EXPERIMENT 9
BUFFERS

PURPOSE:

To understand the properties of buffer solutions.

PRINCIPLES:

A buffer 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 buffer solutions:

1. A weak acid by itself [$HC_2H_3O_2$(aq)], even though it ionizes to form some of its conjugate base [$C_2H_3O_2^-$ (aq)], does not contain sufficient base [$C_2H_3O_2^-$ (aq)] to be a buffer. If acid is added, there is too little conjugate base [$C_2H_3O_2^-$ (aq)], to keep the pH constant.
   Similarly, a weak base by itself [NH_3(aq)], even though it partially ionizes in water to form some of its conjugate acid [NH_4^+(aq)], does not contain sufficient acid to be a buffer If base is added, there is too little conjugate acid [NH_4^+(aq)], to keep the pH constant.

2. Solutions containing comparable amounts of both the weak acid, such as [$HC_2H_3O_2$(aq)], and its conjugate base, such as [$C_2H_3O_2^-$ (aq)], can act as buffers. These solutions have buffer capacity. The [$HC_2H_3O_2$(aq)] present can react with small amounts of added base and the [$C_2H_3O_2^-$ (aq)] present can react with small amounts of added acid.
   The weak acid [$HC_2H_3O_2$(aq)], and its conjugate base [$C_2H_3O_2^-$ (aq)], "work" together to keep the pH relatively 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:

Weak Acid Ionization Equation: $$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad \textbf{(Equation 1)}$$

Chemical Reaction to generate A^-: $$HA(aq) + NaOH(aq) \longrightarrow A^-(aq) + H_2O(l) \qquad \textbf{(Equation 2)}$$

Acid Ionization Constant Expression: $$Ka = \frac{[H^+]\,[A^-]}{[HA]} \qquad \textbf{(Equation 3)}$$

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

Taking negative logarithms of both parts of Equation 4 yields:

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

Recall that:

$-\log[H^+] = pH$ $\qquad\qquad$ $-\log K_a = pK_a$

It follows that:

$$\boxed{pH = pK_a + \log\frac{[A^-]}{[HA]}} \quad \textbf{or} \quad \boxed{pH = pK_a + \log\frac{[Base]}{[Acid]}} \qquad \textbf{Equation 5}$$

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, $[A^-]$ and of the weak acid [HA] must be reasonably close to each other (must be within a factor of 10 of each other).

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

This implies that if in a buffer solution:

$$[Base] \approx [Acid],$$

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 NaOH 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 into six separate, labeled 18 mm x 150 mm test tubes or vials according to the table below. The solutions can be dispensed from the burets set up for this purpose in the lab.
   NOTE:
   The solutions in Table A and Table B are duplicates of the same solutions, but are labeled differently.

TABLE A

Solution #	$HC_2H_3O_2$ (mL)	NaOH (mL)	H_2O (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 #	$HC_2H_3O_2$ (mL)	NaOH (mL)	H_2O (mL)
1B	10.00	0.00	10.00
2B	10.00	5.00	5.00
3B	10.00	7.50	2.50

4. Cover (seal) each test tube with a piece of saran wrap or parafilm.
   If available, stoppers that fit snuggly may be used.
5. Mix the contents of each tube (vial) by inverting the tubes (vials) several times.

PART II: Measurement of pH

1. Calibrate your pH meter for buffer pH = 7.00, followed by calibration for buffer pH = 4.0
2. Measure the pH of each of your six solutions (1A, 2A, 3A and 1B, 2B and 3B) and record these measurements.
3. Turn the pH meter "OFF"
4. Rinse the electrode with a stream of deionized water and catch the water in a beaker.
5. Remove the excess water from the electrode with tissue paper.
6. Store the electrode temporarily in the pH = 7.0 buffer solution.
7. Calculate the average pH for each solution (1, 2 & 3)
8. Calculate the average pH for each solution (1, 2 & 3)

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PART III: Determination of Buffering Capacity

1. **Addition of 0.10 M Hydrochloric Acid to solutions 1A, 2A and 3A**
    - Add **2.00 mL of 0.10 M Hydrochloric Acid (HCl) to solutions 1A, 2A and 3A** by dispensing it from the buret, set up for this purpose in the lab.
    - Cap or seal the tubes (vials) containing the three solutions.
    - Mix the contents of each tube (vial) by inverting the tubes (vials) several times.
    - Measure the pH of each of your three solutions, to which hydrochloric Acid has been added (1A + Acid, 2A + Acid, 3A + Acid) and record these measurements.
    - Turn the pH meter “OFF”
    - Rinse the electrode with a stream of deionized water and catch the water in a beaker.
    - Remove the excess water from the electrode with tissue paper.
    - Store the electrode temporarily in the pH = 7.0 buffer solution.

