Acid–Base Titrations

Introduction

A common question chemists have to answer is how much of something is present in a sample or a product. If the product contains an acid or base, this question is usually answered by a titration. Acid–base titrations can be used to measure the concentration of an acid or base in solution, to calculate the formula (molar) mass of an unknown acid or base, and to determine the equilibrium constant of a weak acid (K_a) or weak base (K_b).

Concepts

- Weak acid
- Equivalent mass
- Equilibrium constant, K_a
- Equivalence point
- Titration curve

Background

Titration is a method of *volumetric analysis*—the use of volume measurements to analyze an unknown. In acid–base chemistry, titration is most often used to analyze the amount of acid or base in a sample or solution. Consider a solution containing an unknown amount of hydrochloric acid. In a titration experiment, a known volume of the hydrochloric acid solution would be "titrated" by slowly adding dropwise a *standard* solution of a strong base such as sodium hydroxide. (A standard solution is one whose concentration is accurately known.) The *titrant,* sodium hydroxide in this case, reacts with and consumes the acid via a neutralization reaction (Equation 1). The exact volume of base needed to react completely with the acid is measured. This is called the equivalence point of the titration—the point at which stoichiometric amounts of the acid and base have combined.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad \textit{Equation 1}$$

Knowing the exact concentration and volume added of the titrant gives the number of moles of sodium hydroxide. The latter, in turn, is related by stoichiometry to the number of moles of hydrochloric acid initially present in the unknown.

Indicators are usually added to acid–base titrations to detect the equivalence point. The endpoint of the titration is the point at which the indicator changes color and signals that the equivalence point has indeed been reached. For example, in the case of the neutralization reaction shown in Equation 1, the pH of the solution would be acidic (< 7) before the equivalence point and basic (> 7) after the equivalence point. The pH at the equivalence point should be exactly 7, corresponding to the neutral products (sodium chloride and water). An indicator that changes color around pH 7 is therefore a suitable indicator for the titration of a strong acid with a strong base.

The progress of an acid–base titration can also be followed by measuring the pH of the solution being analyzed as a function of the volume of titrant added. A plot of the resulting data is called a pH curve or titration curve. Titration curves allow a precise determination of the equivalence point of the titration without the use of an indicator.

In this experiment the equivalent mass of an unknown acid will be determined by titration. The equivalent mass is defined as the mass of the acid that supplies one mole of hydrogen ions. The acid, a solid crystalline substance, is weighed out and titrated with a standard solution of sodium hydroxide. From the moles of base used and the mass of the acid, the equivalent mass of the acid is calculated. The acid is then titrated a second time with the standard solution of sodium hydroxide and the course of the titration is followed using a pH meter. A titration curve is constructed by graphing pH on the vertical (y) axis versus the volume of NaOH on the horizontal (x) axis. The value of the equilibrium constant (K_a) for the dissociation of the weak acid is determined by analyzing the titration curve.

An acid may contain one or more ionizable hydrogen atoms in the molecule. The equivalent mass of an acid is the mass that provides one mole of ionizable hydrogen ions. It can be calculated from the molar mass divided by the number of ionizable hydrogen atoms in a molecule. For example, hydrochloric acid, HCl, contains one ionizable hydrogen atom—the molar mass is 36.45 g/mole, and its equivalent mass is also 36.45 g/mole. Sulfuric acid, H_2SO_4, contains 2 ionizable hydrogen atoms—the molar mass of H_2SO_4 is 98.07 g/mole but its equivalent mass is 49.04 g/mole. Thus, either 36.45 g of HCl or 49.04 g of H_2SO_4 would supply one mole of H^+ ions when dissolved in water.

The equivalent mass is determined by titrating an acid with a standard solution of NaOH. Since one mole of NaOH reacts with one mole of hydrogen ion, at the equivalence point the following relation holds:

$$V_b \times M_b = \text{moles base} = \text{moles } H^+ \qquad \textit{Equation 2}$$

$$EM_a = \frac{\text{grams acid}}{\text{moles } H^+} \qquad \textit{Equation 3}$$

where V_b is the volume of base added at the endpoint, M_b is the molarity of base, grams acid is the mass of acid used, and EM_a is the equivalent mass of the acid.

The concentration of the NaOH solution must be accurately known. To "standardize" the NaOH, that is, to find its exact molarity, the NaOH is titrated against a solid acid, potassium hydrogen phthalate (abbreviated KHP). The KHP is chosen because it is easily dried and weighed and has a relatively high equivalent mass. The formula of KHP is $KHC_8H_4O_4$ (see Figure 1).

