DETERMINING K_{a2} OF SULFURIC ACID BY TITRATION (#10.8)

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Learning Objectives

- 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:

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

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

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.

An analysis of what happens during a titration of 25.00 ml of 0.1 M H_2SO_4 with 0.1 M NaOH is discussed to obtain the equation: $pH = (0.5)pK_{a2} - (0.5)\log[HSO_4^-]$ (3) It is then shown that K_{a2}, is determined at three-quarters of the equivalence point volume to the second ionization reaction.

A discussion of Slope and Derivatives helps the student understand how to calculate the best value for the equivalence point.

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 acids are defined and the rules discussed and applied to some ternary acids.

Procedure

- pH can be very precisely measured by the use of the ***MicroLAB*** . interface, computer and associated software. Since the equivalence point of the second ionization of H_2SO_4 is a pH of about 2, the system will be calibrated using buffers of pH 2,4 and 6.
- Detailed instructions are provided on the setup, and operation of the ***MicroLAB*** and performing the titration.
- A minimum of three good titrations are required in order to get a good average and standard deviation.

Data Treatment

Guidance is given in obtaining the derivatives and performing the calculations.

Resources Provided

- Sample Report Sheets providing the format to organize the data collection with sample data.
- Questions to consider, answer and turn-in with suggested answers.
- Tips and Traps section to assist the instructor with potential problems and solutions.
- Sample ***MicroLAB*** screen shots and graphs.
- Laboratory preparation per student station.

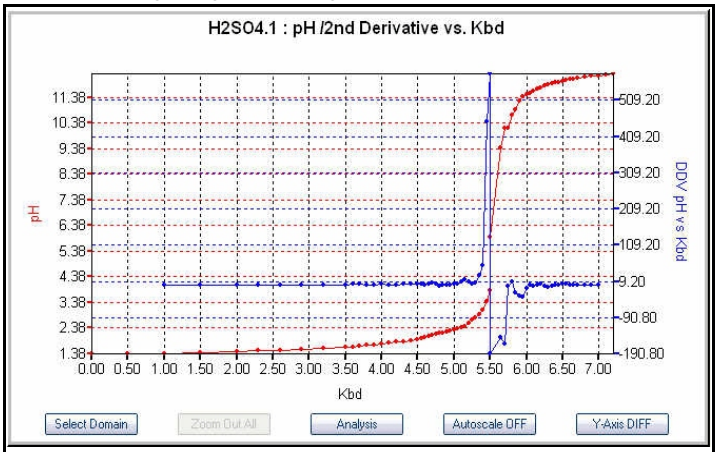

Figure 1. Sample ***MicroLAB*** graph of H_2SO_4 titration, data sampled every 0.1 pH units, with 2nd derivative plot.