Experiment

DETERMINING K_{a2} OF SULFURIC ACID BY TITRATION

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LEARNING OBJECTIVES:

The objectives of this experiment are to . . .

- experience the titration of a diprotic acid.
- learn proper technique in pipette and buret usage.
- determine the second dissociation constant for sulfuric acid from the titration curve.
- become familiar with Pauling's rules for oxyacid strength.

INTRODUCTION:

Sulfuric acid, H_2SO_4, has two ionizable hydrogen atoms; it is a *diprotic* acid. It ionizes in two steps, each step having a distinctive ionization constant expression:

$$H_2SO_4 + H_2O \Rightarrow H_3O^+ + HSO_4^- \qquad K_{a1} = [H_3O^+][HSO_4^-] / [H_2SO_4] \qquad (1)$$

$$HSO_4^- + H_2O \Rightarrow H_3O^+ + SO_4^{2-} \qquad K_{a2} = [H_3O^+][SO_4^{2-}] / [HSO_4^-] \qquad (2)$$

Sulfuric acid is a strong acid in its first ionization step and a weak acid in the second. Ionization is complete in the first step. Therefore, we have essentially no H_2SO_4 molecules in solution, and the concentration of the H_3O^+, contributed by this ionization is equal to the initial concentration of the acid. However, the second dissociation constant of H_2SO_4 is quite large and the H_3O^+ from the second ionization step contributes quite substantially to the total concentration of hydronium ion in solution. Therefore, when we observe the titration curve of sulfuric acid, we cannot distinguish the first equivalence point, since the pH of the solution is still very low at this point and the neutralization proceeds to the second equivalence point.

Let us analyze what happens during a titration of 25.00 ml of 0.1 M H_2SO_4 with 0.1 M NaOH. After 25.00 ml of NaOH have been added, the first H^+ of H_2SO_4 has been completely neutralized (the first equivalence point has been reached). Since H_2SO_4 is a strong acid, the pH at the equivalence point should be about 7. However, we have to consider the contribution of the second ionization step, the dissociation of the weak acid HSO_4^-.

$$HSO_4^- + H_2O \Rightarrow H_3O^+ + SO_4^{2-} \qquad (3)$$

$$K_{a2} = [H_3O^+][SO_4^{2-}] / [HSO_4^-] \qquad (4)$$

Since all the H_3O^+ due to the first hydrogen has been neutralized, the concentration of H_3O^+ from the second step is equal to the concentration of SO_4^{2-}, from the stoichiometry of reaction (3). Therefore, expression (4) can be written as:

$$K_{a2} = [H_3O^+]^2 / [HSO_4^-] \quad (5)$$

having substituted $[H_3O^+]$ for the $[SO_4^{2-}]$ in expression (4). By taking the negative log of both sides of expression (3), we obtain

$$-\log K_{a2} = -2\log[H_3O^+] + \log[HSO_4^-] \quad (6)$$

and rearranging,

$$pH = (0.5)pK_{a2} - (0.5)\log[HSO_4^-] \quad (7)$$

Substituting the accepted values for $pK_{a2} = 1.96$ and $[HSO_4^-] = 0.05$ M (due to the dilution factor), we obtain the pH of the solution at the first equivalence point equal to 1.63. Since the $pK_{a2} = 1.96$, these two equivalence points merge, the titration curve displays just one equivalence point and it is impossible to distinguish the two from each other. It is necessary for the two equivalence points to differ by at least three orders of magnitude to reasonably be able to differentiate them. Thus, the equivalence point we observe in the titration of sulfuric acid represents the complete neutralization of both hydrogens of H_2SO_4.

