

TITRATIONS OF AQUEOUS SOLUTIONS (A two week experiment)

The Problem to be Investigated: A pH meter will be calibrated and used to obtain data for the titration of acetic acid with sodium hydroxide. A complementary titration will be performed with a conductivity probe and the results compared. Finally, a thermometric titration will be performed on the same system to determine the heat of the reaction. The three experiments will allow determination of G° , H° , and S° for the system.

The Nature of this Investigation: This investigation consists of four parts. First you will perform a conventional colorimetric titration of a standard weak acid with a strong base, sodium hydroxide. Then a pH meter will be used for the titration of acetic acid, a weak acid, by sodium hydroxide. The pH of the acetic acid solution will be recorded as a function of the volume of sodium hydroxide solution added. The resulting data will be used to construct a titration curve from which the equivalence point of the titration will be found. Third, the same titration will be performed using the conductivity probe that is available on each meter. A plot of conductivity as a function of volume of sodium hydroxide will provide an alternative method for determining the equivalence volume of the titration. Fourth, a thermister probe will be calibrated to read temperature to better than 0.01°C . A final titration will be performed using the thermister probe as the sensor. From the temperature change of the system you will be able to calculate H for the dissociation of acetic acid.

BEFORE BEGINNING THE EXPERIMENT: enter the following data into a spreadsheet and graph it.

pH	Volume NaOH, ml
1.0	0
1.2	5.00
1.4	10.00
1.6	15.00
2.0	20.00
2.7	24.00
3.0	24.50
7.0	25.00
11.0	25.50
11.4	26.00
12.0	30.00
12.2	35.00
12.3	40.00
12.4	45.00
12.5	50.00

Discuss this graph and then when you meet with your lab instructor the following types of questions will be asked:

- where is the equivalence point?
- what is the significance of this point?
- how will you determine this point?
- how will the $[\text{H}^+]$ be determined at any given place on the graph?

Week I

STANDARDIZATION OF A NaOH SOLUTION WITH POTASSIUM HYDROGEN PHTHALATE

Background Information

Laboratory work frequently involves the use of a standard solution, which is a solution of accurately known concentration. For example, standard solutions are used in the process of titration, which is a common volumetric method of analysis. Titration consists of the careful addition of a solution of unknown concentration to a measured quantity of the standard solution until the reaction between these substances is complete. The known quantity of the standard solution and the measured volume of the other solution can be used in calculations to determine the unknown concentration. Titrations are employed for acid-base reactions, oxidation-reduction reactions, complex formation reactions, and precipitation reactions. An acid-base titration is the subject of this laboratory investigation.

Once the reactants for an acid-base titration are chosen, one reactant must be selected as a standard for the proposed titration. The selection of one of the substances as a standard can be accomplished in two ways. First, one of the substances may be a primary standard, in which case a standard solution of the substance may be prepared and the exact concentration calculated directly from the mass of the solute and the volume of the solution. If neither of the reactants in the titration reaction is a primary standard, then the concentration of one of the reactants must be determined separately using a primary standard. Thus, a primary standard is used, either directly or indirectly, in the preparation of any standard solution.

For a substance to be a primary standard, the following criteria should be met, or at least approached. A primary standard substance should be:

1. Available in very pure form.
2. Reasonably soluble.
3. Stable in the pure form and in solution.
4. Nonhygroscopic and easily dried.
5. A compound with a reasonably high formula weight.

Not very many substances meet these criteria, so the number of useful primary standards is quite limited. Two common primary standard bases are pure sodium carbonate and borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. Some primary standard acids are potassium hydrogen phthalate, oxalic acid dihydrate, sulfamic acid, and benzoic acid. Potassium hydrogen phthalate is a solid organic acid.

Solutions of sodium hydroxide slowly attack glass containers and cause glass stoppers to become stuck. Thus, sodium hydroxide solutions are usually stored in polyethylene bottles fitted with rubber stoppers or screw caps. Also, burets must be thoroughly cleaned immediately after use.

In this experiment, the concentration of a sodium hydroxide solution will be determined by titrating potassium hydrogen phthalate solutions, each containing an accurately known mass of potassium hydrogen phthalate. The sodium hydroxide solution is referred to as the titrant because it is the solution dispensed from the buret into the solution being titrated. The reaction involved in this titration is shown in Equation (3).



