EXPERIMENT 8
BUFFERS

PURPOSE:

1. To understand the properties of buffer solutions.
2. To calculate the pH of buffer solutions and compare the calculated values with the experimentally determined pH values.

PRINCIPLES:

I. Definition

A buffer solution is an aqueous solution that resists changes in pH when small amounts of acid or base are added.

II. Composition

A buffer solution is composed of a weak acid (HA) and its conjugate base (A^-)

III. Effectiveness of Buffer Solutions:

In order for a solution to resist pH change, the weak acid and conjugate base must be within a factor of 10 of each other i.e. in the range of 0.10 to 10. This range assures that there is enough weak base to react with any added acid, or that there is enough weak acid to react with any added base. This implies that in an effective buffer solution: [Base] ≈ [Acid]

It follows that:

$$\text{The closer the ratio of } \frac{[\text{Base}]}{[\text{Acid}]} = \text{ to 1, the more effective the buffer.}$$

1. Effective Buffer Solutions

Solutions containing comparable amounts of both the weak acid and its conjugate base, such as acetic acid, [$HC_2H_3O_2(aq)$] and the acetate ion, [$C_2H_3O_2^-(aq)$], can act as buffers since the [$HC_2H_3O_2(aq)$] can react with small amounts of added base, and the acetate ion [$C_2H_3O_2^-(aq)$] can react with small amounts of added acid.

The weak acid and its conjugate base "work together" in the following way:

The weak acid [$HC_2H_3O_2(aq)$] neutralizes added base:

$$HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l)$$

The conjugate base [$C_2H_3O_2^-(aq)$] neutralizes added acid:

$$C_2H_3O_2^-(aq)] + HCl(aq) \longrightarrow HC_2H_3O_2(aq) + H_2O(l)$$

2. Ineffective Buffer Solutions

Even though a weak acid, such as [$HC_2H_3O_2(aq)$], ionizes to form some of its conjugate base [$C_2H_3O_2^-(aq)$], it 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, such as [$NH_3(aq)$], partially ionizes in water to form some of its conjugate acid [$NH_4^+(aq)$], does not contain sufficient acid to be a buffer. Again, if base is added, there is too little conjugate acid [$NH_4^+(aq)$] to keep the pH constant.

IV. Calculating the pH of Buffer Solutions

There are two methods to calculate the pH of a buffer solution, by using (1) the equilibrium method or by using (2) the Henderson-Hasselbach equation.

1. The Equilibrium Method

Consider the buffer solution below. The acetic acid ionizes according to the following reaction:

	$HC_2H_3O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial Conc:	0.100 M						0.100 M

(Note that this equilibrium reaction is different from the familiar acid ionization equilibrium of acetic acid that initially does not contain any $C_2H_3O_2^-$ ions.)

The initial presence of the $C_2H_3O_2^-$ (aq) in the equilibrium reaction given above acts as a stress on the equilibrium system and causes the equilibrium system to shift to the left. This causes the $HC_2H_3O_2$(aq) to ionize much less that it normally would, resulting in a less acidic solution whose $[H_3O^+]$ ion concentration is practically negligible.

	$HC_2H_3O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:	0.100				≈ 0.00		0.100 M
Change:	- x				+ x		+ x
Equilibrium:	0.100 – x				x		0.100 + x

$$Ka = K_{HC_2H_3O_2} = 1.8 \times 10^{-5} = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x\,(0.100 + x)}{0.100 - x}$$

Assume that "x" is small:

$$1.8 \times 10^{-5} = \frac{x\,(0.100)}{0.100} \qquad x = [H_3O^+] = 1.8 \times 10^{-5}$$

Confirm the assumption that "x" is small by calculating the ratio of "x" and the number it was subtracted from (or added to) in the approximation.
This ratio should be less than 0.05. (or 5%)

$$\frac{1.8 \times 10^{-5}}{0.100} \times 100 = 0.018\ \% < 5\%$$

In this case, the approximation is valid.

$$x = [H_3O^+] = 1.8 \times 10^{-5} \qquad \boxed{\mathbf{pH = -\log [1.8 \times 10^{-5}] = 4.74}}$$

2. **The Henderson-Hasselbach equation**

The Henderson-Hasselbach equation can be used to calculate the pH of any buffer solution from the initial concentrations of the buffer components, as long as “x” is small. Consider a buffer containing the weak acid HA and its conjugate base A^-. The weak acid ionizes as follows:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearrange to solve for $[H_3O^+]$: $\quad [H_3O^+] = Ka\frac{[HA]}{[A^-]}$

To calculate the pH of a buffer solution, take the negative logarithm of both sides of the equation.

