EXPERIMENT

INTRODUCTION TO INDICATORS AND ACID-BASE TITRATIONS

By

Dale A. Hammond, PhD, Brigham Young University Hawaii

LEARNING OBJECTIVES

The objectives of this experiment are . . .

- an introduction to pH as a means of determining the amount of an acid or base present.
- exploration of the change in acidity versus the volume of titrant added during a titration.
- determine the difference between a strong acid and a weak acid titration curve.
- determine the effect of a weak acid/strong base titration on the acidity of the equivalence point.

INTRODUCTION

An acid was originally defined by Svante Arrhenius as a substance which furnishes hydrogen ion in solution, and a base as a substance which furnishes hydroxide ion in solution. Bronsted and Lowry further defined an acid as a proton donor, and a base as a proton acceptor.

INDICATORS

One way we will look at whether a substance is an acid or base is by using "indicators." Using the Boasted-Lorry definition, an indicator is an organic compound which can either accept or donate a proton, depending upon the hydrogen ion concentration of the solution. Indicators have two or more different colors as a function of the hydrogen ion concentration, for example, litmus, a naturally occurring dye with this capability, is red in acid and blue in base. Other indicators have other colors. In addition, different indicators will change color at different hydrogen ion concentrations, or acidities. Many flowers have natural indicators to give them their color.

Acidity, or the hydrogen ion concentration, $[H^+]$, can range over more than 16 orders of magnitude of concentration, i.e., of $[H^+]$ from 10^1 to 10^{-15}. Because this is such an extremely wide range, a logarithmic scale has been adopted to make it more convenient to use. This logarithmic utilizes what is known as the "p function." The "p function" is defined as

$$p(F) = - \log(F)$$

where F is any entity of interest that varies over many orders of magnitude. Using this function, pH is defined as the negative logarithm of the hydrogen ion concentration,

$$pH = - \log[H^+]$$

and ranges from -1 for very acid solutions ($[H^+] = 10^1$ where $[H^+]$ equals the molar hydrogen ion concentration) to 14 for very basic solutions($[H^+] = 10^{-14}$). Neutrality, i.e., when there are equal concentrations of acid and base, occurs at a pH of 7 ($[H^+] = 10^{-7}$). This occurs at this value because in a solution of pure water, the $[H^+] = [OH^-] = 1 \text{ X } 10^{-7}$ at 25 °C. We will use this scale as an approximation to measuring the acidity or basicity of solutions in today's experiments.

Indicators

We will look at whether a substance is an acid or base by using "indicators." An indicator is an organic compound which can either accept or donate a proton, depending upon the hydrogen ion concentration of the solution it is placed in. Indicators have different colors depending on the hydrogen ion concentration. For example, litmus, a naturally occurring dye with this capability, is red in acid and blue in base. Other indicators have other colors. In addition, different indicators will change color at different hydrogen ion concentrations, or acidities. We will also utilize buffer solutions, which are solutions which have a specific acidity and tend to resist a change in that acidity.

Titration

Titration is a process in which a solution of known concentration is quantitatively added to a known volume of a solution of unknown concentration in order to determine its concentration. It requires the use of a buret, which is a glass tube of a uniform bore with accurate calibrations capable of measuring any dispensed volume to a precision of 0.02 ml. The known volume of solution of unknown concentration to be titrated is known as the "analyte," and the solution in the buret of known concentration is termed the "titrant." The titration takes place by incrementally adding the titrant to the analyte solution.

As the titration proceeds, it is necessary to have some mechanism to identify when the proper amount of titrant has been added. Stoichiometrically, this occurs when chemically equivalent amounts of titrant have been added to the analyte. This point in the titration is called the "*equivalence point*," and is in the middle of the steep portion of the titration curve of Figure 1. Macroscopically, this point is not generally observable, and it is necessary to measure it by some artificial means. In an acid base titration such as we have here, there is a change in the acidity of the solution, and monitoring the change in acidity, or pH, can serve the purpose. In practice, several methods are available for determining this change in acidity. One is the use of indicators. As discussed above, each indicator changes color at a particular acidity, or pH. In a titration, the point at which the indicator undergoes its color change is called the "*end point*." It is critical to a good titration to chose the proper indicator that will change color at or very near the pH of the equivalence point.

Another method of determining when the correct amount of titrant has been added is the use of a pH meter. A pH meter measures the pH of the solution as the titration proceeds. We will use the ***MicroLAB*** interface and computer with a pH probe to measure the pH, and the system will graph the progress of the titration on the screen as the titrant is added

In this experiment, our titrant is sodium hydroxide, a strong base. We will be titrating acetic acid, a weak acid that only ionizes about 2% in solution. We will then examine the titration curve as to its general shape, the initial and final pH values, and the pH at the equivalence point.

