<u>EXPERIMENT C2: BUFFERS & TITRATION</u>

Learning Outcomes
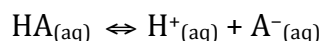
Upon completion of this lab, the student will be able to:

1) Prepare a buffer solution at a given pH and concentration.
2) Analyze the titration curve for the titration of a:
    a. Weak acid with a strong base
    b. Weak base with a strong acid

Introduction

A buffer is a solution that resists changes to pH when a strong acid or base is added to the solution. There are two combinations of solutions that may result in a buffer. 1) a solution prepared by combining a weak acid and a salt of its conjugate base or 2) a solution prepared by combining a weak base and a salt of its conjugate acid.

In a buffer solution, the weak acid (or the weak base) is in equilibrium with its conjugate base (or acid). Assume that the formula of the weak acid is HA and the conjugate base is A^-; in a buffer made by combining HA and A^- the following equilibrium will be established:

$$HA_{(aq)} \Leftrightarrow H^+_{(aq)} + A^-_{(aq)}$$

The pH of the above buffer can be calculated by manipulating the equilibrium constant for the equation given above in the following manner.

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

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

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

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

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

The above equation is referred to as the **Henderson Hasselbach equation** and is (only) used to calculate the **pH of a buffer**. The pK_a in the equation is that of the

weak acid found in the buffer solution. [HA] and [A⁻] are respectively, the concentrations of the weak acid and the conjugate base.

The exact same equation can also be used to calculate the pH of a buffer made from a combination of a weak base and its conjugate acid. In this instance, the pK_a would be that of the conjugate acid in the solution.

When preparing a buffer, it is important to choose an acid/conjugate base pair such that the desired pH of the buffer is within about one unit of the pK_a of the acid in the buffer. This is done in order to maximize the buffer capacity- an indicator of the extent to which the buffer is able to resist changes to pH upon addition of a strong acid or base.

In order to prepare a buffer the following pieces of information are essential:
1. The desired pH
2. The total concentration of the ions in the buffer
3. The required volume
4. The identity of the ions in the buffer

Buffer Preparation

For instance, assume that the following buffer is to be prepared: 100.0 mL of 0.10 M phosphate buffer at a pH of 7.40

100.0 mL is the total volume of the buffer and 0.10 M is the total concentration of the phosphate ions that should be found in the buffer. In order to determine the identity of the phosphate ions that would be required to prepare this buffer, one must consider the various forms of phosphate: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}.

STEP 1: Determine the acid/conjugate base pairs of these different forms of phosphate and use the table of equilibrium constant values to arrive at the pK_a of each acid. This information is provided in Table 1 below.

ACID	CONJUGATE BASE	pK$_a$
H_3PO_4	$H_2PO_4^-$	2.16
$H_2PO_4^-$	HPO_4^{2-}	7.21
HPO_4^{2-}	PO_4^{3-}	12.32

Table 1

From Table 1, it is apparent that the phosphate acid with a pK_a within one unit of the pH of the desired buffer is $H_2PO_4^-$.

Therefore the best combination of weak acid and conjugate base for the buffer would be:

Weak acid = A = $H_2PO_4^-$ (dihydrogen phosphate)

Conjugate base = B = HPO_4^{2-} (monohydrogen phosphate)

STEP 2: Now that the identity of the phosphate ions in the buffer has been established, the next task in hand is to determine the molar concentrations of these ions in the buffer.

Keep in mind that the total concentration of the phosphates in the desired buffer is given to be 0.10 M. This implies that:

[A] + [B] = 0.10   **Equation 1**

In order to determine the exact concentrations of A and B, it is now necessary to use the Henderson Hasselbach equation.

$$pH = pK_a + \log\left(\frac{[B]}{[A]}\right)$$ **Equation 2**

In equation 2, for the present situation, pH = 7.40 and pK_a = 7.21. Substitute these values in equation 2:

$$7.40 = 7.21 + \log\left(\frac{[B]}{[A]}\right)$$ **Equation 3**

Manipulation of equation 3 results in the following:

[B] = 1.55[A]   **Equation 4**

Substitute equation 4 in equation 1 and solve for [A] and [B].

