Experiment 10
Titration Curves

OUTCOMES

After completing this experiment, the student should be able to:

- generate a titration curve for an acid-base reaction.
- identify if an unknown acid is weak or strong and monoprotic or polyprotic.
- calculate initial concentrations of monoprotic acids from titration data.
- calculate K_a values of weak acids from titration data.

DISCUSSION

Titration is a technique used in analytical chemistry to determine the concentration of an unknown solution. When the unknown solution is a weak acid or base, the K_a or K_b of the acid or base can also be calculated. Titration involves the slow addition of one solution of known concentration (the **titrant**) to a known volume of another solution whose concentration is unknown. The addition continues until the reaction reaches a desired level. In an acid-base titration, the desired level is when the amounts of acid and base are stoichiometrically equivalent to each other (the **equivalence point**). This can be determined using an appropriate acid-base indicator or by monitoring the pH over the course of the addition of titrant and analyzing the resulting titration curve.

A **titration curve** is a graph of pH vs. the volume of titrant added. When the titrant is a strong base, the pH will gradually increase until just before the equivalence point is reached. At the equivalence point, the pH will jump drastically and then gradually level off again as addition of titrant continues, resulting in an "S"-shaped curve (Figure 1). The number of jumps observed in the titration curve corresponds to the number of protons that can be removed from the acid being titrated and is therefore indicative of the type of acid in the unknown solution. A similar curve is observed when the titrant is a strong acid being added to an unknown solution of base; the major difference being that the pH decreases as the titrant is added.

In order to determine the concentration of the unknown acid or base, the volume of titrant required to reach the equivalence point must be determined. Because it is situated at the part of the titration curve where the concavity changes, the equivalence point can be calculated by finding the maximum point in the graph of the first derivative of the pH. The volume to reach the maximum derivative is the same as the volume of titrant needed for the equivalence point. Knowledge of the volume and concentration of the titrant as well as the initial volume of the unknown acid or base allows for the calculation of the unknown concentration.

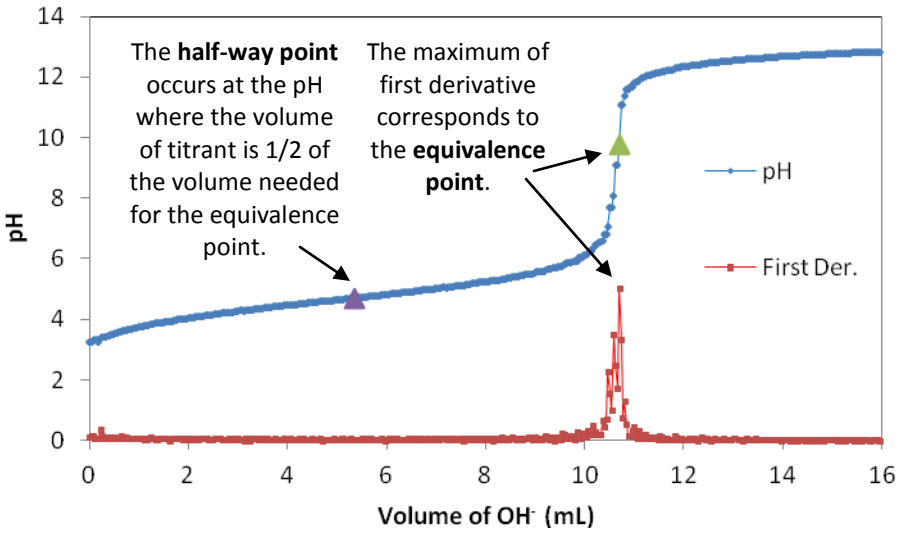

Figure 1. Sample titration curve and first derivative.

If the unknown is a weak acid or base, the corresponding K_a or K_b can be calculated from the titration curve as well in one of two ways. In the first method, the initial concentrations of all solution components are plugged into the equation for K_a or K_b. If, for example, the unknown was a weak acid,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The concentration of HA was already determined using the volume of titrant needed to reach the equivalence point. The concentrations of H_3O^+ and A^- can be calculated from the pH before the titration begins.

The second method utilizes the pH at the **half-way point**, or the pH when one-half of the volume required to reach the equivalence point has been added. As base is added to the weak acid, conjugate base is formed and a buffer system is established. The buffer system remains until the equivalence point is reached and all of the weak acid has been converted to the conjugate base. The pH of this buffer system can be described using the Henderson-Hasselbach equation

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

When the half-way point is reached, exactly half of the weak acid has been converted to its conjugate base, so [HA] = [A^-] and the log term drops out of the equation leaving

$$pH = pK_a$$

Thus, the pK_a and K_a of the weak acid can be determined from the pH at the half-way point.

