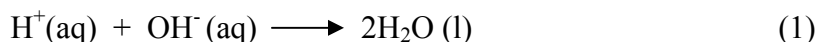


## Introduction to Acid-Base Chemistry

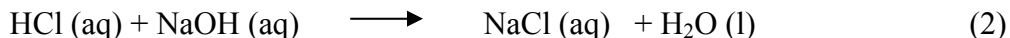
This experiment and the next three permit you to explore most of the important aspects of acid-base chemistry. When doing your pre-laboratory preparation and your post-laboratory data workup, take a few minutes each week to reflect on how the successive laboratories are building on your experience from the previous one. We start with an exploration of the classic acid-base reaction, that of a strong acid with a strong base. The solutions you prepare in the strong acid-strong base experiment will be used as standardized solutions when you explore the additional complexities of a weak-acid titration curve experiment and the titration of a polyprotic acid experiment. Buffers constructed to exploit a property of the weak-acid titration curve are then explored in the fourth of these related experiments.

### **Strong Acid - Strong Base Titration**

In this experiment you will be analyzing the neutralization between a strong acid and a strong base, using the titration skills learned in the earlier parts of this lab. According to the Arrhenius concept when dissolved in water, an acid raises the concentration of hydrogen ion,  $H^+$  while a base increases the hydroxide ion,  $OH^-$  concentration. When reacted together the acid and base will neutralize each other according to the net ionic equation (1).



An acid is considered to be strong if it completely ionizes in water. In this lab, you will be utilizing the strong acid, hydrochloric acid, HCl, to neutralize the strong base, sodium hydroxide, NaOH, according to the neutralization reaction below.



The progression of the reaction will be observed using a pH meter and a titration curve will be created using the experimental data. You will start with sample solely containing the acid and indicator and slowly add your standardized base. A titration curve is simply a plot of the pH of an acid versus the volume of base added, or vice versus. The titration curve gives a good description of how an acid-base reaction proceeds. The pH will start out low and acidic, then quickly rise up and reach the equivalence point, where the concentration of acid equals that of the base, and then as the solution becomes more basic it will slowly rise and level off as an excess amount of base is added. Note that the equivalence point is slightly different from the endpoint of a titration. The endpoint is when the indicator changes color which does not always correspond to the equivalence point.

**As pre-laboratory preparation it is critical that you review the ideas presented in Chapter 17, sections 1-4, 8th edition. These sections address the concepts involved in this experiment.**

**Safety: Remember to wear gloves and use caution whenever handling acids and bases. WEAR YOUR GOGGLES!**

**Work in pairs throughout this laboratory assignment.**

**Each student must collect data and submit a separate report.** The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs.

## **Experimental Procedure**

### **Part I. Preparing your Solutions**

You will prepare about 1 L of approximately 0.15 M sodium hydroxide solution by diluting the stock solution of 6 M NaOH. You will need to calculate the volume of 6M NaOH required in this dilution.

1. Begin by pouring about 200 mL of deionized water into your (clean) plastic bottle. Calculate the appropriate volume of stock solution, use a polyethylene dropper to dispense it into a 25 mL graduated cylinder, and then pour the contents of the graduate into the partially filled plastic bottle. Rinse the graduate out with fresh water at least twice, adding the rinsing to the contents of the plastic bottle. Screw the cap on the plastic bottle and mix the contents thoroughly by inverting the bottle and swirling it repeatedly. Then add the remaining volume of water to bring the total volume to about 1 L, mixing the bottle contents thoroughly. The bottle should be shaken at least 30 times after the last addition. Label this bottle 0.15 M NaOH.
2. Take the second 1 L plastic bottle and label it as 0.2 M HCl. Fill it with about 200 mL of deionized water. You will need to calculate and accurately measure out the volume of 6.0 M HCl needed to make 1 L of 0.2 M HCl. Clean your graduated cylinder before using it to measure the HCl. Add the necessary amount of acid to the plastic bottle, rinse the graduated cylinder several times with deionized water, adding each rinsing to the plastic bottle. Cap and shake the bottle to mix thoroughly and then fill the remainder of the bottle with water. Cap the plastic bottle and shake well. Again, invert the bottle at least 30 times in order to completely mix the solution.

