EXP. 7–DETERMINATION OF THE FORMULA WEIGHT AND \( K_a \) OF A WEAK ACID

LABORATORY OBJECTIVES AND ASSESSMENTS

1. Understand how to perform a pH titration.
   a. Titrate an unknown acid with standard base solution.
   b. Demonstrate proper use of a pH meter.
   c. Identify the end point and half-equivalence point of a titration using a pH meter.
   d. Use a first-derivative plot to identify the end point of a titration.
   e. Understand the purpose of a rough and a careful titration.

2. Understand acid-base equilibria and be able to extract information from an acid-base titration curve.
   a. Determine FW of a known mass of a weak acid using the moles of \([\text{OH}^-]\) required to titrate it.
   b. Calculate the \( K_a \) of a weak acid from the pH at its half-equivalence point it.
   c. Calculate the \( K_a \) of a weak acid from the initial pH of the solution.

INTRODUCTION

TITRATION OF A WEAK ACID

The experiment from last week, Acid-Base Titrations: Prep. of Std. Solutions / Titration of an Unknown Acid, describes the procedure involved in titrating an acid with standard base using phenolphthalein indicator. Near the point at which stoichiometric quantities of acid and base have been mixed together in solution (the equivalence point), the phenolphthalein indicator changes color (the endpoint).

In this experiment a pH meter (instead of a visual indicator) will be used to follow the reaction between our acid and base. We will determine the pH at the half-equivalence point, i.e., that point at which sufficient base has been added to neutralize exactly half the quantity of initial acid.

\[
\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O} \tag{1}
\]

At this point, the concentration of unreacted acid, HA, is equal to the concentration of the \( \text{A}^- \) ion:

\[
[\text{HA}] = [\text{A}^-] \tag{2}
\]

Incorporation of this equality (equation (10)) into the expression for \( K_a \), leads to the following expression for \( K_a \) at the half-equivalence point.

\[
K_a = [\text{H}_3\text{O}^+] \tag{3}
\]

or

\[
\text{p}K_a = \text{pH} \tag{4}
\]

Thus, if we can measure the pH at the half-equivalence point during the titration of a weak acid, we have also determined the \( \text{p}K_a \) value of the acid. In order to do this, it will be necessary to plot a titration curve for the weak acid, i.e., measure the pH during the titration as a function of added base.

Figure 1 shows a titration curve for a weak acid titrated with a standard NaOH solution. If a vertical line is drawn to the x–axis from the inflection point on the nearly
vertical portion of the curve that coincides with the equivalence point, A, the volume of base needed to reach the equivalence point in this example is ~30 mL. The pH at the half-equivalence volume, (i.e. 15 mL), point B (pH=4.9) is the pKa of the weak acid.

**FORMULA WEIGHT**

The measured equivalence point volume times known molarity of base gives the number of moles of base (which, in this case, is OH\(^{-}\) that react:

\[ V_{\text{base}} \cdot M_{\text{base}} = \text{moles} \text{OH}^{-} \]  

One mole of OH\(^{-}\) reacts with one mole of H\(^{+}\),

\[ \text{mole} \text{OH}^{-} = \text{mole} \text{H}^{+} \]  

The formula weight of the acid is determined by dividing the number of grams weighed by the number of moles acid determined by equation (6).

\[ \text{FW}_{\text{acid}} = \frac{\text{g} \text{ acid}}{\text{moles} \text{ acid}} \]  

**EQUIVALENCE POINT DETECTION**

The equivalence point occurs at the inflection point as shown in Figure 1 at point D.

To pinpoint the equivalence point more accurately in the titration, a derivative plot i.e., Derivative vs. \( \overline{V}_{\text{base}} \) (Ave. Vol.\_base), where \( \overline{V}_{\text{base}} = TVol-\Delta TVol / 2 \), can be used. The maximum on this curve gives the volume of standard base required to reach the equivalence point, see Figure 2.
Thus, the equivalence point is pinpointed from a Derivative versus $\overline{V}_{\text{base}}$ plot. Note the importance of having very small volume increments between readings in the vicinity of the equivalence point in Figure 2.

![Figure 2. Derivative plot of the results of the titration in Figure 1 showing A, equivalence volume.](image)

**Determination of the Acid Dissociation Constant (K_a)**

There are two methods that we can use to determine the acid dissociation constant (K_a). The pK_a can be determined from the pH versus True Volume plot, the regular titration curve. The pK_a is equal to the pH at the “half-equivalence” point on the titration curve (see Figure 1). The half-equivalence point can be determined using the Derivative plot, point A in Figure 2.

