Analytical Chemistry Laboratory 319

Experiment 7:

Identification of an Unknown Weak Acid

Formal Report

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Drawer G-1

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INTRODUCTION:

One of the more common reactions seen in chemistry is the acid/base reaction. The most common result of an acid/base reaction is the formation of water and a salt. Such a reaction can be highly useful in the analysis of an unknown acid or base. By titrating the unknown analyte with a standard reagent, several characteristics of the unknown can be determined, as well as the identity of the analyte itself.

One important aspect of an acid/base reaction is the pH of the solution. Since an acid/base reaction is often performed by titrating an acid with a basic solution (or vice versa), monitoring the pH during the titration shows how the acidity is changing as reagent is added. By recording these pH values during the course of the reaction, a titration curve can be generated; from this curve, several characteristics of the reaction can be determined such as equivalence point(s), pK_a(s), and end point(s), etc.

In this experiment, the objective was to identify an unknown weak acid. This was accomplished by titrating the unknown acid with a standardized base. Using a pH meter, the pH values were recorded as the volume of added base increased until the pH reached a specified limit of 11. From these values, the pK_a(s) and molecular weight of the unknown could be determined; these defining characteristics could then be used to determine the identity of the unknown acid.

EXPERIMENTAL:

      The first step of this experiment was the standardization of the NaOH solution. Three samples of KHP were weighed out, and then diluted in deionized water to obtain three solutions. A few drops of phenolphthalein were added to each solution, and then a titration using NaOH was performed; the volume of NaOH solution used was recorded for each titration. The average concentration of the NaOH solution was then calculated using these results.

      Once the NaOH solution had been standardized, it was then used to titrate the unknown acid solution. By assuming that the acid was monoprotic with a molecular weight of 100 g/mol, it was determined that approximately 0.15 g of unknown acid would be needed for titration with 0.1 M NaOH. This mass of unknown was collected in a beaker and diluted with deionized water; the solution dissolved easily without the need for heating.

      With the unknown acid solution properly prepared, it was then titrated with the standardized NaOH. Before titration was begun, the pH meter was calibrated using the available buffers. The solution's initial pH and initial burette reading were recorded. To begin the titration, the pH and burette reading were recorded after every milliliter that was added. Careful attention was paid to the change in pH as each drop was added, however, and when the pH began to rise steeply, the values were recorded with every drop. After reaching a pH of 11, the titration was complete.

RESULTS AND DISCUSSION:

The data obtained from the standardization of NaOH is as follows:

Sample #	Mass (g)	NaOH Volume (L)	Conc. NaOH (M)
1	0.7024	0.03445	0.09984
2	0.7026	0.03465	0.09929
3	0.7026	0.03465	0.09929

Average Conc. (M)	StDev	%RSD
0.09947	3.16E-04	0.3181

Using the mass of each KHP sample and the volume of NaOH used in the titration, the concentrations of each sample and, ultimately, the average concentration of NaOH was determined.

Sample 1:

$$0.7024 \ g \ KHP * \frac{1 \ mol \ KHP}{204.209 \ g \ KHP} * \frac{1 \ mol \ NaOH}{1 \ mol \ KHP} * \frac{1}{0.03445 \ L} = 0.09984 \ M \ NaOH$$

Sample 2:

$$0.7026 \ g \ KHP * \frac{1 \ mol \ KHP}{204.209 \ g \ KHP} * \frac{1 \ mol \ NaOH}{1 \ mol \ KHP} * \frac{1}{0.03465 \ L} = 0.09929 \ M \ NaOH$$

Sample 3:

$$0.7026 \ g \ KHP * \frac{1 \ mol \ KHP}{204.209 \ g \ KHP} * \frac{1 \ mol \ NaOH}{1 \ mol \ KHP} * \frac{1}{0.03465 \ L} = 0.09929 \ M \ NaOH$$

Average:

$$\frac{0.09984 + 0.09929 + 0.09929}{3} = 0.09947 \ M \ NaOH$$

DATA:

The data obtained from the titration is as follows:

NaOH Added (mL)	pH
0.00	1.87
0.85	1.88
2.00	1.91
2.99	1.95
4.00	2.00
5.00	2.05
5.99	2.11
6.95	2.18
7.90	2.25
8.60	2.30
9.00	2.35
9.50	2.40
10.10	2.48
10.61	2.55
11.05	2.62
11.31	2.68
11.71	2.77
12.06	2.86
12.35	2.97
12.80	3.14
12.96	3.29
13.38	3.68
13.60	4.10
13.80	4.34
14.20	4.65
14.49	4.80
15.00	5.02
15.49	5.14
15.80	5.22
16.31	5.32
16.81	5.42

