Potentiometric Determination of the pKₐ and the Equivalent Weight of a Weak Acid

Introduction

In this experiment you will use a pH meter to follow changes in H⁺ concentration during a titration. The laboratory instructor as part of the briefing will explain operation of the pH meter to you. These instruments are expensive and the electrodes are fragile. They should be handled with care. You should be absolutely certain that you understand the correct technique for using the meter.

By plotting pH as a function of the volume of base added during the titration, a titration curve can be readily prepared (Figure 1). Titration curves provide the analyst with significant information concerning the identity of the weak acid. For a monoprotic acid, there will be one equivalence point (as shown in Figure 1). However, diprotic acids exhibit two equivalence points, triprotic acids exhibit three equivalence points, and so on. If the pKᵢ’s for a polyprotic acid are sufficiently far apart (~2 units), then the equivalence points in the titration curve will be distinct. If the pKᵢ’s are too close, the equivalence points merge into a single, irregular shaped equivalence point representing both pKᵢ’s.

The pKᵢ for a monoprotic acid is readily determined from the titration curve by the following procedure. First, determine the volume of base required to reach the equivalence point. Divide this volume in half, and from inspection of the titration curve determine the pH of the solution at 1/2 of the volume of base necessary for equivalence. The pH at this point is the pKᵢ. This is readily confirmed from the Henderson-Hasselbach equation describing buffers:

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]

where A⁻ represents the concentration of neutralized weak acid and HA is the concentration of unneutralized weak acid. At the equivalence point, all of the HA has been converted into A⁻. This conversion required a finite volume of base. If half of the volume of base needed for total conversion is added, then half of the HA has been converted into A⁻. The concentrations of HA and A⁻ will be equal, the ratio of \([A^-]/[HA]\) will be 1.00, the log of 1.00 is 0.00, and the pH = pKᵢ.
Figure 1. Titration curve for a monoprotic weak acid.
Solutions needed for this experiment:

<table>
<thead>
<tr>
<th>Solutions prepared by the student</th>
<th>Solutions provided by the instructor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1N sodium hydroxide (standardized by student)</td>
<td>Phenolphthalein indicator (for standardization of sodium hydroxide solution only)</td>
</tr>
</tbody>
</table>

Specialized equipment needed:

In this experiment, you will be using a pH meter and electrode. Your laboratory instructor will demonstrate the proper calibration and use of this instrument during the laboratory briefing for this experiment.

Experimental Procedure

Preparation and standardization of sodium hydroxide solution.

1. Dry ~2 grams of potassium hydrogen phthalate (KHP) in the oven for 2 hours at 110 °C. Store the dried KHP in a desiccator.

2. Prepare 1 liter of 0.1N sodium hydroxide by adding about 500 mL of deionized water to a clean 1 liter plastic bottle. Add either 4.0 grams of solid sodium hydroxide, or 8.0 grams (~5.3 mL) of 50% sodium hydroxide solution. Shake the contents until the sodium hydroxide is completely dissolved and mixed, and then fill the bottle with deionized water. Cap the bottle and mix by shaking.

3. Using an analytical balance, dispense three 0.5-gram samples of KHP into separate beakers or flasks. Make sure you record the mass of KHP used to four decimal points. Add about 25 mL of water to each sample. The KHP should completely dissolve, but if it doesn't DON'T WORRY ABOUT IT.

4. To each KHP sample, add 2-3 drops of phenolphthalein solution.

5. Titrate each KHP sample with your sodium hydroxide solution to the first, pale pink endpoint that is stable for at least 10 seconds (Figure 2). The entire contents of the beaker/flask must be pale pink, and the palest endpoint possible is the most desirable. Record the volume of sodium hydroxide solution used.
6. Calculate the average normality of your sodium hydroxide solution and label the solution appropriately. The formula weight of KHP is 204.23 g/mole. At the endpoint of the titration the number of moles of sodium hydroxide is equal to the number of moles of KHP. The molarity of the sodium hydroxide solution is equal to the moles of sodium hydroxide divided by the volume (in liters) of sodium hydroxide solution used at the endpoint. The normality of sodium hydroxide is equal to the molarity.

Titration of the weak acid.

1. Obtain an unknown weak acid sample from your instructor and record the unknown number. DO NOT dry the acid in the oven.
2. Using the analytical balance dispense 0.4 – 0.5 grams of the acid into a 250 mL beaker. Add about 50 mL of deionized water and a magnetic stir bar. Turn the magnetic stirrer on, and adjust it so that the solution is constantly and gently stirred. Rinse the pH electrodes with deionized water and place them in the beaker. Make certain that the stir bar does not hit the electrodes.

