

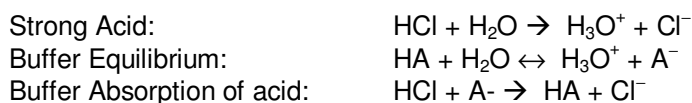
EXPERIMENT 6

Buffer Effects

Introduction

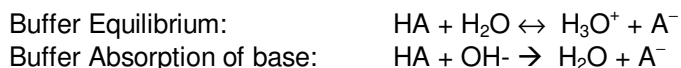
Buffers are solutions that contain an acid and its conjugate base that are designed to resist pH changes. This is important in biological systems to maintain proper blood chemistry and in the environment to help minimize effects of acid rain. A buffer works by using the equilibrium between the acid and its conjugate base to minimize the effect that the addition of a small amount of additional acid or base has on the pH.

Buffers work chemically by shifting the equilibrium between the weak acid and the conjugate base in the following manner. If a strong acid is added, it uses up some of the conjugate base and produces more of the weak acid. The pH may shift slightly downward due to the small amount of dissociation of the weak acid, but it is much less of a shift than would be seen by adding the strong acid directly to water, where each mole of acid added adds directly to the $[H_3O^+]$.

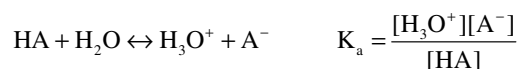


Since no H_3O^+ is produced directly by the addition of the strong acid, there is minimal shift in pH.

Buffers offer similar protection against changes in pH due to the addition of a strong base. In this case, the weak acid absorbs the base

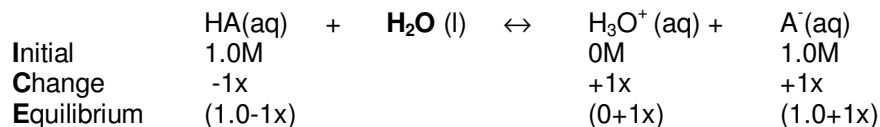


Thus, in a similar manner to the addition of acid, no explicit change in OH^- or H_3O^+ is seen, so there is minimal change in the pH. The pH is governed only by the equilibrium constant, K_a , not directly by the addition of base or acid as would be seen in a water solution.

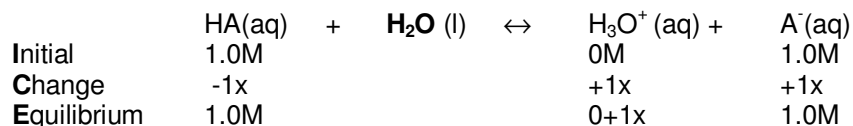


The Henderson-Hasselbalch Equation

There are some restrictions in the preparation of a buffer. Unlike a weak acid equilibrium, where an ICE table is needed to determine the degree of equilibrium concentrations of the weak base, the weak base is added directly to the solution, so the concentrations of HA and A^- in the initial line in the ICE table is already accounted for.



To fully absorb any strong acid or base that is added, the concentrations of the conjugate acid and base must be high enough that the amount that dissociates, x , is negligible in the equilibrium concentrations of both HA and A^- . A rule of thumb is that you must have the acid and base concentrations at least 100x greater than the K_a for the dissociation to become negligible.



Once you have satisfied this criteria, then you can use the Henderson-Hasselbalch equation instead of an ICE table to solve buffer problems. This equation uses the same information given in the equilibrium line in the ICE

table, but is much quicker, especially when multiple pH calculations must be made. The Henderson-Hasselbalch equation is as follows:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

It is a rearrangement of the K_a expression in terms of pH instead of $[\text{H}_3\text{O}^+]$ and can be used to very quickly determine the concentration of buffer components needed to provide a particular pH for a system. It can also be used to determine the ratio of the weak acid and its conjugate base from the pH of the solution.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{pK}_a = -\log \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = -\log[\text{H}_3\text{O}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Finally, because the ratio of the conjugate base to the acid is constant, there are no changes in pH seen in a buffer when it is diluted, as there is no explicit change in the $[\text{H}_3\text{O}^+]$. If a small amount of strong acid is added, it removes some of the conjugate base and increases the acid by the same amount. These changes are made in the actual concentrations of HA and A^- in the Henderson-Hasselbalch equation before the recalculation of pH is made. More explicit instructions on working with the Henderson-Hasselbalch equation and ICE tables are given in the calculations section of the lab.