PROCEDURE

⚠ ***Wear safety glasses or goggles at all times for this experiment.***
⚠ ***Avoid skin contact with the chemicals in this experiment.***
⚠ ***Never pipet by mouth.***

1. Assemble your equipment as shown in Figure 2.

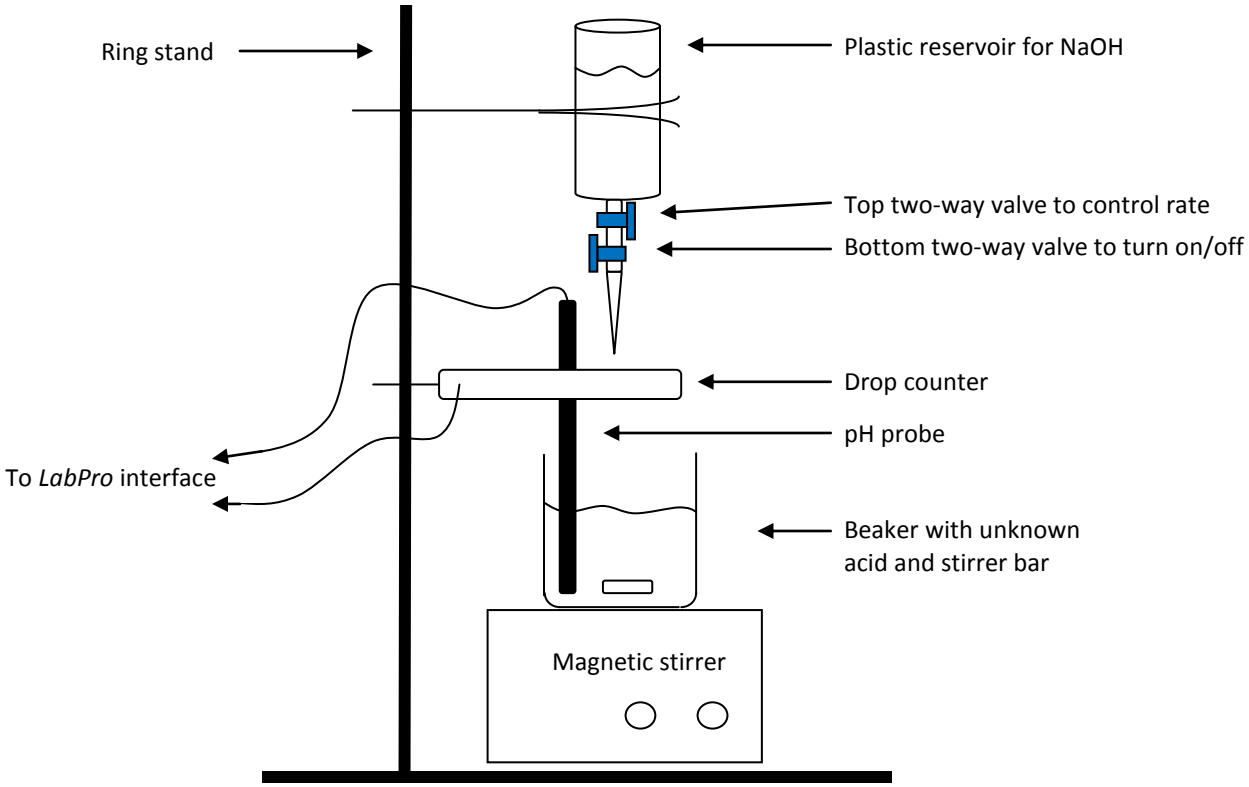

Figure 2. Experimental apparatus for the titration experiment.

2. Rinse and fill the plastic reagent reservoir with NaOH. Write down the concentration of the NaOH in your lab notebook. Remove any air bubbles from the tip of the reservoir.

3. Adjust the flow rate of the NaOH. To do this, completely open the bottom two-way valve. Then, slowly open the top valve until a rate of one drop per second is achieved. Once the desired flow rate has been obtained, **only use the bottom two-way valve** to start and stop the NaOH.

4. Launch *LoggerPro* on your computer. From the *Probes & Sensors* folder, select the Drop Counter folder, then open the *Drop Counter-pH* file.

5. Check to make sure that the drop counter is aligned properly, that the beam lens is free of debris (or dried NaOH), and that drops are being registered by *LoggerPro*.