[A] = 0.039 M

[B] = 0.061 M

STEP 3: Once the molar concentration of the acid and conjugate base pair has been determined, determine the grams or mL of the acid and conjugate base needed for the buffer.

In the laboratory, the weak acid to be used in this buffer, $H_2PO_4^-$, is likely found as a solid in its sodium salt form: NaH_2PO_4 and likewise the conjugate base HPO_4^{2-}, is likely d=found as a solid in its sodium salt form: Na_2HPO_4. So, the exact mass of the acid and conjugate base needed to prepare 100.0 mL of the buffer must be calculated as follows:

$$\text{Grams of NaH}_2\text{PO}_4 = 0.039\frac{moles}{L} \times 0.1000L \times 120\frac{grams}{mole} = 0.47 grams$$

$$\text{Grams of Na}_2\text{HPO}_4 = 0.061\frac{moles}{L} \times 0.1000L \times 142\frac{grams}{mole} = 0.87 grams$$

STEP 4: Using the information from steps 1, 2, and 3, the desired buffer can be prepared as follows:

"Combine 0.47 grams of NaH_2PO_4 and 0.87 grams of Na_2HPO_4 in a 100-mL volumetric flask. Add a small amount of deionized water to completely dissolve the solids and add water to the graduation mark of the volumetric flask. Carefully mix the contents of the flask and measure the pH to confirm that it is indeed 7.40."

Effect of acid on the pH of a buffer

When a strong acid is added to a buffer, the conjugate base present in the buffer neutralizes it. The equilibrium between the weak acid and the conjugate base of the buffer is shifted. The amount of conjugate base in the buffer decreases and consequently the amount of weak acid increases. This leads to a decrease in the overall pH of the buffer. The decrease in the pH would be far more pronounced if the solution were not a buffer, i.e., if no conjugate base was available to neutralize the added acid.

The following calculation demonstrates the effect of adding a strong acid such as hydrochloric acid on the pH of a buffer solution.

Example: Calculate the pH of the buffer prepared earlier (100.0 mL of 0.10 M phosphate buffer at pH 7.40) after the addition of 1.00 mL of 1.0 M HCl.

NOTE: The HCl will react with the conjugate base in the buffer (HPO_4^{2-}). Therefore the new concentrations of the weak acid and conjugate base in the buffer must be calculated.

Millimoles of weak acid ($H_2PO_4^-$) present initially = $100.0 mL \times 0.039\frac{moles}{L} = 3.9$

Millimoles of conjugate base (HPO_4^{2-}) present initially = $100.0 mL \times 0.061\frac{moles}{L} = 6.1$

Millimoles of HCl (H^+) added to the buffer = $1.00 mL \times 1.0\frac{moles}{L} = 1.0$

Reaction: $H^+_{(aq)} + HPO_4^{2-}$ ➜ $H_2PO_4^-$ (NOTE: The H+ here is from HCl)

Initial millimoles:	1.0	6.1	3.9
Reaction:	-1.0	-1.0	+1.0
Amount left:	0	5.1	4.9
Molarity:		$\dfrac{5.1}{101.0}$	$\dfrac{4.9}{101.0}$

Therefore: pH = $7.21 + \log\left(\dfrac{5.1/101.0}{4.9/101.0}\right)$ = 7.23

The pH of the buffer changed from 7.40 to 7.23 upon addition of 1.0 mL of a strong acid such as 1.0 M HCl.

Effect of base on the pH of a buffer

When a strong base is added to a buffer, the weak acid present in the buffer neutralizes it. The equilibrium between the weak acid and the conjugate base of the buffer is shifted. The amount of conjugate base in the buffer increases and consequently the amount of weak acid decreases. This leads to an increase in the overall pH of the buffer. The increase in the pH would be far more pronounced if the solution were not a buffer, i.e., if no weak acid was available to neutralize the added base.

The following calculation demonstrates the effect of adding a strong base such as sodium hydroxide on the pH of a buffer solution.
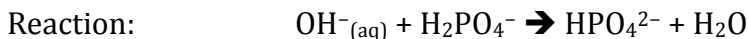
Example: Calculate the pH of the buffer prepared earlier (100.0 mL of 0.10 M phosphate buffer at pH 7.40) after the addition of 1.00 mL of 1.0 M NaOH.

