Titration of a Weak Acid

Pre-Laboratory Reading: Section 16.3 in Olmstead and Williams, *General Chemistry*

Purpose: The identity and concentration of an unknown weak acid is determined by titration with standardized NaOH solution.

Introduction

The reaction of an acid and a base is a *neutralization* reaction. The technique of accurately measuring the volume of solution, such as a strong base, required to react with another reagent, such as a weak acid, is termed a *titration*. The neutralization titration in this experiment is the reaction of an unknown weak acid, HA, with NaOH:

$$HA\ (aq) + OH^-\ (aq) \rightarrow A^-\ (aq) + H_2O \qquad (1)$$

An acid-base titration can be monitored either through the use of an acid-base indicator or through the use of a pH meter. Monitoring the pH during titration of a weak acid with a strong base leads to a titration curve, Figure 1. The equivalence point occurs when enough base has been added to react completely with all of the weak acid originally in solution. As can be seen in equation (1), the predominant species in solution at the equivalence point is the conjugate base A^-. This conjugate base reacts with water to give a basic solution at the equivalence point:

$$A^-\ (aq) + H_2O \rightleftarrows HA\ (aq) + OH^-\ (aq) \qquad (2)$$

Thus, the pH is not neutral at the equivalence point but is greater than 7.0. The equivalence point can be found as the steepest portion of the titration curve as seen in Figure 1. At the equivalence point, the moles of strong base added is equal to the moles of weak acid being titrated:

$$M_tV_t = M_xV_x \qquad (3)$$

where M_t is the concentration of the titrant, V_t is the volume of added titrant, M_x is the concentration of the unknown weak acid, and V_x is the volume of the weak acid that is titrated.

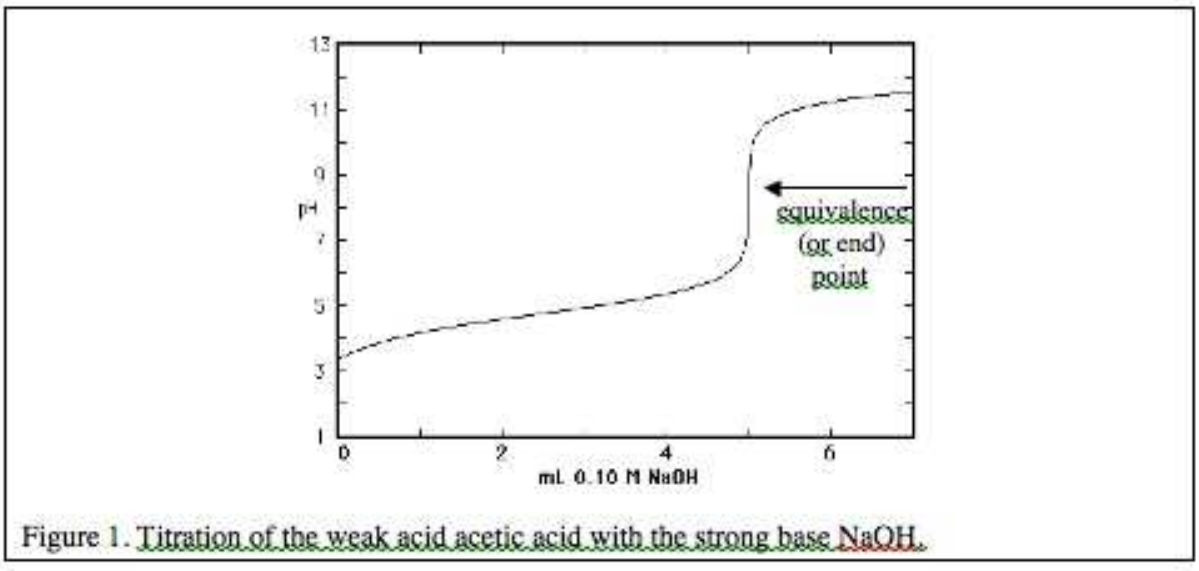


Figure 1. Titration of the weak acid acetic acid with the strong base NaOH.

The equivalence point (or the end point) of the titration can be estimated visually, as in Figure 1. A more accurate approach is to calculate the derivative (d pH/dV) of the titration curve and plot this function versus volume of added base. As shown in Figure 2, the derivative plot exhibits a clear maximum at the equivalence point.

