## Experiment 6

## Determination of the $K_{a}$ of a Weak Acid and the $K_{b}$ of a Weak Base from pH Measurements

## Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly. PAY CLOSE ATTENTION TO INTRODUCTION OR YOU WILL FIND YOURSELF VERY CONFUSED IN THE LAB.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers.
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, and Procedure.


## Purpose

In this experiment you will learn to calibrate and use a pH probe and then construct a titration curve (graph) in order to determine the molarity and $\mathrm{K}_{\mathrm{a}}$ (acid dissociation constant) of an unknown acid. Similarly, you will then titration a weak base $\left(\mathrm{NH}_{3}\right)$ with a strong acid to calculate the value of $\mathrm{K}_{\mathrm{b}}$ (base dissociation constant) for the weak base. Finally, you will use the pH meter in order to determine the effect of dissolved salts on the pH of water through the process of hydrolysis and the effect of adding an acid or base to a buffer.

## Background

In Chem1A, you performed a titration experiment in order to determine the concentration (Molarity) of an unknown acid. In any titration experiment, an accurately known number of moles of one substance (either the acid or the base) is used to determine the number of moles of the other. The point where moles of acid $=$ moles of base is called the equivalence point. In a well-designed experiment, the equivalence point corresponds to the endpoint of the titration-the point at which an indicator changes color due to a large change in pH . In Chem1A, you used the indicator phenolphthalein which turned from colorless to pink to indicate the endpoint of the titration. The concentration of the unknown substance can then be calculated from the data obtained from the equivalence point, the amount of known substance reacted, and volume of the unknown substance that you titrated. An example of this type of calculation is on the next page of the lab.

## Example Problem: Concentration Determination By Titration

Citric acid $\left(\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{7}\right.$ or $\left.\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}\right)$ is the primary acid present in many fruits that gives them a sour taste. Suppose that 18.7 mL of 0.102 M NaOH is required to neutralize 20.0 mL of a citric acid solution. The equation for neutralization is given below. What was the concentration of the citric acid solution?
$3 \mathrm{NaOH}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}(\mathrm{aq}) \rightarrow \mathrm{Na}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}$ (I)
Step 1: Moles of starting compound used:
18.7 mL NaOH solution $\times \frac{1 \mathrm{~L}}{1000 \mathrm{~mL}} \times \frac{0.102 \text { moles } \mathrm{NaOH}}{1 \mathrm{~L} \text { solution }}=0.0019074$ moles NaOH

Step 2: Moles of desired compound:

$$
0.0019074 \text { moles } \mathrm{NaOH} \times \frac{1 \text { mole Citric Acid }}{3 \text { moles } \mathrm{NaOH}}=0.0006358 \text { moles Citric Acid }
$$

Step 3: Finish the Problem
What is the molarity of Citric Acid Solution?
$L$ of solution $=20.0 \mathrm{~mL} \times \frac{1 L}{1000 \mathrm{~mL}}=0.0200 \mathrm{~L}$ solution
Molarity of Citric Acid $=\frac{\text { moles Citric Acid }}{\text { LCitric Acid solution }}=\frac{0.0006358 \text { moles Citric Acid }}{0.0200 \text { L Solution }}$ $=0.0318$ M Citric Acid

If the acid and base react in a 1:1 ratio, you can use a simpler method to determine the concentration of an acid or base.

For a reaction where all coefficients are one,

$$
\begin{array}{r}
M_{A} \times V_{A}=M_{B} \times V_{B} \quad \text { where } M_{A}=\text { molarity of the acid } \\
\\
V_{A}=\text { volume of the acid } \\
\\
M_{B}=\text { molarity of the base } \\
\\
V_{B}=\text { volume of the base }
\end{array}
$$

