

1. An Acid–Base Titration Curve

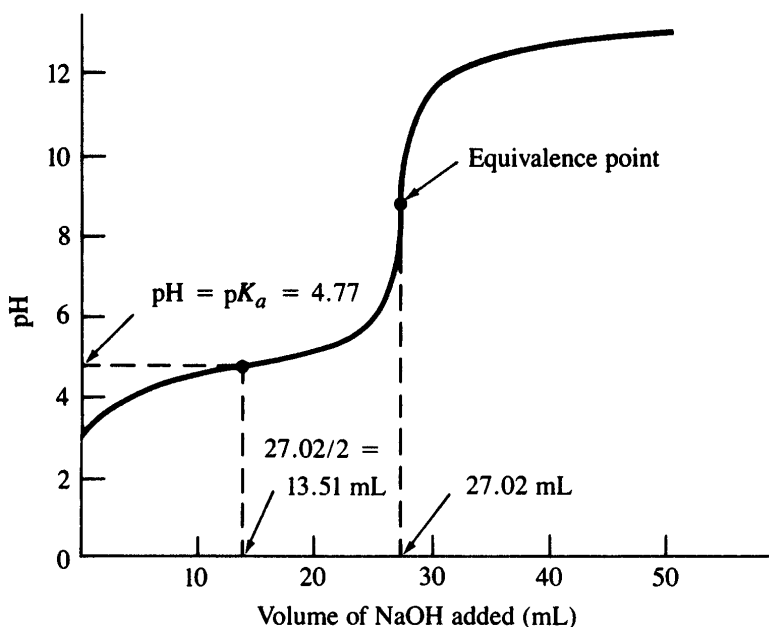
Introduction

Acid–base titration curves (Ebbing/Gammon, Section 17.7) 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 1.1.

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 allow 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 1.1
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. You will accumulate the data that you will use for this graph during the titration of a weak acid, potassium hydrogen phthalate, with a solution of sodium hydroxide. The titration curve

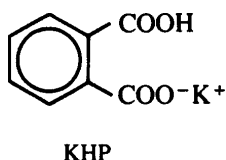
will be used to achieve three goals: standardizing the solution of sodium hydroxide, choosing an indicator that would be suitable for subsequent titrations if you were going to do them, and illustrating the method for obtaining the acid ionization constant for the weak acid.

Standardization of a NaOH solution

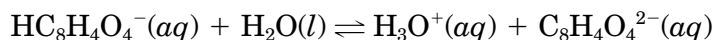
You cannot prepare a solution of sodium hydroxide with an accurately known concentration by adding a known mass of NaOH to an appropriate quantity of water. The hygroscopic (readily taking and retaining water from air) nature of solid NaOH makes measuring the mass of a sample of this substance with accuracy 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 1.2.

FIGURE 1.2
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 1.1. A solution of acetic acid has been titrated with a 0.101 M solution of NaOH. The equivalence point (Ebbing/Gammon, Section 17.7) 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 17.6)

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

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 17.6), 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 between 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 1.1 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

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

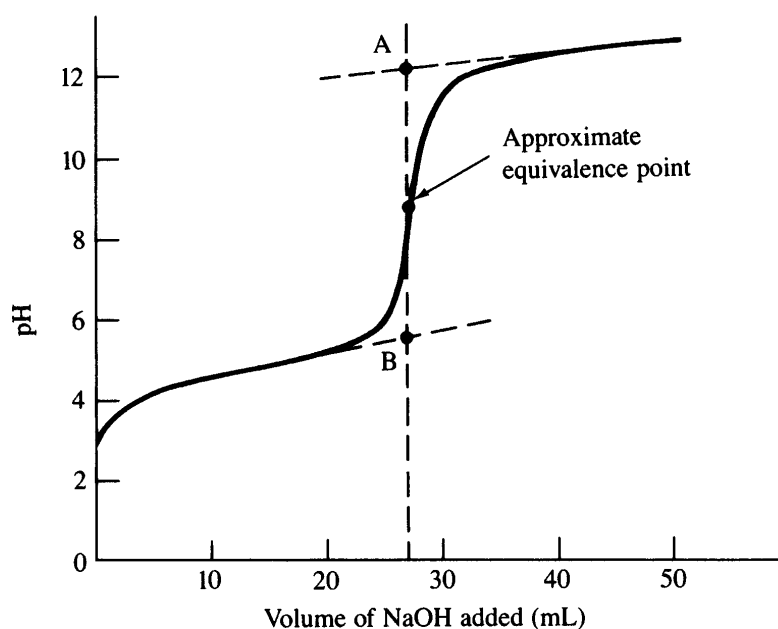
This result agrees with the known value of K_a (Ebbing/Gammon, Table 17.1).

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 1.3. 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 1.3
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 in 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: Indicators, pH Paper, and pH Meters.

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).

An Acid–Base Titration Curve

Date: Student name:
Course: Team members:
Section:
Instructor:

Prelaboratory assignment

1. Provide definitions for the following terms:

a. Acid–base titration curve

b. Equivalence point

c. Standardization

d. pH

e. pH meter

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Results

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

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.

Student name: Course/Section: Date:

