Chapter 9

Titrimetric Methods

Chapter Overview

Titrimetry, in which volume serves as the analytical signal, made its first appearance as an analytical method in the early eighteenth century. Titrimetric methods were not well received by the analytical chemists of that era because they could not duplicate the accuracy and precision of a gravimetric analysis. Not surprisingly, few standard texts from the 1700s and 1800s include titrimetric methods of analysis.

Precipitation gravimetry developed as an analytical method without a general theory of precipitation. An empirical relationship between a precipitate's mass and the mass of analyte—what analytical chemists call a gravimetric factor—was determined experimentally by taking a known mass of analyte through the procedure. Today, we recognize this as an early example of an external standardization. Gravimetric factors were not calculated using the stoichiometry of a precipitation reaction because chemical formulas and atomic weights were not yet available! Unlike gravimetry, the development and acceptance of titrimetry required a deeper understanding of stoichiometry, of thermodynamics, and of chemical equilibria. By the 1900s, the accuracy and precision of titrimetric methods were comparable to that of gravimetric methods, establishing titrimetry as an accepted analytical technique.

9A Overview of Titrimetry

We are deliberately avoiding the term analyte at this point in our introduction to titrimetry. Although in most titrations the analyte is the titrand, there are circumstances where the analyte is the titrant. When discussing specific methods, we will use the term analyte where appropriate.

In TITRIMETRY we add a reagent, called the TITRANT, to a solution containing another reagent, called the TITRAND, and allow them to react. The type of reaction provides us with a simple way to divide titrimetry into the following four categories: acid–base titrations, in which an acidic or basic titrant reacts with a titrand that is a base or an acid; complexometric titrations based on metal–ligand complexation; redox titrations, in which the titrant is an oxidizing or reducing agent; and precipitation titrations, in which the titrand and titrant form a precipitate.

Despite the difference in chemistry, all titrations share several common features. Before we consider individual titrimetric methods in greater detail, let's take a moment to consider some of these similarities. As you work through this chapter, this overview will help you focus on similarities between different titrimetric methods. You will find it easier to understand a new analytical method when you can see its relationship to other similar methods.

9A.1 Equivalence Points and End points

If a titration is to be accurate we must combine stoichiometrically equivalent amount of titrant and titrand. We call this stoichiometric mixture the EQUIVALENCE POINT. Unlike precipitation gravimetry, where we add the precipitant in excess, an accurate titration requires that we know the exact volume of titrant at the equivalence point, V_{eq}. The product of the titrant's equivalence point volume and its molarity, M_T, is equal to the moles of titrant reacting with the titrand.

$$\text{moles of titrant} = M_T \times V_{eq}$$

If we know the stoichiometry of the titration reaction, then we can calculate the moles of titrand.

Unfortunately, for most titrations there is no obvious sign when we reach the equivalence point. Instead, we stop adding titrant when at an END POINT of our choosing. Often this end point is a change in the color of a substance, called an INDICATOR, that we add to the titrand's solution. The difference between the end point volume and the equivalence point volume is a determinate TITRATION ERROR. If the end point and the equivalence point volumes coincide closely, then the titration error is insignificant and it is safely ignored. Clearly, selecting an appropriate end point is critically important.

Instead of measuring the titrant's volume, we may choose to measure its mass. Although we generally can measure mass more precisely than we can measure volume, the simplicity of a volumetric titration makes it the more popular choice.

9A.2 Volume as a Signal

Almost any chemical reaction can serve as a titrimetric method provided it meets the following four conditions. The first condition is that we must know the stoichiometry between the titrant and the titrand. If this is not the case, then we cannot convert the moles of titrant consumed in reaching the end point to the moles of titrand in our sample. Second, the titration reaction must effectively proceed to completion; that is, the stoichiometric mixing of the titrant and the titrand must result in their reaction. Third, the titration reaction must occur rapidly. If we add the titrant faster than it can react with the titrand, then the end point and the equivalence point will differ significantly. Finally, there must be a suitable method for accurately determining the end point. These are significant limitations and, for this reason, there are several common titration strategies.

Depending on how we are detecting the endpoint, we may stop the titration too early or too late. If the end point is a function of the titrant's concentration, then adding the titrant too quickly leads to an early end point. On the other hand, if the end point is a function of the titrant's concentration, then the end point exceeds the equivalence point.

A simple example of a titration is an analysis for Ag^+ using thiocyanate, SCN^-, as a titrant.

$$Ag^+(aq) + SCN^-(aq) \rightleftharpoons Ag(SCN)(s)$$

This is an example of a precipitation titration. You will find more information about precipitation titrations in Section 9E.

This reaction occurs quickly and with a known stoichiometry, satisfying two of our requirements. To indicate the titration's end point, we add a small amount of Fe^{3+} to the analyte's solution before beginning the titration. When the reaction between Ag^+ and SCN^- is complete, formation of the red-colored $Fe(SCN)^{2+}$ complex signals the end point. This is an example of a DIRECT TITRATION since the titrant reacts directly with the analyte.

If the titration's reaction is too slow, if a suitable indicator is not available, or if there is no useful direct titration reaction, then an indirect analysis may be possible. Suppose you wish to determine the concentration of formaldehyde, H_2CO, in an aqueous solution. The oxidation of H_2CO by I_3^-

$$H_2CO(aq) + I_3^-(aq) + 3OH^-(aq) \rightleftharpoons HCO_2^-(aq) + 3I^-(aq) + 2H_2O(l)$$

is a useful reaction, but it is too slow for a titration. If we add a known excess of I_3^- and allow its reaction with H_2CO to go to completion, we can titrate the unreacted I_3^- with thiosulfate, $S_2O_3^{2-}$.

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 3I^-(aq)$$

This is an example of a redox titration. You will find more information about redox titrations in Section 9D.

The difference between the initial amount of I_3^- and the amount in excess gives us the amount of I_3^- reacting with the formaldehyde. This is an example of a BACK TITRATION.

Calcium ion plays an important role in many environmental systems. A direct analysis for Ca^{2+} might take advantage of its reaction with the ligand ethylenediaminetetraacetic acid (EDTA), which we represent here as Y^{4-}.

$$Ca^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CaY^{2-}(aq)$$

Unfortunately, for most samples this titration does not have a useful indicator. Instead, we react the Ca^{2+} with an excess of MgY^{2-}

$$Ca^{2+}(aq) + MgY^{2-}(aq) \rightleftharpoons CaY^{2-}(aq) + Mg^{2+}(aq)$$

MgY^{2-} is the Mg^{2+}–EDTA metal–ligand complex. You can prepare a solution of MgY^{2-} by combining equimolar solutions of Mg^{2+} and EDTA.

This is an example of a complexation titration. You will find more information about complexation titrations in Section 9C.

releasing an amount of Mg^{2+} equivalent to the amount of Ca^{2+} in the sample. Because the titration of Mg^{2+} with EDTA

$$Mg^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons MgY^{2-}(aq)$$

has a suitable end point, we can complete the analysis. The amount of EDTA used in the titration provides an indirect measure of the amount of Ca^{2+} in the original sample. Because the species we are titrating was displaced by the analyte, we call this a DISPLACEMENT TITRATION.

If a suitable reaction involving the analyte does not exist it may be possible to generate a species that we can titrate. For example, we can determine the sulfur content of coal by using a combustion reaction to convert sulfur to sulfur dioxide

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

and then convert the SO_2 to sulfuric acid, H_2SO_4, by bubbling it through an aqueous solution of hydrogen peroxide, H_2O_2.

$$SO_2(g) + H_2O_2(aq) \rightarrow H_2SO_4(aq)$$

This is an example of an acid–base titration. You will find more information about acid–base titrations in Section 9B.

Titrating H_2SO_4 with NaOH

$$H_2SO_4(aq) + 2NaOH(aq) \rightleftharpoons 2H_2O(l) + Na_2SO_4(aq)$$

provides an indirect determination of sulfur.

9A.3 Titration Curves

Why a pH of 7.0 is the equivalence point for this titration is a topic we will cover in Section 9B.

To find a titration's end point, we need to monitor some property of the reaction that has a well-defined value at the equivalence point. For example, the equivalence point for a titration of HCl with NaOH occurs at a pH of 7.0. A simple method for finding the equivalence point is to continuously monitor the titration mixture's pH using a pH electrode, stopping the titration when we reach a pH of 7.0. Alternatively, we can add an indicator to the titrand's solution that changes color at a pH of 7.0.

Suppose the only available indicator changes color at an end point pH of 6.8. Is the difference between the end point and the equivalence point small enough that we can safely ignore the titration error? To answer this question we need to know how the pH changes during the titration.

For the titration curve in Figure 9.1, the volume of titrant to reach a pH of 6.8 is 24.99995 mL, a titration error of -2.00×10^{-4}%. Typically, we can only read the volume to the nearest $\pm$0.01 mL, which means this uncertainty is too small to affect our results.

The volume of titrant to reach a pH of 11.6 is 27.07 mL, or a titration error of +8.28%. This is a significant error.

A TITRATION CURVE provides us with a visual picture of how a property of the titration reaction changes as we add the titrant to the titrand. The titration curve in Figure 9.1, for example, was obtained by suspending a pH electrode in a solution of 0.100 M HCl (the titrand) and monitoring the pH while adding 0.100 M NaOH (the titrant). A close examination of this titration curve should convince you that an end point pH of 6.8 produces a negligible titration error. Selecting a pH of 11.6 as the end point, however, produces an unacceptably large titration error.

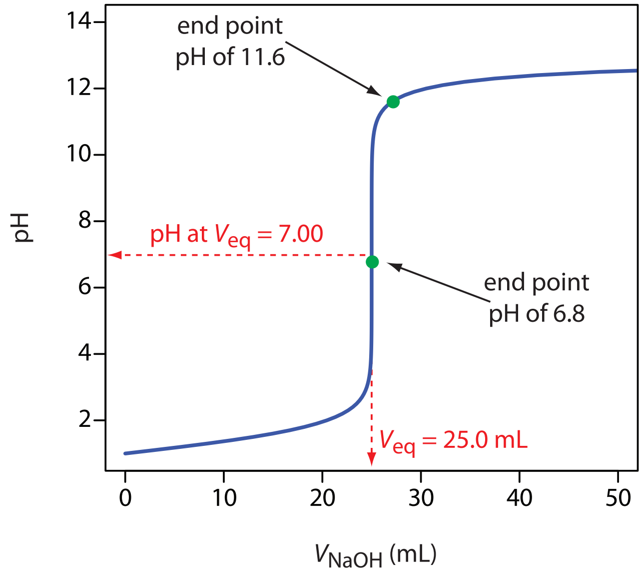


Figure 9.1 Typical acid–base titration curve showing how the titrand's pH changes with the addition of titrant. The titrand is a 25.0 mL solution of 0.100 M HCl and the titrant is 0.100 M NaOH. The titration curve is the solid blue line, and the equivalence point volume (25.0 mL) and pH (7.00) are shown by the dashed red lines. The green dots show two end points. The end point at a pH of 6.8 has a small titration error, and the end point at a pH of 11.6 has a larger titration error.

The titration curve in Figure 9.1 is not unique to an acid–base titration. Any titration curve that follows the change in concentration of a species in the titration reaction (plotted logarithmically) as a function of the titrant's volume has the same general sigmoidal shape. Several additional examples are shown in Figure 9.2.

The titrand's or the titrant's concentration is not the only property we can use when recording a titration curve. Other parameters, such as the temperature or absorbance of the titrand's solution, may provide a useful end point signal. Many acid–base titration reactions, for example, are exothermic. As the titrant and titrand react the temperature of the titrand's solution steadily increases. Once we reach the equivalence point, further additions of titrant do not produce as exothermic a response. Figure 9.3 shows a typical THERMOMETRIC TITRATION CURVE with the intersection of the two linear segments indicating the equivalence point.

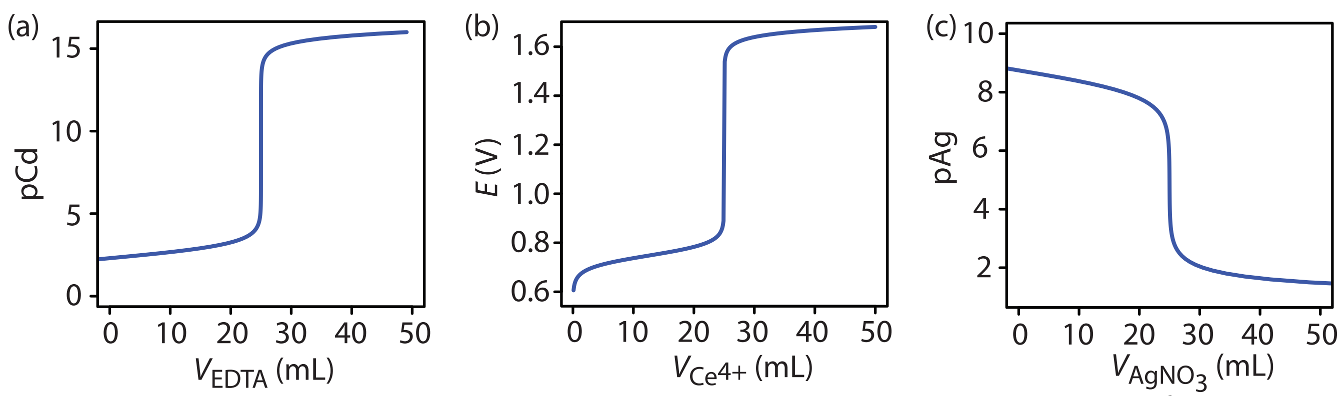


Figure 9.2 Additional examples of titration curves. (a) Complexation titration of 25.0 mL of 1.0 mM Cd^{2+} with 1.0 mM EDTA at a pH of 10. The *y*-axis displays the titrand's equilibrium concentration as pCd. (b) Redox titration of 25.0 mL of 0.050 M Fe^{2+} with 0.050 M Ce^{4+} in 1 M $HClO_4$. The *y*-axis displays the titration mixture's electrochemical potential, *E*, which, through the Nernst equation is a logarithmic function of concentrations. (c) Precipitation titration of 25.0 mL of 0.10 M NaCl with 0.10 M $AgNO_3$. The *y*-axis displays the titrant's equilibrium concentration as pAg.