## Example

HCl and NaOH react in a $1: 1$ ratio. If it takes 54 mL of 0.100 M NaOH to neutralize 125 mL of an HCl solution, what is the concentration of the HCl ?
$M_{A} \times V_{A}=M_{B} \times V_{B}$
$\mathrm{M}_{\mathrm{A}} \times 125 \mathrm{~mL}=0.100 \mathrm{M} \times 54 \mathrm{~mL}$
$\mathrm{M}_{\mathrm{A}}=0.043 \mathrm{M}$

## Titration Curves

A more advanced way to analyze an acid-base reaction is to create a titration curve. A titration curve will have the volume of the titrant added from the burette as the independent variable and the pH of the solution as the acid and base mix as the dependent variable. The graph below is for the addition of a base such as NaOH from a burette into a beaker containing an acid. As the titrant (the base in this example) is added, the pH will slowly rise and then undergo a large sudden rise before leveling off again. As you can see in the graph below, the shape of the curve will be slightly different depending on whether the acid being titrated is a strong or a weak acid. You will gain a more detailed understanding of titration curves during the course of this experiment.


## Strong Acids versus Weak Acids

The strength of an acid is measured by its ability to donate a proton $\left(\mathrm{H}^{+}\right)$; the strongest acids dissociate $100 \%$ in water, donating all of their protons to water. For example, when HCl donates its proton in water, the proton bonds to a water molecule to form a hydronium ion $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$,

$$
\mathrm{HCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}^{-}{ }_{(\mathrm{aq})}
$$

There are six strong acids: $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{HClO}_{4}$, and $\mathrm{H}_{2} \mathrm{SO}_{4}$. For any strong acid, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=[\mathrm{HA}]_{\text {nititial }}$ because it dissociates $100 \%$. Because of this, calculating the pH of the solution of a strong acid is relatively simple. The pH of a solution can be determined:

All Acids: $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
Strong Acids only: $\mathrm{pH}=-\log [\mathrm{HA}]_{\text {initial }}$

Beyond the six acids mentioned above, all other acids are classified as weak acids because they typically dissociate less than $100 \%$ in water. For example, acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, dissociates somewhere around $10 \%$. Because it does not dissociate $100 \%$, we can say that the dissociation of a weak acid is an equilibrium process.

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}{ }_{(\mathrm{aq})}
$$

Similarly for the weak acid benzoic acid, the reaction would be

$$
\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}^{-}{ }_{(\mathrm{aq})}
$$

In general, the equation for the dissociation of the weak acid, HA is

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

Since the reaction of a weak acid with water is an equilibrium process, an equilibrium expression can be written
$\mathrm{K}_{\mathrm{a}}$ provides a quantitative measure of the degree to which an acid dissociates. A small value for $K_{a}(\ll 1)$ indicates that the acid remains mostly as molecules (HA) in solution. On the other hand, a large value for $K_{a}(\gg 1)$ indicates that the acid has dissociated to a greater extent ( $\mathrm{A}^{-}$)

$$
\mathrm{Ka}=\frac{\left[\mathrm{H}_{3}\right.}{} \frac{\mathrm{O}+][\mathrm{A}-]}{[\mathrm{HA}]}
$$

The subscript "a" on $K$ is used to denote that the reaction involves an acid and is called the acid dissociation constant.

## The Henderson-Hasselbalch Equation

Using the Ka expression above we can derive a relationship that is very useful when working with titration curves such as in this lab:

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

First taking the logarithms of both sides of the above equation,

$$
\log K_{\mathrm{a}}=\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

and then multiplying by -1 gives:

$$
-\log K_{\mathrm{a}}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]-\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

Substituting $\mathrm{p} K_{\mathrm{a}}$ for $-\log K_{\mathrm{a}}$ and pH for $-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, (p just means $-\log$ )

$$
\mathrm{p} K_{\mathrm{a}}=\mathrm{pH}-\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

Finally re-ordering, yields

$$
\begin{equation*}
\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \tag{2}
\end{equation*}
$$

This equation is known as the Henderson-Hasselbalch Equation. It relates the pH of solution to the equilibrium constant $\left(\mathrm{K}_{\mathrm{a}}\right)$ of the acid present in the solution and is the basis of how we will determine the value of $\mathrm{K}_{\mathrm{a}}$ for our unknown acid.