To determine the concentration of the sodium hydroxide solution, the number of moles of sodium hydroxide that react with a known number of moles of acid must be calculated.

A small amount of indicator solution containing phenolphthalein is added to each standard acid solution and signals the endpoint of the titration by changing color. Phenolphthalein is colorless in the acid solution but changes to pink at the endpoint (about pH 8.3).

Procedure

Work alone for these titrations.

Weighing bottles containing dried potassium hydrogen phthalate (KHP) are located by each balance in the balance room.

Tare a clean 200- or 250- ml Erlenmeyer flask, then carefully transfer about 0.7 to 0.9 grams of KHP into it. Record the weight to the nearest 0.1 milligram. You will need to prepare three samples.

Dissolve each sample in about 30-50 ml of distilled water. Add three drops of phenolphthalein indicator solution to the contents of each flask.

Standardization of the Sodium Hydroxide Solution

Obtain one liter of approximately 0.1M NaOH from the instructor. Mix thoroughly to make sure you have a homogeneous solution. After cleaning the buret, rinse the buret with three 5-ml portions of the sodium hydroxide solution to be standardized. Make certain that the rinse solution comes in contact with the entire inner surface of the buret and the tip of the buret. Close the buret stopcock and fill the buret with the sodium hydroxide solution to above the top calibration mark on the buret. Be sure to replace the buret cap to avoid carbon dioxide contamination and evaporation of your solution. Lower the meniscus of the solution until it reaches a calibrated portion of the buret. Make certain that the buret tip is filled with the solution. Record the initial buret reading to the nearest 0.01 ml. Use a buret reading card to easily visualize the meniscus.

Place one of the Erlenmeyer flasks containing the potassium hydrogen phthalate solution under the buret and lower the buret tip until it is well into the mouth of the flask, as shown in Figure 1. Swirl the flask containing the solution with one hand while controlling the stopcock with the other hand. Add the titrant slowly to the solution with swirling.

As the titration progresses, the approach of the endpoint will be signaled by a temporary appearance of a pink color where the titrant first comes in contact with the indicator. At this point, add the titrant dropwise to the standard acid solution. As the endpoint is approached more closely, these temporary flashes of color will persist longer and fractional parts of a drop of titrant should be added. Fractions of a drop may be added by allowing a droplet of titrant to begin to form on the

buret tip. After touching the buret tip to the inner surface of the flask, wash down the inner surface of the flask with a stream of distilled water from a wash bottle. The titration is complete when the indicator exhibits a pink color that persists for several seconds. Wait for about 15-20 seconds to allow any solution on the inner wall of the buret to drain down to the meniscus and then read the final buret volume to the nearest 0.01 ml.

Repeat the titration at least two more times with two different samples of standard acid. Titrations should be done until three results are obtained which agree to within less than five parts per thousand.

When all of the titrations are completed, drain and *thoroughly rinse* the buret with distilled water. Label and store your buret, filled with distilled water, on the shelf above your lab bench. The tip of the buret can be cushioned by lowering it into a small beaker containing a paper towel. Thoroughly wash all other glassware used in this experiment. Store the standardized NaOH in a rubber-stoppered bottle in your desk for the next pH titration experiment.

Calculations which should be in your notebook

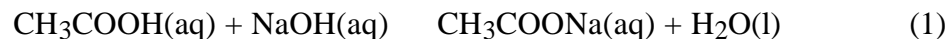
1. For each titration, calculate the molarity of the sodium hydroxide.
2. Calculate the average molarity of the sodium hydroxide solution, the range, and standard deviation of your results. If you wish to reject one of your results, use the Q test.

Week II

Background Information

The neutralization reaction of acetic acid (CH₃COOH) and sodium hydroxide solution occurs as follows:

Molecular:



Ionic:



Net Ionic:



A typical curve for the titration of acetic acid with sodium hydroxide solution is given in Figure 1. The equivalence point is found by determining the steepest portion of the curve, but as seen from Figure 1, the equivalence point does not occur at pH 7, as it would for a strong acid strong base titration.