3. Record the initial pH of the weak acid solution.

4. Mount the burette in an appropriate position for the addition of sodium hydroxide to the beaker.

5. Add standard base to the unknown acid and record the total volume of base added and the pH reading. Try to record pH changes in intervals of 0.2 – 0.3 pH units, or volume increases of ~5 mL, whichever comes first.

6. Continue to titrate until you have reached the equivalence point. Normally, you will be able to tell that you are approaching the equivalence point when a small addition of base causes a dramatic increase in pH. When this happens, add additional smaller increments of sodium hydroxide solution (~0.1 - 0.2 mL). After you have reached the equivalence point, the small volumes of sodium hydroxide will not have significant effects on the pH. Return to adding ~5 mL increments of sodium hydroxide and continue the titration until you have reached a pH that is 2 – 3 pH units higher than the equivalence point pH, or until you reach a pH of 12 (whichever comes first).

7. Repeat the titration on a second sample of the unknown acid.

8. When you are finished, you should have two sets of data similar to that shown in the table below.

<table>
<thead>
<tr>
<th>Total volume of base added</th>
<th>pH of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 mL</td>
<td>4.65</td>
</tr>
<tr>
<td>5.13 mL</td>
<td>4.99</td>
</tr>
<tr>
<td>10.22 mL</td>
<td>5.31</td>
</tr>
<tr>
<td>etc.</td>
<td>etc.</td>
</tr>
</tbody>
</table>

9. For both sets of titration data, plot pH (y-axis) as a function of total volume of sodium hydroxide solution added (x-axis). Draw a smooth curve through all of the data points.
10. Determine the equivalence point on the graph by finding the midpoint of the steep portion of the titration curve. Figure 3 below will help you determine this midpoint. Draw a straight line coinciding with the buffer region of your titration curve, and another straight line coinciding with the post-equivalence region. Draw a third straight line coinciding with the equivalence point region and intersecting the other two lines. The intersection of the straight lines coincides with two volumes, \( V_1 \) and \( V_2 \). The equivalence point volume is equal to the average of \( V_1 \) and \( V_2 \).

11. From the equivalence point volume, calculate the equivalent weight of your acid using the following equations:

\[
N_{\text{base}} \times V_{\text{base,Liters}} = \text{moles,}OH^- = \text{moles,}H^+
\]

\[
\frac{\text{grams}_{\text{Acid}}}{\text{moles,}H^+} = \text{Equivalent weight, grams/mole}
\]

12. Determine the pKₐ for your acid by determining the pH at a volume equal to 1/2 of the equivalence point volume. Report the average equivalent weight and average pKₐ.
Figure 3. Graphical method for determining equivalence point volume.

Laboratory Report

A sample lab report is shown at the end of this procedure.

WASTE DISPOSAL: All wastes can be poured down the sink.
Equivalent Weight and pKₐ

Unknown # 12.5
Washington Irving

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of unknown acid, g</td>
<td>0.5278</td>
<td>0.5093</td>
<td></td>
</tr>
<tr>
<td>Vol. base at equivalence, mL</td>
<td>25.50</td>
<td>24.50</td>
<td></td>
</tr>
<tr>
<td>Vol. base at 1/2 equivalence, mL</td>
<td>12.75</td>
<td>12.25</td>
<td></td>
</tr>
<tr>
<td>Normality of base, N</td>
<td>0.1099</td>
<td>0.1099</td>
<td></td>
</tr>
<tr>
<td>pKₐ, from titration curves</td>
<td>5.50</td>
<td>5.45</td>
<td>5.48</td>
</tr>
<tr>
<td>Equivalent weigh, g/mole</td>
<td>188.3</td>
<td>189.2</td>
<td>188.8</td>
</tr>
</tbody>
</table>

Sample calculations:

\[ N_{\text{base}} \times V_{\text{base,Liters}} = \text{moles,OH}^- = \text{moles,}H^+ \]

\[ 0.1099N \times 0.02550L = 0.00280245\text{moles,OH}^- = 0.00280245\text{moles,}H^+ \]

\[ \frac{\text{grams}_{\text{Acid}}}{\text{moles,}H^+} = \text{Equivalent weight, grams/mole} \]

\[ \frac{0.5278\text{grams}_{\text{Acid}}}{0.00280245\text{moles,}H^+} = 188.3 \frac{\text{grams}}{\text{mole}} \]

Attach one of your titration curves to the report.