EXPERIMENT 14   *Identification of an Unknown Acid*

Objective

The objective in this experiment is to prepare and standardize a sodium hydroxide solution and use it to determine the **equivalent weight, pK$_a$, and melting point** of an unknown acid. Using this information the identify of an unknown acid will be determined. The techniques required for this lab include the preparation of a standard acid solution, standardization of a base solution, titration measurement of pK$_a$ and the melting point of a crystalline solid.

Introduction

Up to now, you have done a number of labs which could be classified as quantitative analysis. Quantitative analysis is the analysis of a sample to determine the concentration of a solute in a mixture. Now you will begin to do what is known as qualitative analysis. Qualitative analysis can be defined as the process of using the properties of an unknown substance in order to identify the substance. It is a common occurrence for a chemist to be given a sample and asked to identify the substances in a mixture. A forensic chemist might be asked to identify the toxin which killed a victim. A chemist working for the IOC might be asked to identify illicit substances in the urine sample from an athlete.

In this experiment, you will be given a sample of an unknown acid. Your job will be to identify this acid from measuring a number of physical properties of the compound. First, quantitative analysis will be used to determine the equivalent weight or gram molar mass (GMM) of an unknown acid.

Titration

The term **titration** refers to the addition of a solution of one reagent, usually from a burette, to a known amount of the other reagent, and then determining the volume of solution added when the reaction is complete. If the titration is done by addition of a base to an acid, typically there is a relatively large and sudden increase in pH as the equivalence point is reached. This point may be

detected visually when a color change occurs by using an appropriate indicator, or by measuring the change in pH with a pH meter.

As mentioned, sodium hydroxide will be used in the titration. However, sodium hydroxide solutions cannot be prepared with adequate precision simply by weighing out solid NaOH, since the commercial material is not sufficiently pure and absorbs water and CO_2 quickly from the air. In order for a titration to be accurate, the base solution must first be standardized. **Standardization** refers to the preparation of a solution of accurately known concentration. To standardize NaOH, **oxalic acid** is used since it can be obtained in a high state of purity and does not absorb moisture readily. Thus, to standardize a sodium hydroxide solution, we first prepare the solution noting the approximate concentration of NaOH and then titrate this solution with an oxalic acid solution of known concentration. The oxalic acid solution is referred to as a **standard solution** since it can be prepared such that its exact concentration is known. This solution is also called a **primary standard solution** and the student should be familiar with both terms. Phenolphthalein will be used as the indicator in this acid/base system.

The **equivalent weight** of an acid is defined as the weight of acid that provides one mole of H^+ in the reaction. The units are grams per equivalent. For a monoprotic acid like HCl, the equivalent weight and the molecular weight are the same. For a diprotic acid like oxalic acid, if both hydrogens are consumed in the reaction, the equivalent weight is one-half the molecular weight. In this experiment, since the formula of the unknown acid is not available, the equivalent weight must be determined by the following relationship:

grams of acid/moles of H^+ reacted. The number of moles of H^+ is equal to the number of moles of OH^- from the base

Some compounds exist as hydrates. A **hydrate** is a compound in which the solid contains one or more molecules of water locked within the ions or molecules that make up the solid. The water molecules are part of the formula unit and are included when writing the formula for the hydrate. Oxalic acid exists as the dihydrate; this means that there are two molecules of water for every molecule of oxalic acid. Thus, the complete formula is written as:

$$H_2C_2O_4 \cdot 2\ H_2O \qquad \text{(EQ 14.1)}$$

Notice the "dot" inserted between the formula and water

Melting Point

The problem with this is that there are many thousands of weak acids.   Knowing the gram molar mass of an acid will certainly eliminate the great majority of possible compounds. However, simply knowing the gram molar mass of an acid does not provide sufficient information to identify the substance unambiguously. More properties of the substance must be measured in order to reach a unique identification.

There are a number of methods used by chemists to do qualitative analysis. These would include measuring the boiling or melting point of the substance, measuring the density of the substance, or the solubility of the substance. Also included are a number of more high tech methods such as various types of spectroscopy. These methods would include infrared spectroscopy, UV/vis spectroscopy, nuclear magnetic resonance (NMR) spectroscopy. Perhaps the qualitative tool of greatest preference to chemists is the gas chromatograph (GC) in tandem with a mass spectrometer (MS) (a GCMS). Your instructor may explain some of these tools. These methods are all fairly expensive.