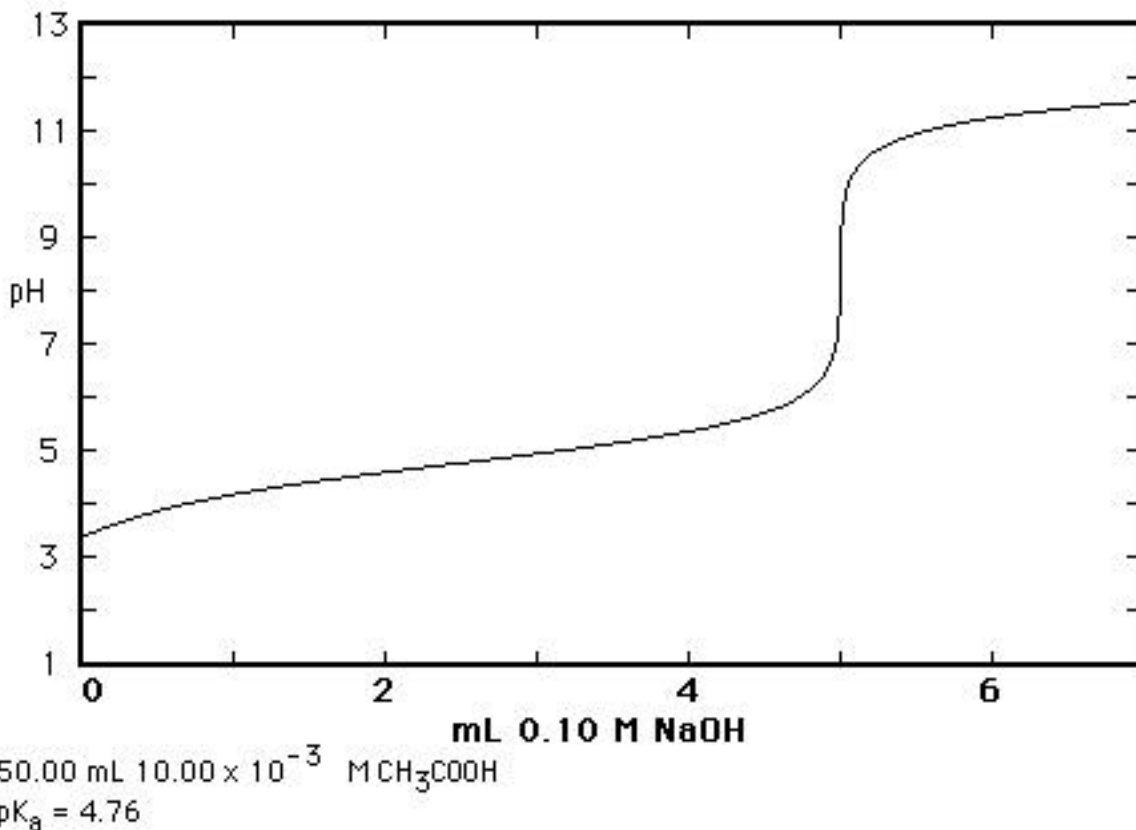


Figure 1. Titration curve of acetic acid with sodium hydroxide.

