pH TITRATION OF A WEAK ACID

Purpose:
To construct a pH titration curve for a weak acid and from it determine the molar weight and $pK_a$ of the acid.

Background:

Remember that at the equivalence point of a titration, the number of moles of acidic hydrogens equals the number of moles of hydroxide added. For example, if the base is NaOH, and if the acid is monoprotic, then:

(1a) \[ \text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \]

(1b) moles HA in sample = moles NaOH used in titration

(1c) grams HA/molar wt. HA = $\frac{\text{MNaOH}}{\text{NaOH used}} \times \text{Liters NaOH used}$

If the acid is diprotic, then:

(2a) \[ \text{H}_2\text{A} + 2\text{OH}^- \rightarrow \text{A}^{2-} + 2\text{H}_2\text{O} \]

(2b) moles H$_2$A in sample = 1/2 x (moles NaOH used in titration)

(2c) grams H$_2$A/molar wt. H$_2$A = 1/2 x $\frac{\text{MNaOH}}{\text{NaOH used}} \times \text{Liters NaOH used}$

Similar reasoning is used for a triprotic acid.

You will titrate a known mass of your weak acid with NaOH which is about 0.1 M, the concentration being known to four decimal places.

Titration Curves:

A pH meter is an instrument that measures the pH of a solution. A pH titration curve is a plot of pH vs. volume of titrant added. The midpoint of the steepest part of the curve corresponds to the equivalence point of the titration.

Consider the titration of a strong acid with a strong base, e.g.,

\[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]

The net-ionic equation is

\[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O} \]

The most important equilibrium at the equivalence point is the dissociation of water,

\[ 2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

resulting in a neutral solution and a pH of 7.0. See Figure 1. Any strong acid–strong base titration would produce a similar curve.

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**Figure 1.** Titration curve for 50.0 mL of 0.100 M HCl with 0.100 M NaOH
You will be titrating a weak acid with a strong base which produces a different curve, depending on the specific acid. For a monoprotic acid,

$$\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-,$$

at the equivalence point you have a solution of $\text{A}^-$, the anion of a weak acid, which can hydrolyze according to the equation:

$$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$$

resulting in a pH at the equivalence point that is basic, above pH 7. The specific pH at the equivalence point depends on what weak acid you are titrating and its concentration.

Figure 2. Titration curve for 50.0 mL 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M $\text{NaOH}$.

Figure 2 shows a titration curve for acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, titrated with NaOH. To determine the actual equivalence point, draw tangents to the lower straight portion, the upper straight portion, and to the steep portion. The half-way point between the intersections of the upper and lower tangents with the steep tangent is the equivalence point. See Figure 3.

Figure 3. Titration curve of $\text{HC}_2\text{H}_3\text{O}_2$ with NaOH with tangents drawn to locate the equivalence point.

Drop a normal (a line at 90°) from the equivalence point to the abscissa to find the volume of NaOH used to titrate to the equivalence point. To calculate the molar weight of your acid, use this volume, your NaOH molarity, and your sample weight. (See equation 1c).
To determine the $pK_a$ of your acid, consider the general equation for the equilibrium constant of a weak acid, HA,

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

Half way through the titration, when the concentrations of $A^-$ and HA are equal, the $[H_3O^+]$ of the solution equals the value of $K_a$, and pH = $pK_a$. For example, if a monoprotic acid sample requires 21.30 mL NaOH to neutralize it, then the pH at 10.65 mL is the $pK_a$ value. See Figure 4.

![Graph showing pH vs. volume NaOH added](image)

Figure 4. The $pK_a$ is found from the half-neutral point of a monoprotic acid.

For a diprotic acid, $H_2A$, you must consider the neutralization of each acidic hydrogen separately.

The net-ionic equations are:

$$H_2A + OH^- \rightarrow HA^- + H_2O$$, extent controlled by $K_{a1}$

$$HA^- + OH^- \rightarrow A^{2-} + H_2O$$, extent controlled by $K_{a2}$.

The first $H^+$ neutralization will result in an inflection point on your pH vs. volume NaOH graph, but the first neutralization region will not be as steep as the second. Figure 5 shows a typical diprotic acid titration curve.

![Graph showing pH vs. volume NaOH added](image)

Figure 5. Titration curve of 50.0 mL of a typical 0.100 M diprotic acid with 0.100 M NaOH.
To locate the first and second equivalence points, draw tangents to the various parts of the titration curve as shown in Figure 6. The first inflection point in the curve is the result of neutralizing the first $H^+$ on $H_2A$. The final inflection point is the result of neutralizing the second $H^+$.