## READ THIS PAGE AND THE NEXT PAGE CAREFULLY. UNDERSTANDING IT IS THE KEY

 TO UNDERSTAND THE LAB.
## Analyzing a Titration Curve- The importance of the pH at the half-equivalence point

When a strong base (from a buret, for example) is added to a weak acid (in a beaker under the buret), the strong base will provide hydroxide $\left(\mathrm{OH}^{-}\right)$ions. These ions will react with the acid $(\mathrm{HA})$ as in the equation below:

$$
\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}
$$

Consider three points during the titration:

1. Before the you have added any base ( OH ): Considering the moment just before the strong base is added to the acid. All that is present in the flask would be the acid HA.

| HA |  |
| :--- | :--- |
| Only HA in beaker |  |
| + |  |
| OH | $\rightarrow$ |
| $\mathrm{H}_{2} \mathrm{O}+$ | $\mathrm{A}^{-}$ |

2. When the acid-base reaction is complete (equivalence point):

On the other hand, considering when the equivalence point is reached. The acid (HA) and the base $\left(\mathrm{OH}^{-}\right)$will have destroyed each other.
All that would be present in the beaker would be the product A :
$\xrightarrow[\text { Have destroyed each other }]{\mathrm{HA}+}$
$\mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}$
Only A- in beaker

3. What about when we have added half the base need to get to the equivalence point?

Half of the acid (HA) will remain, and half the acid will have been turned into $A$ : (its conjugate base) In other words, $[\mathrm{HA}]=[\mathrm{A}-]$.
$\underset{1 / 2}{\mathrm{HA}}+\underset{\mathrm{HA} \text { still present }}{\mathrm{OH}} \rightarrow \quad \underset{1 / 2 \text { of } \mathrm{HA}}{\mathrm{H}_{2} \mathrm{O}}+\underset{\mathrm{A}^{-}}{\mathrm{A}^{-}}$


Considering this point further and returning to the Henderson-Hasselbalch Equation:
$\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
At half-way to the equivalence point, $[\mathrm{HA}]=[A \cdot]$. Therefore, they would cancel
$\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}-1\right.}{[\mathrm{HA}]}$
The equation would therefore simplify to
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log 1$
Since the $\log$ of 1 is 0 ,

## At half- way to the equivalence point

$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$ (The pH of the solution is the $\mathrm{pK}_{\mathrm{a}}$ of the acid.

## Example: Determining the Ka of an acid from a titration curve

A sample of 10.00 mL of dilute $\mathrm{HNO}_{2}$ solution was titrated with 0.1 M NaOH solution. The equivalence point was reached after 10.10 mL . The half-titration point, therefore, was at 5.05 mL . The pH that corresponded to that volume of titrant was 4.75 , so the value of $K_{\mathrm{a}}$ can be calculated as follow is

$$
\begin{aligned}
& \mathrm{pH}=4.75 \text { at } \\
& \text { half-point } \\
& \text { Therefore } \\
& \mathrm{pKa}=4.75 \mathrm{pH} \\
& -\operatorname{log~} \mathrm{Ka}=4.75 \\
& \log \mathrm{Ka}=-4.75 \\
& \mathrm{Ka}=1.78 \times 10-5
\end{aligned}
$$



Volume of NaOH added

## Titration of a weak base with a strong acid

Weak bases will form $\mathrm{OH}^{-}$when they are placed in water. The do this by accepting a proton $\left(\mathrm{H}^{+}\right)$from water. In this lab we will be working with the weak base ammonia $\left(\mathrm{NH}_{3}\right)$. As a weak base, the reaction it undergoes in water is an equilibrium process where the equilibrium constant is called the base dissociation constant $\left(\mathrm{K}_{\mathrm{b}}\right)$. The process for a weak base can be generally described by the equations:

$$
\mathrm{B}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{OH}^{-}{ }_{(\mathrm{aq})}+\mathrm{BH}^{+}{ }_{(\mathrm{aq})}
$$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}{ }^{-1 \mathrm{BH}}{ }^{+}\right]}{[\mathrm{B}]}
$$