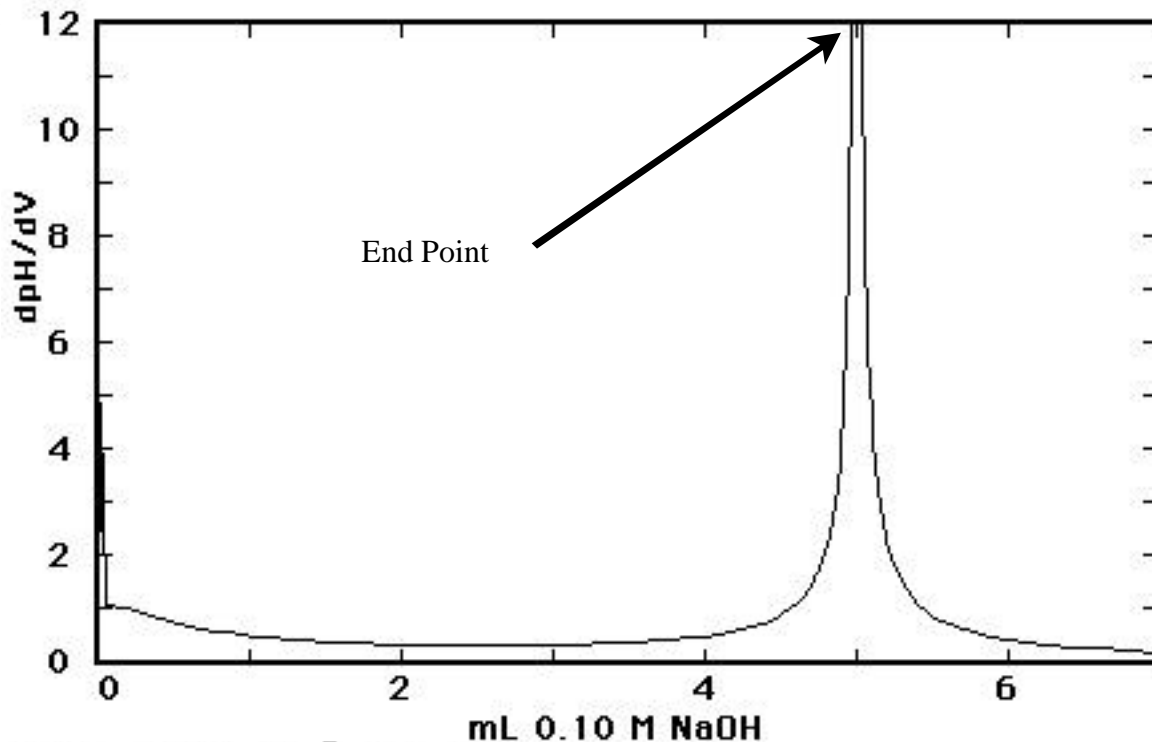
At the equivalence point in the titration, equimolar quantities of acetic acid and hydroxide ions have reacted, so that all of the H^+ ions available from the acetic acid have combined with all of the OH^- ions available from the sodium hydroxide solution. Any H^+ and OH^- ions existing in solution at the equivalence point come from two sources: (1) the dissociation of water molecules, and (2) the hydrolysis of the acetate ion, CH_3COO^- , produced in the neutralization reaction.



Because hydroxide ions are produced by hydrolysis of the acetate ion, the solution is not neutral at the equivalence point; instead, the pH is greater than 7.

At the equivalence point, the moles of sodium hydroxide added will equal the moles of acetic acid being titrated. Dividing the moles of acetic acid by the volume of the acid titrated will provide the concentration of the unknown sample.

The endpoint (we will use the terms endpoint and equivalence point interchangeably in this lab) of the titration can be estimated by eye. An improved approach is to calculate the derivative of the titration curve $\text{d}p\text{H}/\text{d}V$ and plot this function versus volume. As shown in Figure 2, the derivative plot exhibits a clear maximum at the equivalence point.



50.00 mL $10.00 \times 10^{-3}\ M\ CH_3COOH$
 $pK_a = 4.76$

Figure 2. Derivative plot of the acetic acid titration.

The volume half way to equivalence point has particular significance since this is the point where the acetic acid is half titrated. In other words, the moles of acetic acid will equal the moles of sodium acetate. Using the Henderson-Hasselbalch, it is apparent that at this point of the titration the pH will equal the pK_a for acetic acid.

$$pH = pK_a + \log \frac{\text{base}}{\text{acid}}, \text{ and } pH = pK_a \text{ at } V_{1/2}$$

We will confirm the pK_a of acetic acid as part of this experiment.

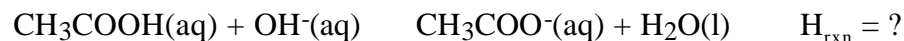
Acid/Base titrations are not restricted to measurements of pH as a function of added titrant. In the previous lab experiment we used conductivity probes to investigate the nature of ions in solution. Recall that the electrical conductivity of a solution is the quantity of electricity which will flow through a solution per unit area, per unit potential gradient, per unit time usually expressed as mho/cm. Note: mho (pronounced "mo") was derived as a unit of conductivity by reversing the letters in "ohm", the unit of resistance. (See Experiment 6 introduction for review of conductivity). Table 1 is an abbreviated table of ionic conductances.

Table 1. Ionic Conductances of Selected Ions	
Ion	Ionic Conductance (mho l eq. ⁻¹ cm ⁻¹ .)
H ⁺	0.34982
Na ⁺	0.05011
OH ⁻	0.1986
CH ₃ COO ⁻	0.0401

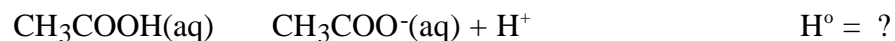
As a consequence of the very different ionic conductance of the acetate anion and the hydroxide anion, the equivalence point of acetic acid titration with sodium hydroxide is indicated as a significant change in conductivity. A typical conductametric titration is shown in Figure 3.

