Experiment

ANALYSIS OF A SOLID MIXTURE

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- learn to analyze a solid unknown with volumetric techniques.
- standardize a solution of NaOH.
- determine the percentage of KHP in solid mixture of KHP and a soluble salt.

BACKGROUND

In this experiment you will use an acid-base titration to determine the composition of a solid mixture, containing potassium hydrogen phthalate (KHP) and an inert, soluble salt (such as NaCl). The analysis will be carried out by weighing out a portion of the unknown solid, dissolving it in water, and titrating the resulting solution with a standard solution of sodium hydroxide.

KHP is an organic weak acid with the structure which corresponds to the formula $KHC_8H_4O_4$. The hydrogen atom of the COOH structure above is acidic and thus will react with a base such as OH^-. When KHP is dissolved in water, it dissociates to produce potassium ions (K+) and hydrogen phthalate ions (HP^-). When OH^- is added to the solution, it extracts the acidic hydrogen atom from the HP^- ion:

$$HP^- + OH^- \Longrightarrow P^{2-} + H_2O$$

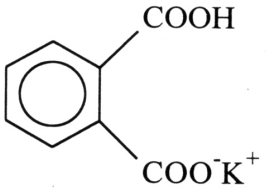

Fig. 1. Structure of KHP

In this experiment, you will titrate the acid in two different ways

- using an acid-base indicator and
- using the ***MicroLAB*** interface to monitor the change in pH.

The first two titrations will be indicator titrations and the second two titrations will use the ***MicroLAB*** system so you can compare the titration methods and their relative accuracy.

The indicator to be used is phenolphthalein, which is colorless in acidic solution and pink in basic solution, with the transition at about pH 9. You will measure a known amount of the solid mixture containing the acid (KHP) into a beaker, dissolve it, add a few drops of phenolphthalein and then use a buret to add an accurately known amount of base (NaOH). The point at which the amount of base added (in moles) equals the original amount of acid in the solution (in moles) is called the **equivalence point, or stoichiometric point.** Because the pH of the solution changes rapidly around the equivalence point and becomes basic, the phenolphthalein will change from colorless to pink in this region. The point at which the indicator changes color is called the **endpoint** of the titration. For a titration to produce an accurate result, the endpoint and the equivalence point must occur at almost exactly the same volume of added titrant.

In the computer portion of the experiment, you will determine the equivalence point by monitoring the pH of the solution as base is added and then plotting a pH curve.

The pH of the solution is a measure of the amount of hydrogen ion in the solution:

$$\mathbf{pH = -\log [H+]}$$

Hydrogen phthalate is a weak acid:

$$\mathbf{HP^- \Leftrightarrow H^+ + P^{2-}}$$

For pure KHP in water, the hydrogen ion concentration will be about 1.0×10^{-4} *M* which corresponds to a pH of about 4.0. The value actually observed depends on the concentration of HP^- in solution.

As base is added to a solution of KHP, the H^+ from dissociation of HP^- will be consumed and the pH of the solution will gradually increase. At first, when there is plenty of HP^- available, th reaction of H+ with base will be offset by more dissociation of HP^-, so there will be little change in the pH. This is called the buffering capacity of HP^-. But when the HP^- is nearly gone, the change in pH with the addition of OH^- becomes greater. At the point where the HP^- is completely consumed, the change in the pH will be the greatest. Consider the following graph of pH vs. ml of base added, (called a titration curve):

At the equivalence point on the curve, the slope of the curve is greatest, since the pH is changing most rapidly in this area of the titration. This is the equivalence point and is very near the phenolphthalein endpoint. Location of the equivalence point enables us to determine how many milliliters of base it took to exactly react with the HP^- in solution. Because we also know the concentration of OH^- in the base solution, we can calculate the number of moles and hence grams, of KHP in the original unknown.

SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted with chemicals should be washed immediately.

BEFORE PERFORMING THIS EXPERIMENT . . .