The pK_a can also be determined from the pH of the initial solution (B in Figure 1) before any base titrant is added. For this method it is important to know the volume of the initial solution. An accurate measurement of the 50 mL (or 100 mL) of water in the beginning is necessary to be able to calculate the concentrations with any confidence. Using the pH of this solution before starting the titration one can determine the [H_3O^+] as well as the [A^-]. With the formula weight determined, one can then calculate the [HA] based on the 50 mL of water added to make up the solution. Be aware there are significant limitations to the pH values. See Harris, pages 344-346.

**Experimental Procedure**

**Each Student will have an Individual Unknown and Work in Pairs Using pH Meter.**

**General Overview**

Because of limitations of equipment, you will work with a partner, but you will be supplied your own solid weak acid unknown. You will obtain a titration curve for this sample by titrating a solution of this acid with your standard NaOH solution for the weak acid and observing the pH after each addition of titrant. From the titration curve you will determine the equivalence point in the titration, the original concentration of the acid in the solution, and the K_a of the acid. Since you will have weighed the acid sample, you will also calculate its formula weight.
Preparation of Weak Acid sample and buret

1. Obtain the unknown acid sample from your instructor; weigh accurately, by difference, about 0.4 g, to the nearest 0.1 mg, **into a 250–mL beaker**.

2. Measure accurately 50 mL of distilled water, with a graduated cylinder, into the 250–mL beaker containing the acid and stir to dissolve. If the sample does not dissolve in a reasonable amount of time, add 50 mL more DI water.

3. Rinse and fill your buret with the standard NaOH solution that you standardized last week. Be sure to remove all air bubbles. Record the initial buret reading.

4. Rinse the pH electrode with distilled water from your wash bottle, and **blot gently (do not rub it)** with a Kimwipe™ or paper towel. Place the beaker onto a magnetic stirrer and add a stirring bar. (If no magnetic stirrer is available, you will need to stir with a stirring rod during the titration.) Center the beaker containing your acid under your buret. Lower the electrode into the solution, making sure that its sensing bulb is fully immersed (yet remains clear of the stirring bar if used.)

5. Use a buret clamp or a utility clamp to clamp the pH electrode to a ring stand. Situate the pH electrode in the acid solution and adjust its position so that it is not struck by the stirring bar.

Prepare the computer for data collection.

If the program is not already started;

6. - Select the file in the Dock titled “**c230 WA Titration**”.
- Press the RETURN key to **START** (or use the mouse to click on the **START** button) the data collection.
- Monitor pH for 5-10 seconds, press the RETURN key again and enter your initial buret reading in mL.

Following the pH during a Titration

“**Rough**” Titration

7. You are now ready to begin the rough titration.
- Before any NaOH solution is added record the pH reading in your notebook. Press KEEP and enter your initial buret reading.
- As pH is being read, add the first increment of NaOH. Add enough NaOH titrant to raise the pH by ~ 0.25 pH units or no more than ~5 mL of NaOH. After the NaOH has been added and the pH stabilizes, press the RETURN key and then enter the new buret reading. Press RETURN to continue.
- Add the next increment of NaOH titrant (enough to raise the pH about 0.15 to 0.25 pH units or ~5 mL of NaOH). When the pH stabilizes, again press the RETURN key. Enter the buret reading. Then press RETURN to continue.
- Continue adding NaOH solution in increments that raise the pH by about 0.25 pH units or ~5 mL of NaOH and input the volume after each increment.
- When the pH begins to change much more rapidly as the equivalence point is approached, change to 1-to-2-drop increments and input after each increment.
- After the equivalence point pH (~10-12) is reached, again add larger increments that raise the pH by about 0.15 to 0.25 pH units or ~5 mL of NaOH and input after each increment.
- Add NaOH solution until the pH remains constant (but not beyond pH 12).

8. Stop the data collection by clicking the STOP button. To make sure you don’t lose the data, at this point save the data to the Desktop. (Give the data a name and select the Desktop button and then the SAVE button.) Be sure to clearly title your saved files when saving on the Desktop.

9. Dispose of the beaker contents in the sink with water.

“Careful” Titration

10. Repeat the procedure, adjusting the sample weight so that about 25 mL of titrant is used to reach the equivalence point. Be sure to save the data as soon as the titration is complete. In this titration focus data collection on the $\frac{1}{2}$-equivalence point and the equivalence point areas (raising the pH in increments not to exceed 0.15 pH units) to obtain a good data set.