The second ionization constant, K_{a2}, can easily be determined from the half equivalence point corresponding to the second ionization reaction. This is due to the fact that in the titration of a weak acid with a strong base, a buffer system is formed after the first few ml of base have been added consisting of the weak acid and the conjugate salt of that weak acid as indicated in expression (8)

$$HSO_4^- + OH^- \Rightarrow SO_4^- + H_2O \quad (8)$$

When the titration has proceeded half way to the equivalence point, then the concentration of the weak acid is equal to the concentration of its conjugate base. The pH can then be determined from the Henderson/Hasselbalch equation (9) as follows.

$$\text{Henderson/Hasselbalch equation} \quad pK_a = pH + \log([HSO_4^-]/[SO_4^{2-}]) \quad (9)$$

When $[HSO_4^-] = [SO_4^{2-}]$ the log term goes to zero, and $pK_a = pH$. Thus, taking 0.75 times the total volume to the second equivalence point will give the volume half way between the first and second equivalence points. The pH at that volume will then represent the pK_a of the weak acid.

SLOPE AND DERIVATIVES:

A straight line that is drawn in such a fashion that it just touches a curved line at some point is said to be tangent to the curve. The slope of such a line is given as $\Delta\mathbf{Y}/\Delta\mathbf{X}$, where Δ (delta) is the change of a variable. The slope is also referred to as rise over run. When such a curve is digitized, giving a table of X and Y values, such as are obtained in the ***MicroLab*** collection of titration data, then the successive differences of the Y values, divided by the successive differences of the X values, will approximate the slope of each segment of the titration curve. This process is termed "taking the derivative," and is

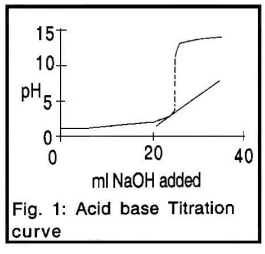

Fig. 1: Acid base Titration curve

Figure 1. pH vs volume titration curve.

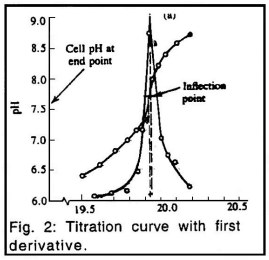

Figure 2. pH vs volume with 1st derivative.

accomplished in an **EXCEL** spreadsheet column by typing in the formula **=(Y2-Y1)/(X2-X1)** where **X1** is the first **X** values cell, **X2** the second **X** values cell, and the same for the **Y** value cells. This reduces to $\Delta Y/\Delta X$ and is termed the "first derivative." If one then takes the $\Delta(\Delta Y/\Delta X)/\Delta X$, this is termed the "second derivative." This is accomplished in the same manner, using the first derivative as the Y array.

In the first part of the curve in Fig. 1, the curvature is up to the left, where as in the second part of the curve, the curvature is up to the right. This means that in an ideal curve, the tangent to the curve is increasing in slope to infinity for the first part, and then decreasing in slope from infinity for the second part. Thus, at the equivalence point, the first derivative is theoretically infinite, but in practice will just be very large. The second derivative is the "slope of the slope," and thus at the equivalence point will be zero. Thus, the first and second derivatives on the pH vs. volume data allows an even more accurate determination of the equivalence point than can be obtained than with indicator "end points."

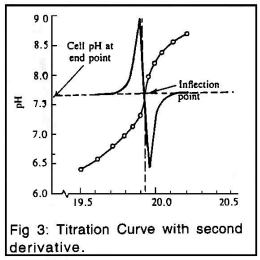

Figure 3. pH vs volume with 2nd derivative.

