GOAL:
The purpose of this experiment is to do a potentiometric titration and use the resulting titration curve to find the equivalence point and $K_a$ value for a weak acid. We also want you to think carefully about the form in which compounds exist at different points in the titration.

INTRODUCTION:
You have done several titrations using the color change of an indicator to find the equivalence point. In this experiment, we will omit the indicator and use an instrument to monitor pH as the titrant is added. This is known as a potentiometric titration. In Part 1, you’ll titrate a solution of acetic acid. In Part 2, you’ll apply your experience to titrate an unknown solid acid. Figure 1 shows a typical titration curve for a weak acid, HA, to which we add NaOH titrant. The reaction, which goes to completion and is not an equilibrium, is

$$\text{HA(aq)} + \text{NaOH(aq)} \rightarrow \text{Na}^{1+}(aq) + \text{A}^{1-}(aq) + \text{H}_2\text{O(l)}$$

Eqn 1

Notice in Figure 1 that as the first few drops of NaOH are added, the pH rises quite sharply, but then levels off (1 mL to 8 mL). This happens because some of the HA is converted to its conjugate base $A^{1-}$. Any solution that contains significant amounts of an acid and its conjugate base is a buffer and resists changes in pH. In the middle, flat region of a titration curve, the mixture is acting as a buffer.

As we near the titration equivalence point (10 mL in the figure), most of the HA has been converted to $A^{1-}$, and the solution loses its buffering ability, so pH rises more rapidly. The titration equivalence point, when just enough NaOH has been added to convert all the HA to $A^{1-}$, corresponds to the sharp rise in pH seen at 10.00 mL. A titration curve also lets us find the acid’s $K_a$ value. Recall that

$$K_a = \frac{[\text{H}_3\text{O}^{1+}] [\text{A}^{1-}]}{[\text{HA}]}$$

Eqn 2

When exactly half of the HA has been converted to $A^{1-}$, then $[A^{1-}] = [HA]$, so these terms cancel out, leaving $K_a = [\text{H}_3\text{O}^{+}]$, or we may say that $pK_a = \text{pH}$ ($pK_a = -\log K_a$) at the half-equivalence point.

In Figure 1, the equivalence point is at 10.00 mL, so at half this volume, 5.00 mL, pH = $pK_a$. We read the pH at 5.00 mL from the graph finding $\text{pH} = 5.70 = pK_a$, and thus $K_a = 2.0 \times 10^{-6}$. For more information on titration curves, see Section 16.4 in your textbook.
In Part 1 of this experiment, you will titrate acetic acid with a strong base. The reaction, shown in Eqn 3, forms sodium acetate.

\[ \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)} + \text{H}_2\text{O(l)} \]  

Eqn 3

In this experiment you will be measuring pH using a pH electrode interfaced to a laptop computer. The computer will assist you in gathering data as well as identifying the titration equivalence point. The computer will monitor pH and prompt you to enter volume measurements. The computer will graph your titration curve, which will be similar to Figure 1 on page 1. You will also use the computer to pinpoint the equivalence point by making a graph of the second derivative of your titration curve. On a graph of second derivative vs. volume, the equivalence point volume is the point where the second derivative passes quickly through zero. On the graph at right (Figure 2), the equivalence point is at 10.0 mL.

While Part 1 focuses on using the half equivalence point to find pK_a, recall that the equivalence volume also provides useful information. When equivalence volume is combined with the titrant’s molarity, you can calculate moles. For a titration in which you know both the mass and moles of the acid, you simply divide to calculate molar mass (g/mole). Recall that stoichiometric calculations from titrations are covered in Chapter 4. In Part 2 of this experiment, you will be given a solid sample of a monoprotic acid. Your titration will allow you to find both its K_a (a chapter 16 topic) and its molar mass (a chapter 4 topic).

PRE-LAB ASSIGNMENT:
In lab you will need to prepare 250.0 mL of 0.0750 M NaOH from solid NaOH. Calculate the mass of NaOH you will need. Record this calculation in your pre-lab notebook entry. Don’t forget to take the prelab quiz online.