We will limit ourselves to more classical and less expensive qualitative measurements to identify your unknown.

Specifically, two additional measurements beyond the gram molar mass will be used to identify the unknown acid. First, the melting point of the substance will be found. This should greatly narrow down the list of possible acids. The **melting point** of a solid occurs when the solid and liquid phases are equilibrium, which occurs at a specific temperature. However, the time required to determine a specific melting point can be impractical, so a melting point range of temperatures between the first sign of melting and the complete melting of a solid is found. A *narrow range* of one to two degrees Celsius implies a high degree of purity, while a *broad range* usually implies an impure sample. As the thermal energy imparted by the melting point apparatus to the sample become large enough to overcome the intermolecular forces that hold the sample together the sample melts. The temperature recorded is when the first solid begins to melt until the last bit of solid disappears.

Solids often decompose or undergo unusual behavior before melting including changes in appearance such as loss of luster or darkening, softening, shrinking, or appearing moist before melting. These changes are not melting but, sintering; the actual melting point occurs when the first drop of liquid is seen until the last solid liquefies. When a substance melts with decomposition the substance will bubble or form a dark char. In these instances, to observe the melting point or decomposition point is dependent on the rate of heating.

In fact, it might be sufficient, in tandem with the GMM to make a sure identification from the given list of possible acids, which will be provided by your instructor. However, to make the identification more definite, the strength of the unknown acid will also be found.

Acid Strength, pK_a

As a measure of the relative strength of an acid, chemists use a measurement known as the **acid dissociation constant**, which usually has the symbol K_a. The acid strength of acids, HA, is a property that can be used to explore the relationship between structure and chemical properties. This can be described using Brønsted-Lowry theory, where an acid has the ability to donate a proton to a base:

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrows A^-_{(aq)} + H_3O^+_{(aq)} \tag{EQ 14.2}$$
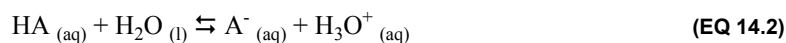
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{EQ 14.3}$$

Actually, because K_a values tend to vary over such a wide range, chemists usually report the pK_a of an acid, which is defined, similar to pH as follows:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{EQ 14.4}$$

when the anion and the acid are at the same concentration (that is, the acid is half-neutralized) the value of the pK_a of an acid is the pH.

When titrating your weak acid, for every mole of hydroxide added, one mole of HA is turned into the conjugate base A^-. While titrating your weak acid, you will create a buffer. A buffer is a mixture of a weak acid and a conjugate base in roughly equal molar proportions. One property of a buffer is

that its pH is changed only slightly by adding strong acid or strong base to it. For this reason, as you titrate your unknown acid, the pH will only change very slowly. Something very interesting happens to the equation for K_a at what is known as the half-titration point. By definition, the half-titration point is the point in the titration where exactly half the original weak acid has been converted to the conjugate base. In a titration, the half-titration point will occur at exactly half the volume of titrant as that required to reach the endpoint. At the half-titration point,

$$[HA] = [A^-] \qquad\qquad \textbf{(EQ 15.15)}$$

In this case, at the half-titration point the K_a equation above simplifies to:

$$K_a = [H^+] \quad \text{or} \quad pK_a = pH \qquad\qquad \textbf{(EQ 15.16)}$$

In other words, for example, if a titration of a weak acid required 9.00 mL to reach endpoint, then if one could measure the pH when the volume of base was 4.50 ml, then the pH at that point would equal pK_a of the acid. Put even more simply, **pK_a = pH at half-titration point**.