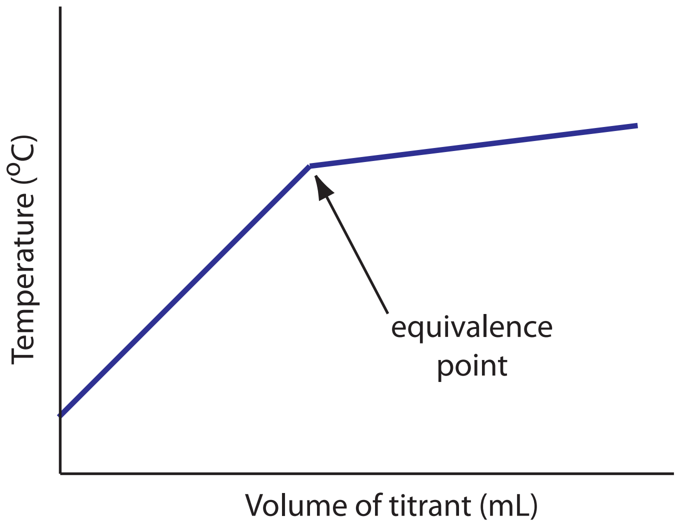


Figure 9.3 Example of a thermometric titration curve showing the location of the equivalence point.

9A.4 The Buret

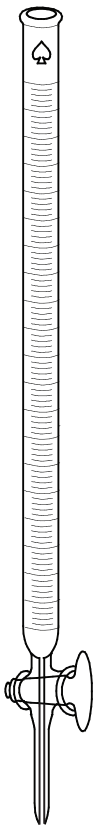


Figure 9.4 Typical volumetric buret. The stopcock is in the open position, allowing the titrant to flow into the titrand's solution. Rotating the stopcock controls the titrant's flow rate.

The only essential equipment for an acid–base titration is a means for delivering the titrant to the titrand's solution. The most common method for delivering titrant is a BURET (Figure 9.4). A buret is a long, narrow tube with graduated markings, equipped with a stopcock for dispensing the titrant. The buret's small internal diameter provides a better defined meniscus, making it easier to read the titrant's volume precisely. Burets are available in a variety of sizes and tolerances (Table 9.1), with the choice of buret determined by the needs of the analysis. You can improve a buret's accuracy by calibrating it over several intermediate ranges of volumes using the method described in Chapter 5 for calibrating pipets. Calibrating a buret corrects for variations in the buret's internal diameter.

A titration can be automated by using a pump to deliver the titrant at a constant flow rate (Figure 9.5). Automated titrations offer the additional advantage of using a microcomputer for data storage and analysis.

Table 9.1 Specifications for Volumetric Burets

Volume (mL)	Class	Subdivision (mL)	Tolerance (mL)
5	A	0.01	±0.01
	B	0.01	±0.01
10	A	0.02	±0.02
	B	0.02	±0.04
25	A	0.1	±0.03
	B	0.1	±0.06
50	A	0.1	±0.05
	B	0.1	±0.10
100	A	0.2	±0.10
	B	0.2	±0.20

Figure 9.5 Typical instrumentation for an automated acid–base titration showing the titrant, the pump, and the titrand. The pH electrode in the titrand's solution is used to monitor the titration's progress. You can see the titration curve in the lower-left quadrant of the computer's display. Modified from: Datamax (commons.wikipedia.org).

9B Acid–Base Titrations

Before 1800, most ACID–BASE TITRATIONS used H_2SO_4, HCl, or HNO_3 as acidic titrants, and K_2CO_3 or Na_2CO_3 as basic titrants. A titration's end point was determined using litmus as an indicator, which is red in acidic solutions and blue in basic solutions, or by the cessation of CO_2 effervescence when neutralizing CO_3^{2-}. Early examples of acid–base titrimetry include determining the acidity or alkalinity of solutions, and determining the purity of carbonates and alkaline earth oxides.

The determination of acidity and alkalinity continue to be important applications of acid–base titrimetry. We will take a closer look at these applications later in this section.

Three limitations slowed the development of acid–base titrimetry: the lack of a strong base titrant for the analysis of weak acids, the lack of suitable indicators, and the absence of a theory of acid–base reactivity. The introduction, in 1846, of NaOH as a strong base titrant extended acid–base titrimetry to the determination of weak acids. The synthesis of organic dyes provided many new indicators. Phenolphthalein, for example, was first synthesized by Bayer in 1871 and used as an indicator for acid–base titrations in 1877.

Despite the increasing availability of indicators, the absence of a theory of acid–base reactivity made it difficult to select an indicator. The development of equilibrium theory in the late 19th century led to significant improvements in the theoretical understanding of acid–base chemistry, and, in turn, of acid–base titrimetry. Sørenson's establishment of the pH scale in 1909 provided a rigorous means for comparing indicators. The determination of acid–base dissociation constants made it possible to calculate a theoretical titration curve, as outlined by Bjerrum in 1914. For the first time analytical chemists had a rational method for selecting an indicator, establishing acid–base titrimetry as a useful alternative to gravimetry.

9B.1 Acid–Base Titration Curves

In the overview to this chapter we noted that a titration's end point should coincide with its equivalence point. To understand the relationship between an acid–base titration's end point and its equivalence point we must know how the pH changes during a titration. In this section we will learn how to calculate a titration curve using the equilibrium calculations from Chapter 6. We also will learn how to quickly sketch a good approximation of any acid–base titration curve using a limited number of simple calculations.

Titrating Strong Acids and Strong Bases

For our first titration curve, let's consider the titration of 50.0 mL of 0.100 M HCl using a titrant of 0.200 M NaOH. When a strong base and a strong acid react the only reaction of importance is

Although we have not written reaction 9.1 as an equilibrium reaction, it is at equilibrium; however, because its equilibrium constant is large—it is equal to $(K_w)^{-1}$ or 1.00×10^{14}—we can treat reaction 9.1 as though it goes to completion.

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l) \qquad 9.1$$

The first task in constructing the titration curve is to calculate the volume of NaOH needed to reach the equivalence point, V_{eq}. At the equivalence point we know from reaction 9.1 that

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

$$\text{moles HCl} = \text{moles NaOH}$$

$$M_a \times V_a = M_b \times V_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point is

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100\text{ M})(50.0\text{ mL})}{0.200\text{ M}} = 25.0\text{ mL}$$

Step 2: Calculate pH values before the equivalence point by determining the concentration of unreacted titrand.

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of unreacted HCl. At the start of the titration the solution is 0.100 M in HCl, which, because HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[H_3O^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

After adding 10.0 mL of NaOH the concentration of excess HCl is

$$[\text{HCl}] = \frac{\text{initial moles HCl} - \text{moles NaOH added}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.200\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 0.0500\text{ M}$$

and the pH increases to 1.30.

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

Step 3: The pH at the equivalence point for the titration of a strong acid with a strong base is 7.00.

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+]^2$$
$$[H_3O^+] = 1.00 \times 10^{-7}\ M$$

Thus, the pH at the equivalence point is 7.00.

For volumes of NaOH greater than the equivalence point, the pH is determined by the concentration of excess OH^-. For example, after adding 30.0 mL of titrant the concentration of OH^- is

Step 4: Calculate pH values after the equivalence point by determining the concentration of excess titrant.

$$[OH^-] = \frac{\text{moles NaOH added} - \text{initial moles HCl}}{\text{total volume}} = \frac{M_bV_b - M_aV_a}{V_a + V_b}$$
$$= \frac{(0.200\ M)(30.0\ mL) - (0.100\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 0.0125\ M$$

To find the concentration of H_3O^+ we use the K_w expression

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.0125\ M} = 8.00 \times 10^{-13}\ M$$

giving a pH of 12.10. Table 9.2 and Figure 9.6 show additional results for this titration curve. You can use this same approach to calculate the titration curve for the titration of a strong base with a strong acid, except the strong base is in excess before the equivalence point and the strong acid is in excess after the equivalence point.

Practice Exercise 9.1

Construct a titration curve for the titration of 25.0 mL of 0.125 M NaOH with 0.0625 M HCl.

Click here to review your answer to this exercise.

Table 9.2 Titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH

Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH
0.00	1.00	26.0	11.42
5.00	1.14	28.0	11.89
10.0	1.30	30.0	12.10
15.0	1.51	35.0	12.37
20.0	1.85	40.0	12.52
22.0	2.08	45.0	12.62
24.0	2.57	50.0	12.70
25.0	7.00		

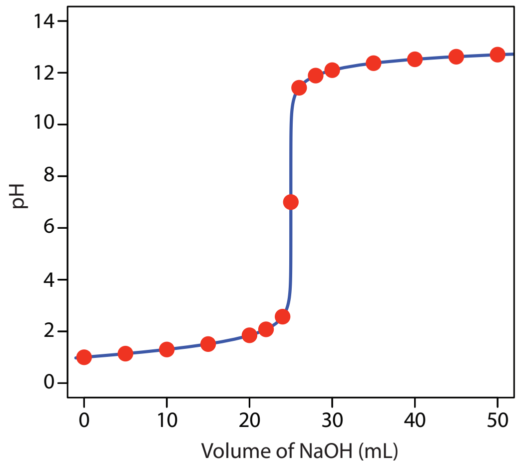


Figure 9.6 Titration curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. The red points correspond to the data in Table 9.2. The blue line shows the complete titration curve.

Titrating a Weak Acid with a Strong Base

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

For this example, let's consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH, with 0.200 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\text{moles } CH_3COOH = \text{moles NaOH}$$

$$M_a \times V_a = M_b \times V_b$$

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{0.200 \text{ M}} = 25.0 \text{ mL}$$

Step 2: Before adding the titrant, the pH is determined by the titrand, which in this case is a weak acid.

Before adding NaOH the pH is that for a solution of 0.100 M acetic acid. Because acetic acid is a weak acid, we calculate the pH using the method outlined in Chapter 6.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [H_3O^+] = 1.32 \times 10^{-3} \text{ M}$$

At the beginning of the titration the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base, CH_3COO^-.

Because the equilibrium constant for reaction 9.2 is quite large

$$K = K_a/K_w = 1.75 \times 10^9$$

we can treat the reaction as if it goes to completion.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq) \qquad 9.2$$

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A^-, is a buffer. As we learned in Chapter 6, we can calculate the pH of a buffer using the Henderson–Hasselbalch equation.

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

Before the equivalence point the concentration of unreacted acetic acid is

Step 3: Before the equivalence point, the pH is determined by a buffer containing the titrand and its conjugate form.

$$[CH_3COOH] = \frac{\text{initial moles } CH_3COOH - \text{moles NaOH added}}{\text{total volume}}$$
$$= \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

and the concentration of acetate is

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_bV_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are

$$[CH_3COOH] = \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}}$$
$$= 0.0500 \text{ M}$$

$$[CH_3COO^-] = \frac{(0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0333 \text{ M}$$

which gives us a pH of

$$pH = 4.76 + \log \frac{0.0333 \text{ M}}{0.0500 \text{ M}} = 4.58$$

At the equivalence point the moles of acetic acid initially present and the moles of NaOH added are identical. Because their reaction effectively proceeds to completion, the predominate ion in solution is CH_3COO^-, which is a weak base. To calculate the pH we first determine the concentration of CH_3COO^-

Step 4: The pH at the equivalence point is determined by the titrand's conjugate form, which in this case is a weak base.

Alternatively, we can calculate acetate's concentration using the initial moles of acetic acid; thus

$$[CH_3COO^-] = \frac{\text{initial moles } CH_3COOH}{\text{total volume}}$$
$$= \frac{(0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}}$$
$$= 0.0667 \text{ M}$$

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}}$$
$$= \frac{(0.200 \text{ M})(25.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}$$

Next, we calculate the pH of the weak base as shown earlier in Chapter 6.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$$

$$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{(x)(x)}{0.0667 - x} = 5.71\times10^{-10}$$

$$x = [OH^-] = 6.17\times10^{-6}\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00\times10^{-14}}{6.17\times10^{-6}} = 1.62\times10^{-9}\ M$$

The pH at the equivalence point is 8.79.

Step 5: Calculate pH values after the equivalence point by determining the concentration of excess titrant.

After the equivalence point, the titrant is in excess and the titration mixture is a dilute solution of NaOH. We can calculate the pH using the same strategy as in the titration of a strong acid with a strong base. For example, after adding 30.0 mL of NaOH the concentration of OH^- is

$$[OH^-] = \frac{(0.200\ M)(30.0\ mL) - (0.100\ M)(50.0\ mL)}{50.0\ mL\ +\ 30.0\ mL} = 0.0125\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00\times10^{-14}}{0.0125\ M} = 8.00\times10^{-13}\ M$$

giving a pH of 12.10. Table 9.3 and Figure 9.7 show additional results for this titration. You can use this same approach to calculate the titration curve for the titration of a weak base with a strong acid, except the initial pH is determined by the weak base, the pH at the equivalence point by its conjugate weak acid, and the pH after the equivalence point by excess strong acid.

Practice Exercise 9.2

Construct a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl.

Click here to review your answer to this exercise.

Table 9.3 Titration of 50.0 mL of 0.100 M Acetic Acid with 0.200 M NaOH

Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH
0.00	2.88	26.0	11.42
5.00	4.16	28.0	11.89
10.0	4.58	30.0	12.10
15.0	4.94	35.0	12.37
20.0	5.36	40.0	12.52
22.0	5.63	45.0	12.62
24.0	6.14	50.0	12.70
25.0	8.79		

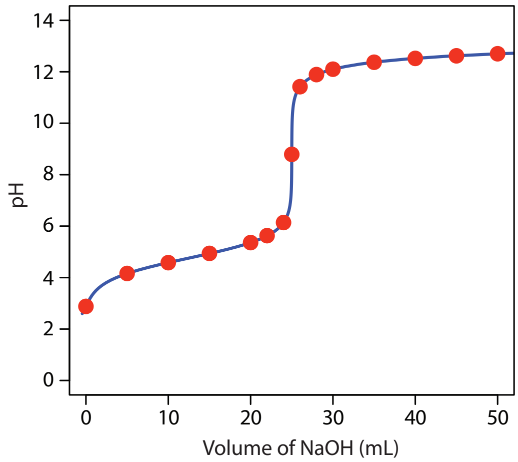


Figure 9.7 Titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH. The red points correspond to the data in Table 9.3. The blue line shows the complete titration curve.