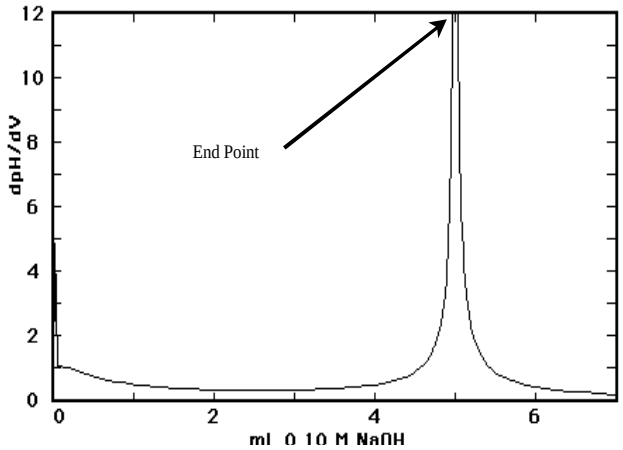


Figure 2. Derivative plot of the acetic acid titration shown in Figure 1.

The derivative of the titration curve is approximated by the finite differences:

$$\frac{d\,pH}{dV} \cong \frac{\Delta pH}{\Delta V} = \frac{pH_2 - pH_1}{V_2 - V_1} \qquad (4)$$

where pH_1 is the measured pH at added volume V_1 and pH_2 is the measured pH at added volume V_2. The derivative is calculated with successive pairs of data points, Table 1.

Table 1: Calculation of the derivative of an example titration curve.

V (mL) NaOH	pH	ΔpH/ΔV	
10.32	3.86	0.5	
10.44	3.92	0.83	
10.56	4.02	1.25	
10.68	4.17	2.58	*(equivalence point)*
10.80	4.48	1.58	
10.92	4.67		

Another significant volume during a titration is when the number of moles of acid (HA) remaining is exactly equal to the number of moles of conjugate base (A^-) produced. This point is called the "half-equivalence point" because it occurs when exactly half the weak acid has been titrated. From the Henderson-Hasselbalch equation (5), the half-equivalence point gives $pH = pK_a$.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (5)$$

Preparation of Standardized 0.10 M NaOH

A solution of NaOH with accurately determined concentration is used as the titrant in this experiment. Solutions of NaOH readily absorb CO_2 from the atmosphere:

$$CO_2\ (g) + 2\ OH^-\ (aq) \rightarrow CO_3^{2-} + H_2O\ (l) \qquad (6)$$

This reaction changes the concentration of the hydroxide, so special precautions are necessary to minimize the effect. The formation of CO_3^{2-} ions in the solution also interferes with the equivalence point, by decreasing the slope of the titration curve at the equivalence point. Solutions must be kept covered while in use and tightly stoppered in storage. Because some CO_2 absorption by the solution can occur in an open burette, it is best to cover the top of the burette with a plastic cap. The absorption of CO_2 must also be avoided when preparing the solution.

Ordinary deionized water is often supersaturated with CO_2, which is absorbed from the air. So-called "equilibrium water" is prepared by boiling deionized water a few minutes to expel excess CO_2 and then cooling to room temperature. The "equilibrium water" is used to prepare NaOH solutions. Solutions of 50% NaOH in water are commercially available. The 50% NaOH solutions are so concentrated that any Na_2CO_3 impurity is virtually insoluble and settles to the bottom of the container. From this concentrated solution, the clear liquid is decanted and diluted with "equilibrium water" to produce a roughly 0.10 M NaOH solution. This solution is then accurately standardized by titration against a primary standard acid.

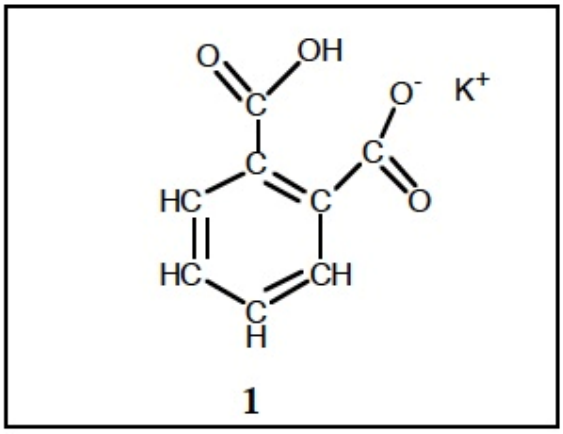
Solutions of sodium hydroxide used for these titrations slowly attack glass containers and cause glass stoppers to become stuck. Thus, sodium hydroxide solutions are usually stored in polyethylene bottles. Also, burettes must be thoroughly cleaned immediately after use.

