GA/7 Potentiometric Titration

INTRODUCTION

The potentiometric titration is a useful means of characterizing an acid. The pH of a solution is measured as a function of the amount of titrant added. The change in pH is small until the end point where there is a sharp change. The strength of an acid or base determines the sharpness of the change. The end point is found by graphing the points and determining the location of the sudden change in pH. It is not necessary to add the titrant dropwise as was required to obtain the exact equivalence point using a visual indicator. The important thing is that a good graph with increments such as 2.00, 1.00, 0.50, 0.20 and 0.10 (2 drops) ml of titrant be added and the resulting pH readings obtained. (Refer to Chap. 7, 10, 11 and 12 of Harris' book).

The hydrogen ion activity of a solution is conveniently measured using a glass indicator electrode. The reference is usually a calomel or silver-silver chloride electrode. In this laboratory, you will be using a “combination electrode” that incorporates both electrodes surrounded by a protective plastic sleeve. The pH meter, a high input impedance millivolt meter, is calibrated by setting the pH to that of a known standard buffer.

In this experiment, three titration curves will be obtained:

1. Strong acid (HCl) with a strong base (NaOH)
2. Weak monoprotic acid (KHP) with a strong base (NaOH)
3. An unknown diprotic acid (H₂A) with a strong base (NaOH)

Determination of the Equivalence Point

A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration. In the case of an acid titration, the slope is increasing before the equivalence point and decreasing after the equivalence point (just the opposite is true for the titration of a base). Note that the slope changes fastest just before and just after the equivalence point. At the equivalence point, it does not change at all, and we say there is an inflection point. The rate of change of the slope is zero.

The equivalence point can be found in three ways. One method is to look at the sigmoid curve and estimate where the central part of the rise is. The second method is to make a first derivative plot. The first derivative, \( \Delta \text{pH}/\Delta \text{ml} \), is the slope of the curve, and can be obtained simply from equation 1 (see the next page). Each first derivative point is plotted against \( V' \) where \( V' \) is the average of the two volumes, \( V_1 \) and \( V_2 \). The endpoint occurs at the volume, \( V' \), where \( \Delta \text{pH}/\Delta \text{ml} \) has the maximum value.

\[
\text{pH}_2 - \text{pH}_1 = \Delta \text{pH}
\]

Equation 1
The third way is to make a second derivative plot. The second derivative, \( \Delta^2 \text{pH}/ \Delta V^2 \), is the rate of change of the slope and can be obtained from equation 2.

\[
\frac{(\Delta \text{pH}_2/\Delta m_{l})_2 - (\Delta \text{pH}_1/\Delta m_{l})_1}{\Delta V_2 - \Delta V_1} = \frac{\Delta^2 \text{pH}}{\Delta m_{l}^2}
\]

Equation 2

Each second derivative point is plotted against \( V'' \) where \( V'' \) is the average of \( V'_{1} \) and \( V'_{2} \). The end point occurs at the volume, \( V'' \), where \( \Delta^2 \text{pH}/ \Delta m_{l}^2 \) is zero. First and second derivative data are given in the table on pages 2-14 and the derivatives plots are shown in the figure on page 2-13.

**PROCEDURE**

**Solutions and Chemicals Required:** standardized 0.1 M HCl from GA/2
standardized 0.1 M NaOH from GA/2
buffer solution, pH 7.00, 4.00 and 3.56 to standardize the pH meter
solid KHP
unknown diprotic acid

**Special Equipment:** To be distributed by the Teaching Assistant:

- pH meter
- combination electrode (glass/SCE reference)
- magnetic stirrer motor
- 50 ml pipet

**NOTE:** The potentiometric titration experiment is to be done with a partner. The same partner should be kept for all parts. No more than two people may work on an experiment together, so if there is an odd number of people in the class, one person will work alone. The use of partners is due to limitations of equipment, NOT with difficulty of experimental procedure.