HAZARDS:
As usual, exercise due care when handling all the acids and bases in this experiment. All solutions may be flushed down the sink with running water at the conclusion of the experiment. For your pre-lab notebook entries, look up the MSDS for glacial acetic acid (the name for concentrated acetic acid). Include the following information in your notebook entry:

- appearance and odor
- a summary of first aid measures recommended
LABORATORY OBSERVATIONS AND DATA:
You will work in pairs during lab. Each student should make notebook entries and each student will write up a separate report. Note that in the procedure, we sometimes add NaOH by different amounts. Pay attention to these variations. Adding NaOH too quickly will hurt your results. Adding NaOH too slowly will slow you unnecessarily.

PROCEDURE:
This procedure will be done in pairs. Record the names of both partners in your lab notebook.

Preparation of the NaOH titrant:
Confirm with your instructor that you have correctly calculated the mass of NaOH needed to prepare 250 mL of 0.0750 M NaOH. Weigh out about this mass. (Record the exact mass.) Transfer it to a 250 mL volumetric flask. Dilute to the mark with distilled water. Cover with parafilm and invert several times to mix thoroughly. Use the mass of NaOH you weighed out to calculate the exact molarity of your prepared NaOH solution. Record this calculation in your notebook.

Part 1. Titration of HC₂H₃O₂ with NaOH:
Your set-up will look something like that shown in Figure 3. One person should manipulate the buret while the other enters data into the computer. Be sure to record what you do and observe in your notebook. The computer will generate your graphs for you, but you will also need to record some important numbers after examining the graph, including the equivalence volume, equivalence pH, half-equivalence volume, and half-equivalence pH.

1. Take a clean 100 mL beaker to the reagent bench and get about 40 mL of 0.0500 M acetic acid, HC₂H₃O₂. You also need a 20 mL pipet and bulb.

2. Use a small amount of the acid to rinse your pipet 3 times. Discard the rinse solutions. Now pipet 20.00 mL of acetic acid into a 50 mL beaker. Place the beaker on a magnetic stirrer and add a stirring bar. Adjust the stir rate so that the bar spins gently. Use a clamp to suspend the pH electrode in the acid solution. Be sure that the spinning stir bar does not strike the electrode.

3. Use a small amount of the NaOH solution you prepared to rinse the buret 3 times. Fill the buret and suspend it from a buret clamp. Be sure to run some NaOH through the stopcock to remove any air. Then carefully bring the volume exactly to the 0.00 mL mark. [This step is not normally done, but we want to make recording the volume of NaOH added in each step especially easy.] Any waste NaOH solution can go down the drain with excess water.

4. If the computer is not already set up, prepare the computer for data collection by opening the Titration Curves file in the “Roanoke Experiments” folder of LoggerPro. The vertical axis has pH scaled from 0 to 14 pH units. The horizontal axis has volume scaled from 0 to 25 mL. With the electrode in the acetic acid solution, the Meter window should show an acidic pH.

5. Before adding any NaOH titrant, click and monitor pH for several seconds. Once the displayed pH reading has stabilized, click . In the edit box, type 0 (for 0 mL added). Press the ENTER key to store the first data pair for this experiment.
6. You are now ready to begin the titration. This process goes faster if one person manipulates and reads the buret while another person operates the computer and enters the volumes.

7. Add about 0.25 mL of NaOH titrant. When the pH stabilizes, again click [Keep]. In the edit box, type the current buret reading, to the nearest 0.01 mL. Press ENTER. You have now saved the second data pair for the experiment. If your solution is being mixed properly and your electrode is working correctly, you should never have to wait more than a few seconds to take a reading. Small fluctuations are normal, just wait a few seconds for mixing, and then click KEEP to take a reading.

8. After this first addition, continue adding NaOH solution in increments of about 1mL and enter the buret reading (to nearest 0.01 mL) after each increment.

9. When a pH value of 6.0 is reached, change to adding NaOH by increments of 2-3 drops. Record a data pair after adding each small increment. Continue these small volume additions until pH reaches about 10.

