## Experiment 7

## Determination of the $\mathrm{K}_{\mathrm{a}}$ of a Weak Acid and the $\mathrm{K}_{\mathrm{b}}$ of a Weak Base from pH Measurements

## Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- 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. Background information can be found in Chapter 16 and 17, especially sections 17.1-17.3 and 16.9 in your textbook (Brown and LeMay).
- 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, Procedure and Data Tables.


## 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 Chem 1a, 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 were moles of acid = moles of base is called the equivalence point. In a welldesigned 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 chem 1a, 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 moles $\mathrm{NaOH} \times \frac{1 \text { mole Citric Acid }}{3 \text { moles } \mathrm{NaOH}}=0.0006358$ moles Citric Acid

Step 3: Finish the Problem
What is the molarity of Citric Acid Solution?

$$
\begin{gathered}
\text { L of solution }=20.0 \mathrm{~mL} \times \frac{1 \mathrm{~L}}{1000 \mathrm{~mL}}=0.0200 \mathrm{~L} \text { solution } \\
\begin{array}{c}
\text { Molarity of Citric Acid }=\frac{\text { moles Citric Acid }}{\text { LCitric Acid solution }}=\frac{0.0006358 \text { moles Citric Acid }}{0.0200 \mathrm{~L} \text { Solution }} \\
=0.0318 \text { M Citric Acid }
\end{array}
\end{gathered}
$$

## 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 buret 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 buret 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, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $[\mathrm{HA}]_{\text {initial }}$ 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:

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

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.
$\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \Leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\text {aq })}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}{ }_{(\text {aq })}$
Similarly for the weak acid benzoic acid, the reaction would be

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

In general, the equation for the dissociation of the weak acid, HA is
$\mathrm{K}_{\mathrm{a}}$ provides a quantitative
measure of the degree to
which an acid dissociates. A
small value for $\mathrm{K}_{\mathrm{a}}(\ll 1)$
indicates that the acid remains
mostly as molecules (HA) in
solution. On the other hand, a
large value for $\mathrm{K}_{\mathrm{a}}(\gg 1)$
indicates that the acid has
dissociated to a greater extent
$\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \Leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
Since the reaction of a weak acid with water is an equilibrium process, an equilibrium expression can be written

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

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

## The Henderson-Hasselback 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:

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

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

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

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-Hasselback 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.

## 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 for example), the strong base will provide hydroxide $\left(\mathrm{OH}^{-}\right)$ions. These ions will react with the acid (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 ( $\mathrm{OH}^{-}$): 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.
$\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}$
Only HA in beaker


## 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 $A^{-}$.
$\mathrm{HA}+\mathrm{OH}^{-} \rightarrow$
Have destroyed each other
$\mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}$
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 $A^{\circ}$. (its conjugate base) In other words, $[\mathrm{HA}]=[\mathrm{A}]$.

$$
\underset{1 / 2}{\mathrm{HA}+\underset{\text { HA still present }}{\mathrm{HA}} \rightarrow \underset{1 / 2 \text { of } \mathrm{HA}}{\mathrm{OH}^{-}} \rightarrow \quad \mathrm{A}^{-}}
$$


$1 / 2$ will be HA, and $1 / 2$ will be $A^{-}$
Considering this point further and returning to the Henderson-Hasselback equation:
$\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
At half-way to the equivalence point, $[\mathrm{HA}]=[\mathrm{A}]$. Therefore, they would cancel
$\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}-\right]}{[\mathrm{HA}]}$
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
$\mathrm{pH}=4.75$ at
half-point
Therefore
$\mathrm{pKa}=4.75$
$-\log \mathrm{Ka}=4.75$
$\log \mathrm{Ka}=-4.75$
$\mathrm{Ka}=1.78 \times 10^{-5}$


## 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:

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

More specifically for this lab:

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

$$
\mathrm{Kb}=\left[\mathrm{OH}^{-}\right]\left[\mathrm{BH}^{+}\right]
$$

[B]

$$
\mathrm{Kb}=\left[\mathrm{OH}^{-}\right]\left[\mathrm{NH}_{4}^{+}\right]
$$

$$
\left[\mathrm{NH}_{3}\right]
$$

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 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
Note: If you just performed part C, start with step 4

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 buret.
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 water using a graduated cylinder.
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 clear 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.

## PART B. Computer Setup and pH Sensor Calibration

## Materials

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

1. Turn on Science Workshop interface and the computer if they are not already on.
2. Connect the plug of the pH Sensor to Analog Channel A on the interface.
3. On the desktop, open the program Data Studio, then select Open Activity, and then open the file weakacid.sws in the Chem 1B folder on the desktop. The file will display a graph display of the pH versus time and a data table of pH and mL added.