A. **Standardization of the pH Meter with Two Standard Buffers**

The laboratory instructor or teaching assistant will demonstrate the proper use of the pH meter. Just before beginning the first titration, standardize the pH meter using the buffers provided. Remember to re-standardize the pH meter with the buffer before each titration. You should note and record in your lab notebook the reproducibility of the pH meter.
readings. If there is any questions about the performance of the electrodes or meter during the titration, the meter please consult either the laboratory instructor or teaching assistant.

**Steps in the Standardization of the pH meter using two Buffers.**

1. Place the combination pH electrode in the pH = 7.00 buffer.

2. Adjust the slope knob to 100% and the temperature knob to the temperature measured for the pH buffer being used. (This temperature needs to be adjusted for only the first buffer and then later for each solution that is to be titrated accurately.

3. Once the pH reading has stabilized, use the standardization knob to bring the meter reading to 7.00. Note the may be some drifting, try to get use to how much your combination pH electrode will drift and about how long before it becomes stable.

4. Remove and carefully rinse the electrode with de ionized water. Place the electrode in the pH = 4.00 buffer.

5. Once the pH meter reading has stabilized, adjust the slope knob until the pH meter reads 4.00.

6. Repeat the entire procedure until you are satisfied that the pH meter is accurately calibrated to within +/- 0.04 pH units.

**B. Standardization of HCl by Potentiometric Titration**

Fill the buret with your standardized 0.1____ M NaOH. Using one of the partnership’s calibrated 25 ml pipets, carefully deliver 25.____ ml. of the ~ 0.1 M HCl into a 250 ml. beaker. Add about 25 ml. of deionized water. Place a magnetic stirrer bar, signed out from the stockroom, in the beaker. (BE SURE TO RETURN THE MAGNET BAR AT THE END OF EACH LAB!) Place the beaker on the magnetic stirrer. Position the electrode system in the solution. making sure the bottom sensing portion of the combination electrode is covered with solution. It might be necessary to add a little deionized water.

Out of interest, add a few drops of phenolphthalein indicator to the titration solution. During the titration, note the color change and the volume and pH at which it occurs. This is to be added to the graph in the lab report.

With the electrodes inserted and the stirrer bar turning, read the initial pH when 0.00 ml. of NaOH has been added. During the titration, keep the pH meter ON and maintain a constant stirring rate. Carefully titrate with standardized NaOH solution starting with increments of 2.00 ml and gradually reducing the increments to 2 drops (about 0.10 ml) at a time in the vicinity of the equivalence point where the pH is changing rapidly. It will simplify graphing if increments are kept constant over the appropriate ranges. For example, add 2.0 ml increments at first. As the slope of the titration curve increases, decrease to 0.5 then 0.20 and finally to 0.10 ml near the equivalence point.

Let the change in pH dictate the volume of NaOH added. The pH change should be on the order of one or two tenths of a pH unit. At the first sign that the pH is changing faster, decrease the NaOH increment. Record all values of volume NaOH solution added and pH. Continue beyond the equivalence point with first smaller and then larger increments as the
change decreases. Stop when the pH has been at or near a pH of 11 for several, consecutive milliliters. Because the pH meter is precise to only 0.02 pH units, there is no need to boil solutions prior to the equivalence point during potentiometric titrations. Turn off the pH meter at the end of the titration; remove and rinse the the electrodes.

C. Potentiometric Titration of Potassium Acid Phthalate (KHP)

IMPORTANT: It will be necessary to know the exact weight, to 0.1 mg, the weight of KHP used. Weigh 2.5 mmoles of KHP to ±0.1 mg., by difference into a 250 ml. beaker. Add exactly, using the large pipet provided, exactly 50.0 ml. of deionized water. Warm slightly to dissolve KHP. Again add 50.0 ml. more of deionized water and quickly cool the solution running tap water around the outside of the beaker until it is close to room temperature.

Add phenolphthalein. Titrate as in part B, recording pH and volume values. Note the color change and the pH and volume at which it occurs.

