Experiment 4 Determination of the Molar Mass and Identity of a Diprotic Acid

Introduction

In many acid-base neutralization reactions, one mole of an acid neutralizes one mole of a base, such as the reaction of hydrochloric acid with aqueous sodium hydroxide:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

However, not all acid-base neutralization reactions have one mole of acid reacting with one mole of base. In the case of the neutralization of sulfuric acid with aqueous sodium hydroxide, one mole of sulfuric acid neutralizes two moles of sodium hydroxide:

$$H_2SO_4(aq) + 2\ NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

Since H_2SO_4 has two acidic protons, it is called a **diprotic acid**. A diprotic acid, generically identified as H_2A, will neutralize two moles of NaOH in the following neutralization reaction:

$$H_2A(aq) + 2\ NaOH(aq) \longrightarrow Na_2A(aq) + 2\ H_2O(l)$$

A weak monoprotic acid (HA) will have an acid ionization constant, K_a, associated with its ionization reaction:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

A weak diprotic acid (H_2A) will have two acid ionization constants, K_{a1} and K_{a2} associated with each of the ionization reactions for the diprotic acid:

$$H_2A(aq) \rightleftharpoons H^+(aq) + HA^-(aq)$$

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$HA^-(aq) \rightleftharpoons H^+(aq) + A^{2-}(aq)$$

$$K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

In order to obtain the information necessary to identify your acid, a **titration curve** will be constructed by performing what is called a **potentiometric titration**. In a potentiometric titration, the progress of the titration is monitored using a device called a **pH meter**. A pH meter measures the pH of a solution by placing an electrode in the solution which is sensitive to $H^+(aq)$ concentration. The potential or voltage that the electrode reads when placed in a solution is related to the concentration of $H^+(aq)$ and, therefore, the pH. In a potentiometric titration, the pH of the solution of the unknown acid is measured as NaOH solution is added to it. You will obtain a set of data of pH versus the volume of NaOH added. A plot of the pH (vertical axis) versus volume of NaOH added (horizontal axis) will yield a titration curve.

For a monoprotic weak acid, such as acetic acid ($HC_2H_3O_2$), a titration curve against a strong base like NaOH is shown in Figure 1. It is an "S"-shaped curve.

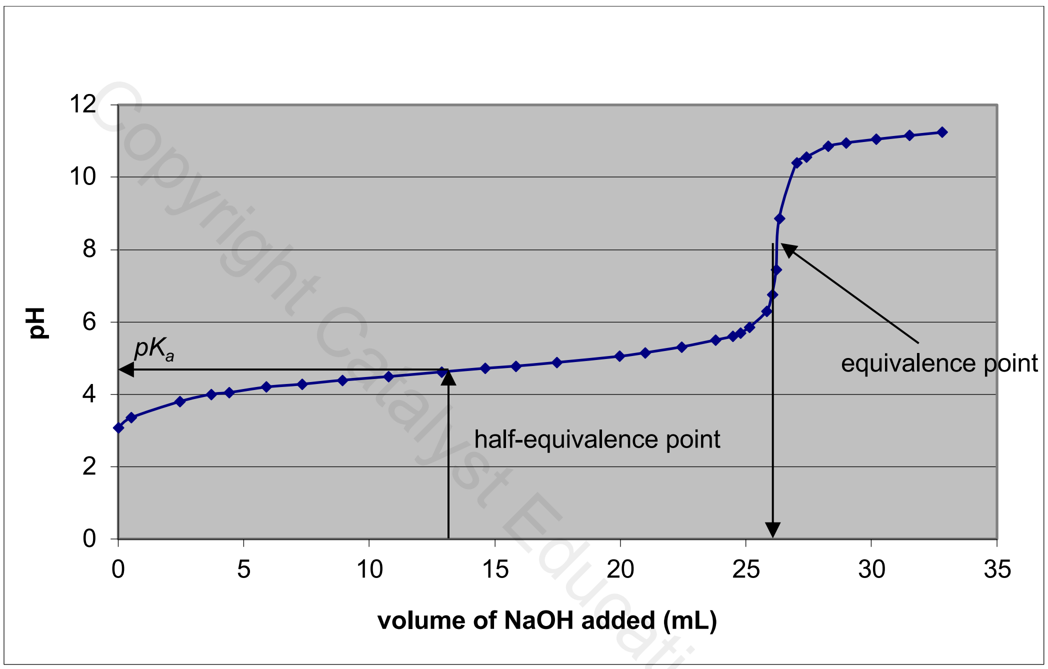

Figure 2 Typical Titration Curve for a Weak Acid against a Strong Base

The inflection point in this curve is the **equivalence point** of the titration. The equivalence point is the point in the titration where the acid has been completely neutralized by the strong base. In this titration, the equivalence point occurs at a pH about 8.0 and a volume of NaOH added of about 26.0 mL. If the volume of NaOH added to reach the equivalence point is divided by two, this volume is called the **half-equivalence point**. At the half-equivalence point, exactly half of the acid has been converted to its conjugate base. Therefore, $[A^-] = [HA]$. Remember that the ionization of a weak monoprotic acid is governed by an **acid ionization constant** (K_a) :

$$K_a = \frac{[H^+][A^-]}{[HA]}$$ If $[HA] = [A^-]$, this reduces to:

$$K_a = [H^+]$$

at the half-equivalence point. If you take the negative log of both sides:

$$pK_a = pH \text{ at the half-equivalence point}$$

Therefore, the K_a for a weak acid may be determined from the titration curve of the acid.