6. To calibrate drops so that the volume of titrant is recorded in units of milliliters, place a 10 mL graduated cylinder below the slot of the drop counter. Start the automatic calibration in LoggerPro and open the bottom valve to begin releasing drops. Continue releasing drops until there are between 9 and 10 mL of NaOH in the graduated cylinder. Type the precise volume of NaOH in the graduated cylinder (to 2 decimal places) in the Volume (mL) box of the calibrate drops dialog box. **Record** the drops per mL calculated under the Volume box and click "Keep."

7. Calibrate the pH probe with the pH 4 and pH 10 buffer solutions. Adjust the precision of the pH to record to the nearest ±0.01 pH units.

8. Using a clean pipet, dispense 50.00 mL of the first acid into a 100-mL beaker. Rinse the pH probe, attach a Vernier microstirrer to the tip of the probe in a manner that allows it to spin freely, and place the probe into the beaker. Alternatively, you may add a magnetic stirrer bar to the acid solution instead of attaching the microstirrer to the probe. Turn on the magnetic stirrer.

9. Before adding any NaOH, click on the green "Collect" button. Open the bottom two-way valve to start the addition of NaOH. Data collection will begin once the first drop passes through the drop counter's slot.

10. Continue adding drop-by-drop until the graph levels off around a pH of 12 to 13.

11. Stop the data collection process by clicking the red "Stop" button. Save your data.

12. Repeat steps 8 through 11 using the other two acids.

13. Waft fumes of each acid toward your nose. Record any familiar odors. This may aid in your identification of the acids.

⚠ ***Dispose of all chemicals in the proper waste container.***

DATA ANALYSIS

1. Copy and paste your data into an *Excel* spreadsheet. In addition to the volume and pH, you will also have columns for the first derivative (d1) and second derivative (d2). You do not

need to keep the second derivative data. If you did not get the first derivative data, your instructor will demonstrate how to calculate the first derivative of your pH and volume data.

2. For each of the acids, graph pH vs. volume. Clearly label each of the graphs.

3. Based on the graphs, classify each of the acids as weak or strong **and** as monoprotic or polyprotic. Keep in mind that there is a slight delay between when a drop is added to the solution and when the pH is recorded. Thus, the pH of the equivalence point may not be exactly what is predicted, especially for strong acids.

4. For each monoprotic acid, use the first derivative to determine the volume of base required to reach the equivalence point.

5. Find the initial molarity of each of the monoprotic acids from the volume of base required to reach the equivalence point, the molarity of the base, and the volume of acid used in the titration.

6. For each weak, monoprotic acid, calculate K_a from its initial pH and initial molarity.

7. For each weak, monoprotic acid, find the pH at the halfway point. Use this pH to determine the pK_a and K_a for the acid.

8. Based on observations in the lab, identify your weak, monoprotic acid(s). Using your textbook, determine the theoretical value of K_a for the acid(s).

9. Compare each of the experimental values of K_a obtained for the weak, monoprotic acid(s) in steps 6 and 7 with the theoretical value of K_a from step 8. Calculate the percent error for each experimental value of K_a.

$$\text{percent error} = \frac{|\text{experimental} - \text{theoretical}|}{\text{theoretical}} \times 100$$

10. Which method of determining K_a gave better results? Why?

11. What were some possible sources of error in this experiment? Explain.

POSTLAB ACTIVITY

You will be turning in a lab report. It may be an individual or group report, depending on instructor preference. The report should include the title, a *detailed* procedure, results, discussion, and references. The information that you obtained from the data analysis should be

included at some point in the report. It is up to you whether it is in the results or discussion or both. (The data tables may be included in an appendix at the end.) However, remember that the report is more than just answering some questions and that it should flow smoothly and logically as you discuss the data obtained, what it signifies, and potential errors or difficulties. Lab report guidelines for how to write the procedure, results, and discussion are found at http://webs.anokaramsey.edu/chemistry/Chem1062.

Follow your instructor's directions for submitting the report. If you are submitting electronically, please submit a single file with all of the required information. Use the following convention for naming your files: *Lastname1 Lastname2 Titration Curves* for a group report or *Lastname Firstname Titration Curves* for an individual report. If you are emailing the report, use a subject line of *Chem 1062: Titration Curves Lab*.

You will need to show sample calculations in the report. For electronic submissions, you may embed data tables which contain the formulas in calculated cells. (Ask your instructor to demonstrate how to do this.) For paper submissions, you will need to show these calculations for one trial of each procedure. You will also need to show these calculations if you submit the report electronically but do NOT include formulas in embedded data tables.