NOTE: The NaOH will react with the weak acid in the buffer ($H_2PO_4^-$). Therefore the new concentrations of the weak acid and conjugate base in the buffer must be calculated.

Millimoles of weak acid ($H_2PO_4^-$) present initially = $100.0 mL \times 0.039 \dfrac{moles}{L} = 3.9$

Millimoles of conjugate base (HPO_4^{2-}) present initially = $100.0 mL \times 0.061 \dfrac{moles}{L} = 6.1$

Millimoles of NaOH (OH^-) added to the buffer = $1.00 mL \times 1.0 \dfrac{moles}{L} = 1.0$

Reaction: $OH^-_{(aq)} + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$

Initial millimoles: 1.0   3.9   6.1
Reaction: -1.0   -1.0   +1.0
Amount left: 0   2.9   7.1
Concentrations: $\dfrac{2.9}{101.0}$ $\dfrac{7.1}{101.0}$

Therefore: $pH = 7.21 + \log\left(\dfrac{7.1/101.0}{2.9/101.0}\right) = 7.60$

The pH of the buffer changed from 7.40 to 7.60 upon addition of 1.0 mL of a strong base such as 1.0 M NaOH.

Titration

The titration of a weak acid with a strong base will be examined theoretically in this section. The calculations will then be used to plot a titration curve. The titration curve provides several useful pieces of information and can often be plotted qualitatively.

Example: Calculate the pH during the titration of 10.0 mL of 0.10 M acetic acid ($K_a = 1.8 \times 10^{-5}$) after the addition of the following volumes (in mL) of 0.10 M sodium hydroxide: a) 0.0 b) 2.5 c) 5.0 d) 7.5 e) 10.0 and f) 11.0

In the following calculations, acetic acid (CH_3COOH), a weak monoprotic acid will be written as HA.

a) **0.0 mL NaOH added**

Since the titration has not begun yet at this point, the pH of the solution is simply the pH of 0.10 M acetic acid.

	$HA_{(aq)}$ $\Leftrightarrow$	$H^+_{(aq)}$ +	$A^-_{(aq)}$
Initial concentration	0.10	~0	0
Change	-x	x	x
Equilibrium concentration	0.10 – x	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.1 - x} \approx \frac{x^2}{0.1}$$

$$x = 0.00134 = [H^+]$$

$$pH = 2.87$$

b) 2.5 mL NaOH added

The OH⁻ from the added NaOH will react with the acetic acid.

Millimoles of HA present = 10.0 mL × 0.10 M = 1.0

Millimoles of OH⁻ added = 2.5 mL × 0.10 M = 0.25

	$HA_{(aq)}$ +	$OH^-_{(aq)}$ →	$A^-_{(aq)}$ +	$H_2O_{(l)}$
Initial milimoles	1.0	0.25		
Amount reacted	-0.25	-0.25	0.25	
Final millimoles	0.75	0	0.25	
Concentrations	$\dfrac{0.75}{12.5}$		$\dfrac{0.25}{12.5}$	

At this point in the titration, since acetic acid (HA) is present in combination with its conjugate base (A⁻), the solution is a buffer. The pH of the solution may therefore be calculated using the Henderson Hasselbach equation.

$$pH = 4.74 + \log\left(\frac{0.25/12.5}{0.75/12.5}\right) = 4.26$$

c) 5.0 mL NaOH added

The OH⁻ from the added NaOH will react with the acetic acid.

Millimoles of HA present = 10.0 mL × 0.10 M = 1.0

Millimoles of OH⁻ added = 5.0 mL × 0.10 M = 0.50

	$HA_{(aq)}$ +	$OH^-_{(aq)}$ →	$A^-_{(aq)}$ +	$H_2O_{(l)}$
Initial milimoles	1.0	0.5		
Amount reacted	-0.5	-0.5	0.5	

Final millimoles	0.5	0	0.5
Concentrations	$\dfrac{0.5}{15.0}$		$\dfrac{0.5}{15.0}$

At this point in the titration, since acetic acid (HA) is present in combination with its conjugate base (A⁻), the solution is a buffer. The pH of the solution may therefore be calculated using the Henderson Hasselbach equation.

$$pH = 4.74 + \log\left(\frac{0.5/15.0}{0.5/15.0}\right) = 4.74$$

NOTE: Here, the amount of NaOH added is exactly one half of the amount of acetic acid present. This point in the titration is referred to as the **HALF EQUIVALENCE POINT**. The pH, as shown above, at the half equivalent point in these types of titrations is always equal to the pK_a of the weak acid.

d) 7.5 mL NaOH added

The OH^- from the added NaOH will react with the acetic acid.