You use the total volume of NaOH added and Eqn. 2-c to calculate the molar weight of the diprotic acid. To find $pK_{a1}$ and $pK_{a2}$ values for $H_2A$, each equivalence point is analyzed separately. You find $pK_{a1}$ from the half-neutral volume for the first equivalence point; $pK_{a2}$ is found from the half-neutral volume for the second equivalence point.

In order to get a good graph from which to determine the equivalence point and $pK_a$ values, extensive data must be available. You will first determine what size sample of your unknown is needed to use about 30 mL of your NaOH. By using about 30 mL of NaOH you will not have to refill your buret in order to get adequate data points before and after reaching the equivalence point.

Because of the rapid change in pH near the equivalence point, it is necessary to add small volumes of NaOH between pH readings in the vicinity of the equivalence point. As noted above, a diprotic acid will have two equivalence points, with one at half the volume of titrant needed for complete neutralization. It is, therefore, necessary to add the titrant in small increments near the half-way point of the titration.
By weighing out a trial 0.1 g sample of your unknown and titrating to the end point using phenolphthalein, you can determine the "volume of NaOH per gram of sample" ratio. This will enable you to calculate the sample weight needed to use about 30 mL of your NaOH. Once you have weighed out this sample, you can calculate the expected volume of NaOH needed for neutralization and the half-neutralized volume (the volume half-way to the equivalence point). These are the volumes (+/- 2mL) through which you must add the NaOH in small (0.2 mL) increments.

Directions for using pH meters are attached to this lab study.

**EXPERIMENTAL PROCEDURE**

Each group needs:  
- standard NaOH solution, 0.1 M (known to four decimal places)  
- solid unknown acid, 2 g, record the number  
- 250 mL beaker for pH titration, waste beaker, beaker for electrode  
- 250 mL Erlenmeyer flask for preliminary titration  
- phenolphthalein, wash bottle  
- pH meter setup (caution: expensive, delicate electrode)  
- magnetic stirrer and stir-bar (caution: do not lose the stir-bar)  
- 50 mL buret, buret reader

(1) **Trial Titration to Determine Optimum Sample Size**

Use the analytical balance to weigh by difference a 0.1 g sample (accurate to 0.0001 g) of your unknown into a clean Erlenmeyer flask. Add about 30 mL distilled water and 2-3 drops of phenolphthalein indicator. Swirl to dissolve the acid. Titrate the sample with the NaOH. You may actually begin the titration before the sample is dissolved, but it must be completely dissolved by the end of the titration.

From the trial sample mass and the volume of NaOH used, calculate the size sample you would need in order to use 30 mL of NaOH to reach the end point. This is your "ideal mass". (You can use a "volume of NaOH per gram of sample" ratio for this calculation.) Weigh a sample fairly close (+/- 20%) to the "ideal mass" sample of your unknown into a clean 250 mL beaker (not an Erlenmeyer flask). Record the mass in your lab notebook to four decimal places.

Calculate the volume at which you expect the equivalence point:

\[
\text{ideal mass} = \frac{30 \text{ mL}}{\text{actual mass of sample in the beaker}} \times \text{expected equivalence point volume}
\]

Divide the mL for the expected equivalence point by 2. This is the expected 1/2 neutralized volume. Record the expected equivalence point volume, and the expected 1/2 neutralized volume in your lab notebook. These are the volumes (+/- 2mL) through which you must add the NaOH in small (0.2 mL) increments.

(2) **pH Titration**

To the sample in the beaker, place a clean magnetic stir bar, add about 75 mL distilled water and 2-3 drops phenolphthalein. Mix the solution with the magnetic stirrer to (at least partly) dissolve the acid. Caution: Do not turn the stirrer too rapidly, or the solution will splash out. The stir bar should be turning smoothly.

Standardize the pH meter as indicated in the attached pH meter directions. Put the pH electrode about one inch into the solution, with at least 1/4 inch clearance between the tip of the electrode and the height of the stir bar. The clearance is necessary to avoid hitting the electrode with the stir bar. Set up your buret stand so that the tip of the buret is about even with the rim of the beaker.
It is handiest to begin this titration with the buret set at 0.00 mL. Record your initial buret reading and the pH of your sample solution. Turn the stirrer on. Titrate by initially adding approximately 1 ml portions of your NaOH and recording the volume NaOH added and the pH of the resultant solution. When you are about 2 ml from your expected half-neutralized volume, add the NaOH in approximately 0.2 ml increments until you are at least 1 ml beyond the half-neutralized point. You can now add the NaOH in 1 ml increments until you are about 2 ml from your expected equivalence point. Again, add the NaOH in 0.2 ml increments until you are 1 ml beyond the expected equivalence point. (Your sample will have changed color because of the phenolphthalein present.) Do not stop titrating. Add an additional 7 ml of NaOH in 1 ml increments to get data for the last part of your graph.

