Chemistry 123

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

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LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- perform the experimental titration of $HC_2H_3O_2$ with NaOH using the LabPro Interface.
- analyze the titration data using the LabPro spreadsheet.

BACKGROUND

In this experiment you and your partner will be issued a sample of an aqueous acetic acid ($HC_2H_3O_2$) solution and a 25.00 mL portion will be titrated with standardized sodium hydroxide (NaOH). Acetic acid is a weak acid and sodium hydroxide is a strong base. The solution pH will be measured after each addition of NaOH using a pH probe connected to the LabPro interface. A graph of measured pH (y-axis) versus mL NaOH (x-axis) will be plotted. This graph is a *titration curve* and has the general features shown in the upper part of Figure 1 on page 2.

Titration curves for weak acids such as $HC_2H_3O_2$ show an initial small rise in pH, but then lead into a region where the pH changes only slowly. The solution composition here is a buffer and this part of the titration curve is the *buffer region*. Eventually the pH climbs very sharply and produces an *inflection* in the curve. Near the center of this inflection is the *equivalence point*, where the stoichiometric amount of base has been added. At the equivalence point, moles of NaOH added equals moles of $HC_2H_3O_2$ present since the reaction is 1:1 on a mole basis. Past the equivalence point the pH again changes slowly as determined by the amount of excess NaOH.

Two important applications of titration curves are illustrated in this experiment. The first is the quantitative determination of the molar concentration of the acetic acid solution. This requires the location of the equivalence point and the titration curve is used to obtain this location. The equivalence point is taken as the steepest point in the titration curve's inflection. To sharpen its location, a titration curve derivative plot is made as illustrated in the lower part of Figure 1. The peak in the derivative plot corresponds to the point of steepest inflection and, scaling in on the second derivative plot provides a precise location of the equivalence point.

The second important application of this titration curve is the determination of the dissociation constant (K_a) of acetic acid. The key data needed are titration curve points located in the buffer region. Three points are selected, occurring at approximately ¼, ½, and ¾ of the distance from the initial point to the equivalence point. Each of these three points yields a K_a value from which an average K_a value is calculated.