Your job, then, is to simply measure the pH of a solution of your unknown acid which has been half-titrated! When you half-titrate a weak acid, you are creating a pH buffer. This solution will be fairly resistant to pH change. For this reason, if you add water to the half-titrated solution, it will not affect the pH significantly.

$$pH = pK_a \qquad\qquad \textbf{(EQ 14.1)}$$

The pH is measured with a pH meter. A graph of pH versus mL of sodium hydroxide added.
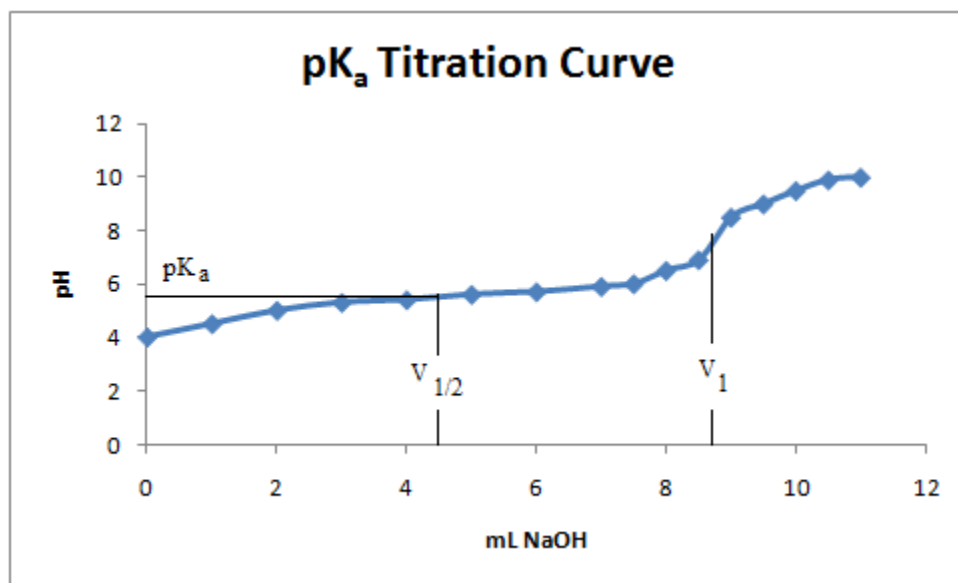
The equivalence point (V_1), which is point where the curve is the steepest, and the half-equivalence point ($V_{1/2}$) of the titration. Using the half-equivalence point the pK_a of the unknown acid, and from the volume of base added at the equivalence point, the equivalent weight of the acid can be calculated. A list of all the possible acids for you to consider along with the pK_a value for each of the acids will be provided by your instructor.

Once you have successfully measured the GMM, the melting point, and the pK_a of your unknown acid, you should to make an unambiguous identification of your acid from the list of possible acids which will be provided by your instructor.

Procedure

Read through the entire procedure first and determine what type of data and observations that you will be collecting. In the data and observations section of your notebook, construct an appropriate data table that facilitates efficient data recording.

Note: Record volumes to 0.01 mL and masses to 0.0001 g

Preparation of the Standard Oxalic Acid Solution

1. Calculate the mass of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\ H_2O$, needed to make 250 mL of 0.050 *M* solution. Do not waste time trying to weigh out the exact amount that you calculated since you will know the final concentration once the solution is prepared.

2. Weigh a sample of the hydrate that is within 20 percent of the calculated amount. Tare a clean, dry beaker on the analytical balance, add an appropriate amount (within 20 percent of calculated) of oxalic acid, and weigh the beaker containing the acid. Do not transfer chemicals inside the analytical balance.

3. Transfer all of the acid to a 250.0 mL volumetric flask, fill the volumetric flask half-full with water and swirl contents until the acid is all dissolved. When you are certain that all of the solid has dissolved, add water to the mark, stopper the flask and invert several times to mix thoroughly. Return the volumetric flask at the end of the lab today!

Standardization of NaOH

1. Prepare one liter of approximately 0.10 *M* NaOH by dilution of the stock solution provided. Mix it thoroughly and store in a properly labeled plastic bottle. Be sure to record the original concentration of the stock solution, the amount of water that you used to dilute the stock solution and the final concentration of your NaOH solution.