More specifically for this lab:

$$
\mathrm{NH}_{3}\left(\mathrm{aq)}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{OH}^{-}{ }_{(\mathrm{aq})}+\mathrm{NH}_{4}^{+}{ }_{(\mathrm{aq})}\right.
$$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{NH}_{4}^{+}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

You will be determining the value of $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{NH}_{3}$ as well as the molarity of an unknown $\mathrm{NH}_{3}$ solution.

## Other Acid-Base Conceptions

In this lab, you will also briefly study solutions which can resist changes when an acid or base is added to them. These solutions contain a weak acid and its conjugate base and are called buffers. In addition, you will briefly look at the effect salt can have on the pH of water through the process of hydrolysis.

## Procedure

Safety: Wear goggles when working with acids and bases. The HCl , and $\mathrm{NH}_{3}$ solutions are relatively dilute; however you should avoid contact and clean up spills immediately.

Waste: All waste can go down the sink

## Part A: Titration of unknown monoprotic acid using NaOH and an indicator

In this part of the lab, you will titrate the unknown acid using the indicator phenolphthalein. This will allow you to determine the molarity of the acid again and compare your results to those obtained with the pH sensor in Part C.

## Materials

For this part you will need the following: a 250 mL beaker, $50-\mathrm{mL}$ buret, funnel, 20 mL pipette

1. Obtain approximately 125 mL of the standardized NaOH from the carboy in the front of the room. Record its molarity in your notebook.
2. Clean a 50 mL buret with deionized water and then rinse the buret three times with the standardized NaOH . Be sure to drain some the solution through the tip. This will get rid of any air bubbles in the tip of the burette.
3. Fill the buret to 0.00 mL mark with the NaOH using a funnel.
4. Pipette 20.00 mL of your unknown acid solution to be titrated into a 250 mL beaker. Also add 3 drops of phenolphthalein. Record the unknown number in your notebook.
5. Add about 20 mL of deionized water using a graduated cylinder to the beaker.
6. Record the initial buret reading of NaOH to the nearest 0.01 mL .
7. Add NaOH from the buret into the sample of the unknown acid until the indicator changes from colorless to pink.
8. Record the final buret reading of NaOH to the nearest 0.01 mL .
9. Dispose of the sample down the sink.
10. Repeat this titration one more time.
11. Using the volume of NaOH , its given molarity, and the volume of acid use, calculate the molarity of the unknown acid. The acid and the NaOH react in a $1: 1$ ratio.

## PART B: pH Sensor Calibration

## Materials

To calibrate the pH Sensor you will need the following: wash bottle, distilled water, two beakers (50-150 mL in size), buffer solutions of high pH (e.g. pH 7) and low pH (e.g. pH 4), pH Sensor.

1. Put distilled water into the wash bottle. Half-fill a beaker with pH 4 buffer solution and half-fill another beaker half-full with pH 7 buffer solution. Label the beakers.
2. Plug in the pH sensor into the USB port on the LabQuest Interface.
3. To calibrate the sensor, tab on Sensor at the top of the screen, then Calibrate. You will be doing a two point calibration.
4. Follow the applicable prompts on the screen. Place the sensor in the pH 4 buffer and wait for the reading to stabilize (1 minute or so). Type in the know pH (4) and then click Keep or Apply.

Then place the sensor in pH 7 buffer. Again wait for the reading to stabilize and then type in the known pH of 7. Click Keep or Apply.

When moving the sensor from one solution to another, thoroughly rinse the pH electrode with distilled water from the wash bottle and dry gently with a Kimwipe.

When not using the sensor, be sure to store it in the storage solution bottle.