### **Part II. Standardizing the base against Potassium Acid Phthalate**

In this step of the experiment you will standardize your sodium hydroxide solution against the primary standard, potassium acid phthalate, KHP. You will also use a technique called *weighing by difference*. This is a very important technique to use because it eliminates systematic errors from the balance. Weighing by difference is quite simple. First, mass the container and the material from which you are going to draw your sample. Then remove some of the material and place it in a separate container. Remeasure the mass of the original container and the remaining material. Calculate the mass removed, and repeat the process until you have removed the mass desired. For preparation of all additional samples, be sure to use the same balance so that systematic errors in the balance will continue to be eliminated when you take the difference readings between masses.

1. In a previous laboratory period you will have obtained about 6 grams of primary-standard grade potassium acid phthalate (KHP) in a vial, dried it in an oven at 110°C for 2 hours, and stored it in a desiccator for use today.
2. In what follows, use a folded paper strip to handle the vial; this will keep oils from your hands from changing the mass of the vial. Accurately weigh a 1.0-1.2 gram sample of dry KHP on to a weighing boat. Using the appearance of this sample as a guide, accurately weigh three more such samples by difference into clean, dry 125 or 250 mL Erlenmeyer flasks. Quantitatively transfer the first sample from the weighing boat into another 500 mL Erlenmeyer flask with the help of a small stream of water from your wash bottle, and then add water to a total of about 35 mL to each of the four flasks and swirl them gently until the solids dissolve. Be careful not to leave drops of the solution on the sidewalls of the flask.
3. With the technique described in the Common Laboratory Procedures section of this manual, condition and fill a 50 mL buret with the NaOH solution you prepared in Part I and which you will now standardize. Remember when filling a buret to make sure the stopcock is closed. Hold the buret at a low enough level that you can safely pour in the needed volume of solution using a funnel. After conditioning, fill the buret with 50 mL of the standardized NaOH. Do not waste time trying to hit 0.00 with the meniscus. Rather, go a few drops below the zero mark and read and record the actual starting point to the nearest 0.02 mL. Be sure always to wipe off the tip of a buret before you begin a titration. Use a laboratory tissue and make one quick stroke downward beginning at the stopcock and ending in the air beyond the buret tip.
4. Add three drops of phenolphthalein indicator and a stir bar to the first KHP solution. Place the flask onto the stir plate underneath the buret and turn on the stirrer and slowly increase the stirring speed. Please note that the stir plates also have a heat control knob that you will not need and must not use in this experiment. The stir motor control knob is on the left, leave the heat control knob turned off. Lower the buret tip well into the Erlenmeyer flask. Perform a cursory titration using the KHP sample in the 500 mL Erlenmeyer flask to determine the approximate endpoint of the titration. If the masses of KHP are approximately the same then the endpoint of each sample will occur at approximately the same volume. After you have reached your endpoint for your cursory titration record the buret reading at the endpoint and calculate the volume of NaOH needed to reach the endpoint.
5. Holding your buret below eyelevel, refill your buret and record the initial buret reading to the nearest 0.02 mL. Add three drops of phenolphthalein indicator to another KHP sample and swirl. Clean and dry your stir bar for your second titration and gently place it in the flask containing your sample. Turn on the stirrer and slowly increase the stirring speed and lower the buret into the flask. Now you are ready to titrate.
6. From your cursory titration you know the approximate position of the endpoint, initially add the titrant fairly rapidly, pausing every few milliliters to allow the solution to mix thoroughly. Pay attention to the region where the two solutions mix and as the indicator color begins to trail out into the solution as you stir, reduce the next amount of titrant added, keeping in mind the target volume. Be prepared to stop adding titrant about 1 mL short of this volume.
7. Gently wash down the walls of the flask with water from your wash bottle, and then resume adding base from the buret but now dropwise. As you approach the endpoint, the pink color will increasingly linger. You should frequently wash down the interior sides of the flask to recover any reagent drops that may be clinging to the sides. Pause after the