For a diprotic acid, the titration curve against a strong base will generally look like the titration curve in Figure 2 below. There are two connected "S"-shaped curves. In the titration, the acidic protons

are removed one at a time, which will give two equivalence points. The 1st inflection point in the curve is the 1st equivalence point when the 1st acidic proton has been removed from the diprotic acid.

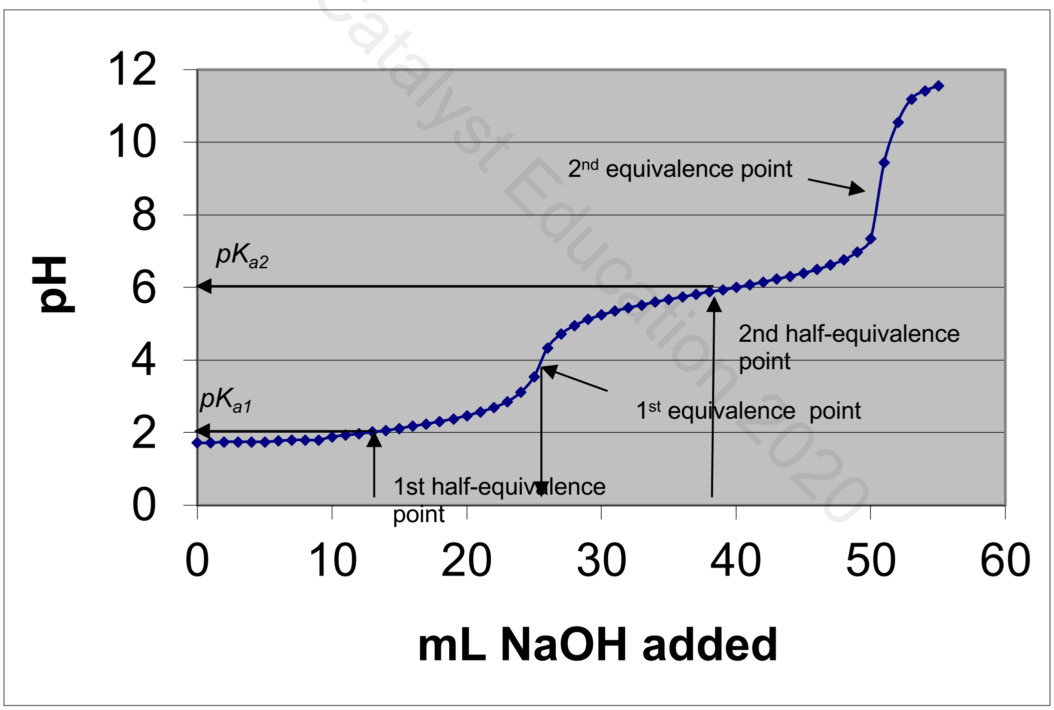

Figure 2 Typical Titration Curve for a Diprotic Acid against a Strong Base

The 2nd inflection point is the 2nd equivalence point, when the 2nd acidic proton has been removed from the acid. The 2nd equivalence point should occur at roughly two times the volume of the first equivalence point. At the volume halfway to the 1st equivalence point is the 1st half-equivalence point. The pH at this volume will be equal to pK_{a1} of the weak diprotic acid. At the volume halfway between the 1st and 2nd equivalence point is the 2nd half-equivalence point. The pH at this volume is equal to pK_{a2} of the weak diprotic acid.

In this experiment, you will weigh out a sample of an unknown diprotic acid and dissolve it in water. Then, you will perform a potentiometric titration against a standard solution of NaOH. The concentration of NaOH will be given to you in prelab. After collecting the data, you will go to the computer room to make a titration curve of your diprotic acid. The values of pK_{a1} and pK_{a2} of your diprotic acid can be obtained from your titration curve. The molar mass of your diprotic acid will be determined from the 2nd equivalence point of your titration. Determine the volume of NaOH added to reach the 2nd equivalence point from your titration curve. Multiply this volume (in liters) by the concentration of NaOH to calculate the number of moles of NaOH added:

$$\text{Moles of NaOH added} = (\text{volume added in liters})(\text{molarity of NaOH})$$

Since this is a diprotic acid, the initial moles of acid is equal to half the number of moles of NaOH added:

$$\text{Initial moles of acid} = \frac{\text{Moles of NaOH added}}{2}$$

The molar mass of the diprotic acid can now be calculated by dividing the weight of the diprotic acid used by the initial number of moles of acid:

$$\text{Molar mass} = \frac{\text{Weight of diprotic acid}}{\text{Initial Moles of Acid}}$$

You should be able to clearly identify your diprotic acid using the molar mass and the values of K_{a1} and K_{a2}.