In Your Lab...

In this experiment, you will compare the pH of differing concentrations of both strong and weak acid solutions to that of an acetic acid buffer. You will then study the pH changes that result when adding small amounts of a strong acid and base to a buffer and directly to an unbuffered (water) solution. You will also learn how to perform the calculations necessary when working with buffers and to calculate the changes in pH that result when the buffer equilibrium is shifted due to the addition of acid and base.

Chemical Hazards

NFPA Health Recommendations For All Chemicals in this Lab

ORAL EXPOSURE

If swallowed, wash out mouth with water provided person is conscious. Call rescue. Do not induce vomiting.

DERMAL EXPOSURE

In case of skin contact, flush with water for at least 15 minutes. Remove contaminated clothing and shoes.

EYE EXPOSURE

In case of contact with eyes, flush with water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Call rescue.

6.0M Acetic Acid

NFPA RATING: HEALTH: 3 FLAMMABILITY: 2 REACTIVITY: 0

0.10M Acetic Acid

NFPA RATING: HEALTH: 1 FLAMMABILITY: 0 REACTIVITY: 0

0.10M $\text{NaC}_2\text{H}_3\text{O}_2$ Solution

NFPA RATING: HEALTH: 1 FLAMMABILITY: 0 REACTIVITY: 1

pH 7 Buffer Solution

NFPA RATING: HEALTH: 0 FLAMMABILITY: 0 REACTIVITY: 0

0.10M Hydrochloric Acid

NFPA RATING: HEALTH: 0 FLAMMABILITY: 0 REACTIVITY: 0

0.10M Sodium Hydroxide Solution

NFPA RATING: HEALTH: 0 FLAMMABILITY: 0 REACTIVITY: 1

Laboratory Equipment Procedures

Using the MeasureNet System for pH Measurements

The pH meter should already be connected to the MeasureNet system at the start of lab. Follow the instructions below to set up for pH measurements.

Setting up system for pH measurements

1. Press the On/Off button to turn on power to the MeasureNet station.
2. Press Main Menu.
3. Press F3- pH/mV.
4. Press F1- pH v TIME.
5. Press DISPLAY.
6. If your display does not read between 6.95 and 7.05, follow the instructions below to calibrate the electrode.

Electrode Calibration

1. Remove cap and pH electrode from the storage bottle.
2. Insert the pH electrode into the storage bottle and screw on the lid.
3. Press CALIBRATE on the MeasureNet station.
4. Ask the TA for room temperature and enter the temperature into the MeasureNet station.
5. Press ENTER.
6. Enter 7 for the pH of the buffer.
7. Press ENTER.
8. When the value stops changing, press ENTER.
9. Press F1.
10. Press DISPLAY to take pH readings.
11. Rinse off the electrode with distilled water and wipe with a kimwipe before returning it to the storage bottle or taking pH measurements.

Using the pH electrode

1. Rinse your electrode with distilled water and wipe off electrode with a kimwipe both before and after each reading. Be especially careful not to bump the glass bulb on the bottom. It is very fragile and the pH electrode is expensive. **You will be charged for the electrode if it is broken.**
2. Return the electrode to the storage bottle between readings and when you are finished with the experiment. **Be careful not to push down too hard on the electrode when returning it to the storage bottle.**
3. Press ON/OFF on the MeasureNet station when you are done with your experiment.
4. Be sure the pH electrode is upright in the storage bottle before leaving the lab.
5. Be sure that the bulb on the pH meter is covered with solution when the electrode is returned to the storage bottle.

Laboratory Procedure

Your TA must sign your data before leaving lab or you will not receive credit for attending the lab.
Both partners must assist with the solution preparation.
Have 1 partner prepare the solutions for part 1 and the other prepare the solutions for part 2.
Be sure to rinse the pH meter with distilled water between readings