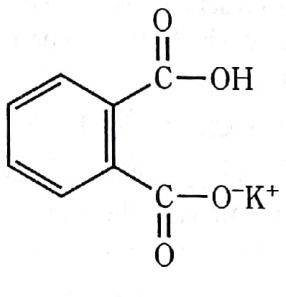

Figure 1. Structure of KHP

KHP contains one ionizable H^+. The titration is followed using phenolphthalein as an indicator.

$$HA(aq) + OH^-(aq) \rightleftarrows A^-(aq) + H_2O(l) \qquad \textit{Equation 4}$$

A graph of pH versus volume of NaOH added (see Figure 2) for the titration of a weak acid with NaOH is obtained by carefully following the titration with a pH meter. There is a significant change in pH in the vicinity of the equivalence point. Note that when a weak acid is titrated with a strong base, the equivalence point is ***not*** at pH 7, but is on the basic side. The value of the equilibrium constant for the dissociation of the acid is determined from a titration curve by considering the pH when the acid is "half-neutralized."

If the dissociation of the acid is represented as:

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad \textit{Equation 5}$$

the equilibrium constant expression is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \textit{Equation 6}$$

When the acid is half neutralized, $[HA] = [A^-]$, these terms cancel in the above equation, and $K_a = [H_3O^+]$. Therefore, when the acid is half-neutralized, the pH = pK_a.

The point where pH is equal to pK_a can be determined from the graph. Refer to Figure 2.

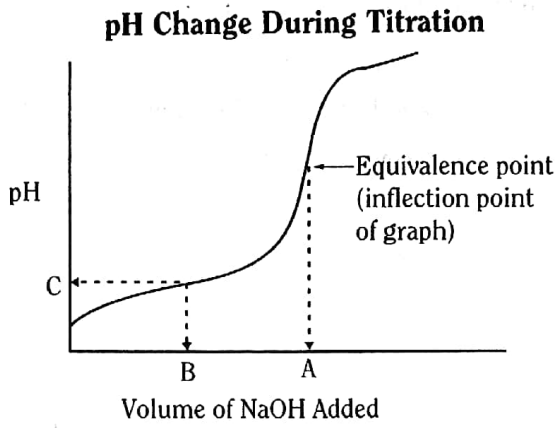

Figure 2. pH during titration of a monoprotic weak acid with sodium hydroxide

A = Volume NaOH at equivalence point

B = ½ A = the volume of NaOH required to neutralize one-half the acid

C = pH when the acid is half neutralized = pK_a

Experiment Overview

The purpose of this experiment is to standardize a sodium hydroxide solution and use the standard solution to titrate an unknown solid acid. The equivalent mass of the solid acid will be determined from the volume of sodium hydroxide added at the equivalence point. The equilibrium constant, K_a, of the solid acid will be calculated from the titration curve obtained by plotting the pH of the solution versus the volume of sodium hydroxide added.

Pre-Lab Questions *(Use a separate sheet of paper to answer the following questions.)*

1. Calculate the equivalent mass of each of the following acids.

   a. $HC_2H_3O_2$ *b.* $KHCO_3$ *c.* H_2SO_3

2. Calculate the molarity of a solution of sodium hydroxide, NaOH, if 23.64 mL of this solution is needed to neutralize 0.5632 g of potassium hydrogen phthalate.

3. It is found that 24.68 mL of 0.1165 M NaOH is needed to titrate 0.2931 g of an unknown acid to the phenolphthalein end point. Calculate the equivalent mass of the acid.

4. The following data was collected for the titration of 0.145 g of a weak acid with 0.100 M NaOH as the titrant:

Volume NaOH added, mL	0.00	5.00	10.00	12.50	15.00	20.00	24.00	24.90	25.00	26.00	30.00
pH	2.88	4.15	4.58	4.76	4.93	5.36	6.14	7.15	8.73	11.29	11.96

   a. Use graph paper to graph the data. Place pH on the vertical axis and volume of NaOH on the horizontal axis.

   b. What is the pH at the equivalence point?

   c. Give the K_a and pK_a value of the acid. Explain.

d. The following acid–base indicators are available to follow the titration. Which of them would be most appropriate for signaling the endpoint of the titration? Explain.