2. **Addition of 0.10 M Sodium Hudroxide to solutions 1B, 2B and 3B**
    - Add **2.00 mL of 0.10 M Sodium Hydroxide (NaOH) to solutions 1B, 2B and 3B** by dispensing it from the buret, set up for this purpose in the lab.
    - Cap or seal the tubes (vials) containing the three solutions.
    - Mix the contents of each tube (vial) by inverting the tubes (vials) several times.
    - Measure the pH of each of your three solutions, to which hydrochloric Acid has been added (1B + Base, 2B + Base, 3B + Base) and record these measurements.
    - Turn the pH meter “OFF”
    - Rinse the electrode with a stream of deionized water and catch the water in a beaker.
    - Remove the excess water from the electrode with tissue paper.

3. **Storing the pH meter**
    - Retrieve the protective cap of the pH meter and drain any water from inside the cap.
    - Place a few drops of Storage Solution (available at the instructor’s desk) in the protective cap of the pH meter. While keeping the pH meter in an upright position, snap the protective cap containing the storage solution onto the bottom of the pH meter.
    - Place the pH meter in an upright position in a 250 mL Erlenmeyer flask and store it in your locker (it will fit in large lockers only). You will use the pH meter again for the next experiment.

4. **Storing the two buffer solutions**
    DO NOT DISCARD THE BUFFER SOLUTIONS!
    The plastic test-tubes containing the two buffer solutions should be kept in your locker (capped) for the next experiment. The test-tubes come with a cap and they should be well capped to preserve the contents. They fit only in the large lockers.

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CALCULATIONS

PART I & PART II

1. Calculate the Ratio $\dfrac{\textbf{[Base]}}{\textbf{[Acid]}}$ **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 mL of 0.10 M of hydrochloric acid is added **(ΔpH_{acid})**

2. Determine the change in pH for solutions 1B, 2B, and 3B, when 2.00 mL of 0.10 M of sodium hydroxide is added **(ΔpH_{base})**

3. Average (ΔpH_{acid}) and (ΔpH_{base}) for solutions:
   - 1A &1B and
   - 2A & 2B and
   - 3A & 3B, respectively.

4. Based on the Average Change in pH, and the Base/Acid Ratio, determine which solution cannot act as a buffer(s) and why
   (Answer the questions listed on the last page of the Report Form).

5. Based on the Average Change in pH, and the Base/Acid Ratio, determine which solutions can act as a buffer(s) and why
   (Answer the questions listed on the last page of the Report Form).

6. Indicate which solution has a highest buffering capacity and why
   (Answer the questions listed on the last page of the Report Form).

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REPORT FORM

NAME: ________________________ Date: ____________ 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						

1. **ADDITION OF HYDROCHLORIC ACID**

   Molarity of Hydrochloric Acid: ________________ M

   Volume of Hydrochloric Acid added ________________ mL

   pH after addition of hydrochloric acid:

   Solution 1A + Hydrochloric Acid: pH = __________

   Solution 2A + Hydrochloric Acid: pH = __________

   Solution 3A + Hydrochloric Acid: pH = __________

2. **ADDITION OF SODIUM HYDROXIDE**

   Molarity of Sodium Hydroxide: ________________ M

   Volume of Sodium Hydroxide solution to be added: ________________ mL

   pH after addition of sodium hydroxide:

   Solution 1B + Sodium Hydroxide: pH = __________

   Solution 2A + Sodium Hydroxide: pH = __________

   Solution 3A + Sodium Hydroxide: pH = __________

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

Original Molarity of $HC_2H_3O_2$: _______________ **M**

Molarity of $HC_2H_3O_2$ solution before mixing (M)	Volume of $HC_2H_3O_2$ solution added (mL)	Volume of water added (mL)	Total Volume of Solution 1 (mL)	**Molarity of $HC_2H_3O_2$ in Solution 1 M**	Average Measured pH of Solution 1	**Average $[H^+]$ in Solution 1 M**

Complete the Equilibrium Table below for Solution 1:

	$HC_2H_3O_2(aq)$	$\rightleftarrows$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
Start:		$\rightleftarrows$		+	

DO NOT USE X! Use actual values indicating the change in concentrations!