We can extend our approach for calculating a weak acid–strong base titration curve to reactions involving multiprotic acids or bases, and mixtures of acids or bases. As the complexity of the titration increases, however, the necessary calculations become more time consuming. Not surprisingly, a variety of algebraic[1] and computer spreadsheet[2] approaches have been described to aid in constructing titration curves.

Sketching An Acid–Base Titration Curve

This is the same example that we used in developing the calculations for a weak acid–strong base titration curve. You can review the results of that calculation in Table 9.3 and Figure 9.7.

To evaluate the relationship between a titration's equivalence point and its end point, we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching an acid–base titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH to illustrate our approach.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pH on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point volume, we draw a vertical line corresponding to 25.0 mL of NaOH. Figure 9.8a shows the result of the first step in our sketch.

Before the equivalence point the titration mixture's pH is determined by a buffer of acetic acid, CH_3COOH, and acetate, CH_3COO^-. Although we can easily calculate a buffer's pH using the Henderson–Hasselbalch equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a buffer operates over a pH range extend-

1 (a) Willis, C. J. *J. Chem. Educ.* **1981**, *58*, 659–663; (b) Nakagawa, K. *J. Chem. Educ.* **1990**, *67*, 673–676; (c) Gordus, A. A. *J. Chem. Educ.* **1991**, *68*, 759–761; (d) de Levie, R. *J. Chem. Educ.* **1993**, *70*, 209–217; (e) Chaston, S. *J. Chem. Educ.* **1993**, *70*, 878–880; (f) de Levie, R. *Anal. Chem.* **1996**, *68*, 585–590.

2 (a) Currie, J. O.; Whiteley, R. V. *J. Chem. Educ.* **1991**, *68*, 923–926; (b) Breneman, G. L.; Parker, O. J. *J. Chem. Educ.* **1992**, *69*, 46–47; (c) Carter, D. R.; Frye, M. S.; Mattson, W. A. *J. Chem. Educ.* **1993**, *70*, 67–71; (d) Freiser, H. *Concepts and Calculations in Analytical Chemistry*, CRC Press: Boca Raton, 1992.

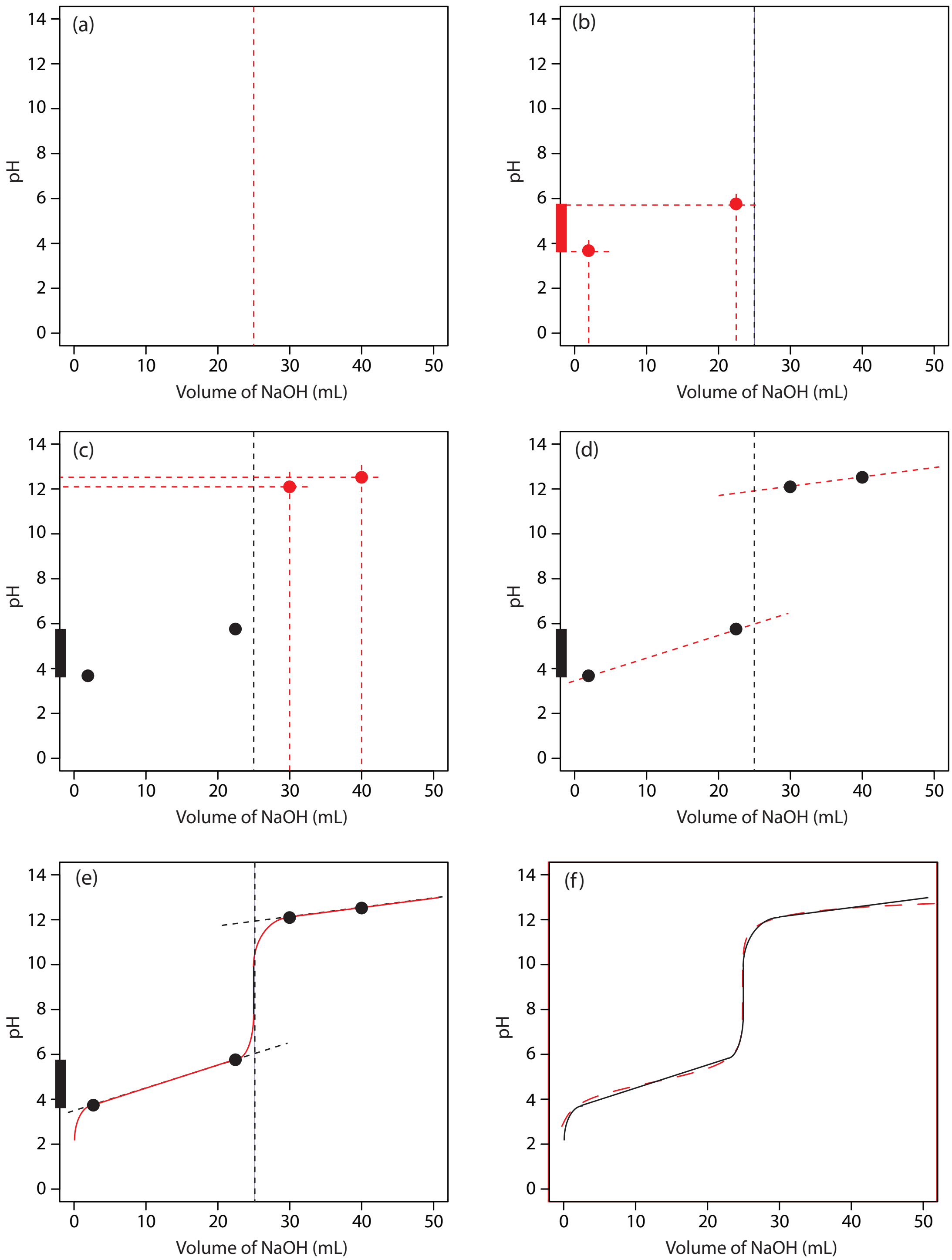


Figure 9.8 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

ing approximately ±1 pH unit on either side of the weak acid's pK_a value. The pH is at the lower end of this range, pH = pK_a − 1, when the weak acid's concentration is 10× greater than that of its conjugate weak base. The buffer reaches its upper pH limit, pH = pK_a + 1, when the weak acid's concentration is 10× smaller than that of its conjugate weak base. When titrating a weak acid or a weak base, the buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure 9.8b shows the second step in our sketch. First, we superimpose acetic acid's ladder diagram on the *y*-axis, including its buffer range, using its pK_a value of 4.76. Next, we add points representing the pH at 10% of the equivalence point volume (a pH of 3.76 at 2.5 mL) and at 90% of the equivalence point volume (a pH of 5.76 at 22.5 mL).

The actual values are 9.09% and 90.9%, but for our purpose, using 10% and 90% is more convenient; that is, after all, one advantage of an approximation! Problem 9.4 in the end-of-chapter problems asks you to verify these percentages.

The third step in sketching our titration curve is to add two points after the equivalence point. The pH after the equivalence point is fixed by the concentration of excess titrant, NaOH. Calculating the pH of a strong base is straightforward, as we have seen earlier. Figure 9.8c shows the pH after adding 30.0 mL and 40.0 mL of NaOH.

See Table 9.3 for the values.

Next, we draw a straight line through each pair of points, extending the lines through the vertical line representing the equivalence point's volume (Figure 9.8d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.8e). A comparison of our sketch to the exact titration curve (Figure 9.8f) shows that they are in close agreement.

Practice Exercise 9.3

Sketch a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl and compare to the result from Practice Exercise 9.2.

Click here to review your answer to this exercise.

As shown by the following example, we can adapt this approach to acid–base titrations, including those involving polyprotic weak acids and bases, or mixtures of weak acids and bases.

Example 9.1

Sketch titration curves for the following two systems: (a) the titration of 50.0 mL of 0.050 M H_2A, a diprotic weak acid with a pK_{a1} of 3 and a pK_{a2} of 7; and (b) the titration of a 50.0 mL mixture containing 0.075 M HA, a weak acid with a pK_a of 3, and 0.025 M HB, a weak acid with a pK_a of 7. For both titrations the titrant is 0.10 M NaOH.

Solution

Figure 9.9a shows the titration curve for H_2A, including the ladder diagram on the *y*-axis, the equivalence points at 25.0 mL and 50.0 mL, two points before each equivalence point, two points after the last equivalence

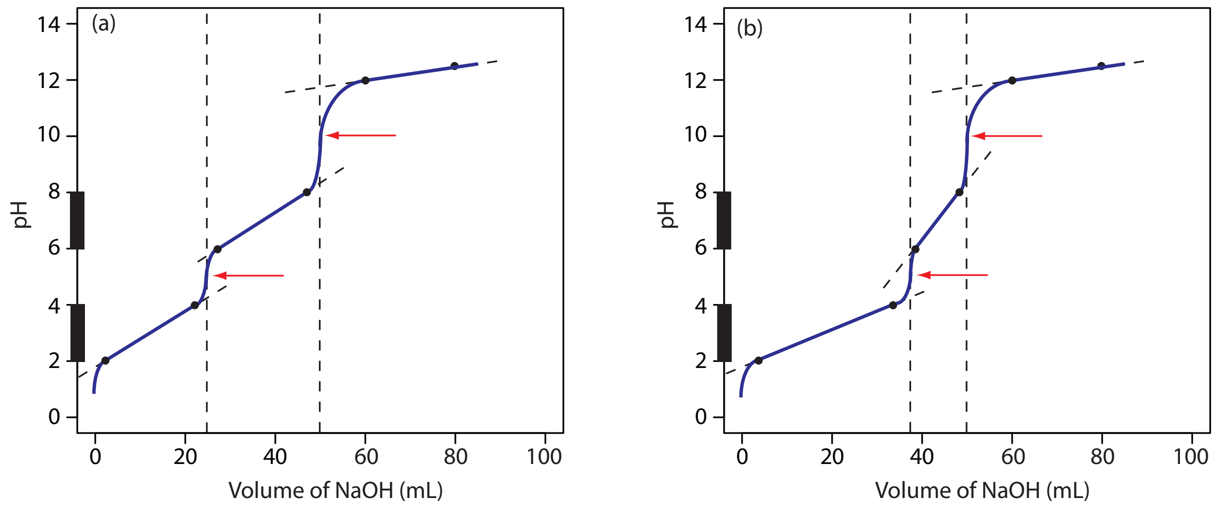


Figure 9.9 Titration curves for Example 9.1. The red arrows show the locations of the equivalence points.

point, and the straight-lines that help in sketching the final curve. Before the first equivalence point the pH is controlled by a buffer consisting of H_2A and HA^-. An HA^-/A^{2-} buffer controls the pH between the two equivalence points. After the second equivalence point the pH reflects the concentration of excess NaOH.

Figure 9.9b shows the titration curve for the mixture of HA and HB. Again, there are two equivalence points. In this case, however, the equivalence points are not equally spaced because the concentration of HA is greater than that for HB. Since HA is the stronger of the two weak acids it reacts first; thus, the pH before the first equivalence point is controlled by a buffer consisting of HA and A^-. Between the two equivalence points the pH reflects the titration of HB and is determined by a buffer consisting of HB and B^-. After the second equivalence point excess NaOH is responsible for the pH.

Practice Exercise 9.4

Sketch the titration curve for 50.0 mL of 0.050 M H_2A, a diprotic weak acid with a pK_{a1} of 3 and a pK_{a2} of 4, using 0.100 M NaOH as the titrant. The fact that pK_{a2} falls within the buffer range of pK_{a1} presents a challenge that you will need to consider.

Click here to review your answer to this exercise.

9B.2 Selecting and Evaluating the End point

Earlier we made an important distinction between a titration's end point and its equivalence point. The difference between these two terms is important and deserves repeating. An equivalence point, which occurs when we react stoichiometrically equal amounts of the analyte and the titrant, is a theoretical not an experimental value. A titration's end point is an experimental result, representing our best estimate of the equivalence point. Any difference between an equivalence point and its corresponding end point is a source of determinate error. It is even possible that an equivalence point does not have a useful end point.

Where is The Equivalence Point?

Earlier we learned how to calculate the pH at the equivalence point for the titration of a strong acid with a strong base, and for the titration of a weak acid with a strong base. We also learned to quickly sketch a titration curve with only a minimum of calculations. Can we also locate the equivalence point without performing any calculations. The answer, as you might guess, is often yes!

For most acid–base titrations the inflection point, the point on a titration curve having the greatest slope, very nearly coincides with the equivalence point.[3] The red arrows in Figure 9.9, for example, indicate the equivalence points for the titration curves from Example 9.1. An inflection point actually precedes its corresponding equivalence point by a small amount, with the error approaching 0.1% for weak acids or weak bases with dissociation constants smaller than 10^{-9}, or for very dilute solutions.

The principal limitation to using an inflection point to locate the equivalence point is that the inflection point must be present. For some titrations the inflection point may be missing or difficult to find. Figure 9.10, for example, demonstrates the affect of a weak acid's dissociation constant, K_a, on the shape of titration curve. An inflection point is visible, even if barely so, for acid dissociation constants larger than 10^{-9}, but is missing when K_a is 10^{-11}.

An inflection point also may be missing or difficult to detect if the analyte is a multiprotic weak acid or weak base with successive dissociation constants that are similar in magnitude. To appreciate why this is true let's consider the titration of a diprotic weak acid, H_2A, with NaOH. During the titration the following two reactions occur.

3 Meites, L.; Goldman, J. A. *Anal. Chim. Acta* **1963**, *29*, 472–479.

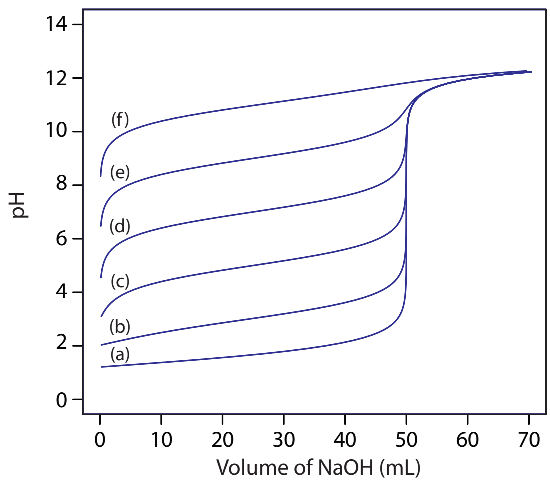


Figure 9.10 Weak acid–strong base titration curves for the titration of 50.0 mL of 0.100 M HA with 0.100 M NaOH. The pK_a values for HA are (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, and (f) 11.