Millimoles of HA present = 10.0 mL × 0.10 M = 1.0

Millimoles of OH^- added = 7.5 mL × 0.10 M = 0.75

	$HA_{(aq)}$ +	$OH^-_{(aq)}$ →	$A^-_{(aq)}$ +	$H_2O_{(l)}$
Initial milimoles	1.0	0.75		
Amount reacted	-0.75	-0.75	0.75	
Final millimoles	0.25	0	0.75	
Concentrations	$\dfrac{0.25}{17.5}$		$\dfrac{0.75}{17.5}$	

At this point in the titration, since acetic acid (HA) is present in combination with its conjugate base (A⁻), the solution is a buffer. The pH of the solution may therefore be calculated using the Henderson Hasselbach equation.

$$pH = 4.74 + \log\left(\frac{0.75/17.5}{0.25/17.5}\right) = 5.22$$

e) **10.0 mL NaOH added**

The OH⁻ from the added NaOH will react with the acetic acid.

Millimoles of HA present = 10.0 mL × 0.10 M = 1.0

Millimoles of OH⁻ added = 10.0 mL × 0.10 M = 1.0

NOTE: This is the equivalence point in this titration.

	$HA_{(aq)}$ +	$OH^-_{(aq)}$ →	$A^-_{(aq)}$ +	$H_2O_{(l)}$
Initial milimoles	1.0	1.0		
Amount reacted	-1.0	-1.0	1.0	
Final millimoles	0	0	1.0	
Concentrations			$\dfrac{1.0}{20.0} = 0.05 M$	

At the equivalence point of the titration, all the acetic acid and the added NaOH are completely consumed. The only remaining species in the solution is the conjugate base, CH_3COO^- (A^-). This solution is no longer a buffer. The pH of the solution must be calculated by considering the equilibrium established by the conjugate base.

	$A^-_{(aq)}$ +	$H_2O_{(l)}$ ⇔	$HA_{(aq)}$ +	$OH^-_{(aq)}$
Initial concentration	0.05		0	0
Change	-x		x	x
Equilibrium concentration	0.05 – x		x	x

Since this is the equilibrium established by the base, the K_b of the base must first be calculated in order to solve for "x".

$$K_a \times K_b = K_W = 1.0 \times 10^{-14}$$
$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.05 - x} \approx \frac{x^2}{0.05}$$
$$x = 5.27 \times 10^{-6} = [OH^-]$$
$$pOH = 5.28$$
$$pH = 8.72$$

NOTE: At the equivalence point in the titration of a weak acid with a strong base, the species present in the solution is the conjugate base of the weak acid. Therefore the pH will always be greater the 7 (basic).

f) <u>**11.0 mL NaOH added**</u>

The OH⁻ from the added NaOH will react with the acetic acid.

Millimoles of HA present = 10.0 mL × 0.10 M = 1.0

Millimoles of OH⁻ added = 11.0 mL × 0.10 M = 1.1

NOTE: Since this point is beyond the equivalence point, the added NaOH is the excess reagent and the acetic acid is the limiting reagent.

	$HA_{(aq)}$ +	$OH^-_{(aq)}$ ➜	$A^-_{(aq)}$ +	$H_2O_{(l)}$
Initial milimoles	1.0	1.1		
Amount reacted	-1.0	-1.0	1.0	
Final millimoles	0	0.1	1.0	
Concentrations		$\dfrac{0.1}{21.0}$	$\dfrac{1.0}{21.0}$	

At this point in the titration, two bases are present in the solution: 1) the strong base NaOH and 2) the conjugate base of acetic acid, A^-. The conjugate base of acetic acid is a weaker base than the strong base NaOH. In solutions that contain a strong base and a weak base, the pH of the solution can simply be determined from the concentration of the strong base. The contribution to the pH from the weak base is negligible in comparison to the strong base.