NaOH Added (mL)	pH
17.50	5.53
18.01	5.63
19.05	5.76
19.85	5.86
20.70	5.97
21.59	6.10
22.41	6.21
23.32	6.36
23.98	6.47
24.65	6.61
25.40	6.76
25.60	6.86
25.99	7.05
26.31	7.24
26.41	7.31
26.50	7.41
26.60	7.52
26.78	7.70
26.85	7.98
27.00	8.63
27.10	9.71
27.20	10.13
27.30	10.36
27.40	10.51
27.50	10.64
27.60	10.71
27.70	10.80
27.85	10.87
27.95	10.93
28.05	10.98
28.15	11.01

Using this data, a titration curve and its first derivative were generated using Microsoft Excel. These graphs are shown on the following pages:
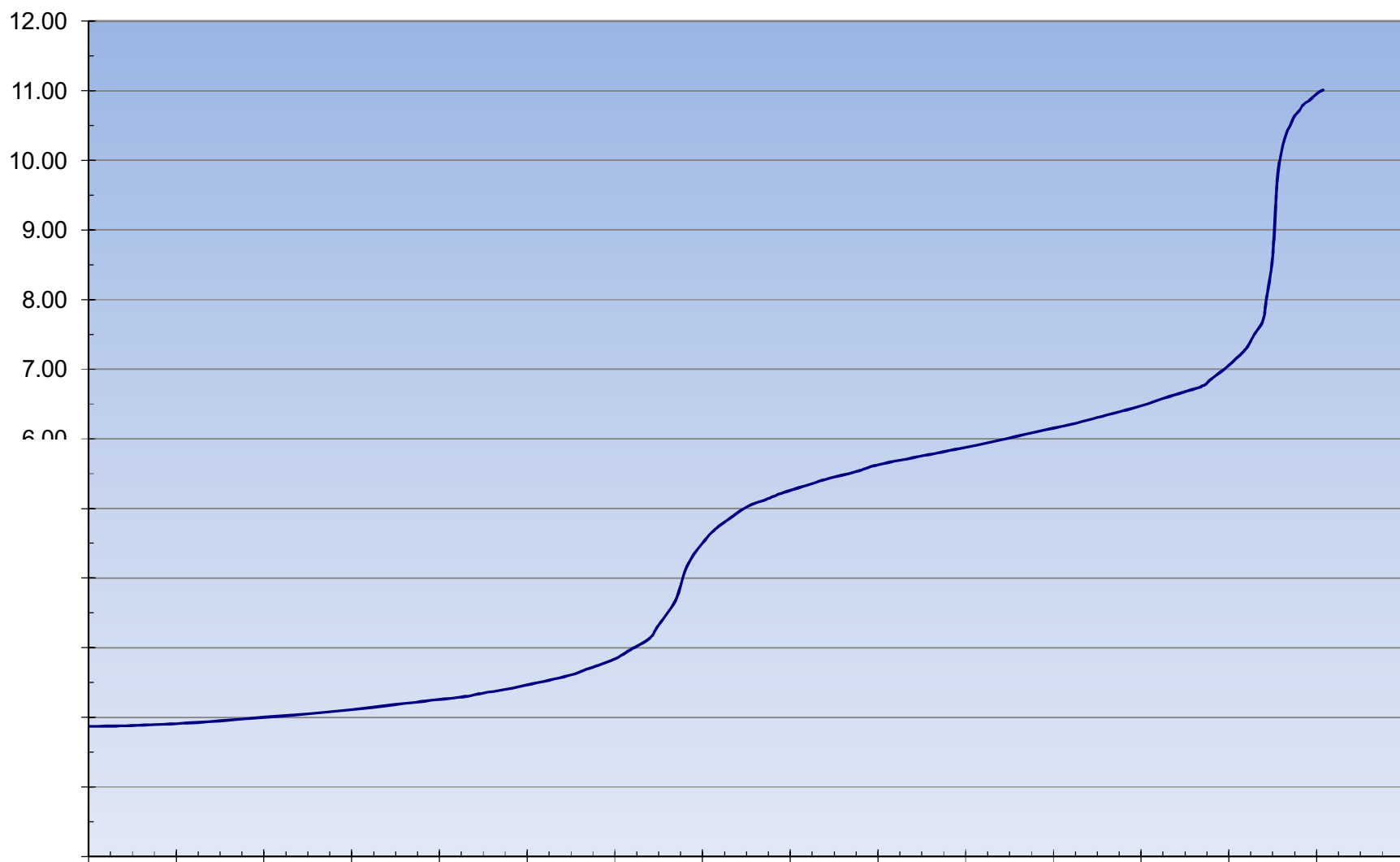
First Derivative Curve of
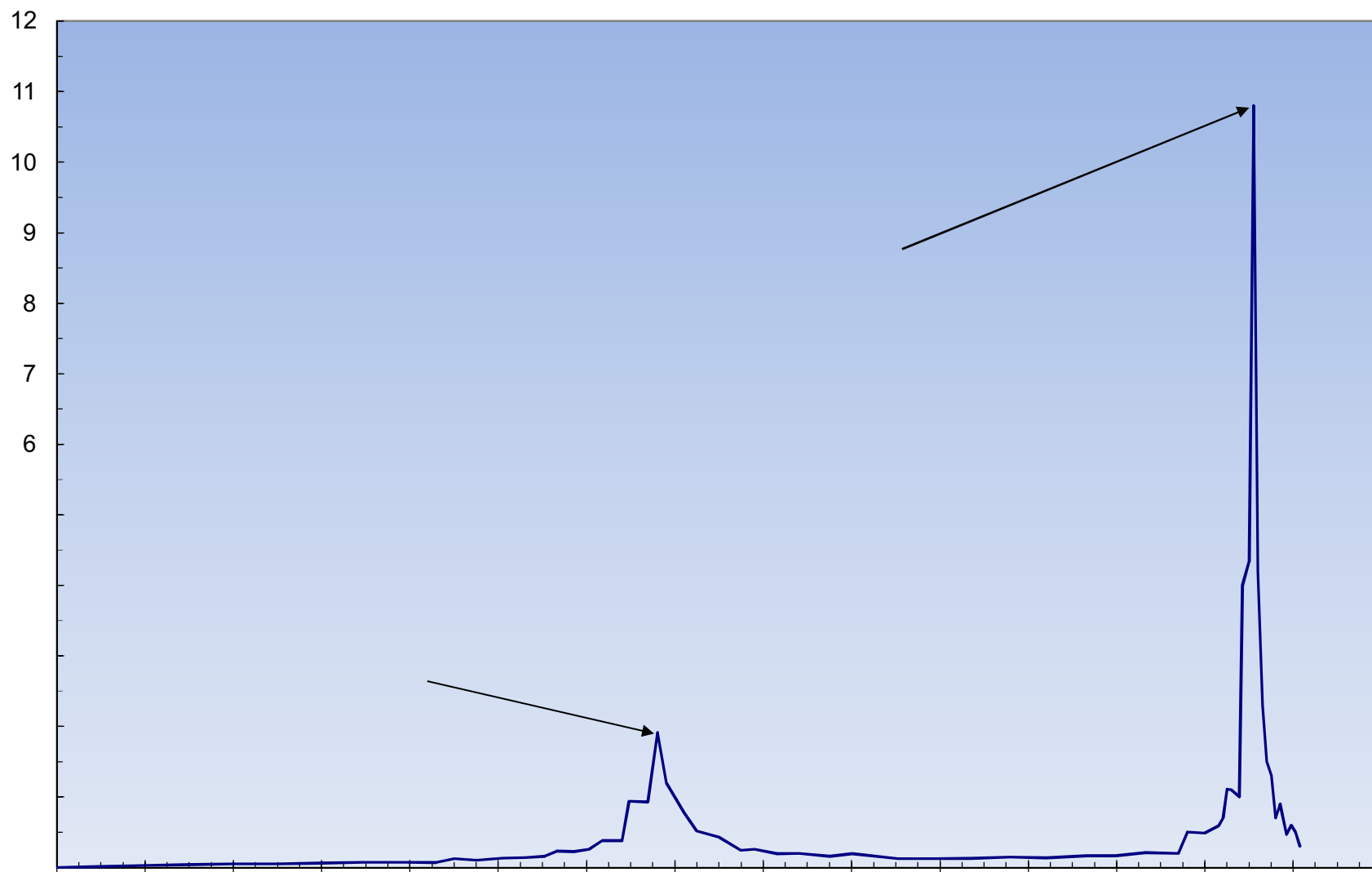
Based on these graphs, it was easily determined that the unknown acid being analyzed was diprotic.

Using the first derivative curve, it was determined that the equivalence points, designated D_1 and D_2, were 13.6 mL and 27.1 mL, respectively.