4. Put distilled water into the wash bottle and into one of the beakers. Put about 50 mL of the pH 4 buffer solution in one of the other two beakers and about 50 mL of the pH 10 buffer solution into the third beaker.
5. Remove the pH electrode from its storage bottle of buffer solution.
6. Use the wash bottle to rinse the end of the electrode. If the pH electrode has not be soaking while stored, soak the electrode in a beaker of distilled water for 10 minutes.
7. In the Experiment Setup window, click Calibrate Sensors at the top.
8. Place the pH sensor in the pH 4 buffer.
9. Find were it says "Calibration point 1" and in the "Standard Value Box" check that the value is set to 4.000 . If is does not say 4.000 , change it to 4.000 .
10. When the voltage stabilizes, click on "Read from Sensor"
11. Thoroughly rinse the pH electrode with distilled water and dry it with a tissue.
12. Place the pH sensor in the pH 7 buffer.
13. Find were it says "Calibration point 2" and in the "Standard Value Box change the value to 7.000 .
14. When the voltage stabilizes, click on "Read from Sensor".
15. Click OK to end the calibration.
16. Thoroughly rinse the pH electrode with distilled water from the wash bottle and dry gently.

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

## Materials

For this part you will need the following: a 250 mL beaker, $50-\mathrm{mL}$ buret, pH Sensor, magnetic stirrer and stir bar, funnel, 20 mL pipette

## Note: If you just performed part A, start with step 4

1. If you haven't already, 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 buret.
3. Fill the buret to 0.00 mL mark with the NaOH using a funnel.
4. Obtain an unknown acid sample solution and record its number in your notebook. Pipette 20.00 mL of your unknown acid solution into a 250 mL beaker. Also add 3 drops of phenolphthalein.
5. Add about 20 mL of water using a graduated cylinder. Then place a magnetic spinning bar in the beaker, and place the beaker on a magnetic stirring plate.
6. Use a clamp and support rod to position the pH electrode so the end of the electrode is submerged in the sample. Make sure the spin bar does not contact the delicate pH sensor
7. Turn on the magnetic stirrer.
8. When you are ready, click START to begin to recording data.
9. After waiting 10 seconds for your reading to stabilize, write down in your notebook the initial pH . Type " 0.0 " in the mL column in the data table on the computer. Then click Keep.
10. Begin adding sodium hydroxide from the buret 1 mL at a time.

11. When the pH stabilizes, read the buret and use the keyboard to enter the volume to the nearest 0.01 mL and click Keep
12. Continue adding approximately 1 mL portions of base. After you add each portion, record the total volume of sodium hydroxide added to the nearest 0.01 in Data Studio using the keyboard and click on Keep.
13. When you notice that the pH is changing by 0.2 units or more as you add 1 mL of the NaOH , begin adding smaller volumes of NaOH (approximately 0.1 mL ) to gather more data near the equivalence point.
14. Continue to add portions of NaOH until you are 5 mL past the equivalence point, recording the volume in Data Studio after each portion is added. You may use larger portions when the pH begins to stabilize.
15. Click the STOP button to end data recording
16. Carefully remove the pH electrode, rinse it thoroughly with distilled water, and place it back in its buffer storage solution. If the storage solution is low, ask your instructor to replace it. If the pH is not stored properly, it may be damaged.
17. Dispose of the mixture in the beaker down the sink.

## Analyzing the Data

1. Click the graph window to make it the active window.
2. Print your graph.
3. 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. This can be found using the smart cursor function in

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.)
4. 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.
5. Use the 'Smart Tool' to 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.
6. Using your value of $K_{a}$, identify your unknown acid. Possible unknowns are listed in table below.

| Name | Formula | $\boldsymbol{K}_{\mathrm{a}}$ | $\mathbf{p} \boldsymbol{K}_{\mathrm{a}}$ |
| :--- | :--- | ---: | ---: |
| 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 |

Record all information your notebook. Show all calculations.

## 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. From your buret 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.
6. Add 1 drop of 6.0 NaOH to the solution. Stir and measure the pH .


Volume added
7. Add 2 drops of 6.0 M HCl to the solution. Stir and measure the pH .
8. Repeat the above adding of drops of NaOH and then HCl to a 30 mL portion of water instead of the half-titrated buffer mixture. Record the intial pH of the water, the pH after adding 1 drop of 6.0 M NaOH and finally after adding 2 drops of 6.0 M HCl .