Part 1: pH of a Strong Acid

1. Obtain exactly 5.0mL of 0.10M HCl in a 25 mL graduated cylinder.
2. Fill your wash bottle with distilled water and use your wash bottle to fill the graduated cylinder to exactly 25.0 mL. Pour the solution into a 30 mL beaker.
3. Use your wash bottle to rinse out the graduated cylinder into the 400 mL beaker used as a temporary waste container and set the graduated cylinder aside until the next dilution is made.
4. Calibrate your pH meter with the pH 7 buffer according to the instructions given to you in the equipment procedures section.
5. Once calibrated, rinse off the bulb of the pH meter with distilled water and insert the pH meter into the beaker containing the diluted acid.
6. Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the value in your lab notebook. Record all decimal places on the pH meter.
7. Rinse the pH meter with distilled water and return it to the buffer solution.
8. Transfer exactly 5.0 mL of the diluted solution from your 30 mL beaker to your 25mL graduated cylinder.
9. Pour the remaining solution in the 30 mL beaker into a 400 mL waste beaker. Rinse out the 30 mL beaker with distilled water from your wash bottle and set aside for the next pH reading.
10. Use your wash bottle to fill the graduated cylinder containing the acid solution to exactly 25.0 mL.
11. Pour the solution from your graduated cylinder into the 30 mL beaker and record the pH.
12. Rinse your pH meter with distilled water and return it to the buffer solution.
13. Repeat steps 8-13 two more times for a total of 4 different dilutions and pH measurements.
14. When finished, pour remaining solution into waste beaker and rinse all equipment with distilled water.

Part 2: pH of a Weak Acid

1. Repeat the steps in part 1 using 0.10 M acetic acid instead of the HCl.

Part 3: Buffer Effects

1. Obtain exactly 5.0 mL of 0.10M acetic acid in a 25 mL graduated cylinder. Obtain exactly 5.0 mL of 0.10M sodium acetate solution in a second 25 mL graduated cylinder.
2. Pour the acetic acid into the graduated cylinder containing the sodium acetate. Use your wash bottle to fill the graduated cylinder to exactly 25.0 mL. Pour the buffer solution into a 30 mL beaker.
3. Check the calibration on the pH meter. Once calibrated, rinse off the bulb of the pH meter with distilled water and insert the pH meter into the beaker containing the buffer solution.

4. Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the value in your lab notebook. Record all decimal places on the pH meter.
5. Rinse the pH meter with distilled water and return it to the buffer solution.
6. Obtain exactly 1 mL 0.10M HCl in a 10 mL graduated cylinder. Pour the 1 mL of HCl into the buffer solution.
7. Rinse the pH meter with distilled water and insert it into the buffer solution. Use it to stir the solution gently before recording the pH of the buffer solution containing the HCl.
8. Pour the solution into the waste beaker when finished and rinse the beaker with distilled water before continuing.
9. Repeat steps 1-8 substituting 0.10M NaOH for the 0.10M HCl.
10. Repeat the entire procedure for part 3 substituting 25 mL of water for the buffer solution.
11. When finished, pour the solution from the waste beaker into the waste container and rinse all equipment with distilled water before returning it to your drawer.

Laboratory Data

Record the data shown in pen.

Include the **signed** copy of this data when you turn in your lab report.

Include the correct number of significant figures for each measurement.

Concentration Data

Concentration of Stock HCl Solution _____

Concentration of Stock Acetic Acid Solution _____

Concentration of Stock Sodium Acetate Solution _____

Concentration of Stock NaOH Solution _____

Tables 1 & 2: pH of Strong Acid Solutions and pH of Weak Acid Solutions (make 2 tables as shown below)

Dilution Number	pH
1	
2	
3	
4	

Table 3: Buffer Effects

Dilution Number	pH
Original Buffer	
Water	
Buffer with HCl	
Water with HCl	
Buffer with NaOH	
Water with NaOH	

Calculations

Remember to show 1 example of each calculation either handwritten or typed on a separate sheet.

Include correct significant figures and units

Units can be included in column or row title as demonstrated in tables below

Brackets, [xx], can be used to designate concentration in molarity.

Include a typed copy of these results in a table with your lab report.

Part 1

Calculating the Molarity of the Diluted HCl Solutions

Each dilution was made by using 5.0 mL of acid and diluting it to 25.0 mL. Use the following equation and solve for the new molarity. Each subsequent concentration, M_1 , is the molarity found from the previous concentration for M_2 .

$$M_1V_1=M_2V_2$$

M_1 = Concentration of HCl from the stock solution.