Primary Standards

Laboratory work frequently involves the use of a standardized solution, which is a solution of accurately known concentration. You will use a standardized solution of NaOH for the titration of a weak acid. The concentration is roughly 0.10 M, but the concentration will be determined to better than three-significant figures. The concentration of the NaOH solution is determined by titration against a primary standard. For a substance to be a primary standard, the following criteria should be met. A primary standard substance should be:

- Available in very pure form
- Reasonably soluble
- Stable in the pure form and in solution
- Nonhygroscopic (doesn't absorb water from the air) and easily dried
- A compound with a reasonably high formula weight

Few substances meet these criteria, so the number of useful primary standards is quite limited. Two common primary standard bases are pure sodium carbonate and borax. Some primary standard acids are potassium hydrogen phthalate (KHP), oxalic acid dihydrate, sulfamic acid, and benzoic acid. The primary standard acid in this experiment is KHP (**1**), which is the monoprotic potassium salt of a diprotic carboxylic acid, $KHC_8H_4O_4$.



The accurate concentration of your sodium hydroxide solution is determined by titration of accurately known masses of KHP. The reaction for the standardization titration is:

$$KHC_8H_4O_4\ (aq) + NaOH\ (aq) \rightarrow KNaC_8H_4O_4\ (aq) + H_2O(l) \qquad (7)$$

To determine the exact concentration of the sodium hydroxide solution, the number of moles of sodium hydroxide that react completely with the known number of moles of KHP must be calculated. A small amount of indicator solution containing phenolphthalein is added to each standard acid solution, which signals the endpoint of the titration by changing color. Phenolphthalein is colorless in the acid solution but changes to pink at the endpoint of the titration. The number of moles of KHP is equal to the number of moles of added base at the equivalence point: M_tV_t = moles KHP, where M_t is the concentration of the titrant and V_t is the volume of added titrant. You then use this standardized NaOH solution for the titration of the weak acid in Part B of this lab. A cartoon of the procedure that you will follow is given in Figure 3.

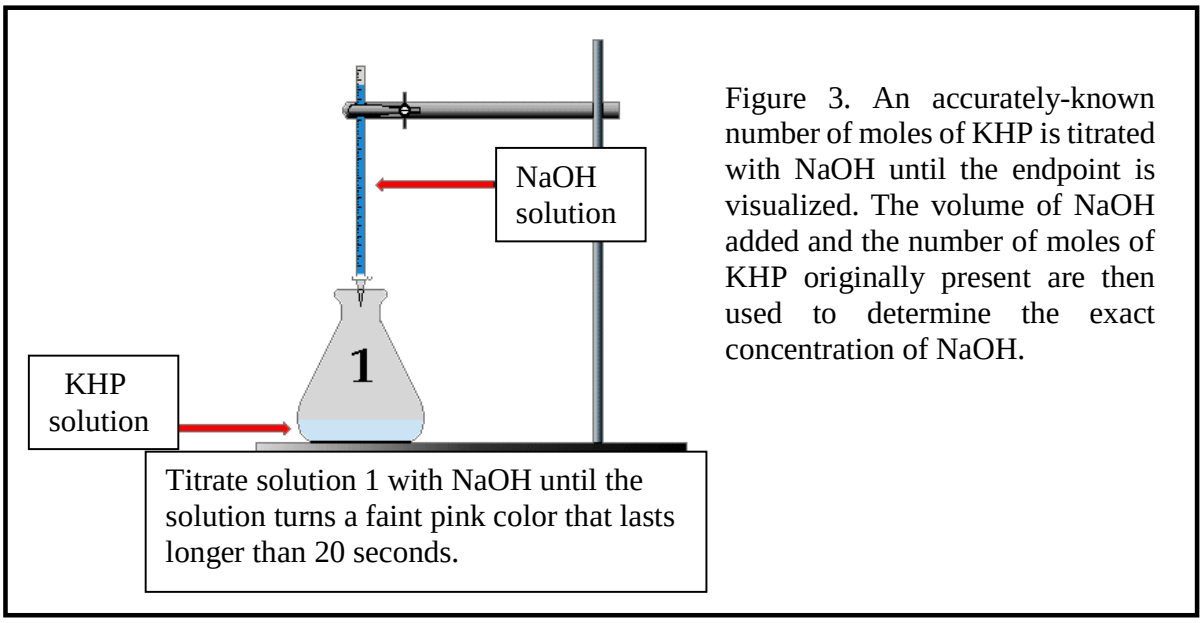


Figure 3. An accurately-known number of moles of KHP is titrated with NaOH until the endpoint is visualized. The volume of NaOH added and the number of moles of KHP originally present are then used to determine the exact concentration of NaOH.