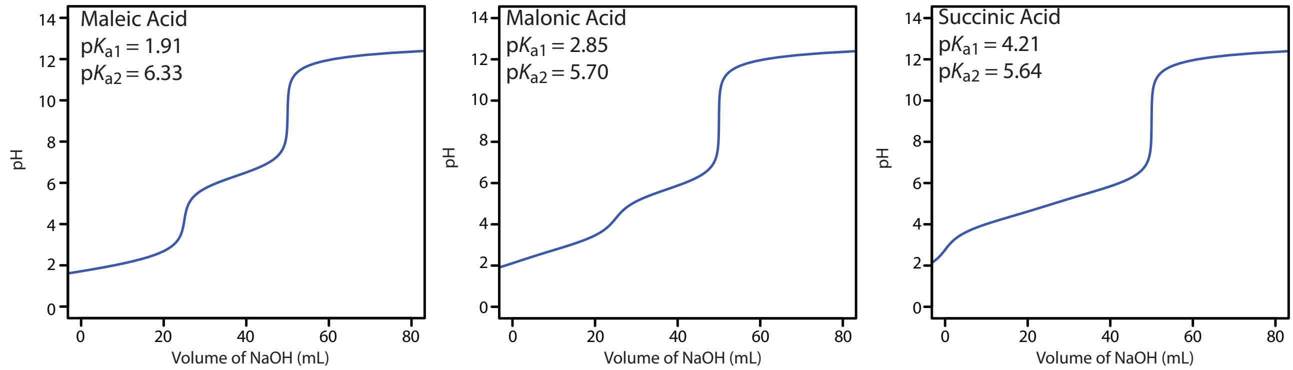


Figure 9.11 Titration curves for the diprotic weak acids maleic acid, malonic acid, and succinic acid. Each titration curve is for 50.0 mL of 0.0500 M weak acid using 0.100 M NaOH. Although each titration curve has equivalence points at 25.0 mL and 50.0 mL of NaOH, the titration curve for succinic acid shows only one inflection point.

$$H_2A(aq) + OH^-(aq) \rightarrow HA^-(aq) + H_2O(l) \qquad 9.3$$

$$HA^-(aq) + OH^-(aq) \rightarrow A^{2-}(aq) + H_2O(l) \qquad 9.4$$

To see two distinct inflection points, reaction 9.3 must be essentially complete before reaction 9.4 begins.

Figure 9.11 shows titration curves for three diprotic weak acids. The titration curve for maleic acid, for which K_{a1} is approximately 20,000× larger than K_{a2}, has two distinct inflection points. Malonic acid, on the other hand, has acid dissociation constants that differ by a factor of approximately 690. Although malonic acid's titration curve shows two inflection points, the first is not as distinct as that for maleic acid. Finally, the titration curve for succinic acid, for which the two K_a values differ by a factor of only 27, has only a single inflection point corresponding to the neutralization of $HC_4H_4O_4^-$ to $C_4H_4O_4^{2-}$. In general, we can detect separate inflection points when successive acid dissociation constants differ by a factor of at least 500 (a ΔpK_a of at least 2.7).

Finding the End point with an Indicator

One interesting group of weak acids and weak bases are organic dyes. Because an organic dye has at least one highly colored conjugate acid–base species, its titration results in a change in both pH and color. We can use this change in color to indicate the end point of a titration, provided that it occurs at or near the titration's equivalence point.

Let's use an indicator, HIn, to illustrate how an acid–base indicator works. Because the indicator's acid and base forms have different colors—the weak acid, HIn, is yellow and the weak base, In^-, is red—the color of a solution containing the indicator depends on their relative concentrations. The indicator's acid dissociation reaction

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

has an equilibrium constant of

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} \qquad 9.5$$

Taking the negative log of each side of equation 9.5, and rearranging to solve for pH leaves with a equation

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} \qquad 9.6$$

relating the solution's pH to the relative concentrations of HIn and In^-.

If we can detect HIn and In^- with equal ease, then the transition from yellow to red (or from red to yellow) reaches its midpoint, which is orange, when their concentrations are equal, or when the pH is equal to the indicator's pK_a. If the indicator's pK_a and the pH at the equivalence point are identical, then titrating until the indicator turns orange is a suitable end point. Unfortunately, we rarely know the exact pH at the equivalence point. In addition, determining when the concentrations of HIn and In^- are equal may be difficult if the indicator's change in color is subtle.

We can establish the range of pHs over which the average analyst observes a change in the indicator's color by making the following assumptions—the indicator's color is yellow if the concentration of HIn is 10× greater than that of In^-, and its color is red if the concentration of HIn is 10× smaller than that of In^-. Substituting these inequalities into equation 9.6

$$pH = pK_a + \log\frac{1}{10} = pK_a - 1$$

$$pH = pK_a + \log\frac{10}{1} = pK_a + 1$$

shows that the indicator changes color over a pH range extending ±1 unit on either side of its pK_a. As shown in Figure 9.12, the indicator is yellow when the pH is less than pK_a–1, and it is red for pHs greater than pK_a+1.

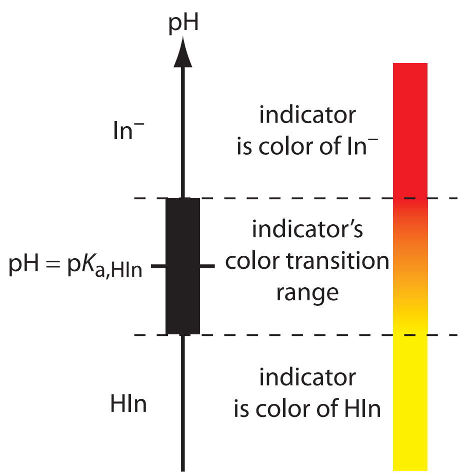


Figure 9.12 Diagram showing the relationship between pH and an indicator's color. The ladder diagram defines pH values where HIn and In^- are the predominate species. The indicator changes color when the pH is between pK_a–1 and pK_a+1.

Table 9.4 Properties of Selected Acid–Base Indicators

Indicator	Acid Color	Base Color	pH Range	pK_a
cresol red	red	yellow	0.2–1.8	–
thymol blue	red	yellow	1.2–2.8	1.7
bromophenol blue	yellow	blue	3.0–4.6	4.1
methyl orange	red	yellow	3.1–4.4	3.7
Congo red	blue	red	3.0–5.0	–
bromocresol green	yellow	blue	3.8–5.4	4.7
methyl red	red	yellow	4.2–6.3	5.0
bromocresol purple	yellow	purple	5.2–6.8	6.1
litmus	red	blue	5.0–8.0	–
bromothymol blue	yellow	blue	6.0–7.6	7.1
phenol red	yellow	blue	6.8–8.4	7.8
cresol red	yellow	red	7.2–8.8	8.2
thymol blue	yellow	red	8.0–9.6	8.9
phenolphthalein	colorless	red	8.3–10.0	9.6
alizarin yellow R	yellow	orange–red	10.1–12.0	–

You may wonder why an indicator's pH range, such as that for phenolphthalein, is not equally distributed around its pK_a value. The explanation is simple. Figure 9.12 presents an idealized view of an indicator in which our sensitivity to the indicator's two colors is equal. For some indicators only the weak acid or the weak base is colored. For other indicators both the weak acid and the weak base are colored, but one form is easier to see. In either case, the indicator's pH range is skewed in the direction of the indicator's less colored form. Thus, phenolphthalein's pH range is skewed in the direction of its colorless form, shifting the pH range to values lower than those suggested by Figure 9.12.

For pHs between p$K_a - 1$ and p$K_a + 1$ the indicator's color passes through various shades of orange. The properties of several common acid–base indicators are shown in Table 9.4.

The relatively broad range of pHs over which an indicator changes color places additional limitations on its feasibility for signaling a titration's end point. To minimize a determinate titration error, an indicator's entire pH range must fall within the rapid change in pH at the equivalence point. For example, in Figure 9.13 we see that phenolphthalein is an appropriate indicator for the titration of 50.0 mL of 0.050 M acetic acid with 0.10 M NaOH. Bromothymol blue, on the other hand, is an inappropriate indicator because its change in color begins before the initial sharp rise in pH, and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining inaccurate results, while the range of possible end point volumes increases the probability of obtaining imprecise results.

Practice Exercise 9.5

Suggest a suitable indicator for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M NaOH. You constructed a titration curve for this titration in Practice Exercise 9.2 and Practice Exercise 9.3.

Click here to review your answer to this exercise.

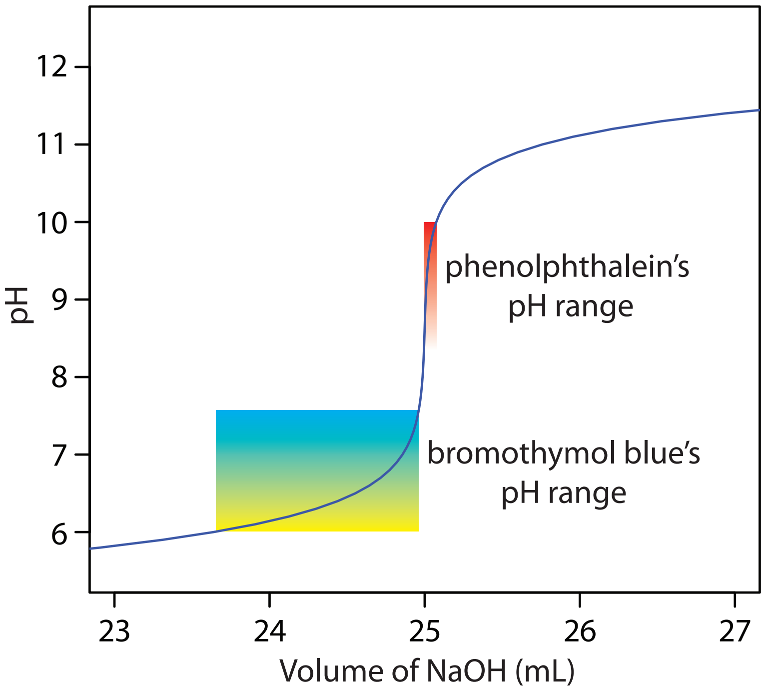


Figure 9.13 Portion of the titration curve for 50.0 mL of 0.050 M CH_3COOH with 0.10 M NaOH, highlighting the region containing the equivalence point. The end point transitions for the indicators phenolphthalein and bromothymol blue are superimposed on the titration curve.

Finding the End point by Monitoring pH

An alternative approach for locating a titration's end point is to continuously monitor the titration's progress using a sensor whose signal is a function of the analyte's concentration. The result is a plot of the entire titration curve, which we can use to locate the end point with a minimal error.

The obvious sensor for monitoring an acid–base titration is a pH electrode and the result is a potentiometric titration curve. For example, Figure 9.14a shows a small portion of the potentiometric titration curve for the titration of 50.0 mL of 0.050 M CH_3COOH with 0.10 M NaOH, focusing on the region containing the equivalence point. The simplest method for finding the end point is to locate the titration curve's inflection point, as shown by the arrow. This is also the least accurate method, particularly if the titration curve has a shallow slope at the equivalence point.

See Chapter 11 for more details about pH electrodes.

Another method for locating the end point is to plot the titration curve's first derivative, which gives the titration curve's slope at each point along the *x*-axis. Examine Figure 9.14a and consider how the titration curve's slope changes as we approach, reach, and pass the equivalence point. Because the slope reaches its maximum value at the inflection point, the first derivative shows a spike at the equivalence point (Figure 9.14b).

The second derivative of a titration curve may be more useful than the first derivative because the equivalence point intersects the volume axis. Figure 9.14c shows the resulting titration curve.

Derivative methods are particularly useful when titrating a sample that contains more than one analyte. If we rely on indicators to locate the end points, then we usually must complete separate titrations for each analyte. If we record the titration curve, however, then a single titration is sufficient.

The precision with which we can locate the end point also makes derivative methods attractive for an analyte with a poorly defined normal titration curve.

Derivative methods work well only if we record sufficient data during the rapid increase in pH near the equivalence point. This is usually not a problem if we use an automatic titrator, such as that seen earlier in Figure 9.5. Because the pH changes so rapidly near the equivalence point—a change of several pH units with the addition of several drops of titrant is not unusual—a manual titration does not provide enough data for a useful derivative titration curve. A manual titration does contain an abundance of data during the more gently rising portions of the titration curve before and after the equivalence point. This data also contains information about the titration curve's equivalence point.

Consider again the titration of acetic acid, CH_3COOH, with NaOH. At any point during the titration acetic acid is in equilibrium with H_3O^+ and CH_3COO^-

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

for which the equilibrium constant is

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Suppose we have the following three points on our titration curve:

volume (mL)	pH
23.65	6.00
23.91	6.10
24.13	6.20

Mathematically, we can approximate the first derivative as ΔpH/ΔV, where ΔpH is the change in pH between successive additions of titrant. Using the first two points, the first derivative is

$$\frac{\Delta\text{pH}}{\Delta V} = \frac{6.10 - 6.00}{23.91 - 23.65} = 0.385$$

which we assign to the average of the two volumes, or 23.78 mL. For the second and third points, the first derivative is 0.455 and the average volume is 24.02 mL.

volume (mL)	ΔpH/ΔV
23.78	0.385
24.02	0.455

We can approximate the second derivative as Δ(ΔpH/ΔV)/ΔV, or Δ^2pH/ΔV^2. Using the two points from our calculation of the first derivative, the second derivative is

$$\frac{\Delta^2\text{pH}}{\Delta V^2} = \frac{0.455 - 0.385}{23.78 - 24.02} = 0.292$$

Note that calculating the first derivative comes at the expense of losing one piece of information (three points become two points), and calculating the second derivative comes at the expense of losing two pieces of information.