Note that the shape of the titration is very different than the pH titration. However, the endpoint of the titration is evident as a distinct change in slope of the conductance plotted versus volume. Two best-fit lines plotted through the data before and after the endpoint allow an accurate estimation of the endpoint volume.

A final titration of the same acid/base system will be performed using a very sensitive electronic thermometer (thermister) to measure the temperature of the titration mixture as a function of added sodium hydroxide. The reaction of acetic acid with base produces heat:



This reaction is really the sum of the acid dissociation and the heat of association for water.



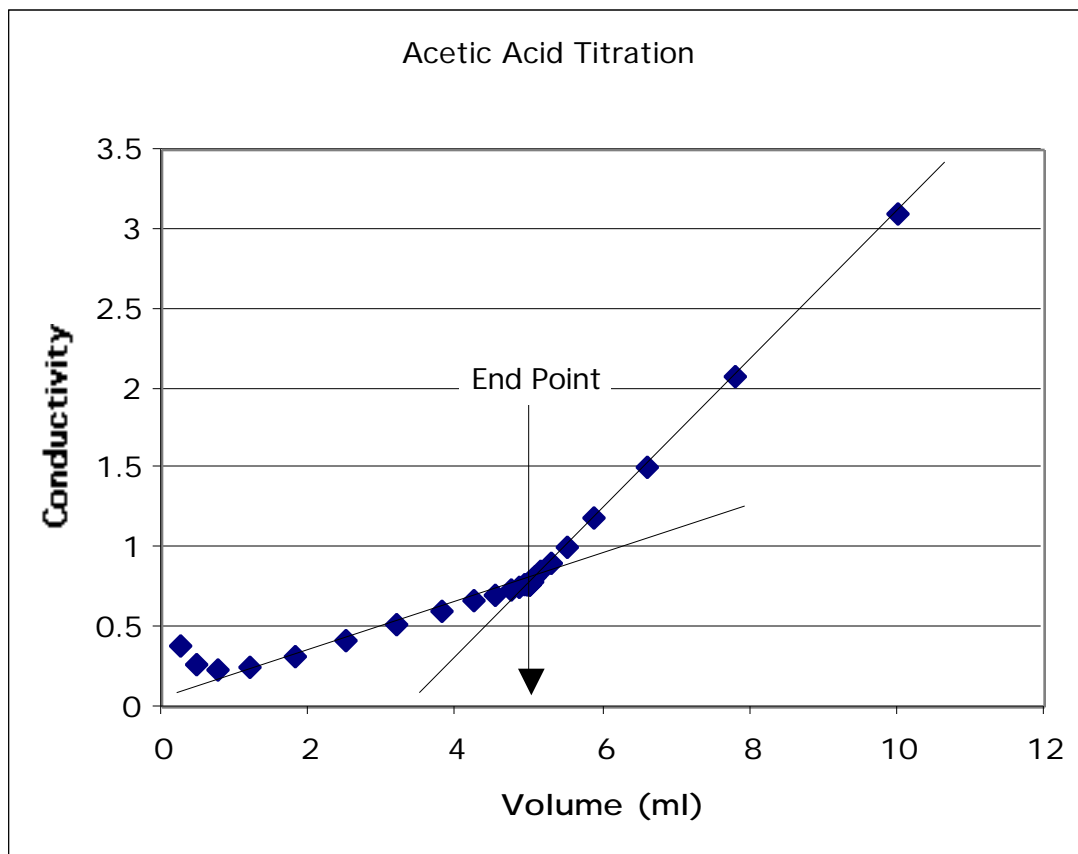


Figure 3. Conductance of an acetic acid solution as a function of added sodium hydroxide.

By measuring the heat produced by the overall reaction the heat of dissociation of acetic acid can be determined. A typical titration curve is shown in Figure 4.