V_1 = 5.0 mL, (the amount of stock solution used)

V_2 = 25.0 mL, (the amount of the final solution)

Solve for M_2 = Concentration of the diluted HCl solution (use this value as M_1 in the next dilution)

Theoretical Concentration of $[H_3O^+]$ for HCl

Strong acids and bases fully dissociate in water, so the molarity of the $[H_3O^+]$ in the diluted solutions is equal to the calculated concentration of the diluted HCl solutions.

$$[H_3O^+] = M_2 \text{ for each of the solutions}$$

Theoretical pH for HCl Solutions

Find the theoretical pH of the HCl solutions using the following equation.

$$pH = -\log [H_3O^+]$$

Part 2

Calculating the Molarity of the Diluted Acetic Acid Solutions

Each dilution was made by using 5.0 mL of acid and diluting it to 25.0 mL. Use the following equation and solve for the new molarity. Each subsequent concentration, M_1 , is the molarity found from the previous concentration for M_2 .

$$M_1V_1=M_2V_2$$

M_1 = Concentration of acetic acid from the stock solution.

V_1 = 5.0 mL, (the amount of stock solution used)

V_2 = 25.0 mL, (the amount of the final solution)

Solve for M_2 = Concentration of diluted acetic acid for each of the 4 dilutions.

(Use the value of M_2 as M_1 in the next dilution)

Theoretical Concentration of $[H_3O^+]$ for Acetic Acid Solutions

Unlike strong acids that fully dissociate, weak acids do not dissociate fully, so an ICE table must be used to calculate the $[H_3O^+]$. However, the amount of acetic acid that dissociates below concentrations of 0.10M is negligible, so you can assume that the initial concentration of acetic acid in the ice table below, M_2 from the previous calculations is the same as the equilibrium concentration.

Set up an ICE table for each concentration of the acetic acid. Use the values calculated for M_2 in the previous section for the initial and equilibrium value of the concentration of the acetic acid, HA. You will need 1 ICE table for each acetic acid concentration.

	HA(aq)	+	H ₂ O (l)	↔	H ₃ O ⁺ (aq)	+	A ⁻ (aq)
Initial	M_2				0M		0M
Change	x				x		x
Equilibrium	M_2				x		x

Use the equation below to solve for x which will be the $[H_3O^+]$ for the acetic acid.

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[x][x]}{[M_2]}$$

Theoretical pH for Acetic Acid Solutions

Find the theoretical pH of the acetic acid solutions using the following equation.

$$pH = -\log [H_3O^+]$$

Part 3

Calculating the Molarity of the Acetic Acid and Acetate Ion in the Buffer Solution

The dilution was made by using 5.0 mL each of acetic acid and sodium acetate and diluting the solution to a total volume of 25.0 mL. The variable, M_1 , in the equation corresponds to the concentration of the stock solution of acetic acid or sodium acetate listed on the bottle. Use the following equation and solve for the diluted molarity for the acetic acid, M_2 acetic acid. Then repeat the calculation for the sodium acetate, M_2 , sodium acetate.

$$M_1V_1 = M_2V_2$$

Theoretical pH of the Buffer Solution before the Addition of HCl or NaOH

Use the Henderson-Hasselbalch equation to calculate the pH of the buffer solution. This equation can be used as long as the amount of dissociation of the acid to $[H_3O^+]$ is considered negligible as it was for the solutions in part 2 of the experiment.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = -\log(1.8 \times 10^{-5}) + \log \frac{[M_2 \text{ acetate ion}]}{[M_2 \text{ acetic acid}]}$$

Concentration of Diluted Acetic Acid and Acetate Ion after the Addition of 1 mL of HCl or NaOH

The addition of 1 mL of any solution to the buffer increases the total volume of the buffer and slightly dilutes the buffer acid and base concentrations. Use the equation, $M_1V_1=M_2V_2$ to find the new concentration of acetic acid and sodium acetate in the buffer.

M_1 is the molarity of the weak acid or base calculated in part 2 for the buffer

V_1 is 25.0 mL: volume of the buffer before the addition of the HCl or NaOH

V_2 is 26.0 mL: volume accounts for the addition of 1 mL of HCl or NaOH in the total volume.

Concentration of Diluted HCl or NaOH in the Buffer Solution

The addition of 1 mL of HCl or NaOH to the buffer increases the total volume of the solution and dilutes the concentration of the HCl or NaOH added. Use the equation, $M_1V_1=M_2V_2$ to find the concentrations of the diluted HCl and NaOH.

M_1 is the molarity of the HCl or NaOH from the stock solution.