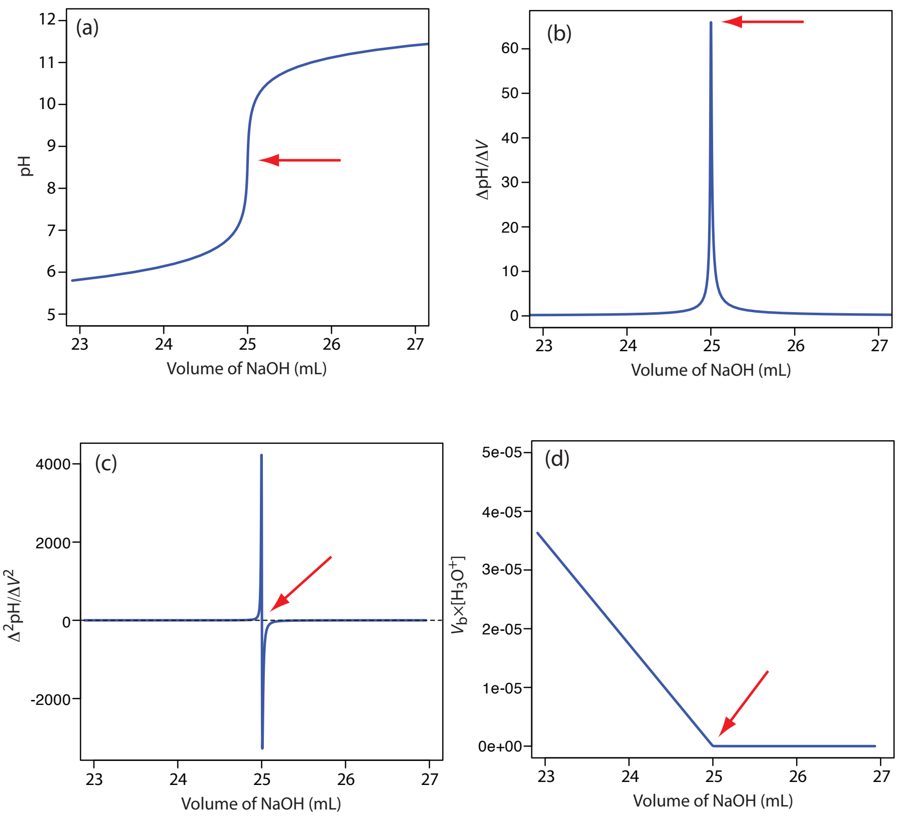


Figure 9.14 Titration curves for the titration of 50.0 mL of 0.050 M CH_3COOH with 0.10 M NaOH: (a) normal titration curve; (b) first derivative titration curve; (c) second derivative titration curve; (d) Gran plot. The red arrow shows the location of the titration's end point.

Before the equivalence point the concentrations of CH_3COOH and CH_3COO^- are

$$[CH_3COOH] = \frac{\text{initial moles } CH_3COOH - \text{moles NaOH added}}{\text{total volume}}$$

$$= \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_bV_b}{V_a + V_b}$$

Substituting these equations into the K_a expression and rearranging leaves us with

$$K_a = \frac{[H_3O^+](M_bV_b)}{M_aV_a - M_bV_b}$$

$$K_aM_aV_a - K_aM_bV_b = [H_3O^+](M_bV_b)$$

$$\frac{K_aM_aV_a}{M_b} - K_aV_b = [H_3O^+] \times V_b$$

Finally, recognizing that the equivalence point volume is

$$V_{eq} = \frac{M_aV_a}{M_b}$$

leaves us with the following equation.

$$[H_3O^+] \times V_b = K_aV_{eq} - K_aV_b$$

For volumes of titrant before the equivalence point, a plot of $V_b \times [H_3O^+]$ versus V_b is a straight-line with an *x*-intercept of V_{eq} and a slope of $-K_a$. Figure 9.14d shows a typical result. This method of data analysis, which converts a portion of a titration curve into a straight-line, is a GRAN PLOT.

Finding the End point by Monitoring Temperature

The reaction between an acid and a base is exothermic. Heat generated by the reaction is absorbed by the titrand, increasing its temperature. Monitoring the titrand's temperature as we add the titrant provides us with another method for recording a titration curve and identifying the titration's end point (Figure 9.15).

Before adding titrant, any change in the titrand's temperature is the result of warming or cooling as it equilibrates with the surroundings. Adding titrant initiates the exothermic acid–base reaction, increasing the titrand's temperature. This part of a thermometric titration curve is called the titra-

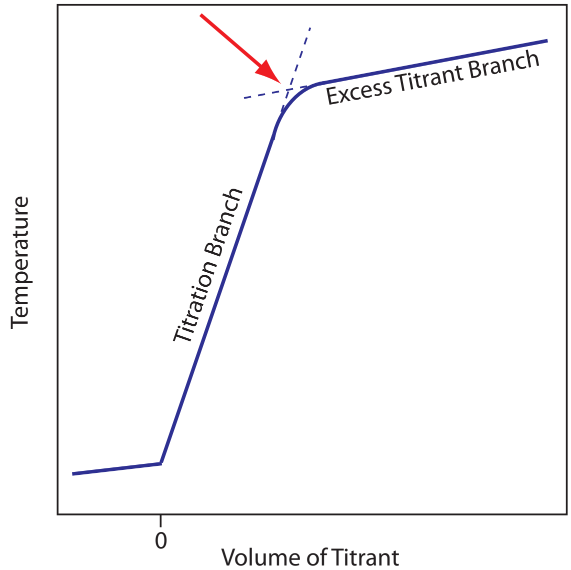


Figure 9.15 Typical thermometric titration curve. The endpoint, shown by the red arrow, is found by extrapolating the titration branch and the excess titration branch.

tion branch. The temperature continues to rise with each addition of titrant until we reach the equivalence point. After the equivalence point, any change in temperature is due to the titrant's enthalpy of dilution, and the difference between the temperatures of the titrant and titrand. Ideally, the equivalence point is a distinct intersection of the titration branch and the excess titrant branch. As shown in Figure 9.15, however, a thermometric titration curve usually shows curvature near the equivalence point due to an incomplete neutralization reaction, or to the excessive dilution of the titrand and the titrant during the titration. The latter problem is minimized by using a titrant that is 10–100 times more concentrated than the analyte, although this results in a very small end point volume and a larger relative error. If necessary, the end point is found by extrapolation.

Although not a particularly common method for monitoring acid–base titrations, a thermometric titration has one distinct advantage over the direct or indirect monitoring of pH. As discussed earlier, the use of an indicator or the monitoring of pH is limited by the magnitude of the relevant equilibrium constants. For example, titrating boric acid, H_3BO_3, with NaOH does not provide a sharp end point when monitoring pH because, boric acid's K_a of 5.8×10^{-10} is too small (Figure 9.16a). Because boric acid's enthalpy of neutralization is fairly large, –42.7 kJ/mole, however, its thermometric titration curve provides a useful endpoint (Figure 9.16b).

9B.3 Titrations in Nonaqueous Solvents

Thus far we have assumed that the titrant and the titrand are aqueous solutions. Although water is the most common solvent in acid–base titrimetry, switching to a nonaqueous solvent can improve a titration's feasibility.

For an amphoteric solvent, SH, the autoprotolysis constant, K_s, relates the concentration of its protonated form, SH_2^+, to that of its deprotonated form, S^-

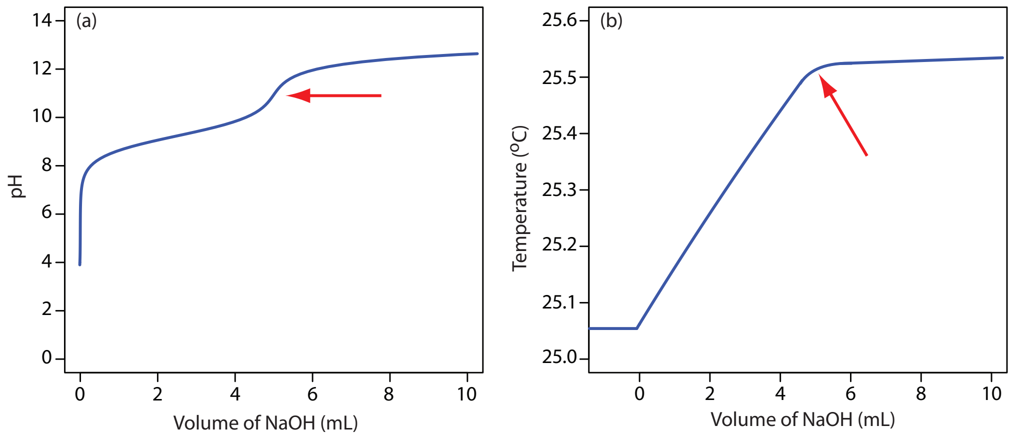


Figure 9.16 Titration curves for the titration of 50.0 mL of 0.050 M H_3BO_3 with 0.50 M NaOH obtained by monitoring (a) pH, and (b) temperature. The red arrows show the end points for the titrations.

$$2\text{SH} \rightleftharpoons \text{SH}_2^+ + \text{S}^-$$

$$K_s = [\text{SH}_2^+][\text{S}^-]$$

You should recognize that K_w is just specific form of K_s when the solvent is water.

and the solvent's pH and pOH are

$$\text{pH} = -\log[\text{SH}_2^+]$$

$$\text{pOH} = -\log[\text{S}^-]$$

The most important limitation imposed by K_s is the change in pH during a titration. To understand why this is true, let's consider the titration of 50.0 mL of 1.0×10^{-4} M HCl using 1.0×10^{-4} M NaOH. Before the equivalence point, the pH is determined by the untitrated strong acid. For example, when the volume of NaOH is 90% of V_{eq}, the concentration of H_3O^+ is

$$[\text{H}_3\text{O}^+] = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$= \frac{(1.0\times10^{-4}\ \text{M})(50.0\ \text{mL}) - (1.0\times10^{-4}\ \text{M})(45.0\ \text{mL})}{50.0\ \text{mL} + 45.0\ \text{mL}}$$

$$= 5.3\times10^{-6}\ \text{M}$$

The titration's equivalence point requires 50.0 mL of NaOH; thus, 90% of V_{eq} is 45.0 mL of NaOH.

and the pH is 5.3. When the volume of NaOH is 110% of V_{eq}, the concentration of OH^- is

$$[\text{OH}^-] = \frac{M_bV_b - M_aV_a}{V_a + V_b}$$

$$= \frac{(1.0\times10^{-4}\ \text{M})(55.0\ \text{mL}) - (1.0\times10^{-4}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 55.0\ \text{mL}}$$

$$= 4.8\times10^{-6}\ \text{M}$$

The titration's equivalence point requires 50.0 mL of NaOH; thus, 110% of V_{eq} is 55.0 mL of NaOH.

and the pOH is 5.3. The titrand's pH is

$$pH = pK_w - pOH = 14 - 5.3 = 8.7$$

and the change in the titrand's pH as the titration goes from 90% to 110% of V_{eq} is

$$\Delta pH = 8.7 - 5.3 = 3.4$$

If we carry out the same titration in a nonaqueous solvent with a K_s of 1.0×10^{-20}, the pH after adding 45.0 mL of NaOH is still 5.3. However, the pH after adding 55.0 mL of NaOH is

$$pH = pK_s - pOH = 20 - 5.3 = 14.7$$

In this case the change in pH

$$\Delta pH = 14.7 - 5.3 = 9.4$$

is significantly greater than that obtained when the titration is carried out in water. Figure 9.17 shows the titration curves in both the aqueous and the nonaqueous solvents.

Another parameter affecting the feasibility of an acid–base titration is the titrand's dissociation constant. Here, too, the solvent plays an important role. The strength of an acid or a base is a relative measure of the ease transferring a proton from the acid to the solvent, or from the solvent to the base. For example, HF, with a K_a of 6.8×10^{-4}, is a better proton donor than CH_3COOH, for which K_a is 1.75×10^{-5}.

The strongest acid that can exist in water is the hydronium ion, H_3O^+. HCl and HNO_3 are strong acids because they are better proton donors than H_3O^+ and essentially donate all their protons to H_2O, LEVELING their acid

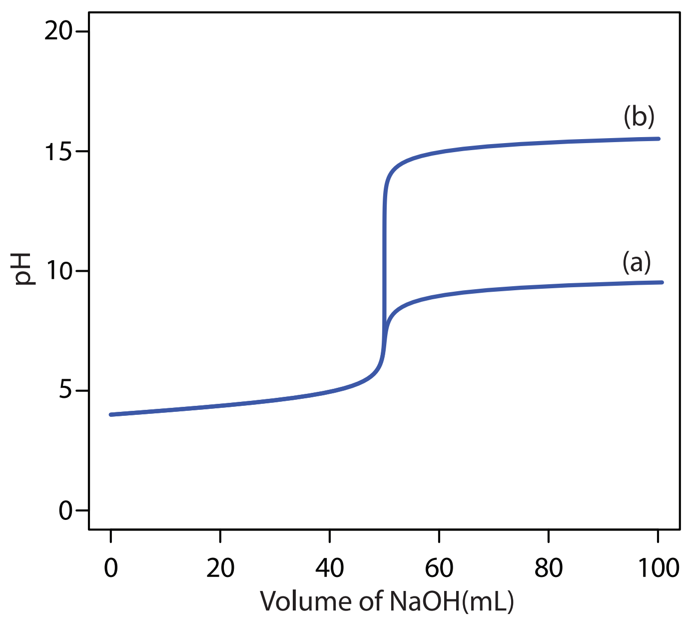


Figure 9.17 Titration curves for 50.0 mL of 1.0×10^{-4} M HCl using 1.0×10^{-4} M NaOH in (a) water, $K_w = 1.0 \times 10^{-14}$, and (b) a nonaqueous solvent, $K_s = 1.0 \times 10^{-20}$.

strength to that of H_3O^+. In a different solvent HCl and HNO_3 may not behave as strong acids.

If we place acetic acid in water the dissociation reaction

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

does not proceed to a significant extent because CH_3COO^- is a stronger base than H_2O, and H_3O^+ is a stronger acid than CH_3COOH. If we place acetic acid in a solvent, such as ammonia, that is a stronger base than water, then the reaction

$$CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$$

proceeds to a greater extent. In fact, both HCl and CH_3COOH are strong acids in ammonia.