Summary of Experiment

- Prepare an approximately 0.10 M solution of NaOH from 50% concentrated NaOH and "equilibrium water."
- Standardize the solution of NaOH with the primary standard KHP (**1**) to determine the exact concentration of NaOH.
- Use the standardized NaOH solution to titrate the unknown weak acid to determine its identity and concentration.
- Next week you will investigate the properties of buffers and then use your weak acid and NaOH to produce a buffer.

Experimental Procedure

Perform at least *three standardization titrations of ~0.10 M NaOH*. For this laboratory exercise, you should obtain a relative standard deviation of the concentrations from the three titrations less than 1%. If the relative standard deviation is too high, more titration trials must be performed to achieve less than 1% relative standard deviation.

Notes: If you have an *obvious* experimental error and need to repeat a trial, you may reject the trial. For example *obvious* errors include if you know that you have spilled some KHP or added too much NaOH, beyond the end-point. However, if you simply have large errors and are doing multiple titrations, you must include *all* the titrations in the data analysis. If you think there is an outlier, a quality statistical test (Q-test) can be performed to identity if it is a valid data point or if the data point can be rejected (check with your lab instructor to do a Q-test).

Part A- Standardization of NaOH of Unknown Concentration

1. Prepare one liter of 0.10 M NaOH using 50% concentrated NaOH and "equilibrium water" in a 1-L volumetric flask. The 50% NaOH solution can be added using a graduated cylinder. Use the volume of base that you calculated in your pre-lab exercise. Invert the 1-L volumetric flask at least 12 times to ensure complete mixing. Transfer the solution to a plastic bottle for storage.
2. Carefully transfer about 0.7 to 0.9 grams of dry KHP (potassium hydrogen phthalate) into a tared, clean 200- or 250- mL Erlenmeyer flask. Record the weight to the nearest 0.1 milligram. Prepare three such samples.
3. Dissolve each sample in about 30-50 mL of deionized water. Add eight drops of phenolphthalein indicator solution to the contents of each flask.
4. Clean your burette, and then rinse with three 5-mL portions of NaOH. Make sure that the rinse solution comes in contact with the entire inner surface of the burette and the tip of the burette.
5. Close the burette stopcock and fill the burette with NaOH to above the top calibration mark on the burette. Lower the meniscus of the solution until it reaches a calibrated portion of the burette. Make certain that the burette tip is filled with the solution. Record the initial burette reading to the nearest 0.01 mL, using a burette reading card. A burette reading card is a piece of white paper with a darkened stripe that you place behind the burette to better visualize the meniscus. Starting below the meniscus, the burette reading card is raised until the reflection of the dark stripe highlights the meniscus.

6. Place one of the Erlenmeyer flasks containing the KHP solution under the burette on top of a stir plate, add a magnetic stirrer, and lower the burette tip until it is well into the mouth of the flask, as shown in Figure 3.
7. Turn on the stirrer (NOT the heating element) so that it is gently mixing and add the NaOH slowly to the solution with mixing.
8. As the titration progresses, the approach of the endpoint will be signaled by brief flashes of pink. At this point, add the NaOH drop-wise to the KHP solution. As the endpoint is approached more closely, these temporary flashes of color will persist longer and fractional parts of a drop of NaOH should be added. Fractions of a drop may be added by allowing a droplet of NaOH to begin to form on the burette tip. After touching the burette tip to the inner surface of the flask, wash down the inner surface of the flask with a stream of distilled water from a wash bottle. The titration is complete when the indicator exhibits a pink color that persists for several seconds. Wait for about 15-20 seconds to allow any solution on the inner wall of the burette to drain down to the meniscus and then read the final burette volume to the nearest 0.01 mL.
9. Repeat the titration with the other 2 samples of KHP.
10. Perform the following calculations to determine whether you need to do another titration.
    - In Excel, calculate the concentration (mol/L) of NaOH for each of your 3 trials.
    - Calculate the average concentration of NaOH, the standard deviation of your data, and the relative standard deviation. If after all of these measures, you are still not within 1%, you must perform a couple more trials to obtain better than 1% error. You must check with your instructor to ensure you have successfully completed the titrations. Once your instructor checks your work, you may continue.
11. When all of the titrations are completed, drain and *thoroughly rinse* the burette with deionized water and leave it hanging upside down on the burette stand. Thoroughly wash all other glassware used in this experiment. **Label your standardized NaOH with your name, lab section, and standardized Molarity. Proceed to part B.**

Part B- Titration of Unknown Weak Acids with Standardized NaOH

Perform two replicate titrations of an unknown weak acid with the NaOH solution that you just standardized in Part A. You will determine the pK_a of this acid by the half-equivalence point of the titration and the concentration of the acid by the equivalence point.

