

16B. An Acid–Base Titration Curve

Introduction

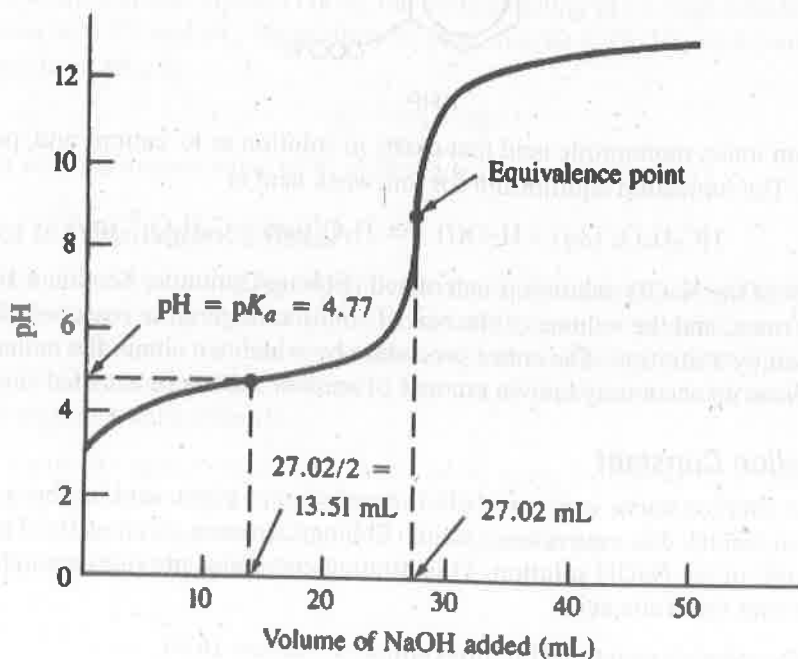
Acid–base titration curves (Ebbing/Gammon, Section 16.7) are graphs that show the successive pH values that occur during the titration of a base with an acid or of an acid with a base. A typical titration curve for the titration of an acid with a base can be found in Figure 16B.1.

The general purpose of a titration is to determine the amount of a particular substance in a sample (Ebbing/Gammon, Section 4.10). An indicator is usually employed to show when a stoichiometric amount of another substance has been added from a buret. An example appears in the experiment “How Much Acetic Acid Is in Vinegar?” The general purpose can also be achieved with a titration curve, but the procedure for obtaining the required data is much slower than one employing an indicator. However, a titration curve will enable an analyst to choose an indicator for subsequent titrations of similar samples with the same reagent.

When a weak acid is titrated with a strong base, or a weak base is titrated with a strong acid, the titration curve is unique for the weak acid or the weak base. As a consequence, there is another use for a titration curve: It can be used to determine the ionization constants for weak acids and weak bases.

FIGURE 16B.1

An acid–base titration curve resulting from the titration of a solution of acetic acid with a 0.101 M solution of NaOH. The equivalence point occurs after the addition of 27.02 mL of the NaOH solution.



Purpose

You will construct an acid–base titration curve on a piece of graph paper. If your laboratory instructor wishes, you can also use materials available online at the student website to see the shape of the

titration curve. However, you will not be able to do any calculations from this curve. Calculation materials can be found at

<http://college.hmco.com/PIC/ebbing9e>

You will accumulate the data that you will use for these graphs during the titration of a weak acid, potassium hydrogen phthalate, with a solution of sodium hydroxide. The titration curve will be used to achieve two goals: standardizing the solution of sodium hydroxide, and illustrating the method for obtaining the acid-ionization constant for the weak acid.

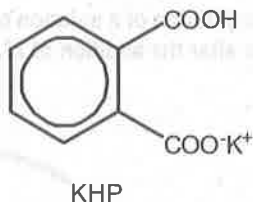
Standardization of a NaOH Solution

You cannot prepare a solution of sodium hydroxide with an accurately known concentration by adding a known mass of NaOH to an appropriate quantity of water. The hygroscopic (readily taking and retaining water from air) nature of solid NaOH makes measuring the mass of a sample of this substance with accuracy virtually impossible. A significant fraction of the measured mass would be due to an unknown quantity of water adsorbed from the air.

