

## POTENTIOMETRIC TITRATION OF AN ACID MIXTURE

Background Reading: Harris, 7<sup>th</sup> ed., Chapter 11. Skoog, West, Holler and Crouch, 7<sup>th</sup> ed., Chapters 11, 13

### Introduction

In this experiment a mixture of two acids is titrated with standard base. Because the pH does not change abruptly enough at either equivalence point to permit estimation with visual indicators, a potentiometric titration with a pH meter and **glass pH electrode**-reference electrode pair is employed. A plot of pH vs. volume of base added yields a curve similar to Figure 13-2 in Skoog (11-6(a) in Harris). From the pH vs. volume curve the two end points, and thus the amount of acid present, can be found. However, a more accurate estimate of the end points can be made from a derivative plot; that is,  $d(\text{pH})/d(\text{vol})$  vs. volume of base added.

A mixture of two acids can be analyzed with a precision of a few parts per thousand, provided the dissociation constants of the two acids differ by at least  $10^3$  to  $10^4$  and the weaker acid is not so weak that its end point is completely obscured. The normality of the sodium hydroxide titrant is determined by titration of a standard acid. For highest precision the end points of the standardization and the acid being titrated are taken at the same pH; this procedure corrects for any error due to carbonate that may be present in the base. Because two end points at substantially different pH values are obtained in this experiment, calculation of two different effective concentrations for the same sodium hydroxide titrant is required.

### Procedure

**Operation of a pH meter.** Your TA will demonstrate the proper use of a pH meter and glass pH electrode. Important points to remember include the following:

- For accurate pH measurements, a pH meter must be calibrated using **buffer solutions** of known pH prior to measurement. For a titration this is less important since it is the change in pH, not the actual pH value, that is used to detect the end point in the titration.
- Always rinse the electrodes with distilled water and wipe dry when transferring them from solution to solution. When finished with the last titration, rinse the electrodes and then immerse them in the buffer reservoir provided. NEVER ALLOW A GLASS ELECTRODE TO SIT IN THE ATMOSPHERE FOR ANY EXTENDED LENGTH OF TIME. A DRY GLASS ELECTRODE IS WORTHLESS.

**Preparation of the 0.1 M NaOH Titrant.** Place about 900 mL of freshly distilled and deionized water in a clean polyethylene bottle. Add sufficient NaOH to make an approximately 0.1 M solution. Keep tightly covered to minimize absorption of atmospheric  $\text{CO}_2$ .

**Titration.** At the beginning of each lab period, BE SURE TO CALIBRATE THE pH METER WITH THE pH STANDARDS PROVIDED. Alternate titrations of sulfamic acid and sample. Three sets of sulfamic acid and sample will be titrated, for a total of six titrations.

Sulfamic acid,  $\text{H}_2\text{NSO}_3\text{H}$ , is also known as amidosulfonic acid. It has a formula weight of 97.10 g.

**Standardization of the 0.1 M NaOH Titrant.** Weigh to the nearest 0.1 mg about 2.5 g of sulfamic acid and then transfer it to a 100 mL volumetric flask. Dissolve the acid in freshly distilled and deionized water, dilute to the mark, and mix thoroughly. Pipet 10 mL portions into 250 mL beakers and add 40 to 50 mL of deionized water to each. Insert the glass/reference electrode pair into the solution so that the tip is completely submerged. Add a stirring bar, positioning it so that it does not strike the electrode. Titrate with the 0.1 M NaOH solution, recording the initial buret reading, then adding titrant until the pH meter indicates a change of about 0.2 pH units. Record the pH and buret readings, and then add titrant again until another change of 0.2 pH units is observed. Continue in this manner until a pH of 3 is reached. Between pH 3 and 8, record pH and buret readings every 0.1 mL of base added. Above pH 8, record pH and buret readings every 0.2 mL of base added. The titration may be terminated at pH 11.