$-\log[H_3O^+] = -\log Ka\frac{[HA]}{[A^-]}$ $\qquad$ Rearrange to: $-\log[H_3O^+] = -\log Ka + \log\frac{[A^-]}{[HA]}$

Utilizing both of these equations: $\boxed{-\log[H_3O^+] = pH}$ $\quad$ $\boxed{-\log Ka = pKa}$

The equation then becomes: $\boxed{pH = pKa + \log\frac{[A^-]}{[HA]}}$

The general form of this equation, known as the Henderson-Hasselbach equation, is:

$$\boxed{pH = pKa + \log\frac{[base]}{[acid]}}$$

Note:
The Henderson-Hasselbach equation can be used to calculate the pH of any buffer solution only if the “x is small” approximation is valid (always confirm).

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PROCEDURE

Part I: Preparation of Solutions

1. The molarity of all the reagent solutions is 0.10 M
2. Measure the volumes of sodium hydroxide solution, acetic acid solution and deionized water into six labeled vials, according to the table below (solutions can be dispensed from the burets).
   Note:
   The solutions in Table A and Table B are duplicates, but are labeled differently.

Table A

Solution #	$HC_2H_3O_2(aq)$ 0.10 M (mL)	NaOH(aq) 0.10 M (mL)	$H_2O(l)$ (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

3. Tightly seal each vial with a # 4 rubber stopper.
4. Mix the contents of each vial by ***slowly*** inverting the vials several times.
   Do not spill or allow any leaks. If you do, discard the solution and make a new solution.
5. Place the six vials in the test tube rack.

Part II: Measurement of pH

1. Calibrate your pH meter for buffer pH = 7.01, followed by calibration for buffer pH = 4.01
2. Measure and record the pH of each of the six solutions (1A, 2A, 3A and 1B, 2B and 3B)
3. Turn the pH meter "OFF".
4. Rinse the electrode with 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 = 7.01 buffer solution.
7. Calculate the average pH for each solution (1, 2 and 3)

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Part III: Determination of Buffer Effectiveness

1. **Addition of 0.10 M hydrochloric acid, HCl(aq), to solutions 1A, 2A and 3A.**
    a. Add 2.00 mL of 0.10 M hydrochloric Acid (HCl) to solutions 1A, 2A and 3A, by dispensing it from the buret. The new mixtures contain:
        i. 1A + 2.00 mL of 0.10 M hydrochloric Acid (HCl)
        ii. 2A + 2.00 mL of 0.10 M hydrochloric Acid (HCl)
        iii. 3A + 2.00 mL of 0.10 M hydrochloric Acid (HCl)
    b. Seal the vials containing the solutions.
    c. Mix the contents of each vial by ***slowly*** inverting the vials several times.
    d. Measure and record the pH of each of your three solutions.
    e. Turn the pH meter "OFF".
    f. Rinse the electrode with deionized water and catch the water in a beaker.
    g. Remove the excess water from the electrode with tissue paper.
    h. Store the electrode temporarily in the pH = 7.01 buffer solution.
    i.
2. **Addition of 0.10 M sodium hydroxide, NaOH(aq), to solutions 1B, 2B and 3B.**
    a. Add 2.00 mL of 0.10 M sodium hydroxide to solutions 1B, 2B and 3B by dispensing it from the buret. The new mixtures contain:
        i. 1B + 2.00 mL of 0.10 M sodium hydroxide
        ii. 2B + 2.00 mL of 0.10 M sodium hydroxide
        iii. 3B + 2.00 mL of 0.10 M sodium hydroxide
    b. Seal the vials containing the solutions.
    c. Mix the contents of each vial by ***slowly*** inverting the vials several times.
    d. Measure and record the pH of each of your three solutions.
    e. Turn the pH meter "OFF".
    f. Rinse the electrode with deionized water and catch the water in a beaker.
    g. Remove the excess water from the electrode with tissue paper.

Part IV: Clean-up Instructions:

a. Storing the pH-meter:
    - Make sure the pH meter is turned "OFF".
    - Rinse the electrode with deionized water and catch the water in a beaker.
    - Remove the excess water from the electrode with tissue paper.
    - Place the pH meter in the common plastic bucket containing the pH = 7.01 buffer solution
b. Storing the two buffer solutions:
    - **DO NOT DISCARD THE BUFFER SOLUTIONS**!
    - Keep the plastic test-tubes containing the two buffer solutions (capped) in your locker for the next experiment.

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CALCULATIONS

I. Calculating [Base]/[Acid] Ratios

1. Calculate the average initial pH obtained from two measurements for each solution
   Note:
   Solutions 1A and 1B, 2A and 2B, 3A and 3B respectively, are initially identical.
2. Calculate the [Base]/[Acid] ratio for :
   a. Solution 1
   The [Base]/[Acid] ratio is an **equilibrium calculation**. Use the concentration of the [H^+] obtained from the pH measurement of solution 1 and then use an equilibrium ICE table.
   b. Solutions 2 & 3
   The [Base]/[Acid] ratio is a **stoichiometry calculation** involving a limiting reagent.