1. Dry 3.5 g KHP for one hour at 110°C.
2. Boil one liter of deionized water and store in a capped Nalgene bottle.

EXPERIMENTAL PROCEDURE

You will do two determinations in this experiment. You should do two manual trials and two trials with the computer interface for both determinations. The first will be the standardization of your NaOH solution (determining the exact molarity) by titrating against pure KHP. After the NaOH is standardized, you will use this same solution of base to titrate the unknown mixture and determine the percentage of KHP.

Solution preparation

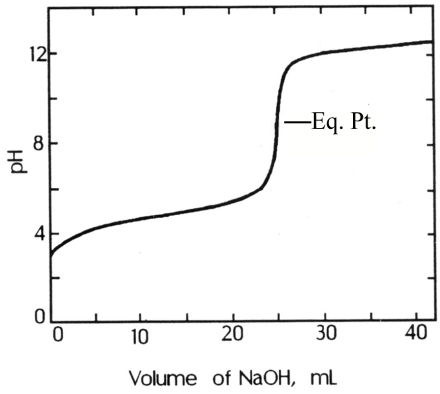

Fig. 2. Typical monoprotic titration curve.

A stock solution of NaOH is provided. Make 500 ml of approximately 0.1 *M* NaOH by adding 7 ml of stock solution to your boiled, deionized water. Mix well and store this solution in a capped **Nalgene** bottle for use as titrant. (Do **NOT** use glass containers, as the NaOH will attack the glass, changing the concentration of the NaOH.) The sodium hydroxide solution will be standardized during the experiment.

Standardization of NaOH

The concentration of the NaOH solution is about 0.1 *M* but for quantitative results it is necessary to know the exact molarity of the base (to four significant figures). This molarity will be determined first by using an indicator and then by using a pH probe attached to the ***MicroLAB*** computer interface.

Using an indicator

Place a precisely weighed sample (about 0.3 g; use the analytical balance) of pure KHP into a beaker and dissolve it in about 40 ml of boiled, deionized water. Add 2-4 drops of phenolphthalein as an indicator. Rinse the buret three times with a few milliliters of your NaOH solution, then fill the buret with base and record the volume (making sure no bubbles appear in the tip). Place the beaker containing the sample of dissolved KHP under the buret and begin adding small increments of base. When you get near the endpoint (the pink color disappears slowly), add the base **drop wise with swirling.** Titrate the sample to the first pale pink color that persists for about 20 seconds upon thorough swirling. Read the buret to the nearest 0.01 ml and record the value. Remember to do a second trial. This information (ml of base added, mass KHP) is enough to calculate the exact molarity of the base.

Using the *MicroLAB*

You will need to use the ***MicroLAB*** interface and computer for two more replications of the standardization titration.

Calibration of drop size

Detailed instructions for this part of the experiment are contained in **The Measurement Manual**. In this part of the experiment the volume of titrant will be determined by electronically counting the number of drops required to reach the equivalence point. Therefore, the volume of a single drop must be known accurately. It is important that the rate of delivery of the NaOH used in the calibration part of the experiment be the same as that used during the actual titration. This ensures that the drop size remains constant.

1. Read the instructions on the attached sheets on setting up and calibrating the drop counter and performing drop counter titrations. Your instructor will also demonstrate how to do this in class. Align the counter by filling the buret with your NaOH solution and allowing it to drip through the counter into a small clean beaker. The buret is correctly aligned when the counter light on the interface flashes every time a drop falls from the buret. Alignment of the buret is a critical step in producing an accurate titration. Do not move the buret or counter once they are aligned or serious errors will result.

2. Load the program ***pH-Acid-Base-Temperature Automatic Titration*** for drop calibration into the program.

3. Read the buret and record the initial volume. Start the buret dripping at a moderately slow rate (about two to four seconds per drop). While one of you watches the buret, the other should watch the drop count. At each 2.00 ml increment, the number of drops should be recorded in your lab notes. This will provide five data points (one each 2.00 ml) to graph. The slope of the regression line through these five points will be your best average for the drop time.