$$pOH = -\log\left(\frac{0.1}{21.0}\right) = 2.32$$

Therefore, pH = 11.68

The data from the above calculation is summarized in the following table:

Volume of base added (mL)	pH
0.0	2.87
2.5	4.26
5.0	4.74
7.5	5.22
10.0	8.72
11.0	11.68

A complete labeled titration curve is shown in Figure 1 below.
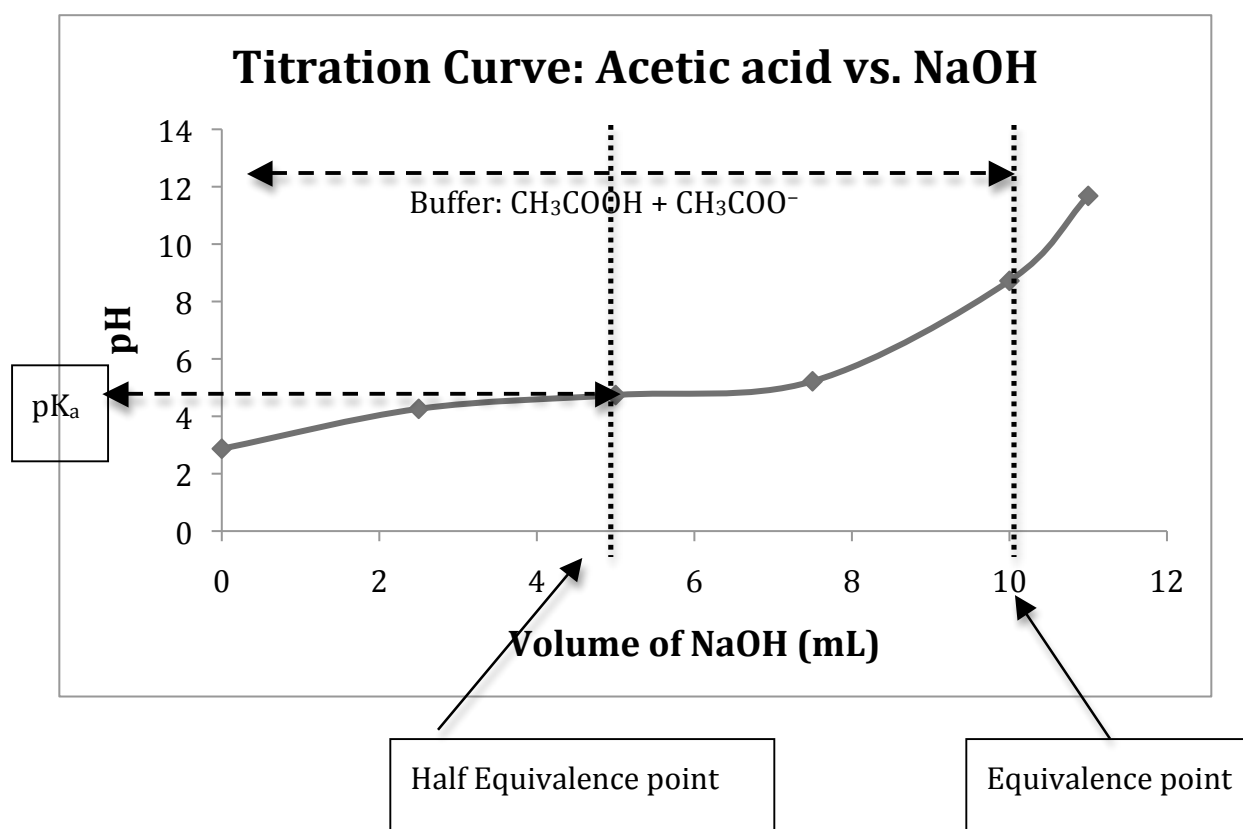

FIGURE 1

Experimental Design

In the first part of the experiment, each student will be required to prepare a buffer. The pH of the prepared buffer will be measured using a pH meter and adjusted to the desired value using either an acid or a base. A strong acid and a strong base will be added to this buffer and the measured pH in each instance will be compared with the calculated value of the pH.

In the second part of this experiment, each student will titrate a weak base with a strong acid and record the pH during the course of the titration. A detailed titration curve will be plotted and labeled using the data from the titration.

