LEARNING OBJECTIVES

The objectives of this experiment are . . .

- To perform the experimental titration of \( \text{HC}_2\text{H}_3\text{O}_2 \) with NaOH.
- To analyze the titration data to determine the \( K_a \) for acetic acid.

BACKGROUND

In this experiment you will be issued a sample of an aqueous acetic acid (\( \text{HC}_2\text{H}_3\text{O}_2 \)) 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 monitored using a pH probe connected to an interface. A graph of measured pH (y-axis) versus Volume of NaOH (mL) (x-axis) will be plotted. This graph is a titration curve and has the general features shown in the upper part of Figure 1.

Titration curves for weak acids, such as \( \text{HC}_2\text{H}_3\text{O}_2 \), 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 \( \text{HC}_2\text{H}_3\text{O}_2 \) 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, with further scaling, provides a well-defined 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 \(\frac{1}{4}\), \(\frac{1}{2}\), and \(\frac{3}{4}\) 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 can be calculated.

Figure 1. Titration and First Derivative Curves for the Reaction of HC₂H₃O₂ with NaOH
SAFETY PRECAUTIONS

If skin contact occurs with any solutions, wash the affected area thoroughly with soap and water. Clean up all spills immediately. Safety goggles must be worn at all times in the laboratory.

BEFORE PERFORMING THIS EXPERIMENT

You will need a pH meter to display pH values. Data collection/tabulation will be done using EXCEL. Active titration curve data will be plotted during the experiment.

EXPERIMENTAL PROCEDURE

pH Probe Calibration
Obtain a pH probe and connect it to the pH meter. Calibrate the probe using pH 7 and pH 4 buffers. Note that a pH probe should always be rinsed with deionized water and carefully patted dry before inserting into any solution, so as to avoid cross-contamination.

Experiment Program
Use the EXCEL program to create columns of volume (x-axis, column A) and pH (y-axis, column B). Create a third column (derivative) for the calculation of change in pH versus change in volume (ΔpH/ΔV). Also create a graph on the spreadsheet so that you can observe the active trend of pH versus volume.

Running the Experiment
Obtain, in a dry beaker, about 100 mL of an aqueous acetic acid solution. Rinse your 25-mL pipet with this solution and pipet 25.00 mL into a 150-mL beaker. Use a graduated cylinder to add about 50 mL of distilled water. Add several drops of the phenolphthalein (PHTH) indicator. The indicator will change from colorless to pale-pink at and slightly after the equivalence point. Darker pink means you have gone well past the equivalence point. (The PHTH indicator should guide you in the additions of NaOH during the titrations.) Add a stir bar and obtain a magnetic stirrer. Rinse and fill your 50-mL buret with standardized NaOH to the 0.00 mL mark (50.0 mL disbursement).

Position the acetic acid solution beaker on the magnetic stirrer. Insert the pH probe. Position the NaOH buret ready for titration. Turn on the magnetic stirrer and adjust the stirring rate to a moderate speed (without splashing).

Start data acquisition by typing in zero volume for a pH reading on the pH meter. Add a small aliquot of NaOH and type the total volume of NaOH added to that point in the spreadsheet. Start with about 1 mL increments. Use 0.1-0.2 mL increments when you get to the equivalence region. You should use the rate of disappearance of the PHTH pink color as your visual guide toward the equivalence point; that is, as you approach closer to the equivalence point, the rate of disappearance of pink color should decrease. Continue until the pH has reached approximately 11-12. Save your data and repeat two more times. You should have three good trials.
DATA ANALYSIS

1. Use the EXCEL spreadsheet to view your titration data. The volume readings should appear in column A, the pH readings should appear in column B.

2. Graph pH versus Volume of NaOH with grid to display your titration data. Use a moving average trend line to produce the titration curve.

3. The next task is to create a data column for the derivative of pH with respect to Volume of NaOH. This is done by taking the difference of pH values and dividing that by the difference in corresponding volume values. Do the first ΔpH/ΔV and then drag/copy/paste the formulation to obtain the rest. Plot derivative versus volume on the same titration graph but plot the derivative on a secondary y-axis. Use a moving average trend line to produce the derivative curve.

4. Use x-axis scaling to expand the derivative plot so as to permit the reading of mL NaOH (directly under the derivative peak) to the nearest 0.01 mL. This mL NaOH reading is the equivalence point volume and will be used in calculating the original acetic acid solution molarity.

5. Enter the equivalence point (NaOH volume to the nearest 0.01 mL) on the report sheet. Using this volume and the molarity of your standard NaOH solution, calculate the molarity of the original acetic acid solution (before dilution) as issued to you. Carefully watch significant figures in this calculation. Report your result on the report sheet and show your calculation.