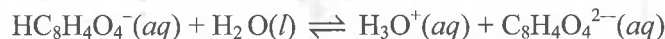
Another approach is available, however; the reaction of NaOH with a known quantity of an acid can be used to determine the molarity of the NaOH solution. Potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, abbreviated here as KHP), a weak acid, is generally used for this purpose. The structure of KHP is shown in Figure 16B.2.

FIGURE 16B.2

The molecular structure of potassium hydrogen phthalate (KHP).



This substance is an ionic, monoprotic acid that exists in solution as K^+ cations and, primarily, $\text{HC}_8\text{H}_4\text{O}_4^-$ anions. The ionization equilibrium for this weak acid is



The exact molarity of the NaOH solution is calculated (Ebbing/Gammon, Section 4.10) from the mass of KHP, its molar mass, and the volume of the NaOH solution required to react completely with the KHP, as determined by a titration. The entire procedure by which we obtain the molarity of a solution of one substance from an accurately known amount of another substance is called *standardization*.

The Acid-Ionization Constant

Again consider the titration curve in Figure 16B.1. A solution of acetic acid has been titrated with a 0.101 M solution of NaOH. The equivalence point (Ebbing/Gammon, Section 16.7) occurs after the addition of 27.02 mL of the NaOH solution. This titration curve also provides enough data to determine the ionization constant for acetic acid.

The Henderson-Hasselbalch equation (Ebbing/Gammon, Section 16.6),

$$\text{pH} = \text{pK} + \log \frac{[\text{base}]}{[\text{acid}]}$$

plays a crucial role in finding the ionization constant. Although this equation can be used to calculate the pH of a buffer (Ebbing/Gammon, Section 16.6), it can also be used to calculate the pH of a point on the titration curve if that point lies within a particular range. The point must lie after the initial point (where none of the NaOH solution has been added) and the equivalence point. As you read about applying this equation, remember that K_a is the ionization constant of the weak acid (acetic acid in this example); that [acid] is the concentration of the weak acid; and that [base] is the concentration of the weak acid's conjugate base.

During the titration, [acid] will be decreasing because the weak acid is reacting with each increment of NaOH. And since the conjugate base of the weak acid is the product of this reaction, [base] will be increasing. These quantities, [acid] and [base], must become equal at some point. The equality will occur halfway to the equivalence point. At this halfway point, half of the NaOH required to react completely with the weak acid will have been added. As a result, half of the weak acid will have been converted to its conjugate base, and so the molar quantities of these substances will be identical. The halfway point in Figure 16B.1 occurs at $27.02/2$, or 13.51 mL. The equality of [acid] and [base] allows us to write

$$\begin{aligned} [\text{acid}] &= [\text{base}] \\ \log \frac{[\text{base}]}{[\text{acid}]} &= \log 1 = 0 \end{aligned}$$

The Henderson-Hasselbalch equation reduces to

$$\text{pH} = \text{p}K_a$$

at the halfway point.

After 13.51 mL is located on the titration curve, the corresponding pH is read directly from the graph. This pH turns out to be 4.77, and $\text{p}K_a$ for acetic acid must also be 4.77. The acid-ionization constant, which is calculated from $\text{p}K_a$, is

$$K_a = 1.7 \times 10^{-5}$$

This result agrees with the known value of K_a (Ebbing/Gammon, Table 16.1).