10. When a pH value of 10 is reached, change back to adding NaOH in 1 mL increments.

11. Continue adding NaOH solution in 1 mL increments until you are at least 3 mL past the equivalence point.

12. When you have finished collecting data, click [Stop]. Discard the solution from the beaker in the sink, but keep your buret of NaOH. Rinse your beaker, stir bar, and pH electrode with distilled water. Be careful to prevent loss of the tiny stir bar.

13. If the data points on your graph are not connected by a line, double click on the graph. In the Graph Options box that pops up, select connect points and click done.

14. Print copies of this titration curve graph (File, Print Graph.) Enter the team members’ names when you have this option. Print a copy for each team member.

15. Move the cursor around on your graph. Note that the (x,y) coordinates display in the lower left corner of the graph. Position your cursor on the equivalence point. Record the coordinates as your equivalence volume and equivalence pH.

16. Divide your equivalence volume in half to get the half-equivalence volume. Move your cursor to this point on the graph. Record the coordinates as your half-equivalence volume and half-equivalence pH.

17. It is often easier to accurately locate the equivalence point by looking at the second derivative graph. Click on the y-axis label (currently pH in pH units) to view the other graph options. Select the second derivative (d 2). Your graph should look something like Figure 2. If your graph goes off-scale, click the Graph Autoscale icon.

18. Print copies of this second derivative graph for each team member. Again use the cursor to find the equivalence volume.

19. When you are sure that you have all the graphs and data needed, delete your data by choosing the Data, Clear All Data.
Part 2. Titration of an Unknown Solid:
For the second part of this experiment, your job is to find the $K_a$ value and molar mass of an unknown solid acid. Get an unknown from the supply bench. Be sure to record its unknown number. In your notebook, outline the steps that you will follow for your titration. When you think you have a good procedure, including what data to record, ask the instructor to check it. You must get the instructor’s initials in your notebook before proceeding. You will have about 0.4 g of solid unknown, enough to do two trials. Complete two trials. When you write up your report, you may choose to average your calculated results or to base your calculations on the single trial you believe is more accurate.

When you are all done with the experiment, discard all solutions down the drain. Rinse all glassware with distilled water. Rinse the pH electrode with distilled water and then return it to its soaking solution.

Be sure that both lab partners have a full set of data and computer print outs before leaving lab. Each student must write up the lab report independently.

RESULTS AND DISCUSSION:
For Part 1, prepare a table giving the equivalence volume, equivalence pH, pH at half equivalence, and $K_a$ value. For Part 2, prepare a table of your data (mass of solid, exact molarity of NaOH, volume, etc for each trial) and calculated results including moles, $K_a$ and molar mass for your unknown. Each trial should have its own column. Don’t forget your sample calculations. Staple your computer printouts to your report.

QUESTIONS:
1. Write the balanced chemical equation for the reaction between HC$_2$H$_3$O$_2$ and NaOH. At the titration equivalence point which of the reactants and products from this equation will actually be present? What was the observed pH at the equivalence point? Without doing any actual calculations, explain why this equivalence point pH wasn’t neutral.

2. Examine your Part 1 results and graphs. Describe how you locate the equivalence point on each of the two types of graphs you used. Did one seem to provide a more accurate way to locate the equivalence point? Explain.

3. Look up an accepted value for the $K_a$ of HC$_2$H$_3$O$_2$ in your textbook. How does your experimental value compare to the accepted value? (Up to 50% error is typical, less than 10% error is excellent.)

4. In Part 1, your titration curve should have a relatively flat region between the volumes of roughly 2 and 10 mL that is often called the “buffer region.” Where did this buffer come from? Give formulas for the chemicals that are in solution and make this a buffer. Why did the buffer eventually go away?

5. Consider your procedure from Part 2. For each proposed change or error below, explain why it would or would not affect your calculated values of $K_a$ and molar mass.
   a. Not weighing the solid sample.
   b. Adding twice as much water to dissolve the solid.
   c. Incorrectly recording the molarity of the NaOH.
   d. Using twice as much solid sample.