Reagents and Supplies

0.10 M acetic acid, solid sodium acetate, solid sodium phosphate, solid sodium monohydrogen phosphate, 0.10 M ammonia, solid ammonium chloride, 0.10 M hydrochloric acid, 0.10 M sodium hydroxide, 1.0 M hydrochloric acid, 1.0 M sodium hydroxide

pH meter kit, 50-mL volumetric flask, 25-mL burette

(See posted Material Safety Data Sheets)

Procedure

1. Obtain one 50-mL volumetric flask and a pH meter kit from the stockroom.

2. Prepare 50 mL of 0.05 M (total concentration of ions) of one of the following three buffers (as assigned by the instructor):
     i. pH = 5.0
     ii. pH = 10.0
     iii. pH = 12.0
   Before preparing the buffer complete the following steps:

   a. Choose the appropriate acid/conjugate base combination from the provided reagents.
   b. Calculate the amounts of acid and conjugate base (in grams or mL) needed to prepare the buffer.
   c. Verify steps a and b with the instructor.

3. Calibrate the pH meter as previously indicated (See Experiment.......).

4. Measure the pH of the prepared buffer and adjust the pH to the required value using 1.0 M HCl or 1.0 M NaOH.

5. Once the buffer has been brought to the required pH value, show the instructor the value of the pH on the pH meter.

6. Transfer exactly two 25 mL potions of the buffer into two 100-mL beakers.

7. Perform the following calculations:

   a. Calculate the pH of the prepared buffer if 0.25 mL of 1.0 M HCl is added to 25 mL of the buffer.
   b. Calculate the pH of the prepared buffer if 0.25 mL of 1.0 M NaOH is added to 25 mL of the buffer.

8. To one 25-mL potion of the buffer, add 0.25 mL of 1.0 M HCl. Thoroughly mix the contents with a stirring rod. Measure the pH and compare the measured pH with the value calculated in 7a.

9. To the second 25-mL potion of the buffer, add 0.25 mL of 1.0 M NaOH. Thoroughly mix the contents with a stirring rod. Measure the pH and compare the measured pH with the value calculated in 7b.

10. Discard the buffer and any other waste generated as directed by the instructor.

PART 2: TITRATION OF A WEAK BASE WITH A STRONG ACID

1. Obtain a 25-mL burette and a pH meter from the stock room.

2. Obtain 20 mL of 0.10 M ammonia solution and 30 mL of 0.10 M HCl solution from the reagent station.

3. Add the 20 mL of 0.10 M ammonia solution into a 125-mL Erlenmeyer flask.

4. Rinse and clean the burette with deionized water and condition and fill the burette with 0.10 M HCl.

5. Measure the pH of the ammonia solution in the flask prior to beginning the titration.

6. Add exactly 1.0 mL of 0.10 M HCl solution from the burette into the Erlenmeyer flask containing the ammonia solution.

7. Thoroughly mix the contents of the Erlenmeyer flask and measure and record the pH.

8. Repeat steps 6 and 7 until a total of 25 mL of HCl has been added.

9. Discard all solutions and any other waste that has been accumulated into a waste container provided by the instructor.

Data Table & Analysis

<u>PART 1: PREPARATION OF A BUFFER</u>

Required buffer (volume, concentration, pH)	
Chosen Acid/Conjugate base pair	

<u>CALCULATIONS (FOR AMOUNTS OF ACID AND BASE)</u>

Amount of acid	
Amount of conjugate base	
Measured pH of the buffer	

Calculate the pH of the prepared buffer if 0.50 mL of 1.0 M HCl is added to 50 mL of the buffer.

Calculated pH value	
Measured pH value	

Calculate the pH of the prepared buffer if 0.50 mL of 1.0 M NaOH is added to 50 mL of the buffer.

Calculated pH value	
Measured pH value	

PART 2: TITRATION OF A WEAK BASE WITH A STRONG ACID

Volume of HCl added (mL)	pH
0.00	

Plot a labeled titration curve using the data obtained and indicate the following:

a. Chemical species before the titration was begun.
b. Buffer region
c. Chemical composition of the buffer
d. Half equivalence point and equivalence point
e. Chemical composition beyond the equivalence point.