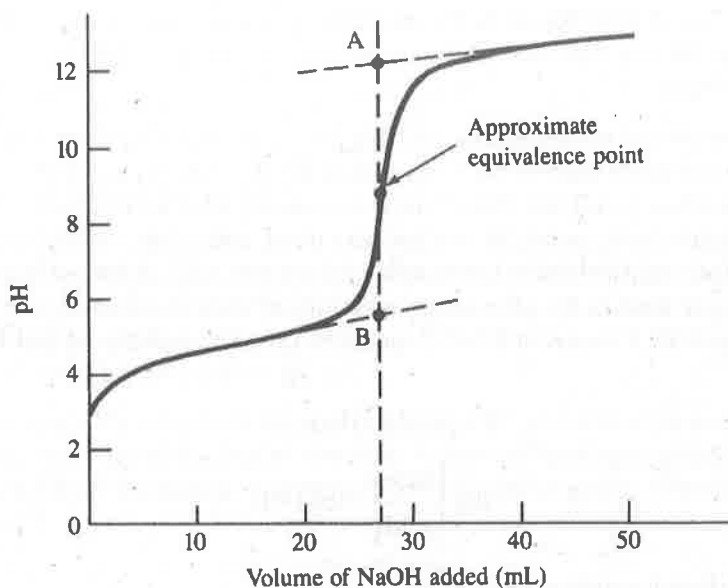
The Location of the Equivalence Point

The most accurate method for finding the equivalence point after the acid-base titration curve has been drawn involves the behavior of $\Delta(\Delta\text{pH}/\Delta V)\Delta V$. This quantity can also be written as $\Delta^2\text{pH}/\Delta V^2$. Those familiar with calculus will know that this is a second derivative. The equivalence point corresponds to the volume at which the second derivative is zero. The use of the second derivative, however, would complicate this experiment unnecessarily.

Instead, you will locate the approximate equivalence point using the following graphical procedure. A titration curve can be approximated by three straight lines, as shown in Figure 16B.3. Two of the lines intersect at A, and another intersection occurs at B. The approximate equivalence point will be located at the midpoint of the *vertical* line between A and B.

FIGURE 16B.3

A method for locating the approximate equivalence point. Note that it lies at the midpoint of the vertical line between A and B.



Concept of the Experiment

You will titrate a sample of KHP whose mass is known with a solution of NaOH. The approximate concentration of that solution will be 0.1 *M*. A question in the Prelaboratory Assignment will require you to calculate the approximate mass of KHP that you will need.

The NaOH solution will be delivered from a buret. Make sure you are familiar with the methods for cleaning, filling, and using a buret; these are described in the Introduction to this manual. However, you will not be able to use the titration technique shown in Figure I.4 because of the presence of the electrodes. A beaker will be used instead of an Erlenmeyer flask. Moreover, the solution in the beaker will have to be stirred, either by hand or mechanically, rather than swirled. Stirring is important because the pH will tend to drift until a completely homogeneous solution is achieved. General instructions for using pH meters can be found in Appendix D.

Follow all instructions carefully during the titration. Remember that the titration must provide sufficient data without consuming an inordinate amount of time.

Procedure

Getting Started

1. Your laboratory instructor may ask you to work with a partner.
2. Obtain a 50-mL buret.
3. If you are going to use a pH meter for the first time, obtain instructions for using it.

Cleaning and Filling Your Buret

1. Instructions for using a buret can be found in the Introduction to this manual. Clean your buret and fill it with the NaOH solution that is available in the laboratory. This solution is approximately 0.1 *M*.

Doing the Titration

1. Measure the mass of a piece of waxed weighing paper, using your most precise balance. Record the mass.
2. Add potassium hydrogen phthalate (KHP) to the paper until you have obtained the quantity that you calculated in the Prelaboratory Assignment. Record the combined masses of the paper and the KHP. Calculate and record the mass of the KHP.
3. Carefully pour the KHP from the paper into a clean, dry 150-mL beaker. Add about 50 mL of distilled water, and swirl gently until the sample has dissolved.
4. Calibrate the pH meter. A buffer solution whose pH is 5.00 is preferred. Be sure to rinse the electrodes with distilled water and dry them gently with tissue paper before and after placing them in the buffer solution.
5. Immediately immerse the electrodes in the solution of KHP. If possible, clamp the electrodes so that they are not touching the beaker.
6. Provide some means of stirring the solution. A magnetic stirring device is preferred. However, stirring by hand with a glass stirring rod will suffice if you are thorough and if you avoid hitting the electrodes.
7. The buret should be clamped so that its tip is within the beaker but above the surface of the solution.
8. Record the initial buret reading.
9. Read and record the initial pH of the solution before any of the NaOH solution has been added.
10. Begin the titration by adding successive portions of about 1 mL of the NaOH solution. Obtain and record the buret reading and the pH after each addition.
11. When the pH begins to increase by more than about 0.3 pH unit after an addition, decrease the portions that you add to about 0.2 mL. Once the equivalence point has been passed, the pH change after each addition will decrease. When the change is again about 0.3 pH unit, return to 1-mL portions. Continue the titration until the pH is about 11.5–12.
12. Repeat Steps 1 through 11 with a new sample of KHP (if time permits).

Date: _____
Course/Section: _____
Instructor: _____

Student name: _____
Team members: _____

An Acid–Base Titration Curve

Prelaboratory Assignment

1. Provide definitions for the following terms:

a. Acid–base titration curve

b. Equivalence point

c. Standardization

d. pH

e. pH meter

2. Estimate the mass of KHP that will require 25 mL of 0.10 M NaOH to reach the equivalence point in a titration. Give the chemical equation for the reaction.