All other things being equal, the strength of a weak acid increases if we place it in a solvent that is more basic than water, and the strength of a weak base increases if we place it in a solvent that is more acidic than water. In some cases, however, the opposite effect is observed. For example, the pK_b for NH_3 is 4.75 in water and it is 6.40 in the more acidic glacial acetic acid. In contradiction to our expectations, NH_3 is a weaker base in the more acidic solvent. A full description of the solvent's effect on the pK_a of weak acid or the pK_b of a weak base is beyond the scope of this text. You should be aware, however, that a titration that is not feasible in water may be feasible in a different solvent.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical acid–base titrimetric method. Although each method is unique, the following description of the determination of protein in bread provides an instructive example of a typical procedure. The description here is based on Method 13.86 as published in *Official Methods of Analysis*, 8th Ed., Association of Official Agricultural Chemists: Washington, D. C., 1955.

Representative Method 9.1

Determination of Protein in Bread

Description of the Method

This method is based on a determination of %w/w nitrogen using the Kjeldahl method. The protein in a sample of bread is oxidized to NH_4^+ using hot concentrated H_2SO_4. After making the solution alkaline, which converts the NH_4^+ to NH_3, the ammonia is distilled into a flask containing a known amount of HCl. The amount of unreacted HCl is determined by a back titration with standard strong base titrant. Because different cereal proteins contain similar amounts of nitrogen, multiplying the experimentally determined %w/w N by a factor of 5.7 gives the %w/w protein in the sample (on average there are 5.7 g protein for every gram of nitrogen).

Procedure

Transfer a 2.0-g sample of bread, which has previously been air-dried and ground into a powder, to a suitable digestion flask, along with 0.7 g of a HgO catalyst, 10 g of K_2SO_4, and 25 mL of concentrated H_2SO_4. Bring the solution to a boil. Continue boiling until the solution turns clear and then boil for at least an additional 30 minutes. After cooling the solution below room temperature, remove the Hg^{2+} catalyst by adding 200 mL of H_2O and 25 mL of 4% w/v K_2S. Add a few Zn granules to serve as boiling stones and 25 g of NaOH. Quickly connect the flask to a distillation apparatus and distill the NH_3 into a collecting flask containing a known amount of standardized HCl. The tip of the condenser must be placed below the surface of the strong acid. After the distillation is complete, titrate the excess strong acid with a standard solution of NaOH using methyl red as an indicator (Figure 9.18).

Questions

1. Oxidizing the protein converts all of its nitrogen to NH_4^+. Why is the amount of nitrogen not determined by titrating the NH_4^+ with a strong base?

   There are two reasons for not directly titrating the ammonium ion. First, because NH_4^+ is a very weak acid (its K_a is 5.6×10^{-10}), its titration with NaOH yields a poorly defined end point. Second, even if the end point can be determined with acceptable accuracy and precision, the solution also contains a substantial larger concentration of unreacted H_2SO_4. The presence of two acids that differ greatly in concentration makes for a difficult analysis. If the titrant's concentration is similar to that of H_2SO_4, then the equivalence point volume for the titration of NH_4^+ is too small to measure reliably. On the other hand, if the titrant's concentration is similar to that of NH_4^+, the volume needed to neutralize the H_2SO_4 is unreasonably large.

2. Ammonia is a volatile compound as evidenced by the strong smell of even dilute solutions. This volatility is a potential source of determinate error. Is this determinate error negative or positive?

   Any loss of NH_3 is loss of nitrogen and, therefore, a loss of protein. The result is a negative determinate error.

3. Discuss the steps in this procedure that minimize this determinate error.

   Three specific steps minimize the loss of ammonia: (1) the solution is cooled below room temperature before adding NaOH; (2) after add-

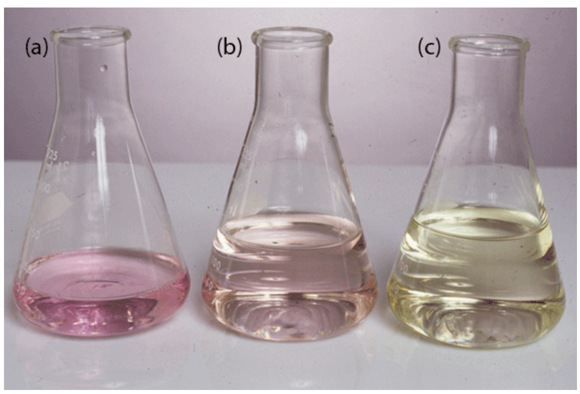


Figure 9.18 Methyl red's endpoint for the titration of a strong acid with a strong base; the indicator is: (a) red prior to the end point; (b) orange at the end point; and (c) yellow after the end point.

ing NaOH, the digestion flask is quickly connected to the distillation apparatus; and (3) the condenser's tip is placed below the surface of the HCl to ensure that the NH_3 reacts with the HCl before it can be lost through volatilization.

4. How does K_2S remove Hg^{2+}, and why is its removal important?

   Adding sulfide precipitates Hg^{2+} as HgS. This is important because NH_3 forms stable complexes with many metal ions, including Hg^{2+}. Any NH_3 that reacts with Hg^{2+} is not collected during distillation, providing another source of determinate error.

9B.4 Quantitative Applications

Although many quantitative applications of acid–base titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In this section we review the general application of acid–base titrimetry to the analysis of inorganic and organic compounds, with an emphasis on applications in environmental and clinical analysis. First, however, we discuss the selection and standardization of acidic and basic titrants.

Selecting and Standardizing a Titrant

The most common strong acid titrants are HCl, $HClO_4$, and H_2SO_4. Solutions of these titrants are usually prepared by diluting a commercially available concentrated stock solution. Because the concentrations of concentrated acids are known only approximately, the titrant's concentration is determined by standardizing against one of the primary standard weak bases listed in Table 9.5.

The nominal concentrations of the concentrated stock solutions are 12.1 M HCl, 11.7 M $HClO_4$, and 18.0 M H_2SO_4.

The most common strong base titrant is NaOH. Sodium hydroxide is available both as an impure solid and as an approximately 50% w/v solution. Solutions of NaOH may be standardized against any of the primary weak acid standards listed in Table 9.5.

Using NaOH as a titrant is complicated by potential contamination from the following reaction between CO_2 and OH^-.

Any solution in contact with the atmosphere contains a small amount of $CO_2(aq)$ from the equilibrium

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l) \qquad 9.7$$

During the titration, NaOH reacts with both the titrand and CO_2, increasing the volume of NaOH needed to reach the titration's end point. This is not a problem if end point pH is less than 6. Below this pH the CO_3^{2-} from reaction 9.7 reacts with H_3O^+ to form carbonic acid.

$$CO_3^{2-}(aq) + 2H_3O^+(aq) \rightarrow H_2CO_3(aq) + 2H_2O(l) \qquad 9.8$$

Combining reaction 9.7 and reaction 9.8 gives an overall reaction that does not include OH^-.

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Table 9.5 Selected Primary Standards for Standardizing Strong Acid and Strong Base Titrants

Standardization of Acidic Titrants		
Primary Standard	Titration Reaction	Comment
Na_2CO_3	$Na_2CO_3 + 2H_3O^+ \rightarrow H_2CO_3 + 2Na^+ + 2H_2O$	a
$(HOCH_2)_3CNH_2$	$(HOCH_2)_3CNH_2 + H_3O^+ \rightarrow (HOCH_2)_3CNH_3^+ + H_2O$	b
$Na_2B_4O_7$	$Na_2B_4O_7 + 2H_3O^+ + 3H_2O \rightarrow 2Na^+ + 4H_3BO_3$	
Standardization of Basic Titrants		
Primary Standard	Titration Reaction	Comment
$KHC_8H_4O_4$	$KHC_8H_4O_4 + OH^- \rightarrow K^+ + C_8H_4O_4^- + H_2O$	c
C_6H_5COOH	$C_6H_5COOH + OH^- \rightarrow C_6H_5COO^- + H_2O$	d
$KH(IO_3)_2$	$KH(IO_3)_2 + OH^- \rightarrow K^+ + 2IO_3^- + H_2O$	

[a] The end point for this titration is improved by titrating to the second equivalence point, boiling the solution to expel CO_2, and retitrating to the second equivalence point. The reaction in this case is

$$Na_2CO_3 + 2H_3O^+ \rightarrow CO_2 + 2Na^+ + 3K^+$$

[b] *Tris*-(hydroxymethyl)aminomethane often goes by the shorter name of TRIS or THAM.

[c] Potassium hydrogen phthalate often goes by the shorter name of KHP.

[d] Because it is not very soluble in water, dissolve benzoic acid in a small amount of ethanol before diluting with water.

Under these conditions the presence of CO_2 does not affect the quantity of OH^- used in the titration and is not a source of determinate error.

If the end point pH is between 6 and 10, however, the neutralization of CO_3^{2-} requires one proton

$$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$

and the net reaction between CO_2 and OH^- is

$$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$$

Under these conditions some OH^- is consumed in neutralizing CO_2, resulting in a determinate error. We can avoid the determinate error if we use the same end point pH in both the standardization of NaOH and the analysis of our analyte, although this often is not practical.

Solid NaOH is always contaminated with carbonate due to its contact with the atmosphere, and can not be used to prepare a carbonate-free solution of NaOH. Solutions of carbonate-free NaOH can be prepared from 50% w/v NaOH because Na_2CO_3 is insoluble in concentrated NaOH.

When CO_2 is absorbed, Na_2CO_3 precipitates and settles to the bottom of the container, allowing access to the carbonate-free NaOH. When preparing a solution of NaOH, be sure to use water that is free from dissolved CO_2. Briefly boiling the water expels CO_2, and after cooling, it may be used to prepare carbonate-free solutions of NaOH. A solution of carbonate-free NaOH is relatively stable f we limit its contact with the atmosphere. Standard solutions of sodium hydroxide should not be stored in glass bottles as NaOH reacts with glass to form silicate; instead, store such solutions in polyethylene bottles.

Inorganic Analysis

Acid–base titrimetry is a standard method for the quantitative analysis of many inorganic acids and bases. A standard solution of NaOH can be used to determine the concentration of inorganic acids, such as H_3PO_4 or H_3AsO_4, and inorganic bases, such as Na_2CO_3 can be analyzed using a standard solution of HCl.

An inorganic acid or base that is too weak to be analyzed by an aqueous acid–base titration can be analyzed by adjusting the solvent, or by an indirect analysis. For example, when analyzing boric acid, H_3BO_3, by titrating with NaOH, accuracy is limited by boric acid's small acid dissociation constant of 5.8×10^{-10}. Boric acid's K_a value increases to 1.5×10^{-4} in the presence of mannitol, because it forms a complex with the borate ion. The result is a sharper end point and a more accurate titration. Similarly, the analysis of ammonium salts is limited by the small acid dissociation constant of 5.7×10^{-10} for NH_4^+. In this case, we can convert NH_4^+ to NH_3 by neutralizing with strong base. The NH_3, for which K_b is 1.58×10^{-5}, is then removed by distillation and titrated with HCl.

Figure 9.16a shows a typical result for the titration of H_3BO_3 with NaOH.

We can analyze a neutral inorganic analyte if we can first convert it into an acid or base. For example, we can determine the concentration of NO_3^- by reducing it to NH_3 in a strongly alkaline solution using Devarda's alloy, a mixture of 50% w/w Cu, 45% w/w Al, and 5% w/w Zn.

$$3NO_3^-(aq) + 8Al(s) + 5OH^-(aq) + 2H_2O(l) \rightarrow 8AlO_2^-(aq) + 3NH_3(aq)$$

The NH_3 is removed by distillation and titrated with HCl. Alternatively, we can titrate NO_3^- as a weak base by placing it in an acidic nonaqueous solvent such as anhydrous acetic acid and using $HClO_4$ as a titrant.

Acid–base titrimetry continues to be listed as a standard method for the determination of alkalinity, acidity, and free CO_2 in waters and wastewaters. **Alkalinity** is a measure of a sample's capacity to neutralize acids. The most important sources of alkalinity are OH^-, HCO_3^-, and CO_3^{2-}, although other weak bases, such as phosphate, may contribute to the overall alkalinity. Total alkalinity is determined by titrating to a fixed end point pH of 4.5 (or to the bromocresol green end point) using a standard solution of HCl or H_2SO_4. Results are reported as mg $CaCO_3$/L.

Although a variety of strong bases and weak bases may contribute to a sample's alkalinity, a single titration cannot distinguish between the possible sources. Reporting the total alkalinity as if $CaCO_3$ is the only source provides a means for comparing the acid-neutralizing capacities of different samples.

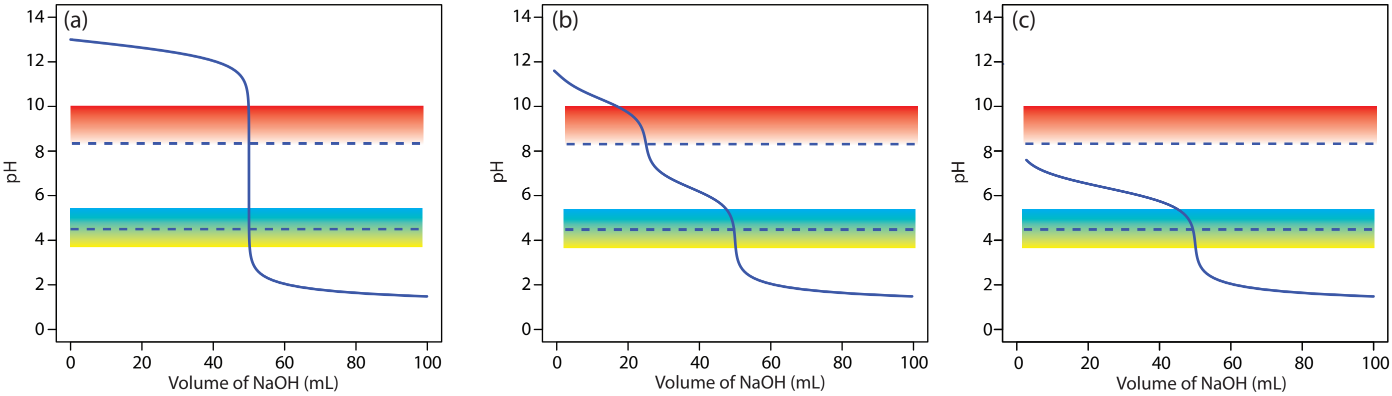


Figure 9.19 Titration curves for 50.0 mL of (a) 0.10 M NaOH, (b) 0.050 M Na_2CO_3, and (c) 0.10 M $NaHCO_3$ using 0.10 M HCl. The dashed lines indicate the fixed pH end points of 8.3 and 4.5. The color gradients show the phenolphthalein (red → colorless) and bromocresol green (blue → green) endpoints. When titrating to the phenolphthalein endpoint, the titration continues until the last trace of red is lost.