## Part C: Titration of unknown monoprotic acid using NaOH and a pH sensor

## Materials

For this part you will need the following: a 150 mL beaker, pH Sensor, magnetic stirrer and stir bar, reagent reservoir, 20 mL pipette, graduated cylinder and drop counter.

1. If you haven't already, obtain approximately 75 mL of the standardized NaOH from the carboy in the front of the room. Record its molarity in your notebook.
2. Connect the pH Sensor to LabQuest interface USB port. Connect the Drop Counter to the DIG 1 port. You will need to open one of the black flaps on the LabQuest to find this port.
3. Calibrate the pH sensor if necessary. See Part B.
4. Obtain the plastic 60 mL reagent reservoir. Close both valves by turning the handles to a horizontal position. Follow the steps below to set up the reagent reservoir for the titration.
a. Rinse the reagent reservoir with a few mL of the NaOH solution and pour the NaOH into an empty 250 mL beaker.
b. Use a utility clamp to attach the reservoir to lab stand.
c. Fill the reagent reservoir with approximately 60 mL of the NaOH solution.
d. Place the 250 mL beaker, which contains the rinse NaOH , beneath the tip of the reservoir.
e. Drain a small amount of the NaOH solution into the 250 mL beaker so it fills the reservoir's tip. To do this, turn both valve handles to the vertical position for a moment, then turn them both back to horizontal.
f. Discard the drained NaOH solution in the 250 mL beaker as directed.
5. Calibrate the Drop Counter so a precise volume of titrant is recorded in units of milliliters.
a. Choose Calibrate from the Sensors menu and select Drop Counter.
b. Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the reagent reservoir.
c. Click on Calibrate Now on the LabQuest interface
d. Open the bottom valve on the reagent reservoir. Keep the top valve closed.
e. Slowly open the top valve of the reagent reservoir so that drops are released at a slow rate ( $\sim 1$ drop every two seconds). You should see the drops being counted on the screen.
f. When the volume of NaOH solution in the graduated cylinder is between 9 and 10 mL , close the bottom valve of the reagent reservoir.
g. Enter the volume of NaOH and select OK.
h. Discard the NaOH solution in the graduated cylinder as indicated by your instructor and set the graduated cylinder aside.
6. Pipette 20.00 mL of your unknown acid solution to be titrated into a 150 mL beaker. Also add 3 drops of phenolphthalein. Record the unknown number in your notebook.
7. Add about 20 mL of deionized water using a graduated cylinder.
8. Assemble the apparatus to perform the titration.
a. Insert the pH Sensor through the large hole in the Drop Counter.
b. Lift up the pH Sensor, and slide the 150 mL beaker containing the unknown acid under the drop counter and reagent reservoir.
c. Place the beaker onto a magnetic stir plate.
d. Add a magnetic stirring bar to the beaker and adjust the position so that the pH Sensor will not be struck when the stirring bar is stirring. The spinning magnetic can damage the pH sensor so be careful.
e. Adjust the reagent reservoir so its tip is just above the Drop Counter slot.
f. Turn on the magnetic stir plate so that the stirring bar is stirring slowly.
9. You are now ready to conduct the titration.

Record the initial pH.
a. Click on the green start button on the Lab Quest interface. No data will be collected until the first drop goes through the Drop Counter slot.
b. Fully open the bottom valve. The top valve should still be adjusted so drops are released at a rate of about 1 drop every 2 seconds. When the first drop passes through the Drop Counter slot, check the graph to see that the first data pair was recorded.
c. Continue watching your graph to see when a large increase in pH takes place-this will be the equivalence point of the reaction. When this jump in pH occurs, let the titration proceed for several more milliliters of titrant.
d. Stop data collection, then turn the bottom valve of the reagent reservoir to a closed (horizontal) position.
9. Dispose of the reaction mixture as directed. Rinse the pH Sensor with distilled water and place back into the storage solution. If the pH is not stored properly, it may be damaged.
10. Examine your titration data to identify the region where the pH made the greatest increase. The equivalence point is in this region.
a. To examine the data pairs on the displayed graph, select any data point.
b. As you move the examine line, the pH and volume values of each data point are displayed to the right of the graph.