D. Potentiometric Titration of a Diprotic Acid

In this experiment, five different diprotic acids will be investigated. These are listed in the table below with their formula weight and pK's. Each of these acids exhibits a different shaped titration curve. From the shape of the curve that are obtained one can obtain the formula weight and the equilibrium constant(s) of the acid. (The laboratory instructor will have given a lab briefing on this subject).
### Possible Diprotic Acids

<table>
<thead>
<tr>
<th>Name of the Acid</th>
<th>Formula Weight</th>
<th>pKₐ₁</th>
<th>pKₐ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glutamic</td>
<td>147.13</td>
<td>4.07</td>
<td>9.47</td>
</tr>
<tr>
<td>Malonic</td>
<td>104.06</td>
<td>2.83</td>
<td>5.69</td>
</tr>
<tr>
<td>Salicylic</td>
<td>138.12</td>
<td>2.97</td>
<td>13.4</td>
</tr>
<tr>
<td>Succinic</td>
<td>118.09</td>
<td>4.16</td>
<td>5.61</td>
</tr>
<tr>
<td>Tartaric</td>
<td>150.09</td>
<td>2.98</td>
<td>4.34</td>
</tr>
</tbody>
</table>

As your group performs the titration, have one of the partners prepare a rough plot in lab then later a more careful plot (with 4 copies) of the titration curve of your unknown diprotic acid. You will need to share these copies with four other pairs of students having different diprotic acids. (The actual assignment of groups of two to the larger study groups will be done by the laboratory instructor). Remember you will need to make time in the laboratory period to discuss and exchange data with the other groups. Do not fail to make time for these important exchanges. The information must be include in your final lab paper, and it is not a valid excuse that "I did not have time to talk to the other groups!"

Weigh by difference the specified weight of the diprotic acid into a 250 ml beaker. Add 50 ml of deionized water to dissolve. Add phenolphthalein indicator. Record the volume at which the indicator changes color. It is suggested that you first perform a rapid, crude titration in order to determine where the equivalence point(s) is/are. Add the titrant in 2.00 ml increments at a time at first recording the pH after each addition. As the pH rises more rapidly, add smaller increments. After the first equivalence point is observed, use once again larger increments until a volume beyond twice that required for the first equivalence point has been added. Continue adding the NaOH for an additional 10 or 15 ml. Plot this rough titration curve, and predict how much sample should be used in the careful titration. Make sure that the final titration jumps occur within the 50 ml limit of the 50 ml buret. Consult the laboratory instructor or teaching assistant if questions arise. Next carry out a careful titration using a sample of your unknown diprotic acid having the appropriate sample weight. Add phenolphthalein and record when it changes color.

### RESULTS AND CALCULATIONS

These calculations should go into the Appendix I section of the lab paper. (See the separate handout- “The Written Laboratory Work- the Lab Papers..."
The results that you calculate as well as the graphs should be incorporated into the Results and Discussion section.

1. Titration Curves

Prepare titration curves for the titrations of HCl, KHP, and your dibasic acid. Be sure to include the following:

   a. a good title
   b. labeled axes
   c. a smoothly drawn curve
   d. indication of the visual indicator transition
   e. position of pk's where applicable and volume(s) at equivalence point(s)
   f. first derivative plots for all acids
   g. second derivative plot for KHP only

   *For the derivative points, it is necessary to use only about sixteen data points, roughly seven derivative points on either side of the equivalence point. DO NOT WASTE TIME CALCULATING DERIVATIVE POINTS FOR EVERY DATA POINT: IT IS ENTIRELY UNNECESSARY.

2. Sketches

Include all of the titration curves for the five diprotic acids done by your group and the other groups. These curves are to be incorporated into your Results and Discussion section of the lab report along the assigned identity and a discussion as to why each of the diprotic acids has a particular shape.

3 Calculations

Part B

From the data and the titration curve, calculate the concentration of HCl. Compare this value with the data obtained in Part D involving the volume ratio section.

Part C

Calculate the pk of KHP from the data and the titration curve. Calculate the formula weight of KHP. Calculate the absolute and relative error for the FW and pKₐ of the KHP (accepted value FW is 204.23 and pKₐ is 5.41).

Part D

Calculate the two pk's of your diprotic acid from the data and the titration curve. Calculate the formula weight of your diprotic acid. Calculate the absolute and relative error of each value to those found in the Table on page 2-9.

