Chemistry 213

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- perform the experimental titration of $HC_2H_3O_2$ with NaOH.

- analyze the titration data to determine the Ka for acetic acid.

BACKGROUND

In this experiment you 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 monitored using a pH probe connected to a pH meter. 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.

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, with further scaling, provides a precise location of the equivalence point.
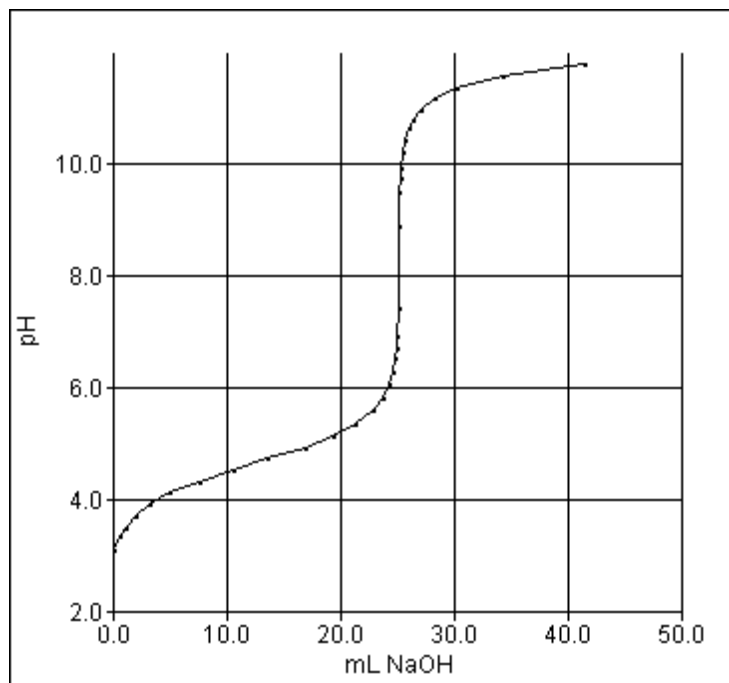
Figure 1. Titration Curve for the Reaction of HC₂H₃O₂ with NaOH

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.

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.

pH Probe Calibration

pH probe must be calibrated with buffer solution before beginning experiment. Your instructor will demonstrate how to do this.

EXPERIMENTAL PROCEDURE

Part A. – Standardization of Acetic Acid

Obtain, in a dry beaker, about 100 mL of an aqueous acetic acid solution. Rinse 10 mL pipet with solution and pipet 10.00 mL into a 150 mL beaker. Use a graduated cylinder to add about 50 mL of distilled water. Add 5 drops of phenolphthalein indicator. Add a stir bar and place on magnetic stir plate. Rinse and fill 50 mL buret with standardized NaOH.

Position the acetic acid solution beaker on the magnetic stirrer. Position the NaOH buret ready for titration. Turn on the magnetic stirrer and adjust the stirring rate to a moderate speed (without splashing). Titrate until faint pink color remains.

Repeat two more times.

Calculate the molarity of the acetic acid and fill in Part A of the report sheet before moving on to Part B.

Part B. – Determination of the K_a of Acetic Acid

Obtain, in a dry beaker, about 100 mL of an aqueous acetic acid solution. Rinse 10 mL pipet with solution and pipet 10.00 mL into a 150 mL beaker. Use a graduated cylinder to add about 50 mL of distilled water. Add 5 drops of phenolphthalein indicator. Add a stir bar and place on magnetic stir plate. Rinse and fill 50 mL buret with standardized NaOH.

Position the acetic acid solution beaker on the magnetic stirrer. Inseert 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).

Set up a spread sheet to record pH vs. volume of NaOH added. Record pH. Add NaOH in small aliquots (less than 1 mL), let solution equilibrate then record pH. Continue until pH reading remains relatively constant at a pH of 11-12. Titration curve should be smooth. If not, try again.

1. Make a graph of pH (y-axis) vs. volume NaOH added (x-axis). Use xy scatter graph with points only (no lines connecting the dots). Turn this graph I with the report sheets.

2. Determine the equivalence point from the graph. Record the NaOH volume (to the nearest 0.01 mL) on the report sheet.

3. From your spreadsheet data, select three *experimental points* (mL NaOH, pH) at 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 the value of K_a 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 K_a value. Report the K_a values to two significant figures but expect one significant figure accuracy. Finally calculate an average value for K_a. Show your calculation for the first K_a value.

4. Look up the literature value for the Ka of acetic acid.

Hints for the Calculation of K_a

Recall that
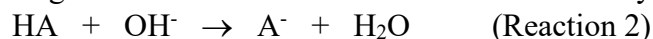
$$HA \leftrightarrow H^+ + A^-$$ (Reaction 1)

and

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

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

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

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,

$$HA + OH^- \rightarrow A^- + H_2O$$ (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

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

$$= 0.0083 \ M$$

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 the addition of NaOH.

Name(s) _____,_____,_____.

Section_____

TITRATION CURVES AND THE DISSOCIATION
CONSTANT OF ACETIC ACID

Turn in report sheets and a full page copy of the titration curve.

Part A. – Standardization of Acetic Acid ($HC_2H_3O_2$)

	Trial 1	Trial 2	Trial 3
mL NaOH added at end point	_____	_____	_____
Molarity of standard NaOH	_____	_____	_____
Calculated $HC_2H_3O_2$ molarity	_____	_____	_____
Average $HC_2H_3O_2$ molarity	_____		

Show example calculation:

Class results – Molarity of Acetic Acid

Average $HC_2H_3O_2$ molarity for the class   _____

1. Discuss the precision of the results and the magnitude of random error for both sets of
    data.

Part B. - Determination of the K_a of $HC_2H_3O_2$

Data Point	mL NaOH	pH	$[H^+]$		K_a calculated
¼ distance				$K_a = [H^+]/3$	
½ distance				$K_a = [H^+]$	
¾ distance				$K_a = 3[H^+]$	

Volume of NaOH added at equivalence point _____mL

Show calculations:

Class K_a Values									

	Experiment Results	**Class Results**
Average K_a value		
Literature K_a value		
Percent error		

1. Discuss the precision and accuracy of the class results.

2. Does there appear to be systematic error in the class results? Explain.