addition of each drop or  $\frac{1}{2}$  drop to allow the solution to mix. A  $\frac{1}{2}$  drop may be added by slowly opening the stopcock until a  $\frac{1}{2}$  drop forms at the tip, then closing the stopcock and washing this  $\frac{1}{2}$  drop into the flask. Stop adding base when the entire flask has a *faint* pink color that persists. You may wish to record the buret volume of several successive drops as you approach the endpoint in case you discover that you have overshot the endpoint. Record the final buret reading to the nearest 0.02 mL. Refill the buret and similarly titrate the remaining two KHP samples.

8. It should be clear to you that the ratio of the NaOH titration volume to the mass of KHP being titrated should be a constant. Calculate this ratio for your three latter titrations and determine if one of them fails the Q-test. If it does, run another sample. You should throw out the data from the first cursory titration since this titration was performed quickly. When you have three samples that can be retained, you may begin part III.

### **Part III. Strong acid Strong base Titration Curve**

This part of the experiment requires the use of a pH meter to measure the pH of various solutions. The pH meter and the accompanying electrode are both very expensive and fragile. Treat both pieces of equipment with great care. Follow the directions provided very carefully. When rinsing the electrode use a light stream of deionized water. Be careful of the electrode when adding strong base or when stirring the solution. After completing the experiment, STORE THE ELECTRODE IN THE STORAGE SOLUTION provided. Additional storage solution is provided in the laboratory if needed.

The information you generate in this part of the experiment has two goals: 1) to standardize the approximately 0.2 M HCl solution and 2) to demonstrate the classic titration curve of acid-base chemistry. You will be doing the titration procedure at least twice. The first titration will familiarize you with the critical pH and volumes for your specific solutions' concentrations after which you may adjust your technique to more accurately locate the endpoint for the specific solutions you are using.

1. Standardize the pH meter nearest your work area using the three buffer solutions at pH 4.00, pH 7.00, and pH 10.00 following the specific directions for use of the pH meters that are provided in the laboratory. Be sure to use your wash bottle to rinse off the pH electrode into a waste beaker before and after using it in each of the buffer solutions. Dry off the end of the electrode by gently wiping it with a Kimwipe before placing it into a new solution. Always keep the pH electrode in a beaker of tap water or a container of pH 7.00 buffer solution.
2. Use your 10.00 mL volumetric pipet to quantitatively transfer 10.00 mL of the approximately 0.2 M HCl solution you prepared in Part I into a 250 mL beaker. Without measuring precisely, add about 40 mL of deionized water to this beaker. Place a magnetic stir bar into the beaker gently so no reagent splashes. Place a magnetic stir plate under a buret clamp that is adjacent to the pH meter you have just standardized near your work area and place the beaker on the stir plate. Use the previously conditioned buret from Part II filled with the approximately 0.15 M NaOH solution that you standardized in Part II and clamp it in place above the beaker. You will now standardize the HCl solution by titrating it with this NaOH solution. You will follow the course of the acid neutralization reaction by monitoring the pH with the pH meter. Using your extension clamp, clamp the pH electrode in place below the level of the liquid in the beaker and away from the stir bar. Also adjust the position of the buret tip so that it is inside the beaker, away from the side

but with the stopcock at a convenient location for you to manipulate. The clearances of all this assembly are rather close. You will probably need to position the beaker so that the stir bar is somewhat displaced away from the center of the beaker to allow room for the pH electrode but make sure that the stir bar is above the center of the stir plate. When assembly is complete, turn on the stir motor (left knob) slowly so that the stir bar is rotating at a smooth, moderate speed and clears the pH electrode. Do NOT turn on the heat.