6. From your spreadsheet data, 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 and enter this information on your report sheet. These points are taken from the buffer region in which appreciable amounts of both acetic acid and acetate ion are present. Using the three data points chosen, calculate three values of Keq for acetic acid. Mark the points chosen on the titration curve printout. Note that various factors (such as temperature variation, electrolyte effects, etc.) will cause considerable error in the Keq value. Report the Keq values to two significant figures but expect one significant figure accuracy. Finally calculate an average value for Keq. Show your calculation for the first Keq value.

Hints for the Calculation of Keq
Recall that:

HA ⇌ H+ + A–  

(Reaction 1)

And that at equilibrium,

\[ Keq = \frac{[H^+][A^-]}{[HA]} \]

To calculate Keq we need to know [H+], [A-], and [HA] at equilibrium. The concentration of hydrogen ion, [H+], is determined directly by measuring the pH,

\[ pH = - \log [H^+] \]

or \[ [H^+] = 10^{-pH} \]
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,

\[
HA + OH^- \rightarrow A^- + H_2O \quad \text{(Reaction 2)}
\]

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

\[
[A^-] = (0.015 \text{ L OH}^-) \left( \frac{0.050 \text{ mol OH}^-}{1 \text{ L}} \right) \left( \frac{1 \text{ mol } A^-}{1 \text{ mol OH}^-} \right) \left( \frac{1}{0.025 + 0.050 + 0.015 \text{ L}} \right)
\]

\[
= 0.0083 \text{ M}
\]

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 the addition of NaOH.

\[
[HA] = [HA]_o - [A^-] ; \quad [HA]_o = 0.040 \text{M} \times \frac{25}{90} = 0.0111 \text{ M} ; \quad [HA] = 0.0028 \text{ M}
\]

Using similar reasoning and calculations, the following table can be obtained:

<table>
<thead>
<tr>
<th>Species Conc’n</th>
<th>[HA]</th>
<th>[A^-]</th>
<th>$K_a = \frac{[H^+][A^-]}{[HA]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1 M</td>
<td>0 M</td>
<td></td>
</tr>
<tr>
<td>1/4-equivalence</td>
<td>3/4 M</td>
<td>1/4 M</td>
<td>$\frac{(<a href="1/4">H^+</a>)/(3/4)}{K_a = [H^+]/3}$</td>
</tr>
<tr>
<td>1/2-equivalence</td>
<td>½ M</td>
<td>½ M</td>
<td>$\frac{(<a href="1/2">H^+</a>)/(1/2)}{K_a = [H^+]}$</td>
</tr>
<tr>
<td>3/4-equivalence</td>
<td>1/4 M</td>
<td>3/4 M</td>
<td>$\frac{(<a href="3/4">H^+</a>)/(1/4)}{K_a = 3 [H^+]}$</td>
</tr>
</tbody>
</table>
**TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID**

**Data Sheet**

<table>
<thead>
<tr>
<th>Molarity of the HC$_2$H$_3$O$_2$ Unknown</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL NaOH at equivalence point</td>
<td>______</td>
<td>______</td>
<td>______</td>
</tr>
<tr>
<td>Molarity of standard NaOH</td>
<td>______</td>
<td>______</td>
<td>______</td>
</tr>
<tr>
<td>Calculated HC$_2$H$_3$O$_2$ molarity</td>
<td>______</td>
<td>______</td>
<td>______</td>
</tr>
<tr>
<td>Average HC$_2$H$_3$O$_2$ molarity</td>
<td>______</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Determination of the $K_a$ of HC$_2$H$_3$O$_2$ (Pick one/best titration curve)**

<table>
<thead>
<tr>
<th>Data Point</th>
<th>mL NaOH</th>
<th>pH</th>
<th>[H$^+$]</th>
<th>$K_a$ calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{4}$ distance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{2}$ distance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{4}$ distance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average $K_a$ value  
Literature $K_a$ value  
Percent error  

**Attach all three titration/derivative curves.** They should have pH on the Y1-axis, Volume NaOH (mL) on the X-axis and the derivative of pH/V on the y2-axis.

**Show sample calculations for Molarity and $K_a$ determinations.**
TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Pre Laboratory Assignment

1. Write a balanced molecular equation for the reaction between acetic acid and sodium hydroxide.

2. 25.0 mL of acetic acid was pipetted into an Erlenmeyer flask. The acid was titrated to the equivalence point with 11.25 mL of 0.998 M NaOH. What is the molarity of the acid solution?