PAULING'S RULES:

Linus Pauling, a Nobel Laureate in chemistry, proposed some simple rules for determining the strengths of oxyacids such as H_2SO_4. Ternary acid strengths (K_a's) may vary from greater than 10^8 to 10^{-13}. If one rewrites the formula in the form of $EO_m(OH)_n$, and then examines the relationship of acid strength (K_a) to the value of "m," an interesting correlation emerges:

m	K_a	Strength	Example	
3	$\sim 10^8$	Very strong	$HClO_4$	$ClO_3(OH)$
2	$\sim 10^3$	Strong	$HClO_3$	$ClO_2(OH)$
1	$\sim 10^{-2}$	Weak	$HClO_2$	$ClO_1(OH)$
0	$\sim 10^{-7}$	Very weak	HClO	$ClO_0(OH)$

Multiple hydroxyacid equilibrium constants (Ka's) will usually differ by about 10^{-5}, e.g., for H_3PO_4, K_{a1} = 7.5 X 10^{-3}, K_{a2} = 6.2 X 10^{-8}, and K_{a3} = 4.2 X 10^{-13}. These general rules are very helpful in estimating ternary acid strengths.

INSTRUMENTATION:

pH can be very precisely measured by the use of an electronic instrument called a pH meter, which consists of a sensor, called the pH probe, associated electronics to modify the signal for proper display, and the readout device for displaying the values to the operator. In order for the information on the display to be meaningful, the system must be calibrated to solutions of known pH. Since the equivalence point of the second ionization of H_2SO_4 is a pH of about 2, the system will be calibrated over the pH range from 2 to 6 using buffers. The ***MicroLab*** interface, computer and associated software will serve as the associated electronics and readout device of the pH meter.

CAUTIONS OF CHEMICAL HAZARDS:

H_2SO_4 solution: Severely corrosive to eyes, skin and other tissue. Toxic, strong skin irritant. Powerful dehydrator causing blistering of the skin.

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

The other chemicals are innocuous, however you should 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.

EQUIPMENT:

You will need to have the following equipment available per pair of students before beginning this experiment.

1 - 50 ml buret
1 - 10 ml pipet
1 - 10 ml beaker
1 - magnetic stirrer with stirring bar
1 - buret clamp
1 - rubber stopper to fit the opening of the buret
1 - pipetting bulb
4 - 250 ml beakers
1 - ring stand
1 - pH probe with BNC connector
1 - ***MicroLAB*** interface and a ***MicroLAB*** program to do the titration

CHEMICALS:

The following chemicals will be provided for you in the laboratory. Please take no more than the recommended amounts.

100 ml of 0.100 M NaOH solution
80 ml of 0.04 M H_2SO_4 solution
15 ml of pH 2 buffer solution per pair of students in a 25 ml beaker.

PROCEDURE:

- Your instructor will give you instructions for the procedure you are to use to carry out the titration. If you are to use a buret, make sure the buret drains clean without any adhering drops within the calibrated region. (Your instructor will provide handouts on cleaning, and using burets, and on proper pipetting techniques.)

- Pipet exactly 10.00 ml of the 0.04 M H_2SO_4 solution into each of four 250 ml beakers and add 30 ml of distilled water.

- Connect your pH probe to the pH BNC connector, and press the "Power ON" button.

- Open the ***MicroLAB***. program provided by your instructor in the normal manner, select **pH Probe** and calibrate your probe with pH 2, 4 and 6 buffers. Be sure to rinse the pH probe with distilled water before you place it in the buffer solution and **CAREFULLY** (the glass bulb is **very** fragile) pat it dry, and again after the calibration and before you place it in your analyte solution. Between titrations, the probe should be stored in the calibration buffer, then rinsed well with distilled water before inserting into your titration beaker. **PLEASE BE VERY CAREFUL NOT TO HIT THE EDGE OF THE BEAKER WITH THE TIP OF THE pH PROBE. IT IS VERY FRAGILE AND EASILY BROKEN. THEY COST ABOUT $90 EACH.**

- When you are ready to begin taking data, follow the instructions provided by your instructor.

- Whichever program you are using for the titration, at the start of each titration, a pH reading should be taken before having added any NaOH titrant, so that you can see that the pH of the solution is indeed below 2. If your reading is not below pH 2, you should recalibrate you probe, and be sure to allow the red line to center in the green area on the calibration window (at least 30 seconds) for it to equilibrate to the pH 2 buffer. It is also recommended that you gently **swirl** the probe and bottle to keep fresh buffer against the probe surface. Titrant addition should be no faster than 4-5 seconds per drop, or, if using the buret, add the volume increment first, key in the volume, then wait at least one minute, then press ENTER.