When the sources of alkalinity are limited to OH^-, HCO_3^-, and CO_3^{2-}, separate titrations to a pH of 4.5 (or the bromocresol green end point) and a pH of 8.3 (or the phenolphthalein end point) allow us to determine which species are present and their respective concentrations. Titration curves for OH^-, HCO_3^-, and CO_3^{2-} are shown in Figure 9.19. For a solution containing only OH^- alkalinity, the volumes of strong acid needed to reach the two end points are identical (Figure 9.19a). When the only source of alkalinity is CO_3^{2-}, the volume of strong acid needed to reach the end point at a pH of 4.5 is exactly twice that needed to reach the end point at a pH of 8.3 (Figure 9.19b). If a solution contains only HCO_3^- alkalinity, the volume of strong acid needed to reach the end point at a pH of 8.3 is zero, but that for the pH 4.5 end point is greater than zero (Figure 9.19c).

Solutions containing OH^- and HCO_3^- alkalinities are unstable with respect to the formation of CO_3^{2-}. Problem 9.15 in the end of chapter problems asks you to explain why this is true.

Mixtures of OH^- and CO_3^{2-}, or of HCO_3^- and CO_3^{2-} also are possible. Consider, for example, a mixture of OH^- and CO_3^{2-}. The volume of strong acid to titrate OH^- is the same whether we titrate to a pH of 8.3 or a pH of 4.5. Titrating CO_3^{2-} to a pH of 4.5, however, requires twice as much strong acid as titrating to a pH of 8.3. Consequently, when titrating a mixture of these two ions, the volume of strong acid to reach a pH of 4.5 is less than twice that to reach a pH of 8.3. For a mixture of HCO_3^- and CO_3^{2-} the volume of strong acid to reach a pH of 4.5 is more than twice that to reach a pH of 8.3. Table 9.6 summarizes the relationship between the sources of alkalinity and the volumes of titrant needed to reach the two end points.

ACIDITY is a measure of a water sample's capacity for neutralizing base, and is conveniently divided into strong acid and weak acid acidity. Strong acid acidity, from inorganic acids such as HCl, HNO_3, and H_2SO_4, is common in industrial effluents and acid mine drainage. Weak acid acidity is usually dominated by the formation of H_2CO_3 from dissolved CO_2, but also includes contributions from hydrolyzable metal ions such as Fe^{3+}, Al^{3+},

Table 9.6 Relationship Between End Point Volumes and Sources of Alkalinity

Source of Alkalinity	Relationship Between End Point Volumes
OH^-	$V_{pH\ 4.5} = V_{pH\ 8.3}$
CO_3^{2-}	$V_{pH\ 4.5} = 2 \times V_{pH\ 8.3}$
HCO_3^-	$V_{pH\ 4.5} > 0$; $V_{pH\ 8.3} = 0$
OH^- and CO_3^{2-}	$V_{pH\ 4.5} < 2 \times V_{pH\ 8.3}$
CO_3^{2-} and HCO_3^-	$V_{pH\ 4.5} > 2 \times V_{pH\ 8.3}$

and Mn^{2+}. In addition, weak acid acidity may include a contribution from organic acids.

Acidity is determined by titrating with a standard solution of NaOH to fixed pH of 3.7 (or the bromothymol blue end point) and a fixed pH 8.3 (or the phenolphthalein end point). Titrating to a pH of 3.7 provides a measure of strong acid acidity, and titrating to a pH of 8.3 provides a measure of total acidity. Weak acid acidity is the difference between the total and strong acid acidities. Results are expressed as the amount of $CaCO_3$ that can be neutralized by the sample's acidity. An alternative approach for determining strong acid and weak acid acidity is to obtain a potentiometric titration curve and use a Gran plot to determine the two equivalence points. This approach has been used, for example, to determine the forms of acidity in atmospheric aerosols.[4]

As is the case with alkalinity, acidity is reported as mg $CaCO_3$/L.

Water in contact with either the atmosphere, or with carbonate-bearing sediments contains free CO_2 that exists in equilibrium with $CO_2(g)$ and aqueous H_2CO_3, HCO_3^-, and CO_3^{2-}. The concentration of free CO_2 is determined by titrating with a standard solution of NaOH to the phenolphthalein end point, or to a pH of 8.3, with results reported as mg CO_2/L. This analysis is essentially the same as that for the determination of total acidity, and can only be applied to water samples that do not contain strong acid acidity.

Free CO_2 is the same thing as $CO_2(aq)$.

Organic Analysis

Acid–base titrimetry continues to have a small, but important role for the analysis of organic compounds in pharmaceutical, biochemical, agricultural, and environmental laboratories. Perhaps the most widely employed acid–base titration is the Kjeldahl analysis for organic nitrogen. Examples of analytes determined by a Kjeldahl analysis include caffeine and saccharin in pharmaceutical products, proteins in foods, and the analysis of nitrogen in fertilizers, sludges, and sediments. Any nitrogen present in a –3 oxidation state is quantitatively oxidized to NH_4^+. Because some aromatic heterocyclic compounds, such as pyridine, are difficult to oxidize, a catalyst is used to ensure a quantitative oxidation. Nitrogen in other oxidation states, such

See Representative Method 9.1 for one application of a Kjeldahl analysis.

4 Ferek, R. J.; Lazrus, A. L.; Haagenson, P. L.; Winchester, J. W. *Environ. Sci. Technol.* **1983**, *17*, 315–324.

Table 9.7 Selected Elemental Analyses Based on an Acid–Base Titration

Element	Convert to...	Reaction Producing Titratable Acid or Base[a]	Titration Details
N	$NH_3(g)$	$NH_3(g) + \mathbf{HCl}(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$	add HCl in excess and back titrate with NaOH
S	$SO_2(g)$	$SO_2(g) + H_2O_2(aq) \rightarrow \mathbf{H_2SO_4}(aq)$	titrate H_2SO_4 with NaOH
C	$CO_2(g)$	$CO_2(g) + \mathbf{Ba(OH)_2}(aq) \rightarrow BaCO_3(s) + H_2O(l)$	add excess $Ba(OH)_2$ and back titrate with HCl
Cl	$\mathbf{HCl}(g)$	—	titrate HCl with NaOH
F	$SiF_4(g)$	$3SiF_4(aq) + 2H_2O(l) \rightarrow 2\mathbf{H_2SiF_6}(aq) + SiO_2(s)$	titrate H_2SiF_4 with NaOH

[a] The species that is titrated is shown in **bold**.

as nitro and azo nitrogens, may be oxidized to N_2, resulting in a negative determinate error. Including a reducing agent, such as salicylic acid, converts this nitrogen to a –3 oxidation state, eliminating this source of error. Table 9.7 provides additional examples in which an element is quantitative converted into a titratable acid or base.

Several organic functional groups are weak acids or weak bases. Carboxylic (–COOH), sulfonic ($-SO_3H$) and phenolic ($-C_6H_5OH$) functional groups are weak acids that can be successfully titrated in either aqueous or nonaqueous solvents. Sodium hydroxide is the titrant of choice for aqueous solutions. Nonaqueous titrations are often carried out in a basic solvent, such as ethylenediamine, using tetrabutylammonium hydroxide, $(C_4H_9)_4NOH$, as the titrant. Aliphatic and aromatic amines are weak bases that can be titrated using HCl in aqueous solution, or $HClO_4$ in glacial acetic acid. Other functional groups can be analyzed indirectly following a reaction that produces or consumes an acid or base. Typical examples are shown in Table 9.8.

Many pharmaceutical compounds are weak acids or bases that can be analyzed by an aqueous or nonaqueous acid–base titration; examples include salicylic acid, phenobarbital, caffeine, and sulfanilamide. Amino acids and proteins can be analyzed in glacial acetic acid using $HClO_4$ as the titrant. For example, a procedure for determining the amount of nutritionally available protein uses an acid–base titration of lysine residues.[5]

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If the titrand is polyprotic, then we must know to which equivalence point we are titrating. The following example illustrates how we can use a ladder diagram to determine a titration reaction's stoichiometry.

5 (a) Molnár-Perl, I.; Pintée-Szakács, M. *Anal. Chim. Acta* **1987**, *202*, 159–166; (b) Barbosa, J.; Bosch, E.; Cortina, J. L.; Rosés, M. *Anal. Chim. Acta* **1992**, *256*, 177–181.

Table 9.8 Selected Acid–Base Titrimetric Procedures for Organic Functional Groups Based on the Production or Consumption of Acid or Base

Functional Group	Reaction Producing Titratable Acid or Base[a]	Titration Details
ester	$RCOOR'(aq) + \mathbf{OH^-}(aq) \rightarrow RCOO^-(aq) + HOR'(aq)$	titrate OH^- with HCl
carbonyl	$R_2C{=}O(aq) + NH_2OH\cdot HCl(aq) \rightarrow R_2C{=}NOH(aq) + \mathbf{HCl}(aq) + H_2O(l)$	titrate HCl with NaOH
alcohol[b]	[1] $(CH_3CO)_2O + ROH \rightarrow CH_3COOR + \mathbf{CH_3COOH}$ [2] $(CH_3CO)_2O + H_2O \rightarrow 2\mathbf{CH_3COOH}$	titrate CH_3COOH with NaOH; a blank titration of acetic anhydride, $(CH_3CO)_2O$, corrects for the contribution of reaction [2]

[a] The species that is titrated is shown in **bold**.

[b] The acetylation reaction [1] is carried out in pyridine to prevent the hydrolysis of acetic by water. After the acetylation reaction is complete, water is added to covert any unreacted acetic anhydride to acetic acid [2].

Example 9.2

A 50.00 mL sample of a citrus drink requires 17.62 mL of 0.04166 M NaOH to reach the phenolphthalein end point. Express the sample's acidity as grams of citric acid, $C_6H_8O_7$, per 100 mL.

Solution

Because citric acid is a triprotic weak acid, we must first determine if the phenolphthalein end point corresponds to the first, second, or third equivalence point. Citric acid's ladder diagram is shown in Figure 9.20a. Based on this ladder diagram, the first equivalence point is between a pH of 3.13 and a pH of 4.76, the second equivalence point is between a pH of 4.76 and a pH of 6.40, and the third equivalence point is greater than a pH of 6.40. Because phenolphthalein's end point pH is 8.3–10.0 (see Table 9.4), the titration proceeds to the third equivalence point and the titration reaction is

$$C_6H_8O_7(aq) + 3OH^-(aq) \rightarrow C_6H_5O_7^{3-}(aq) + 3H_2O(l)$$

In reaching the equivalence point, each mole of citric acid consumes three moles of NaOH; thus

$$0.04166 \text{ M NaOH} \times 0.01762 \text{ L NaOH} = 7.3405 \times 10^{-5} \text{ moles NaOH}$$

$$7.3405 \times 10^{-5} \text{ mol NaOH} \times \frac{1 \text{ mol } C_6H_8O_7}{3 \text{ mol NaOH}} = 2.4468 \times 10^{-4} \text{ mol } C_6H_8O_7$$

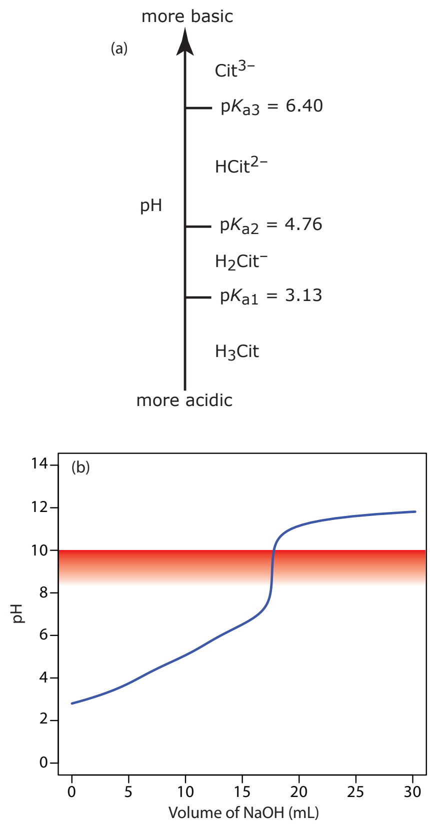


Figure 9.20 (a) Ladder diagram for citric acid; (b) Titration curve for the sample in Example 9.2 showing phenolphthalein's pH transition region.

$$2.4468 \times 10^{-4} \text{ mol } C_6H_8O_7 \times \frac{192.13 \text{ g } C_6H_8O_7}{\text{mol } C_6H_8O_7} = 0.04701 \text{ g } C_6H_8O_7$$

Because this is the amount of citric acid in a 50.00 mL sample, the concentration of citric acid in the citrus drink is 0.09402 g/100 mL. The complete titration curve is shown in Figure 9.20b.

Practice Exercise 9.6

Your company recently received a shipment of salicylic acid, $C_7H_6O_3$, to be used in the production of acetylsalicylic acid (aspirin). The shipment can be accepted only if the salicylic acid is more than 99% pure. To evaluate the shipment's purity, a 0.4208-g sample is dissolved in water and titrated to the phenolphthalein end point, requiring 21.92 mL of 0.1354 M NaOH. Report the shipment's purity as %w/w $C_7H_6O_3$. Salicylic acid is a diprotic weak acid with pK_a values of 2.97 and 13.74.

Click here to review your answer to this exercise.

In an indirect analysis the analyte participates in one or more preliminary reactions, one of which produces or consumes acid or base. Despite the additional complexity, the calculations are straightforward.

Example 9.3

The purity of a pharmaceutical preparation of sulfanilamide, $C_6H_4N_2O_2S$, is determined by oxidizing sulfur to SO_2 and bubbling it through H_2O_2 to produce H_2SO_4. The acid is titrated to the bromothymol blue end point with a standard solution of NaOH. Calculate the purity of the preparation given that a 0.5136-g sample requires 48.13 mL of 0.1251 M NaOH.