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

ΔY / ΔX. 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 until the middle point, then decreases back to a smaller value again. 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. (BY = ∞, and X. = 0, therefore, actually BY / X. is undefined.) The series of data points for BY / X. plotted against the "X" axis is termed a "first derivative plot" of the original data.

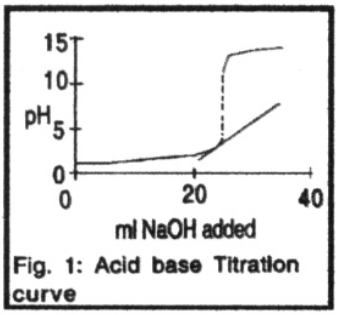

Fig. 1: Acid base Titration curve

Figure 1. pH vs volume titration curve.

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(Δ Y / 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.

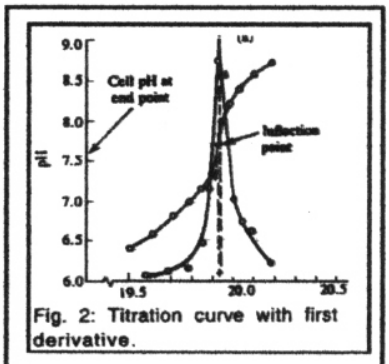

Fig. 2: Titration curve with first derivative.

Figure 2. pH vs volume with 1st derivative.

After completing the titrations for this experiment, we will examine the titration curves generated as to the pH at the equivalence point, their indicator end points, their relative shape, their starting and ending pHs, etc.

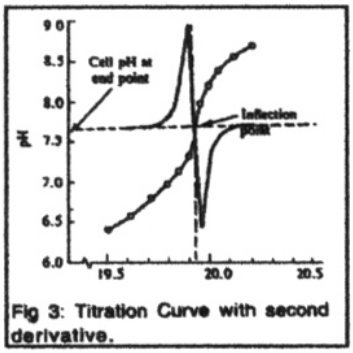

Fig 3: Titration Curve with second derivative.

Figure 3. pH vs volume with 2nd derivative.

SAFETY PRECAUTIONS

SAFETY GOGGLES MUST BE WORN AT ALL TIMES DURING THIS EXPERIMENT

Hydrochloric Acid solution: Corrosive liquid, skin burns are possible, very dangerous to eyes.

Acetic Acid solution: Corrosive liquid, skin burns are possible, very dangerous to eyes.

Sodium Hydroxide solution: Corrosive liquid, skin burns are possible, very dangerous to eyes.

pH 2-12 Buffers: Below pH 6 and above pH 8 should be considered corrosive and dangerous to the eyes and skin.

Keep all chemicals away from eyes and mouth, wash hands after use and before leaving the laboratory, and use prudent laboratory practices at all times.

BEFORE PERFORMING THIS EXPERIMENT . . .

...you will need a ***MicroLAB*** program capable of timing the collection of 5 ml titrant at about 2 - 4 seconds per drop. Your program should also be designed to collect pH data in relation to time and load this information into a spreadsheet. Use the ***pH.Time.exp*** selected from the **Titrations** tab.

EXPERIMENTAL PROCEDURE

Acidity and Indicators: Determining the pH Acid, Transition and Base Range of Indicators

1. Add about 1 ml (one plastic dropper full) of each buffer solution, 2 through 12, in separate wells of the well plate.

2. Dip a stirring rod into each buffer and touch it to a short piece of Alkacid paper, then match the color of the Alkacid paper against the chart on the side of the tube.

3. Under each buffer value on the report sheet, indicate whether the color you observed on the Alkacid paper lighter or darker than the color on the chart.

4. Add one drop of methyl orange indicator to each well, stir with a clean toothpick and note the pH **Acid, Transition** and **Base Range** over which the indicator makes its color transition. Indicate this on the buffer chart on the report sheet.

5. Empty the well plate into a large beaker, rinse and wipe dry, and refill with 1 ml each of buffer.

6. Repeat step four and five, using bromothymol blue, then, phenolphthalein, noting the **Acid, Transition** and **Base Range** for each on the report sheet.

Titrations

1. Connect your pH probe to the pH input on the back of the ***MicroLAB*** interface and press the **Power On** button.

2. Open the ***MicroLAB Experiment program*** in the normal manner, select the experiment indicated by your instructor from the **Titrations** tab, then press **Enter** to open the program. Click on **pH** in the **Variables View** and recalibrate your probe with the pH 4, 7 and 10 buffers supplied. Be sure to rinse the pH probe with distilled water after each buffer and before you place it in your analyte solution. Between titrations, the probe should be stored in the pH 7 buffer, then rinsed well with distilled water before inserting into your titration beaker.