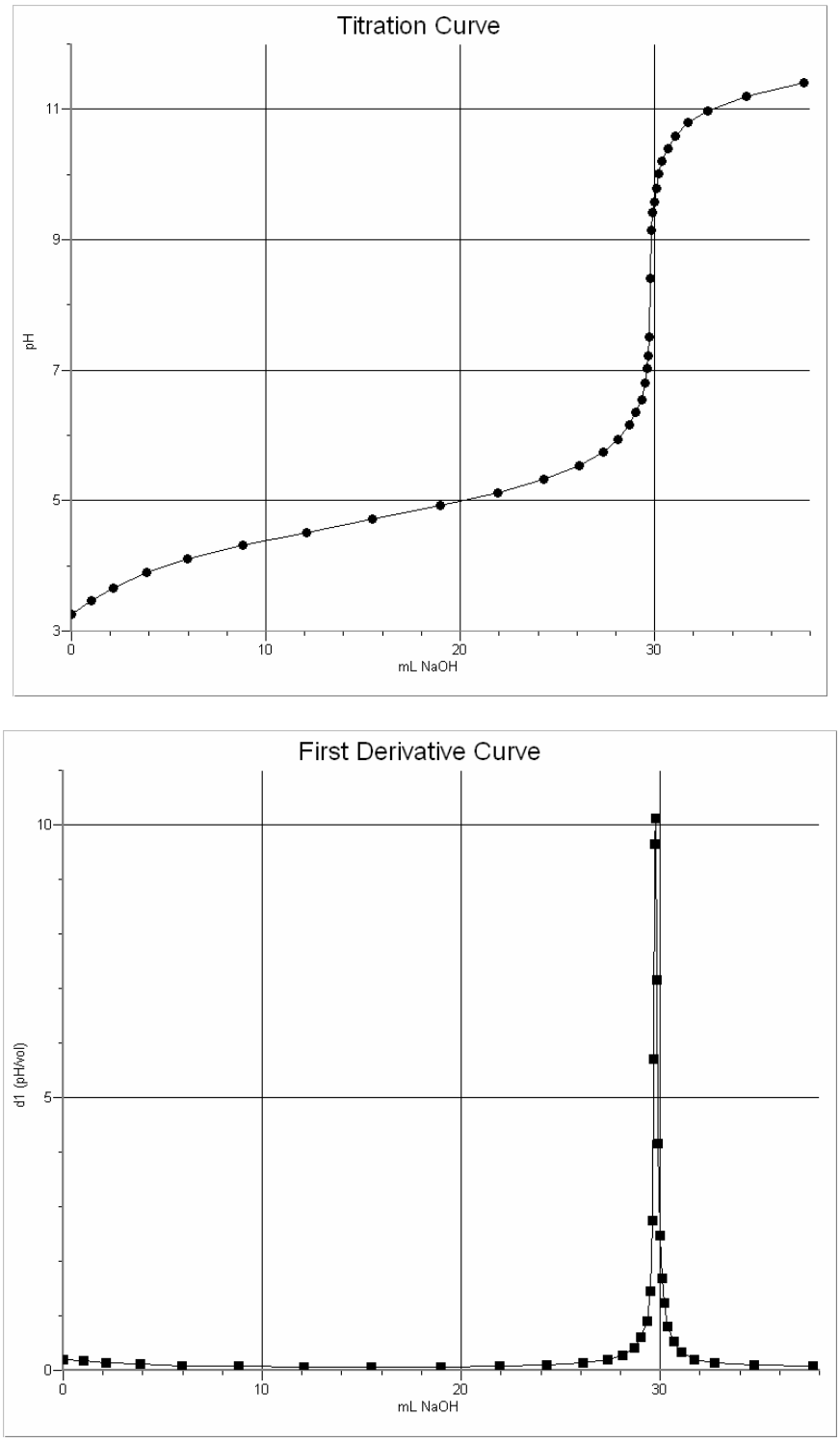

Figure 1. Titration and First Derivative Curves for the Reaction of $HC_2H_3O_2$ with NaOH

SAFETY PRECAUTIONS

Wear departmentally approved eye protection at all times in the laboratory. Follow all additional laboratory rules and regulations provided by your instructor. Know the location and proper use of all laboratory safety equipment (safety showers, eye washers, fire extinguishers, etc.). Dispose of all chemicals in the proper waste containers located in the Waste Hood.

A material safety data sheet (MSDS) for each chemical used in this experiment is located in a binder in the lab. You should be familiar with the hazards associated with each chemical, as well as the instructions on safe handling and appropriate disposal. Your instructor will be available to assist you in interpreting this information.

EXPERIMENTAL PROCEDURE – this lab is to be done in pairs

pH Probe Calibration and Experiment Program

Obtain a pH sensor. Note that the pH sensor comes screwed into a storage bottle containing a storage solution. Do not discard this solution! Connect the sensor to channel CH1 on the LabPro interface. Turn on the computer and open the Logger Pro 3.6.1 software; close the tips window. To open the experiment file, click **File**, *Open*, open the *Chemistry with Vernier* folder and select ***24a Acid-Base Titration.cmbl***. This program collects titration data and displays the titration curve during the experiment as a plot of pH versus buret reading.

Before beginning data collection, you need to calibrate the pH sensor with pH 7 buffer solution. Access the calibration window by clicking **Experiment**, *Calibrate*, and *LabPro: 1 CH1: pH*. Select "One-Point Calibration" and click "Calibrate Now". Remove the storage bottle from the sensor by unscrewing the lid and removing the bottle. Set the storage bottle of storage solution aside. Thoroughly rinse the probe with a DI H_2O squirt bottle, and carefully pat it dry with a KimWipe. Note that a pH probe should always be rinsed with DI H_2O and patted dry before inserting into any solution, so as to avoid cross-contamination. Place the probe in the pH 7 buffer solution provided in the lab. When the voltage reading stabilizes, enter *7* under Reading 1 and click "Keep" and "Done". Rinse the probe with DI H_2O, pat it dry, slide on the storage cap and screw it back on to the storage bottle until you are ready to collect titration data.