For the second and subsequent titrations only the initial pH and data near the equivalence points (pH 3-10) need be recorded, so these titrations can be performed rather quickly. MAKE SURE TO ALTERNATE SULFAMIC ACID AND SAMPLE TITRATIONS.

**Titration of an Unknown Mixture of Acids.** Obtain a sample acid mixture from the TA in a 100 mL volumetric flask. Dilute to volume with deionized water and mix thoroughly. Pipet 10 mL portions of this solution into 250 mL beakers, add 40 to 50 mL of water to each, and titrate with 0.1 M NaOH. Record the initial pH, then add titrant until the pH meter indicates a change of about 0.2 pH units. Record the pH and buret readings. Continue in this fashion until a pH of 3 is reached. Between pH 3 and 6 (region of the first end point), record the pH after the addition of 0.1 mL increments of base. Then, record the pH after addition of each 0.2 mL of base from pH 6 to 8, each 0.1 mL from pH 8 to 10.5 (region of the second end point), and finally each 0.2 mL until pH 11.

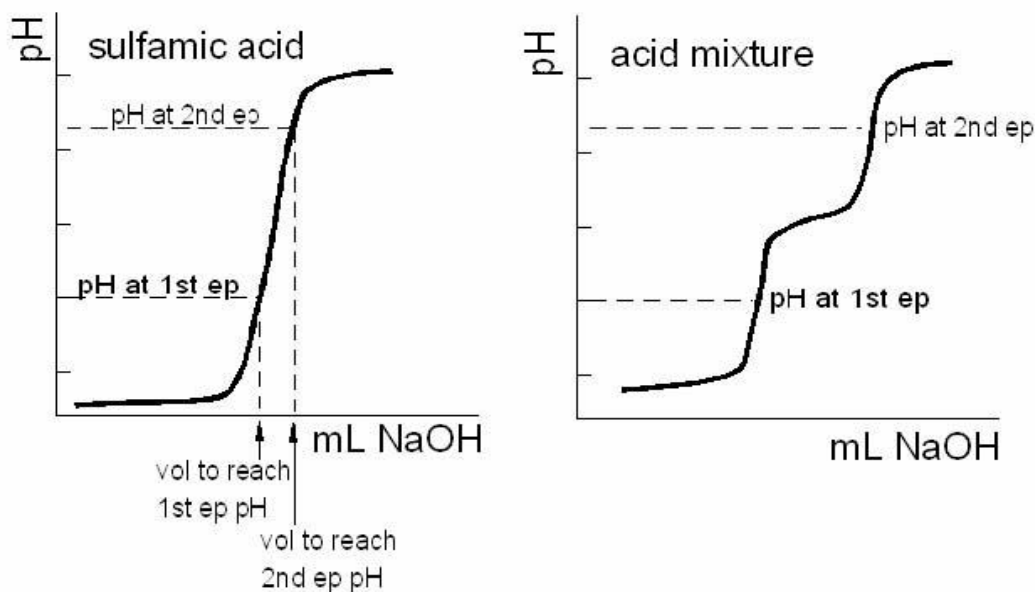
For the second and subsequent titrations only the initial pH and data near the equivalence points need be recorded, so these titrations can be performed rather quickly. **MAKE SURE TO ALTERNATE SULFAMIC ACID AND SAMPLE TITRATIONS.**