11. Stop the data collection and IMMEDIATELY SAVE THE DATA TO THE DESKTOP BEFORE DOING ANY OTHER ACTION WITH THE COMPUTER!!!

12 Dispose of the beaker contents in the sink with water.

Data Analysis

Record in your notebook the mass of unknown acid used, and the molarity of the standard base used. The computer will record the buret reading entered and the pH after each addition of titrant. Be sure to print a copy of the data.

1. Set up the computer to complete the data table by calculating the true volume of titrant added to that point in the titration and also determine the Derivative ($\frac{\Delta pH}{\Delta V}$) and the value of $V$(bar) for each interval for the derivative method.

2. Prepare a graph with the pH on the vertical axis (ordinate) and true volume of titrant added on the horizontal axis (abscissa).

3 Identify the equivalence point in the titration, using the derivative method. Because this determination only needs to be done for the 1 mL interval before and after the equivalence point, expand the x-axis to maximize the resolution of the volume reading.

4. Knowing the equivalence point, determine from your data the number of milliliters of titrant added to reach this point. This is the equivalence volume.

5. Using the equivalence volume, molarity of the titrant used and the mass of the sample, calculate the formula weight of your unknown.

6. Determine the $K_a$ from the pH at half-neutralization point. Additionally, determine the $K_a$ from the pH of the initial solution. Show your calculations.

7. Summarize your results; formula weight, $K_a$ (from each method), for the “careful” titration in a table.
**WHAT TO DO**

**To Be Turned in From Exp. 6- Acid-Base Titrations:**

Create a summary table in your notebook with the following Template. You will only turn in the copy page for this table. **You will be graded only on the accuracy of your results.**

<table>
<thead>
<tr>
<th>All Trials</th>
<th>Standardized NaOH Mean Concentration</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard Deviation</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>% Relative Std. Dev.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95% Confidence Interval</td>
<td>± M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Best three Trials</th>
<th>Standardized NaOH Mean Concentration</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard Deviation</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>% Relative Std. Dev.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95% Confidence Interval</td>
<td>± M</td>
</tr>
</tbody>
</table>

**Mmoles of Acid**

<table>
<thead>
<tr>
<th>Flask 1</th>
<th>Flask 2</th>
<th>Flask 3</th>
</tr>
</thead>
</table>

**For Experiment 7**

**Before Lab:** Read this experiment and the readings in Harris. Fill in the “Title bar”. Prepare your notebook. You should also include the following information:

- Completed Title bar.
- Purpose.
- Reagent Table for NaOH. **BE SURE TO NOTE THE DISPOSAL PROCEDURES IN THIS TABLE.**
- Summarize the experimental procedure in your notebook.

**During the Lab:** Carry out the procedure as written. Record all data. Modify your procedure if you find it necessary, but be sure to record the modifications.

The computer application Logger Pro will tabulate the volumes and pH’s as you do the titration. Save and keep both the rough and the careful titrations. Record **all other pertinent observations and measurements as you do the experiment.** Show sample calculations in your laboratory notebook.

**To Be Turned In:**

**You will be graded on the basis of the results of the titrations and the quality of your report. Include:**

1) A printed copy of your titration curve (in Word or from LoggerPro) with caption. Include a formal title on the first page.

2) **A printed copy of your** first derivative curve covering about 1-2 mL on either side of the equivalence point showing the extrapolation of the equivalence point (by hand) with caption.

3) **A Summary Report.** Use the following template to produce a report page in your lab notebook with a summary of results. You will turn in the copy page of this report.

**SUMMARY OF RESULTS**

[NaOH] __________ M

mass<sub>rough</sub> HA __________ g
mass\textsubscript{careful} HA \hspace{1cm} \underline{\hspace{1cm}} \text{g}

equivalence volume\textsubscript{rough} of titrant \hspace{1cm} \underline{\hspace{1cm}} \text{mL}

equivalence volume\textsubscript{careful} of titrant \hspace{1cm} \underline{\hspace{1cm}} \text{mL}

My \text{K}_a and FW were determined by my \textbf{rough} or \textbf{careful} titration (circle one).

Formula weight of the unknown acid \hspace{1cm} \underline{\hspace{1cm}} \text{g}

\text{K}_a determined from half equivalence point \hspace{1cm} \underline{\hspace{1cm}}

\text{K}_a determined from initial pH \hspace{1cm} \underline{\hspace{1cm}}

4) \textbf{Answer the following question} on your report page in your notebook:

**Q.1.** Of the three pieces of data you determined for your unknown, rank them in terms of increasing accuracy. Briefly explain your answer.