3. Check the buret for cleanliness and proper drainage as directed by your instructor.

4. Rinse the buret three times with about 5 ml amounts of the standard NaOH solution, tipping and rotating the buret to cover all of the inside surface of the buret with each rinse. Be sure to have a stopper in the end of the buret so you don't spill NaOH on the floor or counter top.

5. Fill the buret above the 0 mark with the NaOH solution.

6. Measure exactly 5 ml portions of the 0.1 *M* HCl solutions (the analyte solution) in a graduated cylinder and pour into each of three 250 ml beakers. Add 50 ml of distilled water.

7. To the first beaker of analyte, add eight drops of phenolphthalein indicator, to the second add eight drops of bromothymol blue indicator. If you have time to do a third titration, use the methyl orange indicator so you can see a complete comparison. As you are doing your titration, ***be sure to note the pH at which the indicator changed color***.

8. Place a stirring bar in the 250 ml beaker and position the beaker on top of the stirrer. Place the pH probe in the analyte solution at the side of the beaker and the buret above it to drop the titrant directly into the analyte. Now remove this beaker assembly and temporarily replace it with a "waste solution" beaker to get the titration started.

9. Set the drop rate at two to four seconds per drop. When the drop rate is properly set, while one student quickly replaces the “waste beaker” with the “titration beaker,” the other student clicks the start button so that the program has started at the instant the first drop falls into the “titration beaker.” Immediately turn on the magnetic stirrer and set it to a moderate rate.

10. Be sure to give a descriptive name for each titration when asked for it in the program. ***Do not use*** **data,** as a name, as that will be overwritten with new data each time.

11. When all is ready, click the **Start** button. The pH vs. Time data will immediately appear in **Graph, Digital Display** and **Spreadsheet Views**.

12. While one partner continues to maintain the titrant level near the 0 level with the wash bottle of 0.100 *M* NaOH, ***the other partner should watch for the change of color of the indicator. Be sure to record on the report sheet the pH and the time at which the indicator changes color at the time that the color change occurs***.

13. Continue the titration until the curve has flattened out at the top. Then turn off the stopcock (turn it perpendicular to the length of the buret) and stop the data collection by clicking on **"Stop**.”

14. Repeat the entire process from step 10, using bromothymol blue in the second titration and methyl orange as the indicator for the third titration, if there is time.

Be sure to use a different file name for each of the titrations and record this on your report sheet so you can recover them for printing and calculating later.

15. Repeat the entire series of steps from step six to step 14 by using exactly 5 ml portions of the 0.1 *M* $HC_2H_3O_2$ solution (the analyte solution) in a graduated cylinder and pour into each of three 250 ml beakers. Add 50 ml distilled water.

16. Discard all titration solutions into a large beaker. At the end of the experiment, this should be neutralized and flushed down the drain with large amounts of water. Be sure solids are **NOT** washed into the sink. Any solids from this experiment may be disposed of in the container so labeled.

DATA ANALYSIS

1. When the titrations are completed, reload each of your data files for HCl and $HC_2H_3O_2$ solutions in turn into the ***MicroLAB*** program and perform the following analyses.

2. Click on the **Analysis** button, click on **Plot a Derivative**, use the current variables, **pH** and **Time**, click **OK**, The **Derivative** of pH vs. Time will appear on the **Graph View** in a fine line in red.

3. In the **Variables View**, scroll down to **Analysis (pH vs. Time),** and "click drag" the **f'(x)** to the **Y2** Axis. This will show the derivative in blue, and with data points.

4. Now **Right Click** on the **f'(x)** line in the **Variables View** and click on **Hide this Derivative** to remove the red derivative line.

5. Print this graph of the titration curve and the first derivative. **DO NOT** print your data table, as that will require too much time and paper. However, using the scroll button on the right of the **Spreadsheet View**, scroll up and down to examine how the data in the table is changing.

6. Repeat the above steps to obtain a **Second Derivative**, then print the graph of the titration curve and the second derivative. **Be sure to use this second derivative to calculate the exact equivalence point of the titration, and compare this with the End Point derived from each of the indicators.**

7. **DO NOT** print your data table, as that will require too much time and paper. However, using the scroll button on the right of the **Spreadsheet View**, scroll up and down to examine how the data in the table is changing.

8. Be sure to add your names or initials and a descriptive title to each graph that you print and submit. (The title should be added to the graph ***before*** you print.)