II. Determining Buffer Effectiveness

1. Determine the change in pH for solutions 1A, 2A, and 3A, when 2.00 mL of 0.10 M of hydrochloric acid, HCl(aq) 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, NaOH(aq) is added (ΔpH_{base})
3. Calculate the average (ΔpH_{ave}) for the three solutions:

$$(\Delta pH_{ave}) = \frac{(\Delta pH_{acid}) + (\Delta pH_{base})}{2}$$

III. Evaluating Buffer Effectiveness

Compare, evaluate and account for the relative buffer effectiveness of the three solutions by:

1. Evaluate the **relative buffer effectiveness** of the three solutions, based on **experimental evidence** (the average change in pH of the three solutions),
2. Provide the **reason** that accounts for the different buffer effectiveness of the three solutions, based on the respective **[Base]/[Acid] ratios** of the three solutions:
   - Explain why one solution cannot reasonably act as a buffer, and
   - Explain why one solution is a more effective buffer than another.

IV. Error Analysis

1. Calculate the theoretical initial pH of the two buffer solutions:
   a. By using the equilibrium method, and
   b. By using the Henderson-Hasselbach equation.
2. Compare the theoretical calculated pH values of the two buffer solutions with the experimentally determined pH values.

Bibliography:
1. Nivaldo J. Tro, “Chemistry: A Molecular Approach”, Third Edition

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REPORT FORM

NAME: ______________________ Date: ___________ Partner: _________________________

Part I & Part II
Preparation of Solutions, and pH 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 added: _________ mL

pH after addition of sodium hydroxide: _________

Solution 1B + Sodium Hydroxide: pH: _________

Solution 2B + Sodium Hydroxide: pH: _________

Solution 3B + Sodium Hydroxide: pH: _________

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

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:		$\rightleftharpoons$		+	
Change:		$\rightleftharpoons$		+	
Equilibrium:		$\rightleftharpoons$		+	

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

4. Calculate [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 (illustrates the reaction that takes place in vial with solution 2):

_______________ + _______________ → _______________ + $H_2O(l)$

Net Ionic Equation:

_______________ + _______________ → _______________ + $H_2O(l)$

Start:	**mol**	+	**mol**	→	**mol**	+	
End:	**mol**	+	**mol**	→	**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.

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 (illustrates the reaction that takes place in vial with solution 3):

_______________ + _______________ → ______________ + $H_2O(l)$

Net Ionic Equation:

_______________ + _______________ → ______________ + $H_2O(l)$

Start:	**mol**	+	**mol**	→	**mol**	+	▨
End:	**mol**	+	**mol**	→	**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: $$\frac{[C_2H_3O_2^-]}{[H\ C_2H_3O_2]}$$ to the proper amount of significant figures.

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Part III
Determine Buffer Effectiveness

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 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: $\frac{(\Delta pHacid + \Delta pHbase)}{2}$			
$\frac{[BASE]}{[ACID]}$ **Ratio**			

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Questions:

1. Which solution cannot be an effective buffer? _______________
   a. What is the **experimental evidence** that supports your answer above?
   b. What is the **reason** that this solution cannot be an effective buffer?
2. Which solution(s) can be an effective buffer(s)? _______________
   a. What is the **experimental evidence** that supports your answer above?
   b. What is the **reason** that this (these) solution(s) is (are) effective buffer(s) ?
3. Which of the solutions is the *most effective* buffer? _______________
   a. What is the **experimental evidence** that supports your answer above?
   b. What is the **reason** that this solution is the most effective buffer?

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Part IV
Error Analysis

Calculate the theoretical initial pH of solution 2 and solution 3:

Solution 2:

Molarity of [$HC_2H_3O_2$] ____________ M

Molarity of [$C_2H_3O_2^-$] ____________ M

a. **The Equilibrium Method (use the approximation method)**

Equation:

Initial:

Change:

Equilibrium:

Show Calculations below:

[H_30^+] =

(Check if the approximation is valid. Show calculations below)

pH =

b. **The Henderson-Hasselbach equation**

Show calculations below:

pH =

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Solution 3:

Molarity of [$HC_2H_3O_2$] ____________ M

Molarity of [$C_2H_3O_2^-$] ____________ M

a. **The Equilibrium Method (use the approximation method)**

Equation:

Initial:

Change:

Equilibrium:

Show Calculations below:

[H_30^+] =

(Check if the approximation is valid. Show calculations below)

pH =

a. **The Henderson-Hasselbach equation**

Show calculations below:

pH =

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Summary

Calculated Values

Buffer Solutions	pH calculated by Equilibrium Method	pH calculated by Henderson-Hasselbach equation	Experimentally measured pH values	% Error
Solution 2				
Solution 3				