As the titration proceeds the solution becomes warmer until the endpoint is reached. After the endpoint the solution continues to warm at a much slower rate due to the dilution of sodium hydroxide. Extrapolation of the temperature curve after the endpoint to the start of the reaction corrects for the heat of dilution of sodium hydroxide and also any heat absorbed by the titration vessel.

$$\text{Heat evolved} = q = [(\text{specific heat of solution}) \times (\text{mass of solution})] (T_{\text{extrapolated}} - T_i).$$

The specific heat of the titration solution can be considered the same as pure water (4.18 °C/J g). You may assume that the density of the acetic acid solution is 1.00 g/ml. The enthalpy of the reaction is the heat evolved divided by the moles of acid titrated.

$$H_{rxn} = \frac{-q}{\text{moles}}$$

A consequence of these three experiments is that the pK_a and H° for acetic acid are determined. This allows complete determination of the thermodynamics of the acetic acid system. Recall that the free energy of the system is related to the equilibrium constant:

$$G^\circ = -RT \ln(K)$$

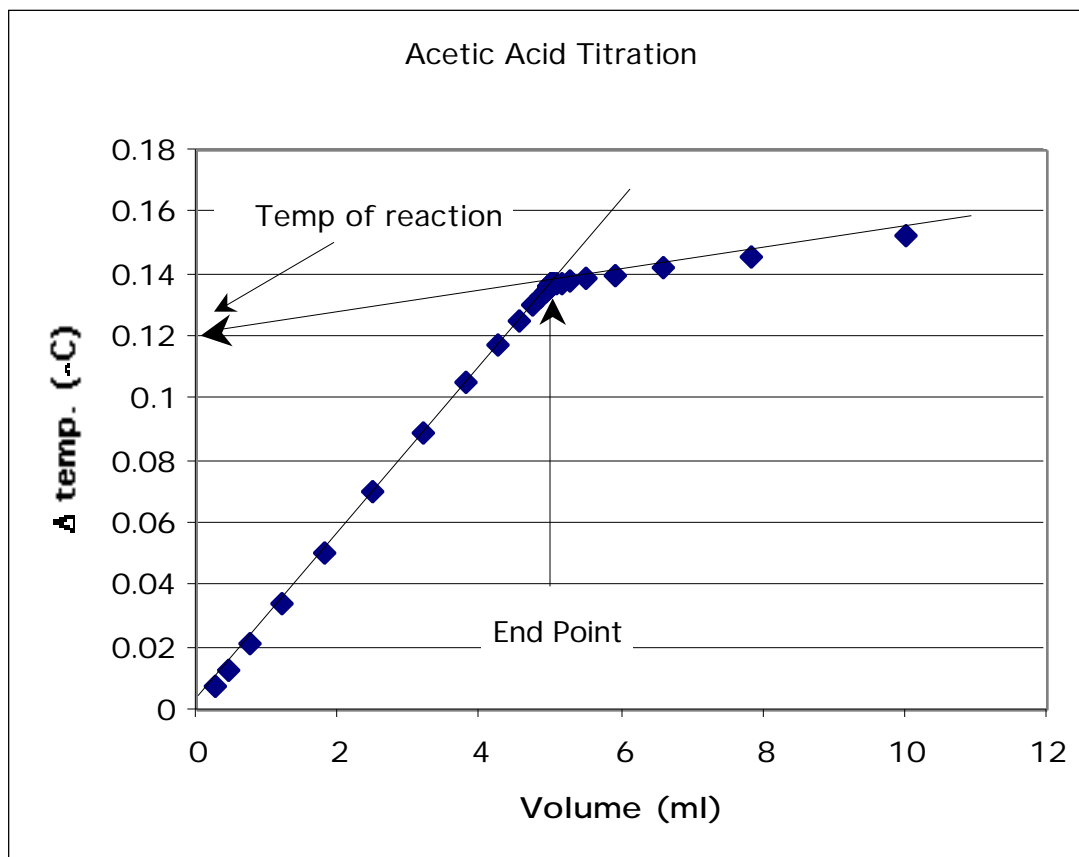


Figure 4. Thermometric titration of acetic acid with sodium hydroxide.

and the free energy change is related to the standard entropy and enthalpy of the reaction.

$$G^\circ = H^\circ - T S^\circ$$

Simple substitution then allows for determination of S° calculated. A typical titration curve is shown below in Figure 4.

PROCEDURE:

Titration of Acetic Acid with Sodium Hydroxide Solution

We will use an automated titration system for all three titrations. You will work with a partner

Your lab instructor will demonstrate the operation of the titration system. Briefly, a precision pump replaces the burette used in traditional titrations. The computer controls the pump to deliver titrant to the reaction vessel. A pH meter is used to measure the pH, conductivity, or temperature in the vessel, and these data are recorded by the computer for display and analysis.