Running the Experiment

In a dry beaker, obtain 50 mL of an aqueous acetic acid unknown solution. Wash your 25-mL pipet, rinse it with DI H_2O and then with the acetic acid solution, and pipet 25.00 mL into a 250 mL beaker. Use a graduated cylinder to add 50.0 mL of DI H_2O. Add a stir bar and obtain a magnetic stirrer. Rinse and fill your 50 mL buret with standardized NaOH. (Use the NaOH solution of the partner who got the lowest RSD on the previous standardization titrations.)

Position the acetic acid solution beaker on the magnetic stirrer. After rinsing, insert the pH probe so that the bulb is fully submerged in the solution. Position the NaOH buret ready for titration. Turn on the magnetic stirrer and adjust the stirring rate to a moderate speed (without splashing).

To start collecting data click the green *Collect* icon on the toolbar. You will see the pH reading displayed in the lower left corner of the screen. When the reading has stabilized, click the *Keep* icon to capture the first pH value. Enter the initial buret reading (which does not need to be 0.00 mL) in the Events window and click "OK". Estimate all buret readings to the nearest 0.01 mL.

As a rough guide, add NaOH in increments which produce pH changes of about 0.2 pH units. After each such increment, capture a stable pH reading and enter the buret reading to 0.01 mL. As you approach the titration curve inflection, less and less NaOH will be required to achieve the desired increase in pH. (Right in the inflection region, even a quick 180° turn of the stopcock will cause a large jump in pH.) Carry the titration about 5 mL beyond the inflection. Press the *Stop* icon when you are finished collecting data.

DATA ANALYSIS

1. View your data in the LabPro spreadsheet. Buret readings are contained in the first column and the pH readings are in the second, followed by first and second derivative columns.

2. If your buret readings do not start at 0.00 mL, create a new column containing the volume NaOH added, which is done by subtracting the initial buret reading from each buret reading in the first column. To add a new column click **Data**, *New Calculated Column*. Name the column *mL NaOH* and enter the appropriate equation. When entering a column as a variable in an equation, the column name must be entered in quotes (i.e. "Volume") or it can be selected under "Variables (Columns)". Finally, under the *Options* tab, change the Displayed Precision to 2 decimal places.

3. To generate a plot pH versus mL NaOH (<u>not</u> buret reading, unless your readings start at 0.00 mL), double-click on the graph, and under the *Axes Options* tab, change the x-axis to *mL NaOH*. Under the *Graph Options* tab, select "Connect Points". Obtain printouts of your titration curve and spreadsheet data by clicking **File**, *Print Graph* and **File**, *Print Data Table*. Submit both with your Summary Sheet.

4. Next plot the first derivative function versus mL NaOH by changing the y-axis from *pH* to *d1(pH/vol)*. The peak on the first derivative plot corresponds to the inflection point, which is the point of steepest inflection in the titration curve. Under **Analyze**, select *Examine* and/or *Interpolate* so that you can trace along the curve, using the mouse or the arrow keys, to estimate the volume at the inflection point. (You do not need to print or record any data.)

5. Now plot the second derivative function, *d2(d1/vol)* versus mL NaOH; be sure to change the graph title. The point at which the connecting line crosses the x-axis (y=0) is the same as the inflection point observed in the first derivative plot and is the titration equivalence point.

6. Click and drag with the mouse to select a small area around the inflection point; the area selected will become highlighted in a dark gray box. Click the *Zoom-In* icon. Use *Interpolate* to find the mL NaOH value with a d2 value closest to zero. (You can zoom in further if needed.) Once the equivalence point volume is displayed on the screen, enter 'Control P' on your keyboard get a printout of the screen. Submit the printout with your Summary Sheet.

7. Using the equivalence point NaOH volume (rounded to the nearest 0.01 mL) and the molarity of your standard NaOH solution, calculate the molarity of the original acetic acid solution as issued to you (before dilution). Fill in the data and calculation result on the Summary Sheet.

8. Finally, re-plot pH versus mL NaOH. Use *Examine* to select three *experimental points* (mL NaOH, pH) at about ¼, ½, and ¾ of the distance between the initial point and the equivalence point of the titration. *Circle these points on the titration curve printout* (printed in step 3), and enter the points on your Summary Sheet. (The pH values should be recorded to two decimal places, as given by the pH sensor.) These points are taken from the *buffer region* in which appreciable amounts of both acetic acid and acetate ion are present.