4. The report for GA/7 is to be in the format of a longer lab paper. Review the requirements for the lab paper. (See the separate handout entitled “Written
Laboratory Work”. The marking will be based about 1/3 on the written report and about 2/3 on the calculations and results. The grade for the written report will be based heavily on the contents of the Introduction, Results and Discussion although the format of the report, and English and style, will also be evaluated.

The Introduction should contain a discussion of general concepts of acid-base behavior, including pH, strong and weak acids, mono- and di-protic acids, titration curves. The Results and Discussion should give a tabulation of the results and discuss them in the context of the material given in the Introduction.

One of the important subsections of the Results and Discussion section is the Statistical Analysis. Since this is the first lab paper that you are doing, included here are a series of specific questions to keep you on the right track. Answer the questions in paragraph form in the Discussion Section. When there are specific calculations to do put them in Appendix.

Statistical Analysis for the Potentiometric Titration

In the potentiometric titration, GA/7, two basic quantities were determined: Formula weights and pK's. In the statistical analysis section, you should present and discuss the accuracy’s of these values and explain what factors are most important in leading to the deviations of the experimental results from the true values as reported in the literature.

A. Formula Weights

The formula weight may be calculated using the following equations:

monoprotic: \[ FW = \frac{mg \text{ acid}}{M_{NaOH} \times ml_{NaOH}} = \text{ gm acid/mole acid} \]

diprotic: \[ FW = 2 \times \frac{mg \text{ acid}}{M_{NaOH} \times ml_{NaOH}} = \text{ gm acid/mole acid} \]

*\[ ml \text{ of NaOH is the volume of base necessary to reach the second point. If you use the ml of NaOH to get to the first equivalence point, then use the same expression as a monoprotic acid.} \]

Questions to be answered in a Separate Section labeled “Questions” in the Discussion Section.

1. What is the accuracy of your experimental FW of KHP and the diprotic acid?

2. To investigate factors affecting accuracy further, suppose a pH meter is inadvertently set to pH 5.00 using a pH 3.56 standard buffer and then the KHP is titrated with standard ~ 0.1 M NaOH. Sketch the titration curve as the experimenter would see it using a solid line. Sketch the titration curve as it should have looked (if the meter were correctly calibrated) using a dashed line.

   How is the precision and accuracy FW affected?

   How is the precision and accuracy pK affected?
Is it reasonable to suppose that the calibration of the pH meter had an adverse effect on the accuracy of your pK’s? FW’s? Explain why?

B. pK’s

To find the pK, the volume of NaOH to reach the equivalence point must be halved and then the pH corresponding to that volume must be found.

1. On your titration curve for KHP, find the volume of NaOH halfway to the equivalence point and identify this point on the curve.

2. What is the accuracy and the relative accuracy for each of your pK’s and the dibasic acids.

In summary, what conclusions can you reach about the most important measurements or factors affecting the accuracy of the FW’s? Of the pK’s?

C. Discuss in your Lab Paper the reproducibility of the pH meter readings as it is being standardized with the three different buffers.
Addendum to GA/7 - Potentiometric Titration

Accepted value for the pKₐ of Potassium Hydrogen Phthalate (KHP) is 5.41.

Sample weight and group assignment for the Unknown Diprotic Acid

<table>
<thead>
<tr>
<th>Unknown #</th>
<th>Suggested Sample Weight</th>
<th>Names Group 1-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6,11</td>
<td>0.16 to 0.18 grams</td>
<td>Names Group 1-15</td>
</tr>
<tr>
<td></td>
<td>dissolve in cold water</td>
<td></td>
</tr>
<tr>
<td>2,7,12</td>
<td>0.18 to 0.21 grams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissolve in warm water</td>
<td></td>
</tr>
<tr>
<td>3,8,13</td>
<td>0.41 to 0.48 grams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissolve in 10 ml ethanol then add 40 ml of water</td>
<td></td>
</tr>
<tr>
<td>4,9,14</td>
<td>0.23 to 0.26 grams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissolve in cold water</td>
<td></td>
</tr>
<tr>
<td>5, 10.15</td>
<td>0.44 to 0.52 grams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissolve in warm water</td>
<td></td>
</tr>
</tbody>
</table>