3. With your first sample do a quick titration by adding 1 mL increments until you reach pH 2.5; then 0.10 mL (2 drops) increments until you reach pH 10.7; after that add 1 mL increments until pH 11.5. DO NOT use your wash bottle to rinse down the sides of the beaker as any added volume will change the pH readings and invalidate the titration curve data being collected. Record your buret readings after the addition of each increment. Allow time for the reaction vessel to become equilibrated and for the pH reading to become stabilized and then record the pH value in your notebook alongside the buret reading. Leave an empty column between the buret reading and the pH in which to place the volume of NaOH added (difference between present buret reading and initial buret reading). Stop the titration when you have reached pH > 11.5. For each pH reading, convert your buret readings to volumes of NaOH added. Examine this data and determine between which volumes the largest change in pH occurs. The NaOH volumes at both ends of the largest pH change, bracket the endpoint.
4. Set up your 2nd titration by repeating step 2. For your 2nd titration, refine your procedure based on your first titration by adding 1 drop of NaOH at a time from well below the endpoint to well above the endpoint. Record your buret readings after the addition of each increment. Allow time for the reaction vessel to become equilibrated and for the pH reading to become stabilized and then record the pH value in your notebook alongside the buret reading. Leave an empty column between the buret reading and the pH in which to place the volume of NaOH added. Stop the titration when you have reached pH > 11.5.
5. Repeat the titration procedure as time allows so that you have as many trials as possible to improve the statistics of your standardization of HCl.
6. Tightly cap and store the bottles containing the standardized NaOH and HCl solutions for use in later experiments.

#### Clean-Up

Pour the contents of the beaker and the remaining solution in the buret down the drain, rinsing with copious amounts of water. Carefully clean the buret by rinsing it with a few mL of acetic acid followed by several rinsings with deionized water. Rinse all remaining glassware with deionized water. Save both of the 1.0 L bottles containing your standardized solutions, for subsequent experiments.

#### Data Analysis

##### **Part I**

1. Calculate the volume of 6 M NaOH stock solution needed to prepare the 1L of 0.15 M NaOH? This should be the same volume of 6 M NaOH you used in part I.
2. Calculate the volume of 6 M HCl stock solution required to prepare the 1L of 0.2 M HCl? This should be the same volume of 6 M HCl you used in part I.

## Part II

3. Calculate the molarity of the NaOH solution as determined by the titration for each of the three acceptable trials. NOTE: KHP has the actual chemical formula  $\text{KHC}_8\text{H}_4\text{O}_4$ , formula mass = 204.23.
4. Calculate the average molarity of the NaOH solution.
5. Calculate the standard deviation of the average molarity of NaOH solution.
6. Calculate the 90% confidence interval for the reported molarity.

## Part III

7. How many trials did you perform to determine the titration curve for the neutralization of HCl by NaOH?
8. Use a spreadsheet program such as Excel to enter your titration data and make your titration curves by plotting pH vs. volume of added NaOH solution. Enter the volume of NaOH as a column headed V and the pH as an adjacent column headed pH. Leave four empty columns to the right of each curve for developing the derivative curves in question 9. Head these columns with the labels  $V_m$ , D1,  $V_d$ , and D2. Use the plot wizard to create a plot from the first two columns. Make sure you use the type of plot that will accept both a randomly spaced x value and a corresponding y value. Such plots are called scatter plots in the jargon of the business world that is commonly used in spreadsheet programs. Use this plot to estimate the position of the endpoint (that volume of NaOH which is midway between the two nearly linear asymptotic regions at low pH and at high pH). What is your best estimate of the volume of NaOH at the endpoint for each of your titration curves based on this plot?
9. A property of the equivalence point of an acid-base titration curve is that it is the volume at which the rate of change of pH is greatest (the first derivative reaches a maximum). It is also that volume at which there is an inflection point in the curve (the second derivative will change sign). These *first and second derivative plots*, which we will approximate by calculating and plotting *forward divided difference curves*, can help you identify this volume, perhaps more precisely than you can from the direct plot of pH vs. NaOH volume.

