DETERMINING Ka2 OF SULFURIC ACID BY TITRATION

INSTRUCTOR RESOURCES

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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.

PROCEDURE OVERVIEW

- the pH electrode is calibrated with buffers of 2, 4, and 6 pH

- the instructor will designate what type of titration, e.g., timed, drop count or buret volume by keyboard input, will be performed and will refer the students to the specific instructions.

- at least three titrations of 10 mL of a 0.04 M H_2SO_4 product are accomplished with standardized 0.1000 M NaOH.

- the exact volume for the equivalence point is determined for each titration.

- The molarity value for each titration is determined from equivalence point volume, and the average and standard deviation are obtained.

NAME: _____   SECTION:_____   DATE: _____

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Report Sheets

Titration Data:

Trial #	Init. Vol.	1st der. vol.	2nd der. high	2nd der. low	2nd der. interp. vol.	2nd der. mmol NaOH	0.75 2nd Equiv. vol.	pH < 0.75 E.P. Vol.	pH > 0.75 E.P. Vol.	pK_{a2} interp from pH	H_2SO_4 conc.
1											
2											
3											
4											
Ave. 2-4											
Std Dev.											
% error											

NOTES: In the above table, be sure to look for 2 or 3 decimal values in all measurements, They should have done at least 3 titrations, and they should have calculated values for all heavily outlined boxes.

Questions for Your Consideration:

1. Show a sample set-up for the calculation of the 2nd derivative interpolated volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.

2. Show a sample set-up for the calculation of the pK_{a2} interpolated value from the pH of the volume 0.05 prior to the 0.75 equivalence point volume, and the pH of the volume 0.05 after the 0.75 equivalence point volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.

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3. On the spreadsheet, calculate the exact concentration of each of the H_2SO_4 solutions you used in your titration. Show a sample calculation below.

4. On the spreadsheet, calculate the standard deviation on these three answers and express your final concentration average as "Ave. value ± Std. Dev." in the space below.

5. According to Linus Pauling's rules for the strengths of oxyacids, what should be the Ka_1 and Ka_2 values for H_2SO_4?

6. How do your results agree with Pauling's values. If there is a significant difference, explain.

7. Explain how the half equivalence point volume of the second ionization can be obtained by taking 0.75 times the total volume used to the second equivalence point.

8. Why must one never pipet a liquid by sucking on the pipet by mouth?

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9. Why is it necessary to rinse the buret or pipette with three rinses of the solution to be placed in it?

10. By discussing in detail what is happening to the pH near the equivalence point verses volume of titrant added, explain why it is necessary to take as small of increments as possible near the equivalence point.

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Tips and Traps

1.
1. During the calibration of the pH probes, students may compare millivolt readings and become concerned that they may differ widely from system to system. Assure them that this is natural and is a function of differences in the nature of the pH electrodes. The values should be around 0 ± 100 millivolts if the pH probe is good.

2. You may find a wide variation in the quality of electrodes depending upon the manufacturer and/or age of the electrode. Some electrodes will reach equilibrium quite rapidly, while others may take a while. All electrodes should be checked out in advance to determine if they obtain equilibration within about 5 to 10 seconds. If not, the electrodes should be treated with an enzymatic cleaner, then soaked in an electrode conditioning solution, both of which can be obtained from Markson.

3. We are looking for absolute pH in this experiment, therefore, make sure that the calibration is done very carefully, and that the students check the pH 2 buffer again after the calibration is completed.

4. There is a tendency for students to leave the pH probe hanging out in the air between titrations. If the time between titrations is small, this probably won't matter much, but it is better to teach them good practice, and that is to store the probe in their pH 2 buffer in a beaker placed at the back of the bench between titrations. There is less chance of breakage this way, and the probe is equilibrating at or near the equivalence point pH.

5. In between uses, all electrodes should be kept in a sealed container with the bulbs covered with the conditioning solution mentioned above.

