Experiment

TITRATION OF AN ACID MIXTURE

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- analyze an acid mixture by titration with NaOH solution.
- use the **MicroLAB** interface to gather and store titration data.
- use the **MicroLAB** spreadsheet to graph the titration curve and accurately determine the endpoints.

BACKGROUND

In this experiment a solution containing either HCl and H_3PO_4, H_3PO_4 alone, or H_3PO_4 and NaH_2PO_4 is titrated using standardized NaOH solution. Progress of the titration will be followed using a pH electrode attached to a computer via the ***MicroLAB*** interface. From the data obtained, titration and first and second derivative curves will be constructed and the two acid concentrations will be determined.

It is often difficult to estimate precisely the equivalence point volume of an acid-base titration from the pH versus ml NaOH plot because it is difficult to determine where the slope of the curve reaches a maximum. Indicators may be chosen to give a good indication of the equivalence point, but they are never exactly accurate. A much more accurate method is to calculate the derivative of the titration curve. A line drawn tangent to the titration curve at any point defines the slope of the curve at that point. The slope of any line is defined as "rise over run," i.e., the change in "Y" direction divided by the change in the "X" direction, or $\Delta Y / \Delta X$. If you mentally move the tangent line along the titration curve from beginning to the middle of the steepest part, you will notice that the slope of the line increases from a small value to a maximum at the middle point, then decreases back to a smaller value again, as illustrated in the figure 2. That is, it rotates to the left to the middle point, then rotates to the right, and at the middle point, the line is vertical and the slope is infinite. ($\Delta Y = \infty$, and $\Delta X = 0$, therefore, actually $\Delta Y / \Delta X$ is undefined.) The series of data points for $\Delta Y / \Delta X$ plotted against the "X" axis is termed a "first derivative plot" of the original data.

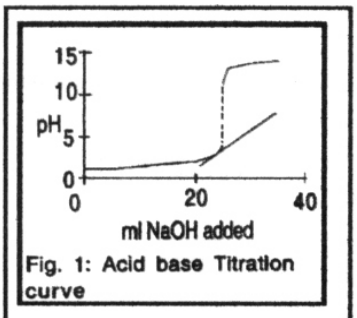

Fig. 1: Acid base Titration curve

Figure 1. pH vs volume titration curve.

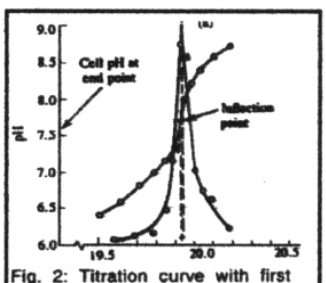

Fig. 2: Titration curve with first derivative.

Figure 2. pH vs volume with 1st derivative.

The ***MicroLAB*** program has a function to carry this out, which will be discussed in the **Data Analysis** section. This derivative can then be plotted on the "Y2 Axis" and will produce a graph as illustrated in Figure 2.

Because we don't have the true mathematical equation for the titration curve, only a collection of "X, Y data points," the likelihood of the maximum in the first derivative being exactly at the equivalence point of the titration is very small. It will, however, be in the near vicinity of the equivalence point. An even more exact measure of the equivalence point can be determined by repeating the derivative process a second time, this

time taking Δ(ΔY / Δ X) / Δ X, i.e., the change in the first derivative with respect to the change in "X." If you analyze the change in the slope of the first derivative with increasing "X", you will see that at the "true" equivalence point, the slope of the second derivative will be zero (0), i.e., a horizontal line. This means that at the equivalence point the slope of the second derivative will go from some positive value, through zero to some negative value as illustrated in Figure 3. Thus, the exact equivalence point corresponds to the zero value of the second derivative. Again, it will rarely occur that the zero value will occur exactly on an "X" data point. This, however, is irrelevant, because the most exact value of the second derivative, and hence also the most exact volume at the equivalence point, can be found by interpolation, a process for accurately calculating an intermediate value between two points, assuming a straight line between the two points. For most situations, even for curved lines, this is a reasonable approximation if the two points are close enough to each other relative to the curve. Instructions for carrying out interpolations are included as an appendix to this experiment.

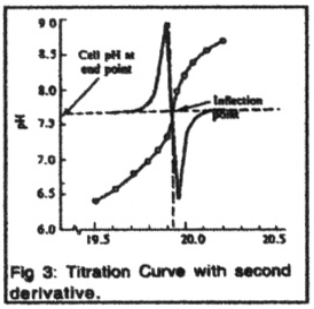

Fig 3: Titration Curve with second derivative.

Figure 3. pH vs volume with 2nd derivative.

SAFETY PRECAUTIONS

Clean up all spills immediately. Safety goggles must be worn at all times. As usual, wash hands with soap and water before leaving the lab.