You will use an automated titration system to perform the titrations. In this system, a precision pump replaces the burette used in traditional titrations. A computer controls the pump to deliver titrant to the reaction vessel. A pH meter is used to measure the pH, and these data are recorded by the computer for display and analysis.

1. Follow the directions on the Vernier LabPro Instructions to calibrate your pump and pH probe.
2. Perform the titration as described in the Vernier LabPro Instructions.
3. Repeat the titration of the unknown weak acid.

4. Analyze your data as described on the Vernier LabPro Instructions. The replicates should agree to 1% or better.
5. Make sure that you keep your NaOH for next week.

Data that should be included in your notebook:

Amount of KHP, initial volumes, final volumes for the NaOH standardization titration.
Standardized NaOH molarity, recorded values for data analysis.
Excel tables, graphs, figures, or charts.
Vernier Titration Graph
Thorough observations and analyses of all your experiments.

Report:

You produce your own report form for this laboratory. The report should contain:

1. Introduction: Give a brief introduction. In the introduction state the purpose of the experiment and the principle means that you are going to use to achieve that purpose. The introduction should be just two sentences. You should not discuss the experimental procedure nor the calculations that will be necessary in the Introduction.

2. Theory: In no more than four (4) sentences, explain how the identity of the unknown acid is determined, give the Henderson-Hasselbalch equation, identify each variable in words, and explain how the pK_a was determined.

3. Procedure: Report that the concentration of the titrant was determined by titration against primary standard potassium hydrogen phthalate (KHP). Name the indicator for the visual detection of the end point in the standardization titration. Report that the weak acid was titrated versus the standardized NaOH using an automated buret. Reference the instructions in this write-up. Give the initial volume of the weak acid that you used in your titrations. List any changes that were made to the written procedure in the lab write-up (there will probably be none). State the manufacturer and model of the data acquisition interface.

4. Results: Provide a table containing the results of each standardization titration that you completed; include the mass of KHP, the volume of titrant to reach the end-point, and the calculated NaOH concentration. Include all titrations. Indicate any titrations that were excluded because of student error or by Q-test. Give the average concentration of your standardized base and the standard deviation of the trials. Report the average volume delivered in each pulse of the automated buret and use the range as the uncertainty in the form "the average volume per pulse was average ± range." Provide plots of each titration curve for the weak acid titrations. Give the volume of weak acid titrated, the volume at the equivalence point, and the corresponding weak acid concentration in tabular form. Report the average and use the range as the uncertainty in the form "the average concentration of the weak acid was average ± range." Report the pK_a for both titrations, the average pK_a, and the range (using the format average ± range). Make sure that each table and figure have captions and that each table or figure is referenced in the body of the text. The captions should summarize the content of the table or figure. The captions on the figures can be hand written. Report all values with appropriate units.

5. Discussion:

(a). Purpose accomplished: Restate the purpose as a completed goal (this sentence is just the introductory sentence for the first paragraph of the discussion).

(b). Final Results: State the experimental pK_a, identity, and concentration of your weak acid.

(c). Factors that influenced the precision and accuracy of the data:

i. Give the measurement that is the predominant source of random error for the concentration of the weak acid: Which experimental measurement, the concentration of the standardized NaOH, the volume of the weak acid, the volume delivered by the automated buret, or the pH gives the largest contribution to the random error in the final weak acid concentration?

ii. Give a source of systematic error in the concentration of the weak acid: Do you have evidence for a systematic error? Give a suggestion for a source of systematic error. Does this systematic error make the final concentration too low or too high? Student mistakes are not systematic errors, they are just mistakes. Systematic errors are consistent for each trial.

(d). Answer the following question in your discussion: Calculate the theoretical pH at the equivalence point using the pK_a and concentration of your weak acid. Compare this theoretical value to the experimentally determined value of the pH at the equivalence point.

6. Literature Cited: Give the citation for this lab write-up.

Attach copies of your two weak acid titration curves as Figures.

Checklist:

Use complete sentences and provide the proper number of significant figures and units.
All Figures and Tables must have captions.
Refer by number to each figure and table in the body of the text or your report.
Acknowledge any data that were not taken by you and your partner (if you had a partner).
Captions start with Figure # or Table # and then a concise description of the contents.
You can write the captions by hand in black pen on attached sheets.
Answer all the questions in the Discussion section of the write-up.