On a (10 mm to the cm or 20 to the inch) graph paper, make a plot of pH vs. volume of NaOH used. Use good graphing techniques: A title, correct labeling of the axes, reflecting the accuracy of your data as closely as possible. The pH scale does not need to begin at 0.00. On the graph, determine the equivalence point and the volume of NaOH used for neutralization. Determine $pK_a$ (or $pK_{a1}$ and $pK_{a2}$) of your acid. Calculate the molar weight of your acid. Using Table 1 and your experimental values, determine the identity of your acid.

Table 1. Possible Unknown Acids:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Molar Weight (g/mol)</th>
<th>$pK_{a1}$</th>
<th>$pK_{a2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic (a)</td>
<td>60.05</td>
<td>4.756</td>
<td></td>
</tr>
<tr>
<td>butyric (a)</td>
<td>88.10</td>
<td>4.817</td>
<td></td>
</tr>
<tr>
<td>crotonic (b)</td>
<td>86.09</td>
<td>4.70</td>
<td></td>
</tr>
<tr>
<td>itaconic (b)</td>
<td>130.10</td>
<td>3.85</td>
<td>5.45</td>
</tr>
<tr>
<td>maleic (a)</td>
<td>116.07</td>
<td>1.910</td>
<td>6.33</td>
</tr>
<tr>
<td>malonic (a)</td>
<td>104.06</td>
<td>2.826</td>
<td>5.696</td>
</tr>
<tr>
<td>mandelic (a)</td>
<td>152.14</td>
<td>3.411</td>
<td></td>
</tr>
<tr>
<td>oxalic 2-hydrate (a)</td>
<td>126.07</td>
<td>1.271</td>
<td>4.272</td>
</tr>
<tr>
<td>potassium hydrogen phthalate (a)</td>
<td>204.23</td>
<td>5.408</td>
<td></td>
</tr>
<tr>
<td>potassium hydrogen tartrate(a)</td>
<td>188.2</td>
<td>4.81</td>
<td></td>
</tr>
<tr>
<td>propionic (a)</td>
<td>74.08</td>
<td>4.874</td>
<td></td>
</tr>
<tr>
<td>sodium hydrogen sulfite (a)</td>
<td>104.06</td>
<td>7.21</td>
<td></td>
</tr>
<tr>
<td>valeric (a)</td>
<td>102.13</td>
<td>4.842</td>
<td></td>
</tr>
</tbody>
</table>

References:


The report:

Each student will turn in a separate report. The complete experiment is to be entered into all lab notebooks. For the procedure, you may say, "See the separate handout titled, pH titration of a weak acid." Please make very ordered places to enter the appropriate data. Include all weights and buret readings. Your main titration table should be headed:

<table>
<thead>
<tr>
<th>Buret Reading</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 mL</td>
<td></td>
</tr>
</tbody>
</table>

At the end of your report make a table showing: unknown number, mass of sample, volume of ____/M NaOH used, experimental molar weight, experimental $pK_a$’s, your identification of the acid.

You will turn in the carbon copies plus a graph.
pKₐ p7
You may turn these in on a separate piece of paper attached to your report. All is due one week after the lab work is done.

QUESTIONS

1. Explain why you should use a sample weight that will use about 30 mL of NaOH at the end point of the titration.

2. A 30.00 mL sample of 0.100 M HOBr is titrated using 0.100 M NaOH.
   \[ K_a = 2.5 \times 10^{-9} \] for HOBr.
   a) Write a balanced net-ionic equation for the titration reaction.

   b) Calculate the pH of the titration mixture at the equivalence point.

   c) Would bromthymol blue be a suitable indicator for the titration? Refer to the discussion of indicators in your textbook. Explain your answer.

3. Why is it necessary to determine pH vs. volume of titrant for volumes beyond the equivalence point in this experiment?

4. If your measured pKₐ value and equivalent weight values do not agree exactly with values in Table 1, which should you trust more, the pKₐ or the equivalent weight? Why?