Find the pH at the equivalence point (the midpoint of the nearly vertical section of the plot). More precisely, the midpoint of this rise occurs at the inflection point of the titration curve- the point on a curve at which the curvature or concavity changes sign from plus to minus or from minus to plus.

An alternate way of determining the equivalence point of the titration is to take the first derivatives of the pH -volume data.

Determine the peak value on the first derivative vs. volume plot.
a. Tap the Table tab and choose New Calculated Column from the Table menu.
b. Enter d1 as the Calculated Column Name. Select the equation 1st Derivative (Y,X). Use Volume as the Column for X and pH as the Column for Y . Select OK.
c. On the displayed plot of d 1 vs . volume, examine the graph to determine the volume at the peak value of the first derivative.

Record in your notebook the $x$ value ( mL needed to reach the equivalence point) and the y -coordinate of this point ( pH of the equivalence point).
10. Use the volume of NaOH used to reach the equivalence point, the given molarity of the NaOH used, and the volume of acid used to calculate the molarity of the acid.
11. Find the pH at the point when $1 / 2$ of the NaOH needed to reach the equivalence was added. Use this to find the $\mathrm{pK}_{\mathrm{a}}$ of the acid, and the $\mathrm{K}_{\mathrm{a}}$ of the acid.
12. Using your value of $\mathrm{K}_{\mathrm{a}}$, identify your unknown acid. Possible unknowns are listed in table below.

| Name | Formula | $\boldsymbol{K}_{\mathrm{a}}$ | $\mathrm{p} K_{\mathrm{a}}$ |
| :--- | :--- | ---: | ---: |
| Acetic acid | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $1.76 \times 10^{-5}$ | 4.75 |
| Sodium bisulfite | $\mathrm{NaHSO}_{4}$ | $1.02 \times 10^{-2}$ | 1.99 |
| Formic acid | $\mathrm{HCHO}_{2}$ | $1.77 \times 10^{-4}$ | 3.75 |
| Propionic Acid | $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{2}$ | $1.34 \times 10^{-5}$ | 4.87 |
| Chloroacetic Acid | $\mathrm{HClCH}_{2} \mathrm{O}_{2}$ | $1.40 \times 10^{-3}$ | 2.85 |

13. Print a copy of the graph of the titration. You can print the graph directly from LabQuest.

## Part D: Addition of an acid and base to a buffer solution

1. In order to create a buffer, add 20.00 mL of your weak acid into a clean 125 mL flask using a pipette.
2. Using a graduated cylinder, add approximately $1 / 2$ of the amount of base needed to reach the endpoint.
3. Your solution is now at half-way to the equivalence point.
4. Notice that at this point on the graph, the pH is relatively stable even as more base is added. This region is called the buffering region of the titration graph.
5. Measure the pH of the solution using your calibrated pH sensor.


Volume added
6. Add 1 drop of 6.0 NaOH to the solution. Stir and measure the pH .
7. Add 2 drops of 6.0 M HCl to the solution. Stir and measure the pH .

## Part E: Titration of the Weak Base $\mathrm{NH}_{3}$ with HCl using a pH Sensor

## Materials

For this part you will need the following: a 150 mL beaker, pH Sensor, drop counter, magnetic stirrer and stir bar, and 20 mL pipette

1. Obtain approximately 60 mL of the standardized HCl (approximately 0.1 M ) from the carboy in the front of the room. Record its exact molarity in your notebook.
2. Place the 60 mL of HCl in the reagent reservoir.
3. Pipette 20.00 mL of the $\mathrm{NH}_{3}$ solution to be titrated into a 150 mL beaker. Also add 3 drops of methyl orange.
4. Add about 20 mL of water using a graduated cylinder to the beaker. Then place a magnetic spinning bar in the beaker and place the beaker on a magnetic stirring plate.
5. Repeat the titration with the pH sensor as done in Part C .
6. Dispose of the mixture in the beaker down the sink.