Equipment

- 150-mL beaker
- 250-mL Erlenmeyer flask
- Burette
- pH meter

You will be instructed in use of the pH meter. You will be working in pairs on this experiment. Each student will turn in a report sheet.

Procedure

1. You will be assigned an unknown acid. Record the number of your unknown acid on the data sheet.
2. Weigh out about 0.75 g of the unknown acid in a clean pre-weighed 150-mL beaker. Record the weight of the acid on your data sheet.
3. Obtain a pH meter which has been calibrated by the Stockroom Manager. Your lab instructor will tell you how to operate the pH meters in pre-lab.
4. Dissolve the acid in about 50 mL of deionized water and place the pH probe into the solution to measure its pH. Make certain that the pH reading has stabilized on the pH meter before continuing on. One lab partner should do the titration while the second lab partner records the data.
5. Record the pH of the solution for each 1-mL increment of NaOH solution added and record on the data sheet provided. Swirl the solution after each addition and be certain that the pH has stabilized before recording the pH.
6. Continue the titration until the pH remains constant for approximately 3 mL (usually at a pH of approximately 12).
7. After you have completed the titration, go to the computer lab and graph the data using MS Excel. (Review graphing procedure in Exp.3 if necessary).
8. Enter mL NaOH in the first column and pH in the second column.
9. For "chart type" select "XY scatter" and select "Scatter with data points connected by smoothed lines."
10. Title the graph "**Titration of Unknown Acid**" and label the x-axis "**mL NaOH**" and the y-axis "**pH**".
11. Make the graph approximately square and print it so that both the graph and the data appear on the printout. Each partner should have a copy of the graph and data.
12. When you have finished your calculations, empty the burette, rinse it with deionized water and leave it upside down in the burette holder to dry.
13. Turn in your graphs with your Data Sheets.

Name: ______________________________________ CHEM 1412 Section: _________

Partner: ____ Date: ___/___/___

Report Sheet EXP4: Determination of the Molar Mass and Identity of a Diprotic Acid

[NaOH] = ______ Unknown #: ______ Identity of unknown acid: ______________

Weight of acid and beaker ____________

Weight of beaker ____________

Weight of acid ____________

Burette reading at 2nd eq. point ____________

Initial burette reading ____________

Volume used to reach 2nd eq point ____________

Molar mass of acid ____________

Calculations:

Burette reading at 1st eq. point ____________

Volume at 50% of 1st eq. pt. ____________

K_1 of acid ____________

Calculations:

Burette reading at 2nd eq. point ____________

Volume at midpoint between eq, points ____________

K_2 of acid ____________

Calculations:

Titration Data Sheet

mL NaOH added	pH	mL NaOH added	pH	mL NaOH added	pH
0.00		18.00		36.00	
1.00		19.00		37.00	
2.00		20.00		38.00	
3.00		21.00		39.00	
4.00		22.00		40.00	
5.00		23.00		41.00	
6.00		24.00		42.00	
7.00		25.00		43.00	
8.00		26.00		44.00	
9.00		27.00		45.00	
10.00		28.00		46.00	
11.00		29.00		47.00	
12.00		30.00		48.00	
13.00		31.00		49.00	
14.00		32.00		50.00	
15.00		33.00			
16.00		34.00			
17.00		35.00			

Make a plot of pH (vertical axis) versus mL NaOH added. You must make this plot before you can determine the burette readings at the 1st and 2nd equivalence points, the values of K_1 and K_2 of the acid and the molar mass of the acid.

Possible Unknown Acids

Name	Molar mass	K_1	K_2
maleic acid	116.08 g/mol	1.5×10^{-2}	2.6×10^{-7}
malonic acid	104.06 g/mol	1.5×10^{-3}	2.0×10^{-6}
oxalic acid	126.50 g/mol	5.9×10^{-2}	6.4×10^{-5}
tartaric acid	150.10 g/mol	1.0×10^{-3}	4.6×10^{-5}

Name: ______________________________ Date: ___/___/___ CHEM1412 Section: ________

Experiment 4: Pre-Lab Exercise

Following instructions in the Lab Manual, you have weighed out 0.755g of an unknown monoprotic weak acid and titrated it with 0.497 M NaOH. You have monitored the progress of the reaction with a pH meter and obtained the following data.

mL	**pH**	**mL**	**pH**
0	3.97	13	7.73
1	4.13	14	8.49
2	4.13	15	9.31
3	4.39	16	9.71
4	4.54	17	9.95
5	4.70	18	10.24
6	4.88	19	10.45
7	5.07	20	10.64
8	5.31	21	10.80
9	5.58	22	10.95
10	5.99	23	11.08
11	6.54	24	11.19
12	7.06	25	11.24

1. Using excel, construct a titration curve for the above data and print it out.

2. Determine the equivalence point of the titration.

3. Determine the molar mass of the unknown acid. Show calculations.

4. Calculate the K_a value for the unknown acid. Show calculations.