Therefore:

At $A_1 = 0.25(13.6) = 3.4$ mL, pH = 1.97 $pK_{a1} = pH - \log\dfrac{.25}{.75} = 1.97 - \log\dfrac{.25}{.75} = 2.45$

At $B_1 = 0.5(13.6) = 6.8$ mL, pH = 2.17 $pK_{a1} = pH = 2.17$

At $C_1 = 0.75(13.6) = 10.2$ mL, pH = 2.49 $pK_{a1} = pH - \log\dfrac{.75}{.25} = 2.49 - \log\dfrac{.75}{.25} = 2.02$

Average:

$$pK_{a1,avg} = \frac{2.45 + 2.17 + 2.02}{3} = 2.21$$

From graph, $D_2 - D_1 = (27.1 - 13.6)$ mL = 13.5 mL.

Therefore:

At $A_2 = 0.25(13.5) + 13.6 = 16.98$ mL, pH = 5.45 $pK_{a2} = pH - \log\dfrac{.25}{.75} = 5.45 - \log\dfrac{.25}{.75} = 5.92$

At $B_2 = 0.5(13.5) + 13.6 = 20.35$ mL, pH = 5.92 $pK_{a2} = pH = 5.92$

At $C_2 = 0.75(13.5) + 13.6 = 23.73$ mL, pH = 6.43 $pK_{a2} = pH - \log\dfrac{.75}{.25} = 6.43 - \log\dfrac{.75}{.25} = 5.95$

Average:

$$pK_{a2,avg} = \frac{5.92 + 5.92 + 5.95}{3} = 5.93$$

The data obtained for the pK$_a$ values are shown in tabular form below:

	A (1/4)	B (1/2)	C (3/4)
pK$_{a1}$	2.45	2.17	2.02
pK$_{a2}$	5.92	5.92	5.95

	Avg	StDev	%RSD
pK$_{a1}$	2.21	0.218	9.880
pK$_{a2}$	5.93	0.015	0.256

The average experimental values of 2.21 and 5.93 are relatively close to the listed values for maleic acid, 1.83 and 6.59.

A percent error calculation yields:

$$\frac{2.21 - 1.83}{1.83} * 100 = 20.82\% \text{ for pK}_{a1}, \text{ and}$$

$$\frac{6.59 - 5.93}{6.59} * 100 = 10.02\% \text{ for pK}_{a2}$$

Lastly, using the average concentration obtained from the NaOH standardization along with D$_2$, the second equivalence point, and the grams of analyte used in preparing the unknown acid solution (0.1509 g), the molecular weight of the unknown acid was calculated.

H$_2$A = unknown acid

$$0.0271 \; L \; NaOH * \frac{0.09947 \; mol \; NaOH}{L} * \frac{1 \; mol \; H_2A}{2 \; mol \; NaOH} = 0.001348 \; mol \; H_2A$$

$$\frac{0.1509 \; g \; H_2A}{0.001348 \; mol \; H_2A} = 111.96 \; g / mol \; H_2A$$

This experimental value is also relatively close to the listed value for maleic acid, which is 116.1 g/mol.

A percent error calculation yields:

$$\frac{116.1 - 111.96}{116.1} * 100 = 3.57\%$$

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CONCLUSIONS:

The unknown acid appeared diprotic with experimental values of pK_{a1} = 2.21, pK_{a2} = 5.93, and a MM = 111.96 g/mol. The pK_a values corresponded closely to those of maleic (1.83, 6.59) and phthalic (2.89, 5.41) acid. However, based on the experimentally observed molar mass of 111.96 g/mol, phthalic acid was dismissed because its molecular weight of 166 was determined to be too high, while maleic acid's molar mass of 116.1 g/mol seemed quite reasonable. Therefore, it was determined that the unknown acid in question was maleic acid. Of all the possibilities, its pK_a values and molecular mass most closely corresponded to the experimentally observed values of the unknown.

Both the standardization of the NaOH and the observed pK_a values show satisfactory precision. Much patience was spent in obtaining barely discernible shades of pink during the NaOH standardization, and the data obtained reflects this. However, if any amount of the mass of KHP weighed was lost in transferring to solution, the resulting concentration values would be skewed. Extra time was also spent in obtaining as many points as possible for the titration curve of the unknown acid. The higher standard deviation of the pK_{a1} values may have occurred in the interpolation of the pH values for A, B, and C of the first equivalence point, as this region was not quite as steep as the region of the second equivalence point, making interpolation more difficult. The pH meter was calibrated prior to analyzing the unknown acid, and therefore did not likely introduce any error. Care was taken to rinse all glassware before use in preparation or titration of the unknown acid. However, if any external chemicals were introduced from the glassware used, the pH values would be skewed.

REFERENCES:

Harris, D C., (**2007**); **"Quantitative Chemical Analysis 7th Edition"**; W.H. Freeman and Company, New York, NY.