## Analyzing the Data

Follow the directions under Part C of the lab to save and print your graph

## Determine:

- The initial pH
- The mL of HCl needed to reach the equivalence point.
- The Molarity of the $\mathrm{NH}_{3}$ used.
- The pH at the equivalence point
- The pH at half-way to the equivalence point
- The $\mathrm{K}_{\mathrm{b}}$ of $\mathrm{NH}_{3}$.

Record all information your notebook. Show all calculations.

## Part F: pH of Salt Solutions

Not only do acids and bases effect the pH of aqueous solutions, salts can also raise or low the pH when placed in water. This occurs when one of the ions from the salt reacts with water to for hydronium or hydroxide ions in a process called hydrolysis. A summary of these kind of processes can be found in your textbook.

1. PREDICT whether each of the salt solutions below is expected to be acidic, neutral, or basic. The six salt you will be testing are::

$$
\begin{array}{llllll}
\mathrm{NaCl} & \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} & \mathrm{Na}_{2} \mathrm{CO}_{3} & \mathrm{NH}_{4} \mathrm{Cl} & \mathrm{KNO}_{3} & \mathrm{ZnCl}_{2}
\end{array}
$$

2. Obtain approximately 50 mL of each solution in a 150 mL beaker.
3. Using the calibrated pH sensor (see part B ), determine the actual pH of the six salt solutions:
4. Dispose of the solutions down the drain.

## Data Tables

Part A: Titration of unknown monoprotic acid using NaOH and an indicator

Given molarity of NaOH
Unknown acid sample number

|  | Trial 1 | Trial 2 |
| :--- | :---: | :---: |
| Final buret reading |  |  |
| Initial buret reading |  |  |
| Volume delivered |  |  |
| Molarity of unknown acid |  |  |

Part C: Titration of unknown monoprotic acid using NaOH and a pH sensor
Initial pH
From your analysis of the titration curve:
mL of NaOH used to reach the equivalence point $\qquad$
Calculated Molarity of the unknown acid $\qquad$
pH at the half-way to the equivalence point $\qquad$
$\mathrm{pK}_{\mathrm{a}}$ the unknown acid $\qquad$
$\mathrm{K}_{\mathrm{a}}$ of the unknown acid
Identity of unknown acid $\qquad$

Part D: Addition of an acid and base to a buffer solution

|  |  |  |
| :--- | :--- | :--- |
| Initial pH |  |  |
| pH after adding 1 drop of 6 M <br> NaOH |  |  |
| pH after adding 2 drops of 6.0 M <br> HCl |  |  |

## Part E: Titration of the Weak Base $\mathrm{NH}_{3}$ with HCl using a pH Sensor

Given molarity of HCl
Initial pH
From your analysis of the titration curve:
pH at the equivalence point
pH at the half-way to the equivalence point
$\mathrm{pK}_{\mathrm{b}}$ of $\mathrm{NH}_{3}$
$\mathrm{K}_{\mathrm{b}}$ of $\mathrm{NH}_{3}$
mL of HCl used to reach the equivalence point
Calculated Molarity of the $\mathrm{NH}_{3}$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

## Part F: pH of Salt Solutions

PREDICT whether each of the salt solutions below is expected to be acidic, neutral, or basic:
0.1 M NaCl $\qquad$
$0.1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ $\qquad$ $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ $\qquad$
$0.1 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ $\qquad$ $0.1 \mathrm{M} \mathrm{KNO}_{3}$ $\qquad$ $0.1 \mathrm{M} \mathrm{ZnCl}_{2}$ $\qquad$