Change:		$\rightleftarrows$		+	
Equilibrium:		$\rightleftarrows$		+	

Calculate the Ratio: $\dfrac{[C_2H_3O_2^-]}{[H\ C_2H_3O_2]}$ **to the proper amount of significant figures.**

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

Original Molarity of $HC_2H_3O_2$: ___________ M Molarity of NaOH: ___________ M

Table II A

Molarity of $HC_2H_3O_2$ solution before mixing (M)	Volume of $HC_2H_3O_2$ solution added (mL)	**Number of moles of $HC_2H_3O_2$ 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/vial:

_______________ + _______________ $\rightarrow$ _______________ + **$H_2O(l)$**

Net Ionic Equation: _______________ + _______________ $\rightarrow$ _______________ + **$H_2O(l)$**

Start:	**mol**	+	**mol**	$\rightarrow$	**mol**		
End:	**mol**	+	**mol**	$\rightarrow$	**mol**		

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

Calculate the molarity of [**$HC_2H_3O_2$**] **after mixing:** _______________ **M**
(show calculations below)

Calculate the molarity of [**$C_2H_3O_2^-$**] **after mixing:** _______________ **M**
(show calculations below)

Calculate the Ratio: $\dfrac{[C_2H_3O_2^-]}{[H\ C_2H_3O_2]}$ **to the proper amount of significant figures.**

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

Original Molarity of $HC_2H_3O_2$: _______________ M   Molarity of NaOH: ___________ M

Table III A

Molarity of $HC_2H_3O_2$ solution before mixing (M)	Volume of $HC_2H_3O_2$ solution added (mL)	**Number of moles of $HC_2H_3O_2$ 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:

_____________ + _______________ $\rightarrow$ ____________ + **$H_2O(l)$**

Net Ionic Equation:

_____________ + _____________ $\rightarrow$ _____________ + **$H_2O(l)$**

Start:	**mol**	+	**mol**	$\rightarrow$	**mol**	
End:	**mol**	+	**mol**	$\rightarrow$	**mol**	

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

Calculate the molarity of [**$HC_2H_3O_2$**] **after mixing:** ______________ **M**
(show calculations below)

Calculate the molarity of [**$C_2H_3O_2^-$**] **after mixing:** ______________ **M**
(show calculations below)

Calculate the Ratio: $\mathbf{\dfrac{[C_2H_3O_2^-]}{[H\ C_2H_3O_2]}}$ **to the proper amount of significant figures.**

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6. Comparing the buffering capacity of the three solutions

TABLE IV A: Change in pH upon addition of acid (ΔpHacid)

	Solution 1	**Solution 2**	**Solution 3**
	10.00 mL $HC_2H_3O_2$ + 10.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 5.00 mL NaOH + 5.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 7.50 mL NaOH + 2.50 mL H_2O
Initial Average pH			
pH after the addition of 2.00 mL of 0.10 M HCl			
Change in pH (ΔpH acid)			

TABLE IV B: Change in pH upon addition of base (ΔpHbase)

	Solution 1	**Solution 2**	**Solution 3**
	10.00 mL $HC_2H_3O_2$ + 10.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 5.00 mL NaOH + 5.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 7.50 mL NaOH + 2.50 mL H_2O
Initial Average pH			
pH after the addition of 2.00 mL of 0.10 M NaOH			
Change in pH (ΔpH 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 $HC_2H_3O_2$ + 10.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 5.00 mL NaOH + 5.00 mL H_2O	10.00 mL $HC_2H_3O_2$ + 7.50 mL NaOH + 2.50 mL H_2O
Change in pH (ΔpHacid)			
Change in pH (ΔpHbase)			
Average change in pH: $\frac{(\Delta pHacid + \Delta pHbase)}{2}$			

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7. Which solution DOES NOT MEET the criteria for being a buffer solution?

(a) ________________

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

(c) What is the **reason** that this solution DOES NOT MEET the criteria for being a buffer solution?

8. Which solutions DO MEET the criteria for being buffer solutions?

(a) ________________ and ________________

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

(c) What is the **reason** that these solutions meet the criteria for being buffer solutions?

9. Which of the solutions listed in # 8. above has the highest Buffering Capacity?

(a) __________________

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

(c) What is the **reason** that this solution has the highest Buffering Capacity?