3. Calculate the molarity of the acetic acid solution in Figure 16B.1 if 25.0 mL of that solution has been titrated with the 0.101 M solution of NaOH.

Date: _____

Student name: _____

Course/Section: _____

Team members: _____

Instructor: _____

An Acid-Base Titration Curve

Results

Sample	1	2
Mass of KHP and paper (g)	_____	_____
Mass of paper (g)	_____	_____
Mass of KHP (g)	_____	_____

Sample 1

Initial pH: _____

Initial buret reading (mL): _____

Buret Reading (mL)	Volume Added (mL)	pH	Buret Reading (mL)	Volume Added (mL)	pH
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
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_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Student name: _____ Course/Section: _____ Date: _____

Sample 2

Initial pH: _____

Initial buret reading (mL): _____

Buret Reading (mL)	Volume Added (mL)	pH	Buret Reading (mL)	Volume Added (mL)	pH
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
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_____	_____	_____	_____	_____	_____
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_____	_____	_____	_____	_____	_____

Questions

1. a. Use the graph paper that is available to plot the titration curves. Locate the equivalence point on each graph. Complete the following table.

Sample	1	2
Volume at equivalence point (mL)	_____	_____
pH at equivalence point	_____	_____

- b. Calculate the molarity of the NaOH solution from each result, and calculate the mean.

- c. Use your graphs to obtain the data required in the following table.

Sample	1	2
Volume at halfway point (mL)	_____	_____
pH at halfway point	_____	_____
pK_a	_____	_____
Mean pK_a	_____	

- b. Use K_b , the number of moles of $\text{C}_8\text{H}_4\text{O}_4^{2-}$ at the equivalence point, and the total volume at that point to calculate the pH for each sample at the equivalence point. Compare these calculated results with the experimental results.

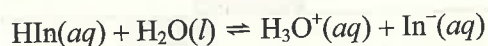
Appendix D: Indicators, pH Paper, and pH Meters

The pH of a solution can be either estimated, using acid–base indicators or pH paper, or measured directly with a pH meter. Each of these methods will be discussed in turn.

Indicators

Acid–base indicators (Ebbing/Gammon, Chapter 15) are usually very complicated molecules that are intensely colored. These substances are also weak acids or bases. For that reason, many aspects of the chemistry of these indicators are very similar to those of other weak acids or bases.

Methyl orange, for example, is an acid–base indicator and a weak acid. Because of its complicated nature, we write its formula in abbreviated form as HIn. This substance dissociates partially in solution according to



The color of the acid form of this indicator is red, whereas the color of In^- is yellow.

The position of the equilibrium between HIn and In^- depends on the pH of the solution to which the indicator has been added. According to Le Châtelier's principle (Ebbing/Gammon, Chapter 14), a large concentration of H_3O^+ ions (low pH) will cause the equilibrium to shift almost completely to the left. The color of the solution will then be red, the color of HIn. At lower concentrations of H_3O^+ ions (higher pH), the equilibrium will shift from left to right, resulting in various hues of orange. If the equilibrium is shifted almost completely to the right, the color of the solution will be yellow, the color of In^- .

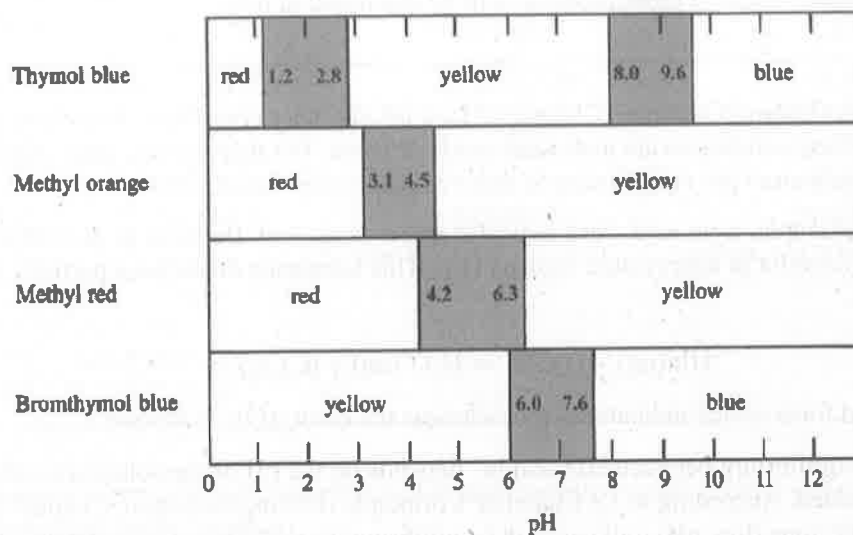
It is important to note that because an indicator is intensely colored, only small amounts are required. Because only small amounts are used, the indicator does not measurably alter the pH of the solution to be tested.