## Part E Titration of the Weak Base $\mathrm{NH}_{3}$ with $\mathbf{H C l}$ using a pH Sensor

## Materials

For this part you will need the following: a 250 mL beaker, a 150 mL beaker, $50-\mathrm{mL}$ buret, pH Sensor, magnetic stirrer and stir bar, funnel, 20 mL pipette

1. Obtain approximately 75 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. Clean a 50 mL buret with deionized water and then rinse the buret three times with the standardized HCl . Be sure to drain some the solution through the tip. This will get rid of any air bubbles in the tip of the buret.
3. Fill the buret with the HCl to the 0.00 mL mark using a funnel.
4. Pipette 20.00 mL of the $\mathrm{NH}_{3}$ solution to be titrated into a 250 mL beaker. Also add 3 drops of phenolphthalein.
5. Add about 20 mL of water using a graduated cylinder. Then place a magnetic spinning bar in the beaker, and place the beaker on a magnetic stirring plate.
6. Use a clamp and base and support rod to position the pH electrode so the end of the electrode is in the sample. Make sure the spin bar does not contact the delicate pH sensor
7. Turn on the magnetic stirrer.
8. When you are ready, click START to begin to recording data.
9. After waiting 10 seconds for your reading to stabilize, write down in your notebook the initial pH . Type " 0.0 " in the mL column in the data table on the computer. Then click Keep.
10. Begin adding HCl from the buret 1 mL at a time.
11. When the pH stabilizes, read the buret and use the keyboard to enter the volume to the nearest 0.01 mL and click Keep
12. Continue adding approximately 1 mL portions of acid. After you add each portion, record the total volume of hydrochloric acid added to the nearest 0.01 in Data Studio using the keyboard and click on Keep.
13. When you notice that the pH is changing by 0.2 units or more as you add 1 mL of the HCl , begin adding smaller volumes of HCl (approximately 0.1 mL ) to gather more data near the equivalence point.
14. Continue to add portions of HCl until you are 5 mL past the equivalence point, recording the volume in Data Studio after each portion is added. You may use larger portions when the pH begins to stabilize.
15. Click the STOP button to end data recording
16. Carefully remove the pH electrode, rinse it thoroughly with distilled water, and place it back in its buffer storage solution. If the storage solution is low, ask your instructor to replace it. If the pH is not stored properly, it may be damaged.
17. 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 Kb 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 on pg of 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::
$\begin{array}{lllllll}\mathrm{NaCl} & \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} & \mathrm{Na}_{2} \mathrm{CO}_{3} & \mathrm{NH}_{4} \mathrm{Cl} & \mathrm{KNO}_{3} & \mathrm{ZnCl}_{2}\end{array}$
2. Obtain approximately 50 mL of each solution in a 150 mL beaker.
3. Using the calibrated pH sensor (see part A ), 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 $\qquad$
Unknown acid sample number $\qquad$

|  | Trial 1 | Trail 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 $\qquad$

From your analysis of the titration curve:
mL of NaOH used to reach the equivalence point $\qquad$
Molarity of the unknown acid $\qquad$
pH at the equivalence point $\qquad$
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 $\qquad$
Identity of unknown acid $\qquad$

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

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

## Part E Titration of the Weak Base $\mathrm{NH}_{3}$ with $\mathbf{H C l}$ 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 $\mathrm{NH}_{3}$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\mathrm{K}_{\mathrm{b}}$ of $\mathrm{NH}_{3}$ $\qquad$
mL of HCl used to reach the equivalence point $\qquad$
Calculated molarity of the $\mathrm{NH}_{3}$ $\qquad$

## 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 M 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 M ZnCl 2 $\qquad$
For each salt that reaction with water, write balanced NET-IONIC equations for the hydrolysis reactions what occurred and the Expression for the equilibrium constant ( $\mathrm{K}_{\mathrm{a}}$ or $\mathrm{K}_{\mathrm{b}}$ ). Then using the measured pH , calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, and $\left[\mathrm{OH}^{-}\right]$

| Salt | Balanced NET-IONIC <br> equations for the <br> hydrolysis reactions | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $[\mathrm{OH}]$ |
| :--- | :--- | :--- | :--- |
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## 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. Sketch the following titration curve. Then, label the (a) equivalence point (b) the halfequivalence point (c) the initial pH , (d) the buffer region.

4. What is the $\mathrm{K}_{\mathrm{a}}$ of acid whose $\mathrm{pK}_{\mathrm{a}}$ is 3.78 ?
5. 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.

## 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 Ka 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 Ka 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 he 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) $0.20 \mathrm{M} \mathrm{HCl}^{2}$ 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: $\mathrm{Na}^{+}, \mathrm{Cu}^{2+}, \mathrm{F}^{-}, \mathrm{SO}_{3}{ }^{2-}$, $\mathrm{Br}, \mathrm{Cl}^{\prime}$ ?
b. For those ions in the above question that reacted, write the net ionic equations for the hydrolysis reaction.

