2B and 3B:

Molarity of Sodium Hydroxide: _____ M

Number of moles of Sodium Hydroxide to be added: _____ moles

Volume of Sodium Hydroxide solution to be added: _____ mL
(Show calculations below)

pH after addition of sodium hydroxide::

Solution 1B: _____ Solution 2B: _____ Solution 3B: _____

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3. Calculate the Base/Acid Ratio for solution 1:

Original Molarity of HC₂H₃O₂ : _____ M

Molarity of HC ₂ H ₃ O ₂ solution before mixing (M)	Volume of HC ₂ H ₃ O ₂ solution added (mL)	Volume of water added (mL)	Total Volume of Solution 1 (mL)	Molarity of HC ₂ H ₃ O ₂ in Solution 1	Average Measured pH of Solution 1	Average [H ⁺] in solution 1

Complete the Equilibrium Table below for Solution 1:

	$\text{HC}_2\text{H}_3\text{O}_2$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$
Start:					
Change:					
Equilibrium:					

Calculate the Ratio: $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$ to the proper amount of significant figures.

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4. Calculate the Base/Acid Ratio for solution 2:

Original Molarity of $\text{HC}_2\text{H}_3\text{O}_2$: _____ M Molarity of NaOH: _____ M

Table II A

Molarity of $\text{HC}_2\text{H}_3\text{O}_2$ solution before mixing (M)	Volume of $\text{HC}_2\text{H}_3\text{O}_2$ solution added (mL)	Number of moles of $\text{HC}_2\text{H}_3\text{O}_2$ added

Table II B

Molarity of NaOH solution before mixing (M)	Volume of NaOH solution added (mL)	Number of moles of NaOH added

Balanced Chemical Equation that illustrates the reaction that takes place in test tube:



Net Ionic Equation:



Start:	_____ mol	+	_____ mol	\rightarrow	_____ mol	
End:	_____ mol	+	_____ mol	\rightarrow	_____ mol	

What is the total volume of solution after mixing? _____ mL

Calculate the molarity of $[\text{HC}_2\text{H}_3\text{O}_2]$ after mixing: _____ M
(show calculations below)

Calculate the molarity of $[\text{C}_2\text{H}_3\text{O}_2^-]$ after mixing: _____ M
(show calculations below)

Calculate the Ratio: $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$ to the proper amount of significant figures.

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5. Calculate the Base/Acid Ratio for solution 3:

Original Molarity of $\text{HC}_2\text{H}_3\text{O}_2$: _____ M Molarity of NaOH : _____ M

Table III A

Molarity of $\text{HC}_2\text{H}_3\text{O}_2$ solution before mixing (M)	Volume of $\text{HC}_2\text{H}_3\text{O}_2$ solution added (mL)	Number of moles of $\text{HC}_2\text{H}_3\text{O}_2$ added

Table III B

Molarity of NaOH solution before mixing (M)	Volume of NaOH solution added (mL)	Number of moles of NaOH added

Balanced Chemical Equation that illustrates the reaction that takes place in test tube:



Net Ionic Equation:



Start:

	_____ mol	+	_____ mol	_____ mol	
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End:

	_____ mol	+	_____ mol	_____ mol	
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What is the total volume of solution after mixing ? _____ mL

Calculate the molarity of $[\text{HC}_2\text{H}_3\text{O}_2]$ after mixing: _____ M
(show calculations below)

Calculate the molarity of $[\text{C}_2\text{H}_3\text{O}_2^-]$ after mixing: _____ M
(show calculations below)

Calculate the Ratio: $\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$ to the proper amount of significant figures.

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6. Testing the buffering capacity of the three solutions

TABLE IV A: Change in pH upon addition of acid ($\Delta\text{pH}_{\text{acid}}$)

	Solution 1	Solution 2	Solution 3
	10.00 mL HC ₂ H ₃ O ₂ + 10.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 5.00 mL NaOH + 5.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 7.50 mL NaOH + 2.50 mL H ₂ O
Initial Average pH			
pH after the addition of 2.00×10^{-4} moles HCl			
Change in pH ($\Delta\text{pH}_{\text{acid}}$)			

TABLE IV B: Change in pH upon addition of base ($\Delta\text{pH}_{\text{base}}$)

	Solution 1	Solution 2	Solution 3
	10.00 mL HC ₂ H ₃ O ₂ + 10.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 5.00 mL NaOH + 5.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 7.50 mL NaOH + 2.50 mL H ₂ O
Initial Average pH			
pH after the addition of 2.00×10^{-4} moles NaOH Sodium hydroxide			
Change in pH ($\Delta\text{pH}_{\text{base}}$)			

**TABLE IV C: Summary of change in pH upon addition of acid or base
(transfer and average your data from Table IV A and IV B above)**

	Solution 1	Solution 2	Solution 3
	10.00 mL HC ₂ H ₃ O ₂ + 10.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 5.00 mL NaOH + 5.00 mL H ₂ O	10.00 mL HC ₂ H ₃ O ₂ + 7.50 mL NaOH + 2.50 mL H ₂ O
Change in pH ($\Delta\text{pH}_{\text{acid}}$)			
Change in pH ($\Delta\text{pH}_{\text{base}}$)			
Average change in pH: $\frac{(\Delta\text{pH}_{\text{acid}} + \Delta\text{pH}_{\text{base}})}{2}$			
$\frac{\text{BASE}}{\text{ACID}}$ Ratio (see pages 6 through 8)			

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7. Which one (or more) of the solutions meets the criteria for being a buffer solution?

(a) What is the **experimental evidence** that supports your answer above?

(b) **Why** does (*do*) this (*these*) solution(s) have buffering capacity ?

8. If more than one solutions meets the criteria for being a buffer solution, which solution has the highest Buffering Capacity?

(a) What is the **experimental evidence** for your answer in (c) above?

(b) **Why** does the solution in (c) above have the highest Buffering Capacity?