BEFORE PERFORMING THIS EXPERIMENT . . .

...you will need a **MicroLAB** program capable of measuring and displaying pH and volume data. It is suggested that ***pH,temp.vs.drop.titr.0.1pH.exp***, supplied by your instructor, be used to give the best derivatives and the most accurate calculations. It is also suggested that the drop counter be calibrated using ***Drop Counter Calibration*** program.

EXPERIMENTAL PROCEDURE

At the work bench

Submit a clean, dry, and stoppered 250 ml Erlenmeyer flask to receive a sample of unknown. Pipet 25 ml of this sample into a 250 ml beaker. Add 35 ml of distilled water using a graduated cylinder. Prepare your buret by rinsing and filling with standardized NaOH solution.

At the computer

Turn on the computer and monitor. Make sure the interface is on by pressing the power switch in the back right corner of the interface module.

1. Click on the **MicroLAB** icon on the desk top, click on the *Titrations* tab, and select the drop calibration program

2. Attach the pH electrode to the pH connector on the back.

3. Perform a three point calibration, following the on-screen instructions using pH 4.00, 7.00 and 10.00 buffers. The pH probe should always be rinsed with distilled water and *patted* dry with a Kimwipe before inserting into any solution so as to avoid cross-contamination.

4. Calibrate the drop counter by collecting five, cumulative two ml volumes, determining the number of drops at each cumulative two ml. Do this before and after your titrations.

Titrations

1. Titrate at least three samples of the mixture with standard 0.1 *M* NaOH solution using a pH electrode to monitor the reaction. Using the above titration program, each titration will first obtain an initial pH value, i.e., one when no NaOH has been added. **NOTE:** The above program will collect data only every 0.1 pH units. Initially the volumes necessary to achieve this change will be on the order of one or more mls. As you approach the equivalence points, increments will be much smaller.

2. **NOTE**: If you are using a buret for the titration, you should have a 125 ml wash bottle filled with 0.100 M NaOH to keep the buret filled within the top one ml in order to keep the drop rate reasonably constant.

3. As you begin the titration, if you are using a buret, adjust the drop rate to between two and four seconds per drop so that the base has time to mix before the pH is measured just as the next drop falls.

4. Continue the titration until the titration curve begins to flatten out beyond the second inflection point. When finished, click on **STOP**, then turn of the stopcock.

5. Save each titration with an appropriate name, e.g., Mix.H1.10.22.04.DH, where the H1 changes to H2, etc. for each titration, the 10.22.04 is the date and the DH is your initials.

DATA ANALYSIS

1. Recall each titration run in turn, using the names you gave them. Column A is the drop count; Column B is the pH of the solution.

2. Click on the **Analysis** button and obtain the first and second derivatives. "Click-drag" the first derivative function from the **Data Sources/Variables** view to the **Spreadsheet**, column C, then to the **Y2** axis of the graph and set it to **Auto-scale**, then right click on the first derivative function again and select **Hide this Derivative** so both will not be on the graph.

3. Scroll the **Spreadsheet** down to center the first derivative in the **Spreadsheet** window.

4. Print this screen as follows:
   a. Press **Ctrl-Print Screen** to capture the screen image.
   b. Open WordPad by clicking **Start > Programs > Accessories > WordPad**.
   c. Press **Ctrl-V** to paste the screen image into WordPad.
   d. Press **Ctrl-P** to print the item.

5. "Click-drag" the second derivative function from the **Data Sources/Variables** view to the **Y2** axis on the graph and set it to **Auto-scale**, then right click on the second derivative function again and select **Hide this Derivative** so both will not be on the graph.

6. Scroll the **Spreadsheet** window to center the second derivative value and print this screen as in step 3.

CALCULATIONS AND RESULTS

Depending on the composition of the mixture, two of the following reactions are possible:

$$HCl + NaOH \Longrightarrow NaCl + H_2O$$

$$H_3PO_4 + NaOH \Longrightarrow NaH_2PO_4 + H_2O$$

$$NaH_2PO_4 + NaOH \Longrightarrow Na_2HPO_4 + H_2O$$

One can thus calculate the amounts of either HCl and H_3PO_4, H_3PO_4 alone, or H_3PO_4 and NaH_2PO_4 in the original unknown from these two equivalence point volumes.

Calculate the molarities of the two acids in the original unknown (to the correct number of significant figures).

You will need to write a brief report on this analysis, very briefly describing your procedure, describing in some detail your analysis of how you arrived at the composition of your mixture, and their concentrations. Be sure to tabulate your results in the report, and make reference to the original data table and graphs. For best results, you should interpolate the second derivative data to obtain the most accurate equivalence volume. Be sure to attach copies of your printouts to the report, and also to your lab book.