Remember that all of these concentrations of NaOH are approximate; the first goal is to determine the exact concentration of NaOH by standardization

2. Using a volumetric pipet, transfer 25.00 mL of your oxalic acid solution into a 125 or 250 mL Erlenmeyer flask. Add two drops of phenolphthalein indicator to the acid solution. Fill the burette with your NaOH solution and titrate the acid in the flask with the NaOH from the burette. The titration is complete when the first pink color persists in the flask. Swirl the flask during the addition of base to ensure complete mixing.

3. Be sure to rinse the pipet with the acid solution and the burette with base before use, to remove any traces of water. The inside of the titration flask should be washed down with water just before reaching the end point to remove any drops of acid or base stuck on the side of the flask.

4. Try to add not more than one drop in the last addition as you approach the end point.

5. Perform titrations until you get three that differ in only the second decimal place for the mL of base used. Calculate the concentration of the base for each trial, and obtain a mean and standard deviation. The average concentration that you calculate is the concentration of your now standardized NaOH. Your standardized base will be used to titrate your unknown acid so be sure to cover the solution to prevent loss of water (which changes the concentration) and save it for use later in the experiment.

Molar Mass of a Monoprotic Unknown Acid

Using standardized sodium hydroxide titrate the unknown monoprotic acid to determine the equivalent weight of the acid. Since the unknown acid is a monoprotic acid, you will not need to worry about the distinction between equivalent weight and gram molar mass.

1. On the analytical balance, measure out approximately 0.50 g of your unknown acid. **Be sure to record your unknown number in your lab book**. Being very careful not to lose any of the acid, transfer to a 250 mL Erlenmeyer flask which has been cleaned but not necessarily dried. Add 50-100 mL of water as well as two drops of phenolphthalein indicator to the flask.

2. If the acid does not dissolve easily, you may need to heat the mixture gently. If most, but not all the acid dissolves, you may proceed with the titration, as the conjugate base of the acid created during the titration will be quite soluble in water.

3. Clean, rinse and condition a 50-mL buret with standardized approximately 0.10 M sodium hydroxide solution. **Be sure to record the concentration of the NaOH in your lab book**. Fill the buret to somewhere near the top and titrate your sample to phenolphthalein endpoint.

4. Repeat the procedure three times. To be sure your results are good, calculate the ration of grams of unknown used to volume of titrant used. The ratios should agree within 1%. At this point, you may want to calculate the GMM of your unknown acid from the three titrations and calculate the average of your values.

The Melting Point

First, you will be measuring the melting point of your acid. (If the melting point apparatus is crowded, you can go on and do the experiment to measure pK_a first if you like). The melting point of a substance is the temperature at which the solid crystals of that compound turn to a liquid. This will be a fairly simple measurement.

1. Place just a few small crystals of your unknown acid in the center of the top of your melting point apparatus. Only a very small amount of solid is required to determine a melting point. Insert a thermometer in the appropriate channel in the apparatus.

2. Allow the temperature to increase fairly slowly and record the temperature at which it melts. You should not bother to be extremely careful in this first attempt, as you are just trying to get an approximate melting point the first time around.

3. Once you have an approximate melting point, now you will measure the melting point much more carefully by approaching the melting point very gradually. Clean off the surface of the melting point apparatus and put more crystals on top as before. This time, when you are a few degrees below the melting point, begin to raise the temperature quite slowly. This can be done by turning down the hot plate or by putting a few layers of paper between the hot plate and the melting point apparatus. You may have to use your imagination a bit at this point! The temperature should rise at no more than two degrees per minute at the melting point to measure an accurate melting point.

4. If you have any doubt at all about the melting point, perform the procedure one additional time. If you have two fairly good values which are slightly different, you can take the melting point to be the average of those two values. Record your results in the data section.

Measuring pK_a

Your job, then, is to simply measure the pH of a solution of your unknown acid which has been half-titrated! When you half-titrate a weak acid, you are creating a pH buffer. This solution will be fairly resistant to pH change. For this reason, if you add water to the half-titrated solution, it will not affect the pH significantly.

Using the Vernier Interface

The volume of sodium hydroxide added to the acid solution will be measured using a drop counter.