Calibration of the pH electrode

1. Attach the electrode to the interface unit at the pH position and place the electrode in a buffer solution of pH 4. Click on **pH** in the **Variables View** and recalibrate your probe with the pH 4, 7 and 10 buffers supplied. Be sure to rinse the pH probe with distilled water after each buffer and before you place it in your analyte solution. Between titrations, the probe should be stored in the pH 7 buffer, then rinsed well with distilled water before inserting into your titration beaker.
2. Remove the electrode from the buffer solution and rinse it with deionized water for each buffer solution.

Standardization of NaOH

1. Dissolve approximately 0.3 g of dry KHP in about 70 ml of boiled, deionized water. Be sure to use the analytical balance and record the exact mass of KHP used. Prepare one more sample in the same manner.
2. Refill the buret with 0.1 *M* NaOH. Check to be sure the alignment of the drop counter is still correct.
3. Place a magnetic stirring bar in one of the KHP solutions. Place the container under the buret and counter assembly. See the sample setup in the lab. Put the pH electrode through the probe hole in the drop counter.
4. Use the ***MicroLAB*** program **pH-Acid-Base-Temperature Automatic Titration, OR *pH.vs.drop.titr.0.1pH.exp*** supplied by your instructor, as instructed for the titrations. Open the ***MicroLAB*** program according to the instructions in the **Measurement Manual**.
5. To maintain a constant head pressure keep the buret full by using the wash bottle to add standardized NaOH.
6. When approaching the equivalence point, slow the drop rate down to allow more time for mixing and for the pH electrode equilibration. Past the equivalence point, you can again increase the drop rate.
7. When the titration curve begins to flatten out, stop the titration by closing the buret stopcock, then clicking **Stop.**
8. Run the program again for the other KHP samples. Be sure to name each data file appropriately so you can identify it later.

Titration of an unknown solid mixture

1. Dissolve approximately 1.0 g (record the exact mass from the analytical balance) of the unknown solid mixture in about 70 ml of boiled, deionized water. Prepare three more samples in the same manner.
2. Titrate the first two samples using phenolphthalein as you did the standardization of the NaOH. Titrate your other two samples with your standardized NaOH using the *MicroLAB* program as described above.
3. Rinse the pH electrode with deionized water when you are finished, replace in the storage bottle and screw the top snugly tight to avoid leakage during storage.

DATA ANALYSIS

Standardization of NaOH

Indicator titration

1. Use the volume of base and the mass of KHP to calculate the molarity of NaOH.

MicroLAB titration

Calibration of drop size

1. Reopen your calibration data into the *MicroLAB* program. Use the graph option to plot ml vs. drops.
2. Use this plot and the linear regression equation to determine the equation necessary to convert drops to ml. Title your graph.
3. After you have obtained the approval of your instructor, print the graph and record the calibration equation for use in your titrations.

Standardization of NaOH

1. Reopen your data into the ***MicroLAB*** program.
2. From the information in the Appendix, set up the first and second derivatives for the data, and "click and drag" them, one at a time, to the Y2 axis of the titration graph, and print out the graph.
3. From the second derivative information, calculate the exact equivalence point for each of the ***MicroLAB*** titrations.
4. Determine the concentration of your NaOH solution from the equivalence point and the mass of KHP.
5. Repeat this analysis for each standardization trial and average the values for the molarity of your NaOH. Record this average for use in subsequent calculations.

Titration of an unknown solid mixture

Indicator titration

Use the volume of standard NaOH to calculate the mass of the unknown acid in the mixture, then the mass of the solid mixture sample to calculate the percentage KHP in the mixture.

MicroLAB titration

Determination of the percent KHP in an unknown solid mixture

1. Load your data from the titrations of your unknown acid into the spreadsheet program.
2. Using the **Analysis and Graph** options, construct titration curves and derivative plots for your unknown acid.
3. Using your graphs, determine the equivalence point(s) for the titration of your unknown acid.
4. Calculate the percent KHP in the solid mixture.