Consider the chart in Figure D.1, which gives the colors of four indicators as a function of pH. Returning to methyl orange, you will see from the chart that a solution containing this indicator will be red if the pH is less than 3.1, orange if the pH lies between 3.1 and 4.5, and yellow if the pH is greater than 4.5. By using all of the indicators given in the chart, you should be able to estimate an unknown pH that lies between 1.2 and 9.6. If the pH does not lie within this range, you will at least be able to say that it is less than 1.2 or greater than 9.6.

Because we must depend on the color of an indicator to estimate the pH, the solution to be tested must be colorless or very nearly colorless. This is one of the principal drawbacks to the use of indicators.

FIGURE D.1

Color changes for four acid–base indicators. Shaded areas indicate the pH intervals in which the colors change.



pH Paper

Paper strips that have been treated with a mixture of indicators can be used to estimate the pH of a solution. The indicators are chosen such that each one will change color at a different pH. The pH is estimated by moistening the paper with the solution being tested and then matching its color with a color on a chart provided by the manufacturer of the paper. The strips of paper are called *pH paper*. Again, colored solutions cannot be used.

Both wide-range and short-range papers are available. A wide-range paper might cover eight to eleven pH units (say, pH 1 to 11), whereas a short-range paper might cover only two or three pH units (say, pH 1 to 2.5).

pH Meters

A pH meter and its electrodes form a sensitive electrochemical device that makes possible the accurate, reproducible, and reliable measurement of the pH of a solution. Moreover, the solution does not need to be colorless.

There are several exterior designs for commercial pH meters. Meters may appear to differ from one another because they come from different manufacturers or, if they come from the same manufacturer, because they are different models with different prices. The differences usually lie in the way the measured pH is displayed, the positions of the control knobs, the types of electrodes, and the manner in which these electrodes are held in position.

Any pH meter, no matter how it looks, is just a voltmeter that measures the voltage of an electric current flowing through a solution between two electrodes. There is a direct relationship between the voltage and the pH of the solution (Ebbing/Gammon, Section 19.7). As a result, the meter on the instrument is calibrated directly in pH units rather than in volts.

Two electrodes are required. One of them is called a *glass electrode*. This electrode is sensitive to the concentration of H_3O^+ ions in the solution. The other is called the *reference electrode*. Its operation is virtually independent of the composition of the solution. These electrodes are sometimes combined into

a single entity called a *combination electrode*. However, there are really two different electrodes present.

Although the operating rules for a pH meter depend on the model and the manufacturer, there are several steps you will need to follow with any instrument.

1. The electrodes should always be kept in a solution except when you are transferring them from one solution to another. When you transfer them, avoid contaminating the solutions. During the transfer, rinse the electrodes with a stream of distilled water, and catch the water in a beaker. Remove the excess water from the electrodes with tissue paper before you immerse the electrodes in the next solution. Do not touch the electrodes with your hand. Handle them with care because they are fragile.
2. If there is a knob that adjusts the pH meter for different temperatures, it should be set to the temperature of the solution whose pH is to be measured. More often than not, this temperature is also the temperature of the laboratory.
3. The pH meter must be calibrated or standardized with a solution whose pH is known before you can measure an unknown pH with accuracy. These solutions of known pH are called *buffer solutions*.
4. Place your solution in the smallest container that is consistent with the experiment. Under the simplest of circumstances, you can measure the pH of a few milliliters of a solution in a large test tube with a combination electrode or in a 50-mL beaker with two electrodes.
5. You should be able to read the pH of a solution about 10 s after the electrodes have been immersed. The reading should be steady and not abruptly changing. If sudden changes do occur, consult your laboratory instructor. Additional operating rules may be issued by your laboratory instructor.