Following the directions below, use your spreadsheet program to calculate the forward divided difference approximation to the first derivative (rate of change) of the titration curve and the second forward divided difference approximation to the second derivative (rate of change of the rate of change) of the titration curve. Sample data and plots are shown below.

The first forward divided difference best represents the derivative or rate of change of the titration curve at the volume midway between volumes  $V(i)$  and  $V(i+1)$ . Here  $i$  is one of the data points and  $i+1$  is the next data point in the sequence. In the column immediately to the right of the pH values, enter the formula that will calculate the volume midway between  $V(i)$  and  $V(i+1)$ ,

$$V_m(i) = (V(i) + V(i+1))/2.$$

The forward divided difference approximation for a series of data points of the type  $\text{pH}(i)$ ,  $V(i)$  is given by:

$$D1(i) = [pH(i+1) - pH(i)]/[V(i+1) - V(i)].$$

In the column to the right of  $V_m$ , enter the formula for  $D1$ . It is easy to set up a formula by referencing the data in the cells for  $pH(2)$ ,  $pH(1)$ ,  $V(2)$ , and  $V(1)$  to calculate this forward difference for the first data point in the sequence in a column adjacent to the  $pH$  of the first point. This formula may then be copied down the column and the spreadsheet will update the references to the correct cells for the  $pH$  and Volume for each row automatically. The column then is the forward divided difference approximation to the derivative. Notice that of course, you will not be able to calculate a forward difference for the last row of the data since there are no data values beyond the last row to use for  $pH(N+1)$  or  $V(N+1)$ .

Likewise in the next column enter the formula for the volume midway between  $V_m(i)$  and  $V_m(i+1)$  given by,

$$V_d(i) = (V_m(i) + V_m(i+1))/2$$

Then in the next and final column to the right enter the formula for the second forward divided difference approximation to the second derivative (rate of change of the rate of change)

$$D2(i) = [D1(i+1) - D1(i)]/[V_m(i+1) - V_m(i)]$$

Invoke the plot wizard to plot the first forward divided difference ( $D1$ ) vs.  $V_m$ , and then again to plot the second forward divided difference ( $D2$ ) vs.  $V_d$ . These approximations to the first and second derivative illustrate the properties, mentioned above, of the titration curve.

The forward divided difference expressions do tend to amplify experimental error (commonly called noise), but your data should be good enough that these plots of the forward divided differences can help you to identify the equivalence point. You will find some plots at the end of this section of the laboratory manual that work up the first and second forward divided difference plots for some old titration data. You can see what the expressions do to the data. Your plots should look similar. **Print copies of all your graphs and turn them in to your teaching assistant. Make sure your name is on each of the graph. Clearly, title and label the vertical and horizontal axes.**

10. Using the combined representations of the titration curves developed in questions 8 and 9, what is your best estimate of the equivalence point volume of NaOH for each of your titration curves? You should be able to make this estimate to within 0.02 mL i.e. 32.46 mL.
11. Using the average molarity of your NaOH solution from part II, and the equivalence point volume of NaOH determined from the derivative plots, calculate the molarity of your HCl solution for each trial to four significant figures, i.e. 0.2314 M HCl.

12. Calculate the average molarity of your HCl solution. Keep the average values of your standardized NaOH and HCl solutions in a prominent place in your notebook and perhaps write the value on the bottle labels. You will need these values in subsequent experiments.

**Conclusion.** Take a moment to reflect on the standardization of NaOH, the titration curves, the forward divided difference approximation (derivative) treatment of the data, and the standardization of your HCl solution and then compose a summary paragraph that describes today's experiment and your new understanding of acid-base neutralization reactions.