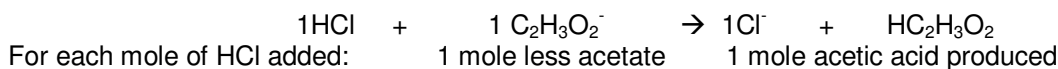
V_1 is 1.0 mL: volume of the HCl or NaOH solution

V_2 is 26.0 mL: total volume of the solution = 25 mL buffer + 1 mL HCl or NaOH

Solve for M_2 , the molarity of the diluted HCl or NaOH

Equilibrium Concentrations of Acetic Acid and Acetate Ion after the addition of HCl

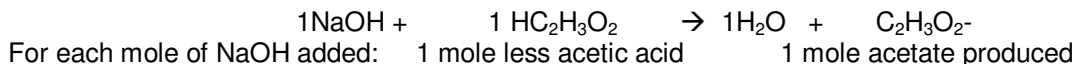
Each mole of HCl added to the buffer solution uses up 1 mole of the acetate ion and produces 1 mole of acetic acid. Calculate the equilibrium value of the base by subtracting the diluted HCl concentration from the diluted acetate concentration in the buffer. Calculate the concentration of the weak acid to be used in the Henderson-Hasselbach equation by adding the concentration of the HCl to the concentration of the concentration of the diluted acetic acid in the buffer.



$$\begin{array}{l} \text{Equilibrium value of } M_{\text{C}_2\text{H}_3\text{O}_2^-} = \text{Buffer } M_{\text{C}_2\text{H}_3\text{O}_2^-} - M_{\text{HCl}} \\ \text{Equilibrium value of } M_{\text{HC}_2\text{H}_3\text{O}_2} = \text{Buffer } M_{\text{HC}_2\text{H}_3\text{O}_2} + M_{\text{HCl}} \end{array}$$

Equilibrium Concentrations of Acetic Acid and Acetate Ion after the addition of NaOH

Each mole of NaOH added to the buffer solution uses up 1 mole of the acetic acid and produces 1 mole of acetate ion. Calculate the equilibrium value of the acetic acid by subtracting the diluted NaOH concentration from the diluted acetic acid concentration in the buffer. Calculate the equilibrium value of the base by adding the diluted NaOH concentration to the concentration of the acetate.



$$\begin{array}{l} \text{Equilibrium value of } M_{\text{C}_2\text{H}_3\text{O}_2^-} = \text{Buffer } M_{\text{C}_2\text{H}_3\text{O}_2^-} + M_{\text{NaOH}} \\ \text{Equilibrium value of } M_{\text{HC}_2\text{H}_3\text{O}_2} = \text{Buffer } M_{\text{HC}_2\text{H}_3\text{O}_2} - M_{\text{NaOH}} \end{array}$$

Theoretical pH of the Buffer Solution after the Addition of Acid or Base

Use the Henderson-Hasselbach equation to calculate the pH of the buffer solution after the addition of HCl and NaOH by substituting the equilibrium values of acetic acid and acetate ion calculated in the previous sections. The pH should decrease slightly to account for the addition of the HCl and increase slightly for the addition of the NaOH when compared to the pH of the original buffer.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = -\log(1.8 \times 10^{-5}) + \log \frac{[\text{M}_2 \text{ acetate}]}{[\text{M}_2 \text{ acetic acid}]}$$

Concentration of Diluted HCl or NaOH in the Water

The addition of 1 mL of HCl or NaOH to the water increases the total volume of the solution and dilutes the concentration of the HCl or NaOH added. Use the equation, $M_1V_1=M_2V_2$ to find the concentrations of the diluted HCl and NaOH solutions.

M_1 is the molarity of the HCl or NaOH from the stock solution.

V_1 is 1.0 mL: volume of the HCl or NaOH solution

V_2 is 26.0 mL: total volume of the solution = 25 mL water + 1 mL HCl or NaOH

Solve for M_2 , the molarity of the diluted HCl or NaOH

Theoretical Concentration of $[H_3O^+]$ for HCl in Water

Strong acids and bases fully dissociate in water, so the molarity of the $[H_3O^+]$ in the diluted solutions is equal to the calculated concentration of the diluted HCl solutions.

$$[H_3O^+] = M_2 \text{ for each of the solutions}$$

Theoretical pH for HCl in Water

Find the theoretical pH of the HCl solutions using the following equation.