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Suggested Answers to Report Sheets

Titration Data:

Trial #	Init. Vol.	1st der. vol.	2nd der. high	2nd der. low	2nd der. interp. vol.	2nd der. mmol NaOH	0.75 2nd Equiv. vol.	pH < 0.75 E.P. Vol.	pH > 0.75 E.P. Vol.	pK_{a2} interp from pH	H_2SO_4 conc.
1	0.00	20.00	27.63	-35	20.022	2.002	15.017	1.78	2.05	1.96	0.0518
2	0.00	20.05	38.24	-23	20.031	2.003	15.023	1.63	2.17	1.98	0.0486
3	0.00	19.95	42.89	-19	19.985	1.999	14.989	1.75	2.03	1.94	0.0497
4	0.00	20.00	24.62	-30	20.032	2.003	15.024	1.59	2.11	1.97	0.0496
Ave.		20.00			20.008	2.002	15.012			1.963	0.0499
Std Dev.		0.05			0.033	0.002	0.020			0.017	0.001
% error		0.25			0.16	0.1	0.13			0.13	2.69

NOTES: In the above table, be sure to look for 2 or 3 decimal values in all measurements, They should have done at least 3 titrations, and they should have calculated values for all heavily outlined boxes.

Questions for Your Consideration:

1. Show a sample set-up for the calculation of the 2nd derivative interpolated volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.

   Ans: *20.00* *27.63*   *X = 0.05(27.63/62.90) = 0.022*
       X   *0*   *Eq. Pt. Vol. = 20.00 + 0.022 = 20.022 ml*
       20.05 *-35.27*

2. Show a sample set-up for the calculation of the pK_{a2} interpolated value from the pH of the volume 0.05 prior to the 0.75 equivalence point volume, and the pH of the volume 0.05 after the 0.75 equivalence point volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.

   Ans: *3.18* *20.00*   *X = 0.02(0.022/0.05) = 0.0088*
       0   *20.022*   *Eq. Pt. PH= 3.18 + 0.0088 = 3.189*
       3.20 *20.05*

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3. On the spreadsheet, calculate the exact concentration of each of the H_2SO_4 solutions you used in your titration. Show a sample calculation below.

   Ans: $\underline{20.031 \text{ ml NaOH soln}}$ | $\dfrac{0.1000 \text{ mmol NaOH}}{1.00 \text{ ml NaOH soln}}$ | $\dfrac{1 \text{ mmol } H_2SO_4}{2 \text{ mmol NaOH}}$ | $\dfrac{1}{25.00 \text{ ml } H_2SO_4}$ = 0.04003 mmol $\underline{H_2SO_4}$

4. On the spreadsheet, calculate the standard deviation on these three answers and express your final concentration average as "Ave. value ± Std. Dev." in the space below.

   Ans: *$[H_2SO_4]$ = 0.0499 ∓ 0.001*

5. According to Linus Pauling's rules for the strengths of oxyacids, what should be the Ka_1 and Ka_2 values for H_2SO_4?

   Ans: *$H_2SO_4 = SO_2(OH)_2$ m = 2, therefore Ka1 > 1000, Ka2 ~ 10^{-2}*

6. How do your results agree with Pauling's Values. If there is a significant difference, explain.

   Ans: *Pauling's rules predict a2 ~ 10^{-2}, and experimental results indicated Ka2 ~ 10^{-2}, therefore, there is no significant difference.*

7. Explain how the half equivalence point volume of the second ionization can be obtained by taking 0.75 times the total volume used to the second equivalence point.