### **Sample Data and Plots**

Since you may not have dealt with graphing first and second derivatives of curves, some sample graphs have been provided for you. The graphs are based on dummy data. A graph of the titration curve and of the first and second derivative curves of this data have been provided. Your graphs should have the same main features as the following graphs, although they will vary because your data will be different from this.

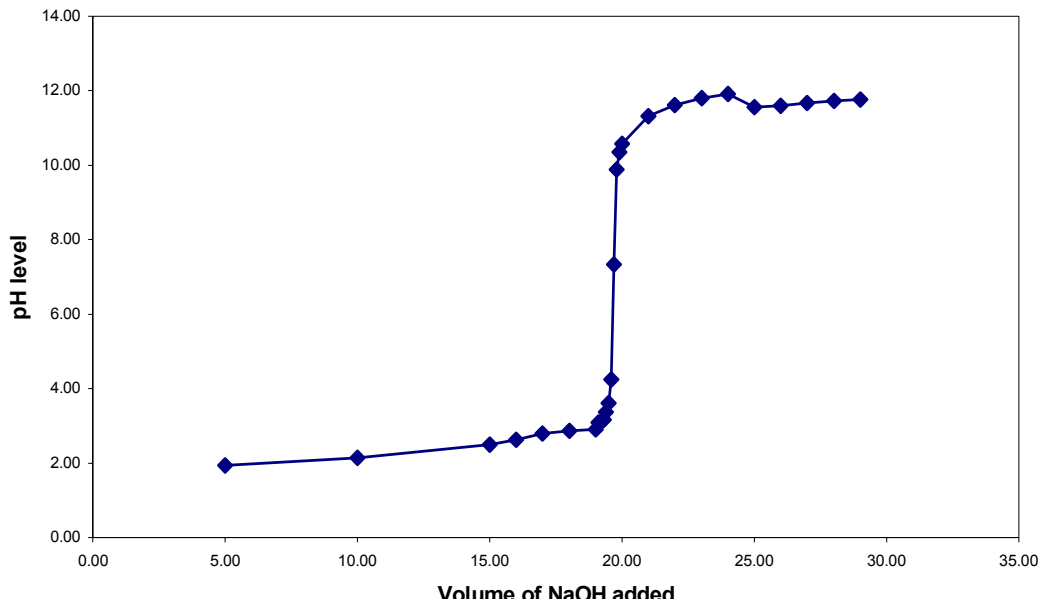
The first curve is just the titration curve. It is based on the data presented on the following page. As you can see, there is some room for error in estimating the precise volume for the equivalence point.

It is because of this difficulty in estimating the equivalence point that the two "derivative" curves are plotted. When the first derivative vs. NaOH Volume ( $D1$  vs.  $V_m$ ) is plotted, a strikingly different curve is the result. In this curve the equivalence point shows up as a large spike on the graph. The equivalence point of the titration is the maximum point on this curve. The second derivative plot ( $D2$  vs.  $V_d$ ) is also made for convenience. When this plot is made the equivalence point is the value of the volume for which the plot passes through the x-axis. Both curves are useful in more accurately determining the equivalence point of titrations.