### Calculations

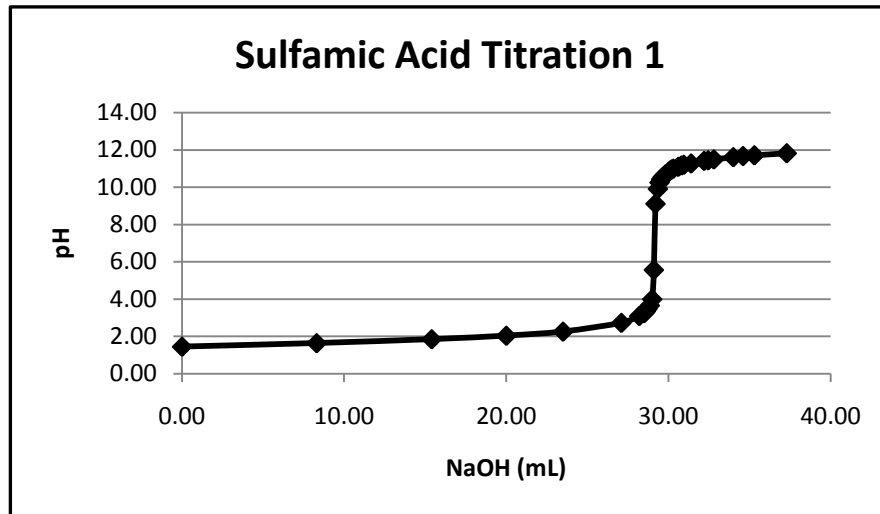
Using Excel, plot the data for each titration (pH vs. volume of base added). The sulfamic acid (standardization) titrations will have one end point, the unknown mixture two. Sodium carbonate present in the NaOH titrant causes the molarity of the solution to vary as a function of the strength of the acid. The best way to correct for the carbonate error is to obtain two effective NaOH molarities from the standardization curves. This process is illustrated in the figure below.

On the mixture titration curve find the pH at each end point. For purposes of illustration assume one is at pH 5 and the other at pH 10. On the sulfamic acid titration curve find the volumes of NaOH required to titrate to pH = 5 and to pH = 10. Use the first volume and the mmol of sulfamic acid used to find the effective molarity of the NaOH in titrating the strong acid and the second volume and the same mmol of sulfamic acid used to find the effective molarity of the NaOH in titrating the weak acid. Thus, the NaOH titrant will have a 'strong acid' molarity,  $M_s$ , and a 'weak acid' molarity,  $M_w$ . If there is no carbonate error, the pH vs. volume curves will be essentially vertical in the region of these end points, and  $M_s$  and  $M_w$  will be indistinguishable.

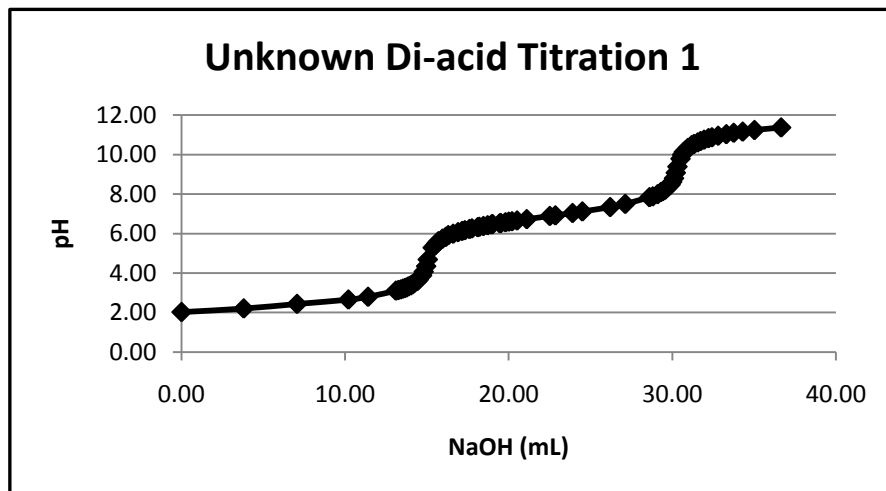
The end points for the unknown acid titration correspond to the inflection points in the pH vs. volume curves. However, these points are more accurately determined by a derivative plot;  $d(\text{pH})/d(\text{vol})$  vs. volume. The end points correspond to the tops of the peaks that will be apparent.