CALIBRATION OF PUMP

Fill a beaker with water and place the pump intake into the beaker. Flush the system with water to remove any bubbles. Weight a clean, dry weighing bottle (with cap) on an analytical

balance. Handle the bottle with a dry towel to prevent adding mass from your hands. Next, deliver 100 pulses from the pump into the weighing bottle. Reweigh the bottle and calculate the mass of water delivered. Dividing this mass by the number of calibration pulses provides a calibration for the volume the pump delivers with each pulse.

Rinse your pump with 3-5 mls of your standardized hydroxide solution. Clamp the pump tubing to the edge of the titration vessel. Make sure that no bubbles remain in the pump tubing.

TITRATION SETUP

Obtain a 250 ml volumetric flask from the instructor (It must be returned at the end of the period). Quantitatively transfer your sample to the cleaned 250 ml volumetric flask, dilute to the mark with distilled water, and *mix thoroughly*.

Rinse a clean 10 ml volumetric pipette with a *small* portion of unknown solution by drawing solution from the volumetric flask. Then use this pipette to take a 10.00 ml aliquot of unknown from the volumetric flask, transfer it to a clean 250 ml beaker, and add 50 ml distilled water.

Calibrate the pH meter by referring to the instructions next to each meter.

Carefully place a magnetic stir-bar into your beaker, and place the beaker on a magnetic stirrer. Immerse the rinsed electrode of the pH meter into your solution, making sure that the magnetic stir-bar does not strike the electrode. Ask the laboratory instructor to check the equipment set up.

Titrate with your standardized NaOH solution. Continue until the pH meter reads about 11. From your data, estimate the volume of base required to reach the equivalence point.

DETERMINATION OF STEEPEST SLOPE:

Place a second 25.00 ml aliquot of unknown in a clean 250 ml beaker and add 50 ml of distilled water and titrate again. Using an Excel spreadsheet plot slope vs. mL to determine the equivalence point(see Figure 1..

Setup the experiment again using the conductivity probe instead of the pH electrode.

Perform the titration using the conductivity probe. Determine the endpoint of the titration (see figure 3) and compare your results with the pH titration.

The thermometric titration procedure is the same except you will measure the temperature instead of the pH or conductivity of the solution. Your lab instructor will demonstrate the operation of the temperature probe.

The temperature probe (thermister) must be calibrated before use. Start with a 250 ml beaker containing water at room temperature. Measure the temperature carefully using a mercury thermometer. Insert the thermister probe into the water and record the signal measured by the computer. Next repeat the measurement in a Styrofoam cup of warm water. From these two measurements a calibration equation for the thermister can be established

$$t (^{\circ}\text{C}) = (S - S_1) * (t_2 - t_1) / (S_2 - S_1)$$

where S is the signal measured on the computer and t is the actual temperature.

Perform the thermometric titration and calculate the average ΔH for the reaction. Using your temperature data calculate the enthalpy of acetic acid dissociation. Determine the endpoint of the titration (see figure 4) and compare your results with the pH and conductivity titrations.

LABORATORY NOTEBOOK

Keep track of all measurements in your lab notebook. Record all observations in your lab notebook. Remember to include units on all numbers that have them. Copy and tape printouts of your calculations (from Excel) into your lab notebook. **All partners should have a copy of the final graphs taped into their notebooks.**

REPORT

Part 1

1. What is the significance of the equivalence point in a titration? (5 points)
2. How would the results of the pH titration be different if 25.00 mL of unknown and 100 mL of distilled water were used? (10 points)
3. Which solution has a greater conductance 0.01 M NaOH or 0.01 M CH₃COOH? Why? (10 points)

Part 2

4. Plot pH versus volume of sodium hydroxide solution. Also attach a *copy* of the pH/ ml versus volume of titrant plots that you used to find the equivalence points. (20 points)
5. Plot conductivity versus volume of sodium hydroxide solution. Also include the equations of the best fit lines used to find the equivalence volume. (15 points)
6. Report the mean concentration and standard deviation of your acetic acid unknown. (10 points)
7. Report the pK_a of acetic acid determined from your pH titrations. How does this compare with literature values? (10 points)
8. Plot ΔT versus volume of sodium hydroxide solution. Calculate the heat produced in the titration and the standard enthalpy of dissociation for acetic acid. (10 points)
9. Determine the ΔG° and ΔS° for acetic acid dissociation. (10 points)