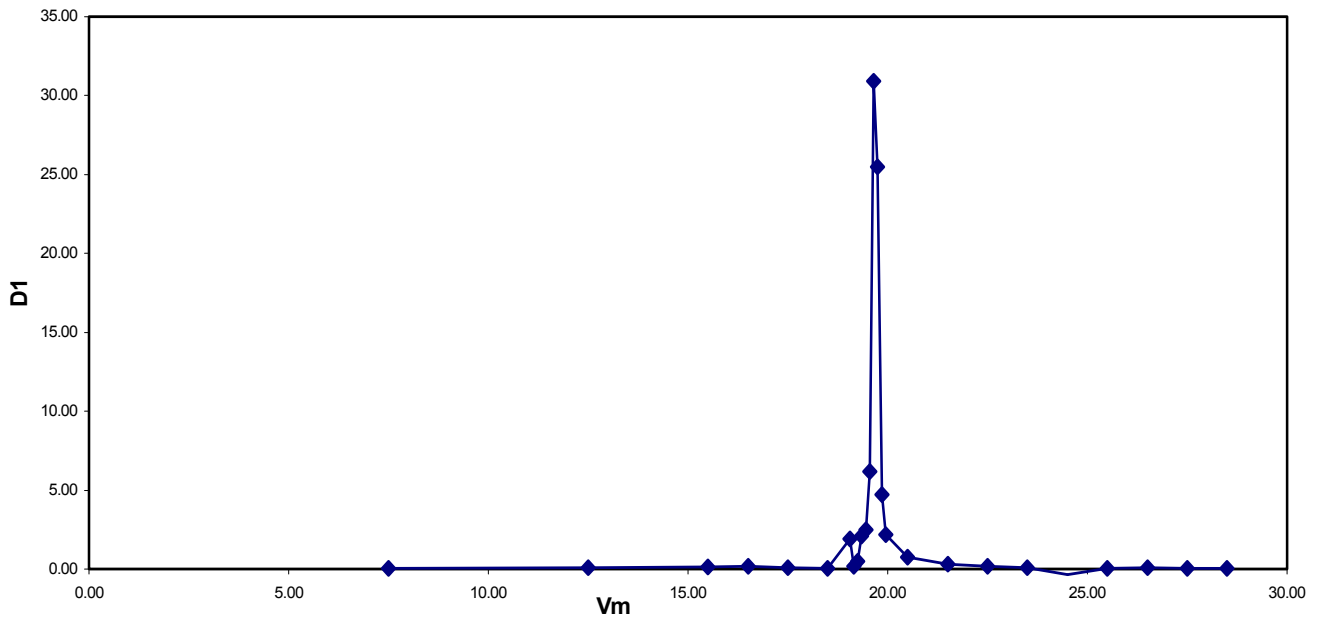
TITRATION EXAMPLE: Titration of 30 mL HCl with 0.10 M NaOH

mL NaOH (Vol)	pH	Vm	D1	Vd	D2
5.00	1.93				
10.00	2.15	7.50	0.04		
15.00	2.50	12.50	0.07	10.00	0.0052
16.00	2.63	15.50	0.13	14.00	0.02
17.00	2.80	16.50	0.17	16.00	0.04
18.00	2.87	17.50	0.07	17.00	-0.1
19.00	2.90	18.50	0.03	18.00	-0.04
19.10	3.09	19.05	1.90	18.78	3.4
19.20	3.11	19.15	0.20	19.10	-17
19.30	3.16	19.25	0.50	19.20	3
19.40	3.37	19.35	2.10	19.30	16
19.50	3.62	19.45	2.50	19.40	4
19.60	4.24	19.55	6.20	19.50	37
19.70	7.33	19.65	30.90	19.60	247
19.80	9.88	19.75	25.50	19.70	-54
19.90	10.35	19.85	4.70	19.80	-208
20.00	10.57	19.95	2.20	19.90	-25
21.00	11.31	20.50	0.74	20.23	-2.65455
22.00	11.61	21.50	0.30	21.00	-0.44
23.00	11.80	22.50	0.19	22.00	-0.11
24.00	11.91	23.50	0.11	23.00	-0.08
25.00	11.56	24.50	-0.35	24.00	-0.46
26.00	11.60	25.50	0.04	25.00	0.39
27.00	11.68	26.50	0.08	26.00	0.04
28.00	11.72	27.50	0.04	27.00	-0.04
29.00	11.77	28.50	0.05	28.00	0.01

Titration Curve (pH vs. vol of NaOH)



First Derivative



Second Derivative