   Ans: *The observed equivalence point represents the 2nd equivalence point of the titration, therefore, 0.5 fo that volume would be where the first equivalence point should be (2/4 of the observed equivalance point volume), but is not observable due to the strength of Ka1. Exactly half way between these two volumes is where the [HSO4-] = [SO42-]. 2/4 to the first equivalence point, plus 1/4 to the equal concentration conditions results in 3/4 or 0.75 of the 2nd equivalence point volume.*

8. Why must one never pipet a liquid by sucking on the pipet by mouth?

   Ans: *Pipetting by mouth is extremely dangerous due to the ease with which the liquid being pipetted can be sucked up into the mouth, and possibly swallowed, which can result in sever tissue damage or poisoning.*

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Suggested Answers to Report Sheets

9.   Why is it necessary to rinse the buret or pipette with three rinses of the solution to be placed in it?

Ans: Pipettes and burets should be stored containing water to prevent their becoming dirty. It is necessary to rinse out the water and obtain a film of original concentration of the solution to be dispensed from the buret or pipette.

10. By discussing in detail what is happening to the pH near the equivalence point verses volume of titrant added, explain why it is necessary to take as small of increments as possible near the equivalence point.

Ans: Because the concentration of acid is very small near the equivalence point, a very small addition of base can cause a large change in the remaining acid concentration, thus significantly changing the pH of the solution.

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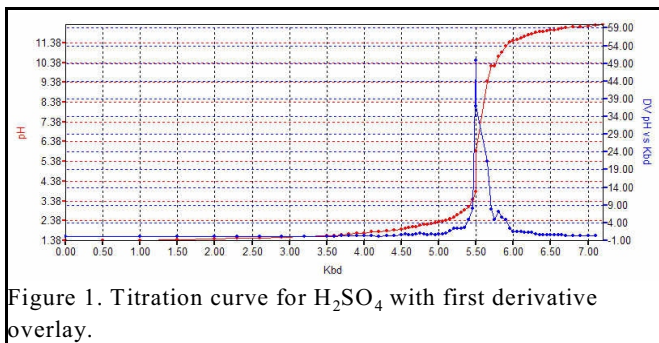
Sample *MicroLAB* Main Screens

Figure 1. Titration curve for H_2SO_4 with first derivative overlay.
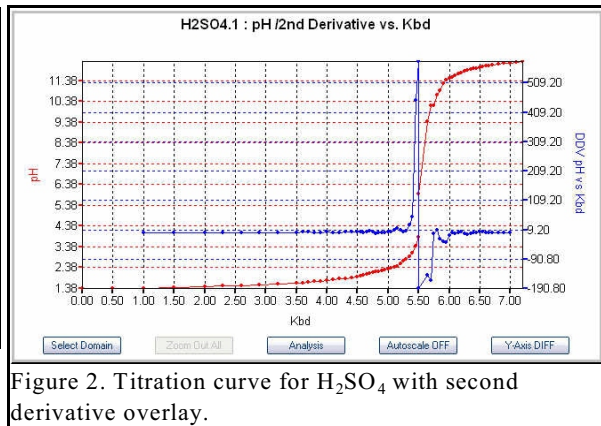

Figure 2. Titration curve for H_2SO_4 with second derivative overlay.

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Laboratory Preparation (per student station)

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

1 - The appropriate buret system   1 utility clamp for the dropping buret
1 - 10 ml pipet   1 - pipetting bulb
3 - 10 ml beakers   4 - 250 ml beakers
1 - magnetic stirrer with stirring bar   1 - ring stand
1 *MicroLAB* drop counter   1 - clamp for the counter
1 - pH probe with BNC connector
1 - *MicroLAB* interface and two *MicroLAB* programs (*Drop Counter Calibration* and one of the titration programs under the **Titration** tab) to do the titration.

CHEMICALS:

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

- 150 ml of 0.100 M NaOH solution
- 30 ml of 0.040 M H_2SO_4 solution
- 15 ml of pH 2,4 and 10 buffer solutions per pair of students in 25 ml beakers.

CAUTIONS OF CHEMICAL HAZARDS:

- H_2SO_4 solution: Severely corrosive to eyes, skin and other tissue. Toxic, strong skin irritant.

- 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.

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