- If using the buret, for the first titration, begin with 5 ml volume increments, As the graph at the top right of the screen begins to curve upward, take 0.05 ml increments by holding the buret firmly near the stopcock with one hand, then rotating the stopcock rapidly with the other hand. (Practice this process such that you can read volumes on and halfway between the finest divisions on the buret, i.e., 0.05 ml.) When you are in the vertical portion of the titration curve, rotate even more rapidly so that you introduce approximately 0.02 ml, which is about the smallest increment you can read on the buret.

- Continue step 7 until the titration curve has begun to flatten out at the top. **Generally speaking, the first titration is a familiarization titration and usually is not used for quantitative data, so you should try to do at least four (4) titrations total, to get three good ones.**

- After performing your first titration, use the **Analysis** function to determine the first derivative and drag this to **Column C** and to the **Y2** axis**.** Place your cursor on the top point of the derivative plot and hold it still until the X, Y coordinates appear, then enter those values (volume and pH) in your notes. Scroll down the columns until you find the row with that point. This point represents the closest point to the equivalence point volume. **Multiply that volume value by 0.75. In the next three titrations, for 1 ml before this value to 1 ml after this value,** take 0.02 ml increments.

- As you approach within 1 ml of the equivalence point volume, take 0.02 ml increments until 1 ml after the equivalence point volume, then 1 ml and 5 ml increments after the equivalence point volume. **Allow at least a whole minute for equilibration to occur after each addition of base in both of these regions.**

- If you are doing a drop counter titration, set your drop rate to about five seconds per drop for the entire titration.

- After you have collected your first titration data, click Stop, **Repeat Experiment**, save the data with a meaningful name such as **H2SO4Titr1.DH**, where **DH** should be your initials. The application will then be ready to take the next titration data.

- Repeat the above process for each of the 10.00 ml samples of sulfuric acid. **REMEMBER:** Refill the buret to the 0 mark each new titration.

- **CAUTION:** Be sure to use and record in your lab notes and on your report sheet a different file name for each of the titrations so you can recover them for printing and calculating later.

DATA TREATMENT:

1. For each of the data files, do the following:
   a. Reload each data file into ***MicroLAB*** and calculate the first derivative of pH vs. volume, click-drag to column C, and then calculate the second derivative and click-drag to column D.

b. Make three graphs for each titration. The first graph will show pH vs. volume only. The second graph will show pH on Y1, the 1st derivative on Y2 and volume. The third will show pH on Y1, the 2nd derivative on Y2 and volume.

c. Print out the data table with the three graphs on a single page.

d. Show all of the following calculations in your lab notes for each of the titrations, but also do them on the spreadsheet. Using the second derivative, calculate, by interpolation (see the appendix), the exact volume needed to the second equivalence point for each of the titrations

e. Calculate the number of mmols of NaOH used for each titration from the milliliters used and the given concentration of the standard and enter the values on the report sheet.

f. Calculate the volume to 0.75 the second equivalence point volume from this value as indicated in the introduction.

g. Locate the region of the data table containing this calculated volume.

h. Calculate by interpolation the exact pH corresponding to this second half equivalence volume. This will be the pK_a value for that titration as indicated in the introduction. Enter these values on the report sheet.

2. Along with your report sheets, be sure to submit the printout of the spreadsheet with the three graphs.

TO DISCARD YOUR SOLUTIONS, COMBINE ANY LEFT OVER ACID WITH THE LEFT OVER BASE TO NEUTRALIZE, AND DISCARD THEM DOWN THE SINK WITH LOTS OF WATER TO DILUTE THEM DOWN.