$$pH = -\log [H_3O^+]$$

Theoretical Concentration of $[H_3O^+]$ for NaOH in Water

Strong acids and bases fully dissociate in water, so the molarity of the $[OH^-]$ in the water after the dilution is the same as the diluted concentration of the NaOH. The $[H_3O^+]$ in the diluted solutions is related to the molarity of the $[OH^-]$ in the water through the K_w . Rearrange the following equation below to calculate the $[H_3O^+]$ from the concentration of the diluted NaOH solution and the K_w .

$$K_w = 1 \times 10^{-14} = [H_3O^+][OH^-].$$

Theoretical pH for HCl or NaOH in Water

Find the theoretical pH of the water solutions with added acid or base using the following equation.

$$pH = -\log [H_3O^+]$$

Laboratory Results

Create the following tables in your lab report

Include the correct number of significant figures for each measurement.

Part 1

Table 1: Comparison of Theoretical pH to Experimental pH for a Strong Acid

Dilution Number	1	2	3	4
$M_{\text{dil. HCl}}$				
$[\text{H}_3\text{O}^+]$				
Theoretical pH				
Experimental pH				

Part 2

Table 2: Comparison of Theoretical pH to Experimental pH for a Weak Acid

Dilution Number	1	2	3	4
$M_{\text{dil. acid, (M}_2\text{)}}$				
$[\text{H}_3\text{O}^+]$				
Theoretical pH				
Experimental pH				

Part 3

Table 3

Concentration of the Acetic Acid in the Buffer Solution _____ M

Concentration of the Acetate Ion in the Buffer Solution _____ M

Theoretical pH of the Buffer Solution before the Addition of Acid or Base _____

Experimental pH of the Buffer Solution before the Addition of Acid or Base _____

Concentration of Diluted Acetic Acid after the Addition of 1 mL of HCl _____ M

Concentration of Diluted Acetate Ion after the Addition of 1 mL of HCl _____ M

Concentration of Diluted HCl _____ M

Equilibrium Concentrations of Acetic Acid after the addition of HCl _____ M

Equilibrium Concentrations of Acetate Ion after the addition of HCl _____ M

Theoretical pH of the Buffer Solution after the Addition of HCl _____

Experimental pH of the Buffer Solution after the Addition of HCl _____

Concentration of Diluted Acetic Acid After the Addition of 1 mL of NaOH _____ M

Concentration of Diluted Acetate Ion After the Addition of 1 mL of NaOH _____ M

Concentration of Diluted NaOH _____ M

Equilibrium Concentrations of Acetic Acid after the addition of NaOH _____ M

Equilibrium Concentrations of Acetate Ion after the addition of NaOH _____ M

Theoretical pH of the Buffer Solution after the Addition of NaOH _____

Experimental pH of the Buffer Solution after the Addition of NaOH _____

Concentration of Diluted HCl _____ M

Concentration of the $[\text{H}_3\text{O}^+]$ in the Acidic Water Solution _____ M

Theoretical pH of the Water Solution after the Addition of HCl _____

Experimental pH of the Water Solution after the Addition of HCl _____

Concentration of Diluted NaOH _____ M

Concentration of the $[\text{H}_3\text{O}^+]$ in the Basic Water Solution _____ M

Theoretical pH of the Water Solution after the Addition of NaOH _____

Experimental pH of the Water Solution after the Addition of NaOH _____

Discussion Questions

You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.

1. Note the large pH change that resulted when a dilution was made to the strong acid solution. Why was a large pH change not noticed when a weak acid was used?
2. Make a table of the percent errors for the pH measurements in Table 3 of your results. Are you confident that your pH measurements are accurate? Briefly explain why or why not. If not, explain where error could have resulted in your experiment.

$$\%Error = \frac{|Theoretical\ pH - Experimental\ pH|}{Theoretical\ pH} \times 100$$

3. Compare the change in pH due to the addition of HCl to the buffer solution to the pH change seen when HCl was directly added to water. Briefly explain why there is such a large pH change in the water, but little pH change in the buffer solution.
4. What would be the result if you added an amount of HCl that exceeded the amount of acetate ion in the buffer solution? Explain how you would calculate the pH of the solution under these conditions.
5. The increase in pH noted upon adding the NaOH to the buffer solution should have been approximately equal to the decrease in pH recorded when adding the HCl to the buffer solution. Explain why this would make sense using the Henderson-Hasselbalch equation.