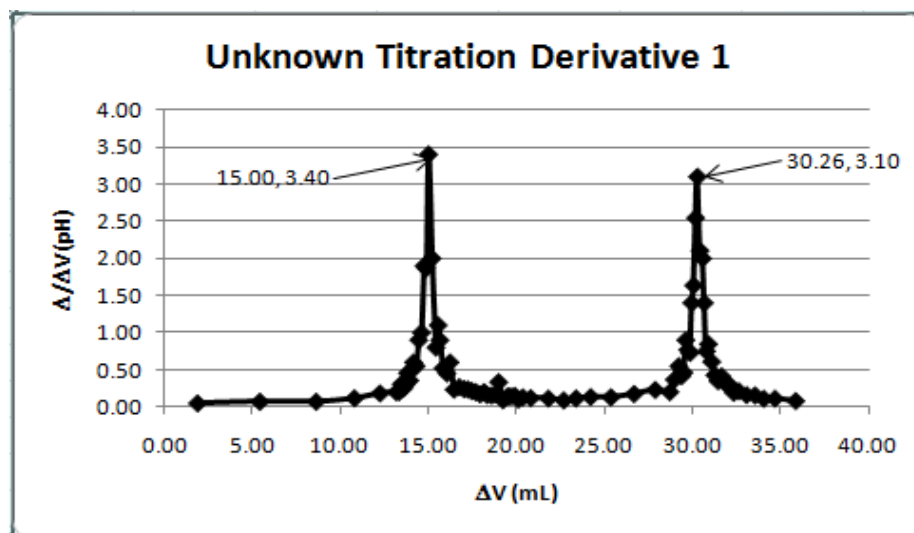
The following is a sample calculation using real data. Using Excel, plot the data for the first sulfamic acid titration (pH vs. volume of base added). For example:



Plot the data for the first unknown acid mixture titration.



Calculate and plot the derivative of the unknown acid titration curve to determine the equivalence points<sup>1</sup>.



Use the mixture titration data to find the pH at each equivalence point. The first equivalence pH lies between a pH of 4.35 & 4.69. For this example, an average pH of 4.52 will be used. The second equivalence lies between a pH of 9.08 & 9.39 for a compromise pH of 9.24. These two pHs are the numbers used to find the milliliters of NaOH needed to titrate the sulfamic and any carbonic acid that may be present.

	V, mL	pH
90	14.80	4.07
91	14.95	4.35
92	15.05	4.69
93	15.35	5.29

	V, mL	pH
135	30.10	8.80
136	30.21	9.08
137	30.31	9.39
138	30.50	9.79

Turning to the sulfamic acid data, a pH of 4.52 correlates with a sodium hydroxide volume close to 29.03 mL and a pH of 9.24 correlates with a sodium hydroxide volume of 29.22 mL. Both of the previous numbers are arrived at by a simple linear interpolation between data points, which may or may not be a good approximation.

	V, mL	pH
40	29.00	4.00
41	29.10	5.57

	V, mL	pH
42	29.20	9.12
43	29.35	9.92

The 29.03 mL & 29.22 mL volumes of NaOH are effective volumes; they account for both the titration of the sample acid and the presence of carbonic acid at the selected pH values. For your data, use the first equivalence volume (29.03 mL in sample data) and the exactly known sulfamic acid concentration to find  $M_s$ , the “strong acid” molarity of NaOH. Use the second equivalence for the determination of the “weak acid” molarity of NaOH,  $M_w$ .

<sup>1</sup> When generating the abscissa,  $\Delta V$  has the following form:   
 the  $\Delta V$  is simply the difference

———. On the other hand, when calculating ——

Now use  $M_s$  molarity of NaOH and your data from the unknown acid titration to calculate the molarity of the strong acid. Likewise, use  $M_w$  to calculate the molarity of the weak acid. Do not forget the assumption that the weak acid's titration starts only after all strong acid has reacted with NaOH.

Repeat the above calculation for each pair of sulfamic and unknown acid titrations.

### **Report**

For sulfamic acid and your unknown report one titration curve plot and one derivative plot.

In tabular form, report  $M_s$  and  $M_w$  and the average and standard deviation for each for the replicate titrations of your NaOH solution. Report the mmoles of strong acid and weak acid in your mixture for at least three determinations. Report the average and standard deviation for your determinations.