9. Using the three data points, calculate three values of K_a for acetic acid (see tips on next page). Various factors (such as temperature variation, electrolyte effects, etc.) will cause considerable error in the K_a value, so *report the K_a values to two significant figures* but expect one significant figure accuracy. Finally, calculate an average value for K_a. (Note that K_a does not have units.)

10. On the back of the Summary Sheet, show the complete calculation of the K_a value for the first buffer region point. You should show all calculation details.

11. Also using the first buffer region point, fill in the titration reaction table on the Summary Sheet (also shown below). For the initial moles of NaOH and $HC_2H_3O_2$, consider the reaction at the imaginary point after the portion of NaOH has been added but before any of it has reacted with the $HC_2H_3O_2$.

Titration Reaction:	$NaOH$	+ $HC_2H_3O_2$	→ $NaC_2H_3O_2$	+ H_2O
Initial Moles				----
Change in moles				----
Final Moles				----

Tips for the Calculation of K_a

Recall that for a weak acid, HA:

$$HA + H_2O \leftrightarrows H_3O^+ + A^- \qquad \text{(Reaction 1)}$$

and $$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

To calculate K_a we need to know $[H_3O^+]$, $[A^-]$, and [HA]. The concentration of hydronium ion, $[H_3O^+]$, is determined directly by measuring the pH, and using the equation below. According to significant figure rules for log calculations, $[H_3O^+]$ values should have 2 significant figures.

$$pH = -\log [H_3O^+]$$

Unfortunately, calculating [HA] and $[A^-]$ is not as straightforward. Consider first $[A^-]$. Most A^- is generated during the reaction of acetic acid with NaOH from your buret,

$$HA + OH^- \rightarrow A^- + H_2O \qquad \text{(Reaction 2)}$$

However, a small additional amount of A^- also comes from Reaction 1. There are thus two sources of A^- (Reactions 1 and 2). In principle we could just add these two sources together and then, dividing by the total volume of the solution, compute $[A^-]$. The problem with this approach is that in order to calculate how much A^- comes from Reaction 1, we have to know the acid dissociation constant of acetic acid, K_a, which is precisely the quantity we are trying to calculate in the first place!

The solution to this paradox is simply to ignore Reaction 1 and treat the problem as though all A^- comes from Reaction 2. This approximation is justified because acetic acid is a weak acid, and therefore the equilibrium in Reaction 1 lies far to the left (i.e. relatively little A^- is generated by Reaction 1 in comparison to the amount produced by Reaction 2).

To see how this works, consider the following example. Suppose 25.0 mL of 0.040 *M* HA was diluted with 50.0 mL of water, and then titrated with 15.0 mL of 0.050 *M* NaOH using a buret.

Based on the stoichiometry of Reaction 2, [A^-] can be computed as

$$moles\ OH^- = \left(0.0150\ L\ OH^-\right)\left(\frac{0.050\ mol\ OH^-}{1\ L}\right) = 0.00075\ mol\ OH^-$$

$$moles\ A^- = \left(0.00075\ mol\ OH^-\right)\left(\frac{1\ mol\ A^-}{1\ mol\ OH^-}\right) = 0.00075\ mol\ A^-$$

$$[A^-] = \left(\frac{0.00075\ mol\ A^-}{(0.0250+0.0500+0.0150)\ L\ solution}\right) = 0.0083\ M$$

You can apply similar reasoning to calculate [HA]. In this calculation, assume that the amount of HA in solution can be determined based on Reaction 2 alone. Remember that you must take into account that some of the HA has reacted with added NaOH. You should calculate the amount (concentration) of HA *remaining* after reacting with the added NaOH.

Laboratory Report

Read the Data Analysis section carefully for instructions on calculations, significant figures and units. Be sure to show the complete calculation of one K_a value and to fill out the titration reaction table on the Summary Sheet.

Leave ample space in your lab notebook to neatly attach your spreadsheet, titration curve and second derivative plot after your graded Summary Sheet is returned.