Actual pH from pH sensor:
0.1 M NaCl $\qquad$ $0.1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ $\qquad$ $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ $\qquad$
$0.1 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ $\qquad$ $0.1 \mathrm{M} \mathrm{KNO}_{3}$ $\qquad$ $0.1 \mathrm{M} \mathrm{ZnCl}_{2}$ $\qquad$
For each salt that reaction with water, write balanced NET-IONIC equations for the hydrolysis reactions that occurred. Then using the measured pH , calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, and $\left[\mathrm{OH}^{-}\right]$

| Salt | Balanced NET-IONIC equations <br> for the hydrolysis reactions for <br> those that reacted. If no reaction, <br> write NO REACTION | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{OH}^{2}\right]$ |
| :---: | :---: | :---: | :---: |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
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|  |  |  |  |

## Post-Lab Questions

1. Using your data from Part C and Part E including your initial pH, calculate the percent dissociation for your unknown acid and in your sample of $\mathrm{NH}_{3}$.
2. Using the value of $\mathrm{Ka}_{\mathrm{a}}$ you found for your unknown acid in Part C and its molarity, calculate the initial pH of your unknown acid. Compare to your measured value of the initial pH and comment on any differences.
3. The $\mathrm{K}_{\mathrm{a}}$ of acetic acid is $1.8 \times 10^{-5}$. Calculate the pH of the following solutions.
a. A solution consisting of 0.50 M acetic acid $\left(\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)$ and 0.50 M sodium acetate $\left(\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)$
b. A solution consisting of 0.10 M acetic acid and 0.50 M sodium acetate.
c. Suppose it is desired to maintain the pH of a solution at 4.2 using only acetic acid and sodium acetate. Would the concentration of acetic acid or sodium acetate have to be higher in the solution? What would be the ratio of acetate to acetic acid need to be?
4. Identify which of the following will result in a buffer solution when equal volumes of the two solutions are mixed. (Circle all that apply.)
(a) $0.10 \mathrm{M} \mathrm{KNO}_{3}$ and $0.10 \mathrm{M} \mathrm{HNO}_{3}$
(b) 0.10 M HCl and $0.10 \mathrm{M} \mathrm{NH}_{3}$
(c) $0.10 \mathrm{M} \mathrm{NaNO}_{2}$ and $0.10 \mathrm{M} \mathrm{HNO}_{2}$
(d) 0.20 M HCl and $0.10 \mathrm{M} \mathrm{NH}_{3}$
(e) $0.20 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ and $0.10 \mathrm{M} \mathrm{NH}_{3}$
5. A typical aspirin contains 324 mg of aspirin $\left(\mathrm{HC}_{9} \mathrm{H}_{7} \mathrm{O}_{4}\right)$ with $\mathrm{K}_{\mathrm{a}}=2.8 \times 10^{-4}$. If you dissolve two aspirin tablets in a 475 mL glass of water, what is the pH of the solution?

6a. Which of the following ions will react with water in a hydrolysis reaction: $\mathrm{Na}^{+}, \mathrm{Cu}^{2+}, \mathrm{F}^{-}, \mathrm{SO}_{3}{ }^{2-}, \mathrm{Br}, \mathrm{Cl}$ ?
b. For those ions in the above question that reacted, write the net ionic equations for the hydrolysis reaction.

## Pre-Lab Questions

1. Write the chemical equation for the reaction that occurs when benzoic acid $\left(\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right)$ reacts with water.
2. A titration experiment reveals that 11.6 mL of 3.0 M sulfuric acid are required to neutralize the sodium hydroxide in 25.00 mL of NaOH solution. What is the molarity of the NaOH solution?

$$
\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}
$$

3. If it takes 25 mL of $0.05 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ to neutralize 345 mL of NaOH solution, what is the concentration of the NaOH solution? $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and NaOH react in a 1:1 ratio
4. Sketch the following titration curve. Then, label the (a) equivalence point (b) the half- equivalence point (c) the initial pH , (d) the buffer region.

5. What is the $\mathrm{K}_{\mathrm{a}}$ of acid whose $\mathrm{pK}_{\mathrm{a}}$ is 3.78 ?
6. Draw the setup for the titration in Part C. Label the various parts including the types and volume of glassware used. Indicate the contents in the beaker and in the burette, including the chemical formula, and volume.