	Color Change		
Indicator	**Acid Form**	**Base Form**	**pH Transition Interval**
Bromphenol blue	yellow	blue	3.0–5.0
Bromthymol blue	yellow	blue	6.0–7.6
Thymol blue	yellow	blue	8.0–9.6

Materials

Chemicals

Buffer solution, pH 7.0, 50 mL

Phenolphthalein indicator solution, 1.0%, 1 mL

Potassium hydrogen phthalate, $KHC_8H_4O_4$, 2 g

Sodium hydroxide solution, NaOH, 0.1 M, 150 mL

Unknown weak acid, 1.5 g

Water, distilled or deionized

Equipment

Balance, (0.001- or 0.0001-g precision)

Beaker, 250-mL

Buret, 50-mL

Desiccator

Erlenmeyer flask, 125-mL or 250-mL

Funnel

Magnetic stirrer and stir bar

Oven, drying

pH sensor or pH meter

Ring stand and buret clamp

Wash bottle with distilled or deionized water

Weighing dishes, 2

Safety Precautions

Dilute sodium hydroxide solutions are irritating to skin and eyes. Phenolphthalein is an alcohol-based solution and is flammable. It is moderately toxic by ingestion. Keep away from flames and other ignition sources. Avoid contact of all chemicals with eyes and skin and wash hands thoroughly with soap and water before leaving the laboratory. Wear chemical splash goggles and chemical-resistant gloves and apron.

Procedure

Part 1. Standardization of a Sodium Hydroxide Solution

1. Obtain a sample of potassium hydrogen phthalate (KHP) that has been previously dried in an oven and stored in a desiccator.
2. On an analytical balance, accurately weigh 0.4 to 0.6 grams of KHP in a previously tared weighing dish. Record the precise mass of KHP in Data Table 1.
3. Transfer the KHP into an Erlenmeyer flask—pour the solid through a funnel into the flask. Use water from a wash bottle to rinse all of the remaining solid from the weighing dish or the funnel into the flask as well.
4. Add about 40 mL of distilled or deionized water to the Erlenmeyer flask and swirl until all the KHP is dissolved.
5. Obtain about 75 mL of the sodium hydroxide, NaOH, solution.

6. Clean a 50-mL buret, then rinse it with three small portions (about 7 mL each) of the NaOH solution.
7. Fill the buret to above the zero mark with the NaOH solution.
8. Open the buret stopcock to allow any air bubbles to escape from the tip. Close the stopcock when the liquid level is between the 0- and 10-mL marks.
9. Measure the precise volume of the solution in the buret and record this value in Data Table 1 as the "initial volume." *Note:* Volumes are read from the top down in a buret. Always read from the bottom of the meniscus, remembering to include the appropriate number of significant figures. (See Figure 3.)

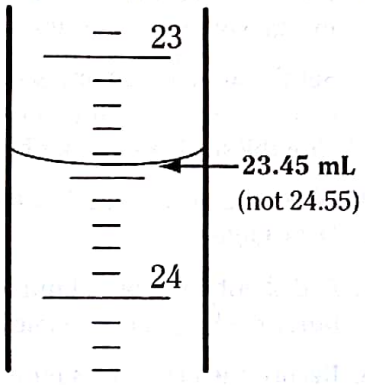

Figure 3. How to read a buret volume.

10. Position the buret over the Erlenmeyer flask so that the tip of the buret is within the flask but at least 2 cm above the liquid surface.
11. Add three drops of phenolphthalein solution to the KHP solution in the flask.
12. Begin the titration by adding 1.0 mL of the NaOH solution to the Erlenmeyer flask. Close the buret stopcock and swirl the flask to mix the contents.
13. Repeat step 12 until 15 mL of the NaOH solution have been added to the flask. Be sure to continuously swirl the flask.
14. Reduce the incremental volumes of NaOH solution to 0.5 mL until the pink color starts to persist. Reduce the rate of addition of NaOH solution to drop by drop until the pink color persists for 15 seconds. Remember to constantly swirl the flask and to rinse the walls of the flask with distilled or deionized water before the endpoint is reached.
15. Measure the volume of NaOH remaining in the buret, estimating to the nearest 0.01 mL. Record this value as the "final volume" in Data Table 1.
16. Repeat the standardization titration two more times. Rinse the Erlenmeyer flask thoroughly between trials with distilled or deionized water.

Part 2. Determination of the Equivalent Mass of an Unknown Acid

1. Weigh about 0.3–0.4 g of a sample of the unknown acid in a weighing dish using an analytical balance. Record the precise mass in Data Table 2.
2. Dissolve the unknown acid in 40 mL of distilled or deionized water and titrate to the phenolphthalein endpoint as above in steps 5 through 16.
3. Record the initial and final volumes of NaOH solution in Data Table 2.
4. Repeat one more time. Choose a mass for the second sample so that the volume of NaOH needed will be about 45 mL if using a 50-mL buret, or about 22 mL if using a 25-mL buret.