Calibrating the Drop Counter

1. Place a clean, dry beaker underneath the drop counter.

2. Press calibrate and start measuring drops. **Make sure that the drops are not added too fast.** Open the stopcock on the buret and begin to slowly drop between 2-3 mL of the sodium hydroxide solution into the beaker counting the number of drops added. The computer will then begin recording the number of drops added to the beaker. After approximately 2-3 mL of sodium hydroxide has been added to the beaker, close the stopcock on the buret, and stop measuring the number of drops.

3. Enter the actual volume of sodium hydroxide added to the beaker to the 0.01 mL into the apparatus.

Collecting Titration Data

Once the drop counter is calibrated, the pH meter needs to be calibrated and the titration data may be collected.

1. Calibrate the pH electrode using two buffer solutions of known pH. Once the reading stabilizes, follow the directions on the screen.

2. Now, the collection of pH as a function of number of drops added may be determined. Make sure that the solutions to be titrated are prepared in advance. Begin measuring the pH as you added the NaOH dropwise. Collect the data until 1.5 times the volume at the equivalence point has been added.

3. The pK_a can be read off of the graph by determining the volume at the steepest point of the graph i.e the equivalence point and taking half of that volume.

Determining the Identity of Your Unknown Acid

At this point, you should use the pK_a you measured to begin to eliminate possible weak acids from the list provided. Once you have narrowed the list down a bit, you should narrow it further, either by determining the GMM of your candidates from their formulas and comparing the result to your measurements, or by looking up the melting points of the candidates in the Handbook of Chemistry and Physics (known as the CRC).

With any luck, the pK_a in combination with either the melting point or the GMM should reduce your possibilities down to just a couple of acids. Now, use the third measurement (MP of GMM) to narrow your choice to one. This is your proposed choice of the identity of your unknown acid.

If you like, you may use the template provided below for recording your experimental values for your unknown acid, as well as the values your find in the literature for your best guess as to the actual acid, as well as your second best guess.

Sample Data Sheet

Do not use this data sheet for your records. This is provided as an example of what should be in your lab notebook before you begin the experiment.

TABLE 14.1 Preparation of Standard Oxalic Acid Solution

mass of oxalic acid

volumetric flask (mL)

TABLE 14.2 Standard Solution Preparation

Initial. conc. of stock solution

Pipet size (mL)

Amount of water used for dilution

Approximate concentration of your standard solution

TABLE 14.3 Standardization of NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Initial buret reading				
Final buret reading				
Volume of base used				

TABLE 14.4 Melting Point of Unknown Solid Acid

	Trial #1	Trial #2	Trial #3	Average
Melting Point Range				

TABLE 14.5 Titration of Unknown Solid Acid

	Trial #1	Trial #2	Trial #3	Trial #4
Initial buret reading				
Final buret reading				
Volume of base used				
Mass of unknown				

Sample Calculation Sheet

Do not use this sheet for your records. This is provided as an example of what should be in your lab notebook before you begin the experiment.

TABLE 14.6 Standard Oxalic Acid Solution

Mass of oxalic acid	
Moles of oxalic acid	
Volumetric flask (mL)	
Molarity of oxalic acid	
Molarity of H$^+$ions in oxalic acid	

TABLE 14.7 Standardization of NaOH Solution

	Trial #1	Trial #2	Trial #3	Trial #4
Moles of oxalic acid				
Vol. of NaOH				
Molarity of NaOH				
Average molarity				

TABLE 14.8 Determination of Equivalent Weight

	Trial #1	Trial #2	Trial #3	Trial #4
Mass of unknown				
Vol. of NaOH				
Moles of NaOH				
Moles H$^+$ reacted				
Equivalent weight				
Average equivalent weight				

TABLE 14.9 Identification of Unknown Acid

	Average Measured Values	Identity of Acid	Literature Values	Second Best Guess	Literature Values
Gram Molar Mass					
Melting Point					
pK$_a$					

Post Lab Questions

1. What mass of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\ H_2O$, is needed to prepare 250.0 mL of 0.050 M solution?

2. If 0.750 grams of oxalic acid dihydrate required 31.0 mL of NaOH solution in a titration, what was the concentration of the base?

3. What was the equivalent weight of an acid if 0.250 grams of it just neutralized 41.0 mL of 0.161 M NaOH solution?