Part 3. Determination of the pK_a of the Unknown Acid

1. Set up a pH meter and electrode. Calibrate the pH meter using a pH 7.0 buffer solution. Rinse the electrode well with distilled or deionized water.
2. Using the analytical balance, weigh a sample of the unknown acid that will require approximately 20 mL of titrant.
3. Dissolve the acid in approximately 100 mL distilled or deionized water in a 250-mL beaker.

4. Fill the buret with the standardized NaOH solution used in Part 1. Record the initital volume as the "initial buret reading" in Data Table 3.
5. Set the beaker containing the unknown acid solution on a magnetic stirrer. Clamp the pH electrode so it is submerged in the acid solution (Figure 4). Be sure the stir bar does not hit the electrode. Set the stir bar gently spinning.
6. When the pH reading has stabilized, record the initial pH of the solution in Data Table 3.
7. Add about 1 mL of sodium hydroxide solution to the beaker. Record the exact buret reading in Data Table 3.
8. Record the pH of the solution next to the buret reading in Data Table 3.
9. Add another 1-mL increment of sodium hydroxide solution. Record both the buret reading and the pH in Data Table 3.
10. Continue adding sodium hydroxide in 1-mL portions. Record both the buret reading and the pH after each addition.

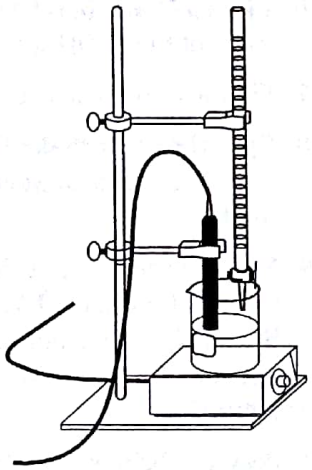

Figure 4. Setup.

11. When the pH begins to increase by more than 0.3 pH units after 1 mL of NaOH is added, decrease the amount of sodium hydroxide added to about 0.2 mL.
12. Continue adding sodium hydroxide in about 0.2-mL increments. Record both the buret reading and the pH after each addition.
13. When the pH change is again about 0.3 pH units, resume adding the sodium hydroxide in 1-mL increments. Continue to record both the buret reading and the pH after each addition.
14. Stop the titration when the pH of the solution is greater than 12. Record the final volume of solution in the buret and the final pH.
15. Graph the data, with pH on the vertical (y) axis and volume NaOH on the horizontal (x) axis. Make the graph large enough to reflect the care taken with the pH and volume measurements.

Disposal and Cleanup

Your teacher will provide disposal and cleanup instructions.

Data Tables

Data Table 1

	Trial 1	Trial 2	Trial 3
Mass KHP, g			
Final volume, mL			
Initial volume, mL			
Volume of NaOH added, mL			

Molarity NaOH (Average) _____ M

Data Table 2

	Trial 1	Trial 2
Mass of unknown acid, g		
Final volume, mL		
Initial volume, mL		
Volume of NaOH added, mL		

Equivalent Mass (Average) _____ g/mol

Data Table 3

Mass of unknown acid	
Standard NaOH concentration	
Initial buret reading	
Initial pH	

Buret reading (mL)	pH	Buret Reading (Con't.)	pH

Post-Lab Calculations and Analysis

(Use a separate sheet of paper to answer the following questions.)

1. From the standardization data in Part 1, calculate the molarity of the sodium hydroxide solution for each trial. Average the values and enter the average in Data Table 1.
2. From the equivalent mass data in Part 2, calculate the equivalent mass of the unknown acid for each trial. Average the values and enter the average in Data Table 2.
3. Why is the answer obtained in Question #2 the equivalent mass of the acid rather than the molar mass?
4. Why must the KHP and the acid samples be dried? If they are not dried, would the calculated molarity of the NaOH be higher or lower than the actual value? Explain.
5. Why must NaOH be standardized? Why can't an exact solution of NaOH be prepared?
6. From the titration curve of pH versus volume of NaOH added in Part 3, determine the pK_a of the unknown acid. Calculate the value of K_a for the unknown acid.
7. Why is the equivalence point in the titration of the unknown acid with sodium hydroxide not at pH 7?