Solution

The bromothymol blue end point has a pH range of 6.0–7.6. Sulfuric acid is a diprotic acid, with a pK_{a2} of 1.99 (the first K_a value is very large and the acid dissociation reaction goes to completion, which is why H_2SO_4 is a strong acid). The titration, therefore, proceeds to the second equivalence point and the titration reaction is

$$H_2SO_4(aq) + 2OH^-(aq) \rightarrow 2H_2O(l) + SO_4^{2-}(aq)$$

Using the titration results, there are

$$0.1251 \text{ M NaOH} \times 0.04813 \text{ L NaOH} = 6.021 \times 10^{-3} \text{ mol NaOH}$$

$$6.021 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol NaOH}} = 3.010 \times 10^{-3} \text{ mol } H_2SO_4$$

produced by bubbling SO_2 through H_2O_2. Because all the sulfur in H_2SO_4 comes from the sulfanilamide, we can use a conservation of mass to determine the amount of sulfanilamide in the sample.

$$3.010\times10^{-3}\ \text{mol H}_2\text{SO}_4\times\frac{1\ \text{mol S}}{\text{mol H}_2\text{SO}_4}\times$$
$$\frac{1\ \text{mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol S}}\times\frac{168.18\ \text{g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}$$
$$=0.5062\ \text{g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$$

$$\frac{0.5062\ \text{g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{0.5136\ \text{g sample}}\times100=98.56\%\ \text{w/w C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$$

Practice Exercise 9.7

The concentration of NO_2 in air can be determined by passing the sample through a solution of H_2O_2, which oxidizes NO_2 to HNO_3, and titrating the HNO_3 with NaOH. What is the concentration of NO_2, in mg/L, if a 5.0 L sample of air requires 9.14 mL of 0.01012 M NaOH to reach the methyl red end point

Click here to review your answer to this exercise.

Example 9.4

The amount of protein in a sample of cheese is determined by a Kjeldahl analysis for nitrogen. After digesting a 0.9814-g sample of cheese, the nitrogen is oxidized to NH_4^+, converted to NH_3 with NaOH, and distilled into a collection flask containing 50.00 mL of 0.1047 M HCl. The excess HCl is back titrated with 0.1183 M NaOH, requiring 22.84 mL to reach the bromothymol blue end point. Report the %w/w protein in the cheese assuming that there are 6.38 grams of protein for every gram of nitrogen in most dairy products.

For a back titration we must consider two acid–base reactions. Again, the calculations are straightforward.

Solution

The HCl in the collection flask reacts with two bases

$$\text{HCl}(aq)+\text{NH}_3(aq)\rightarrow\text{NH}_4^+(aq)+\text{Cl}^-(aq)$$

$$\text{HCl}(aq)+\text{OH}^-(aq)\rightarrow\text{H}_2\text{O}(l)+\text{Cl}^-(aq)$$

The collection flask originally contains

$$0.1047\ \text{M HCl}\times0.05000\ \text{L HCl}=5.235\times10^{-3}\ \text{mol HCl}$$

of which

$$0.1183 \text{ M NaOH} \times 0.02284 \text{ L NaOH} \times \frac{1 \text{ mol HCl}}{\text{mol NaOH}} = 2.702 \times 10^{-3} \text{ mol HCl}$$

react with NaOH. The difference between the total moles of HCl and the moles of HCl reacting with NaOH

$$5.235 \times 10^{-3} \text{ mol HCl} - 2.702 \times 10^{-3} \text{ mol HCl} = 2.533 \times 10^{-3} \text{ mol HCl}$$

is the moles of HCl reacting with NH_3. Because all the nitrogen in NH_3 comes from the sample of cheese, we use a conservation of mass to determine the grams of nitrogen in the sample.

$$2.533 \times 10^{-3} \text{ mol HCl} \times \frac{1 \text{ mol NH}_3}{\text{mol HCl}} \times \frac{14.01 \text{ g N}}{\text{mol NH}_3} = 0.03549 \text{ g N}$$

The mass of protein, therefore, is

$$0.03549 \text{ g N} \times \frac{6.38 \text{ g protein}}{\text{g N}} = 0.2264 \text{ g protein}$$

and the % w/w protein is

$$\frac{0.2264 \text{ g protein}}{0.9814 \text{ g sample}} \times 100 = 23.1\% \text{ w/w protein}$$

Practice Exercise 9.8

Limestone consists mainly of $CaCO_3$, with traces of iron oxides and other metal oxides. To determine the purity of a limestone, a 0.5413-g sample is dissolved using 10.00 mL of 1.396 M HCl. After heating to expel CO_2, the excess HCl was titrated to the phenolphthalein end point, requiring 39.96 mL of 0.1004 M NaOH. Report the sample's purity as %w/w $CaCO_3$.

Click here to review your answer to this exercise.

Earlier we noted that we can use an acid–base titration to analyze a mixture of acids or bases by titrating to more than one equivalence point. The concentration of each analyte is determined by accounting for its contribution to each equivalence point.

Example 9.5

The alkalinity of natural waters is usually controlled by OH^-, HCO_3^-, and CO_3^{2-}, which may be present singularly or in combination. Titrating a 100.0-mL sample to a pH of 8.3 requires 18.67 mL of a 0.02812 M HCl. A second 100.0-mL aliquot requires 48.12 mL of the same titrant to reach a pH of 4.5. Identify the sources of alkalinity and their concentrations in milligrams per liter.

Solution

Because the volume of titrant to reach a pH of 4.5 is more than twice that needed to reach a pH of 8.3, we know, from Table 9.6, that the sample's alkalinity is controlled by CO_3^{2-} and HCO_3^-. Titrating to a pH of 8.3 neutralizes CO_3^{2-} to HCO_3^-

$$CO_3^{2-}(aq) + HCl(aq) \rightarrow HCO_3^-(aq) + Cl^-(aq)$$

but there is no reaction between the titrant and HCO_3^- (see Figure 9.19). The concentration of CO_3^{2-} in the sample, therefore, is

$$0.02812 \text{ M HCl} \times 0.01867 \text{ L HCl} \times \frac{1 \text{ mol } CO_3^{2-}}{\text{mol HCl}} = 5.250 \times 10^{-4} \text{ mol } CO_3^{2-}$$

$$\frac{5.250 \times 10^{-4} \text{ mol } CO_3^{2-}}{0.1000 \text{ L}} \times \frac{60.01 \text{ g } CO_3^{2-}}{\text{mol } CO_3^{2-}} \times \frac{1000 \text{ mg}}{\text{g}} = 315.1 \text{ mg/L}$$

Titrating to a pH of 4.5 neutralizes CO_3^{2-} to H_2CO_3, and HCO_3^- to H_2CO_3 (see Figures 9.19).

$$CO_3^{2-}(aq) + 2HCl(aq) \rightarrow H_2CO_3(aq) + 2Cl^-(aq)$$

$$HCO_3^-(aq) + HCl(aq) \rightarrow H_2CO_3(aq) + 2Cl^-(aq)$$

Because we know how many moles of CO_3^{2-} are in the sample, we can calculate the volume of HCl it consumes.

$$5.250 \times 10^{-4} \text{ mol } CO_3^{2-} \times \frac{2 \text{ mol HCl}}{\text{mol } CO_3^{2-}} \times \frac{1 \text{ L HCl}}{0.02812 \text{ mol HCl}} \times \frac{1000 \text{ mL}}{\text{L}} = 37.34 \text{ mL}$$

This leaves 48.12 mL - 37.34 mL, or 10.78 mL of HCl to react with HCO_3^-. The amount of HCO_3^- in the sample is

$$0.02812 \text{ M HCl} \times 0.01078 \text{ L HCl} \times \frac{1 \text{ mol } HCO_3^-}{\text{mol HCl}} = 3.031 \times 10^{-4} \text{ mol } HCO_3^-$$

$$\frac{3.031 \times 10^{-4} \text{ mol } HCO_3^-}{0.1000 \text{ L}} \times \frac{61.02 \text{ g } HCO_3^-}{\text{mol } HCO_3^-} \times \frac{1000 \text{ mg}}{\text{g}} = 185.0 \text{ mg/L}$$

Practice Exercise 9.9

Samples containing the monoprotic weak acids 2–methylanilinium chloride ($C_7H_{10}NCl$, $pK_a = 4.447$) and 3–nitrophenol ($C_6H_5NO_3$, $pK_a = 8.39$) can be analyzed by titrating with NaOH. A 2.006-g sample requires 19.65 mL of 0.200 M NaOH to reach the bromocresol purple end point and 48.41 mL of 0.200 M NaOH to reach the phenolphthalein end point. Report the %w/w of each compound in the sample.

Click here to review your answer to this exercise.

9B.5 Qualitative Applications

Example 9.5 shows how we can use an acid–base titration to assign the forms of alkalinity in waters. We can easily extend this approach to other systems. For example, by titrating with either a strong acid or a strong base to the methyl orange and phenolphthalein end points we can determine the composition of solutions containing one or two of the following species: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HCl, and NaOH. As outlined in Table 9.9, each species or mixture of species has a unique relationship between the volumes of titrant needed to reach these two end points.

9B.6 Characterization Applications

An acid–base titration can be use to characterize the chemical and physical properties of matter. Two useful characterization applications are the

Table 9.9 Relationship Between End Point Volumes for Mixtures of Phosphate Species with HCl and NaOH

Solution Composition	Relationship Between End Point Volumes with Strong Base Titrant[a]	Relationship Between End Point Volumes With Strong Acid Titrant[a]
H_3PO_4	$V_{PH} = 2 \times V_{MO}$	—[b]
$H_2PO_4^-$	$V_{PH} > 0$; $V_{MO} = 0$	—
HPO_4^{2-}	—	$V_{MO} > 0$; $V_{PH} = 0$
PO_4^{3-}	—	$V_{MO} = 2 \times V_{PH}$
HCl	$V_{PH} = V_{MO}$	—
NaOH	—	$V_{MO} = V_{PH}$
HCl and H_3PO_4	$V_{PH} < 2 \times V_{MO}$	—
H_3PO_4 and $H_2PO_4^-$	$V_{PH} > 2 \times V_{MO}$	—
$H_2PO_4^-$ and HPO_4^{2-}	$V_{PH} > 0$; $V_{MO} = 0$	$V_{MO} > 0$; $V_{PH} = 0$
HPO_4^{2-} and PO_4^{3-}	—	$V_{MO} > 2 \times V_{PH}$
PO_4^{3-} and NaOH	—	$V_{MO} < 2 \times V_{PH}$

[a] V_{PH} and V_{MO} are, respectively, the volume of titrant at the phenolphthalein and methyl orange end points.
[b] When no information is provided, the volume of titrant to each end point is zero.

determination of a compound's equivalent weight and its acid or its base dissociation constant.

Equivalent Weights

Suppose we titrate a sample containing an impure weak acid to a well-defined end point using a monoprotic strong base as the titrant. If we assume that the titration involves the transfer of n protons, then the moles of titrant needed to reach the end point is

$$\text{moles titrant} = \frac{n \text{ moles titrant}}{\text{moles analyte}} \times \text{moles analyte}$$

If we know the analyte's identity, we can use this equation to determine the amount of analyte in the sample

$$\text{grams analyte} = \text{moles titrant} \times \frac{1 \text{ mole analyte}}{n \text{ moles titrant}} \times \text{FW analyte}$$

where FW is the analyte's formula weight.

But what if we do not know the analyte's identify? If we can titrate a pure sample of the analyte, we can obtain some useful information that may help in establishing its identity. Because we do not know the number of protons being titrated, we let $n = 1$ and replace the analyte's formula weight with its equivalent weight (EW)

$$\text{grams analyte} = \text{moles titrant} \times \frac{1 \text{ equivalent analyte}}{1 \text{ moles titrant}} \times \text{EW analyte}$$

where

$$\text{FW} = n \times \text{EW}$$

Example 9.6

A 0.2521-g sample of an unknown weak acid is titrated with 0.1005 M NaOH, requiring 42.68 mL to reach the phenolphthalein end point. Determine the compound's equivalent weight. Which of the following compounds is most likely to be the unknown weak acid?

ascorbic acid	$C_8H_8O_6$	FW = 176.1	monoprotic
malonic acid	$C_3H_4O_4$	FW = 104.1	diprotic
succinic acid	$C_4H_6O_4$	FW = 118.1	diprotic
citric acid	$C_6H_8O_7$	FW = 192.1	triprotic

Solution

The moles of NaOH needed to reach the end point is

$$0.1005 \text{ M NaOH} \times 0.04268 \text{ L NaOH} = 4.289 \times 10^{-3} \text{ mol NaOH}$$

which gives the analyte's equivalent weight as

$$EW = \frac{\text{g analyte}}{\text{equiv. analyte}} = \frac{0.2521 \text{ g}}{4.289 \times 10^{-3} \text{ equiv.}} = 58.78 \text{ g/equivalent}$$

The possible formula weights for the weak acid are

$$n = 1: \text{ FW} = \text{EW} = 58.78 \text{ g/equivalent}$$
$$n = 2: \text{ FW} = 2 \times \text{EW} = 117.6 \text{ g/equivalent}$$
$$n = 3: \text{ FW} = 3 \times \text{EW} = 176.3 \text{ g/equivalent}$$

If the analyte is a monoprotic weak acid, then its formula weight is 58.78 g/mol, eliminating ascorbic acid as a possibility. If it is a diprotic weak acid, then the analyte's formula weight is either 58.78 g/mol or 117.6 g/mol, depending on whether the titration is to the first or second equivalence point. Succinic acid, with a formula weight of 118.1 g/mole is a possibility, but malonic acid is not. If the analyte is a triprotic weak acid, then its formula weight is 58.78 g/mol, 117.6 g/mol, or 176.3 g/mol. None of these values is close to the formula weight for citric acid, eliminating it as a possibility. Only succinic acid provides a possible match.

Practice Exercise 9.10

Figure 9.21 shows the potentiometric titration curve for the titration of a 0.500-g sample an unknown weak acid. The titrant is 0.1032 M NaOH. What is the weak acid's equivalent weight?

Click here to review your answer to this exercise.

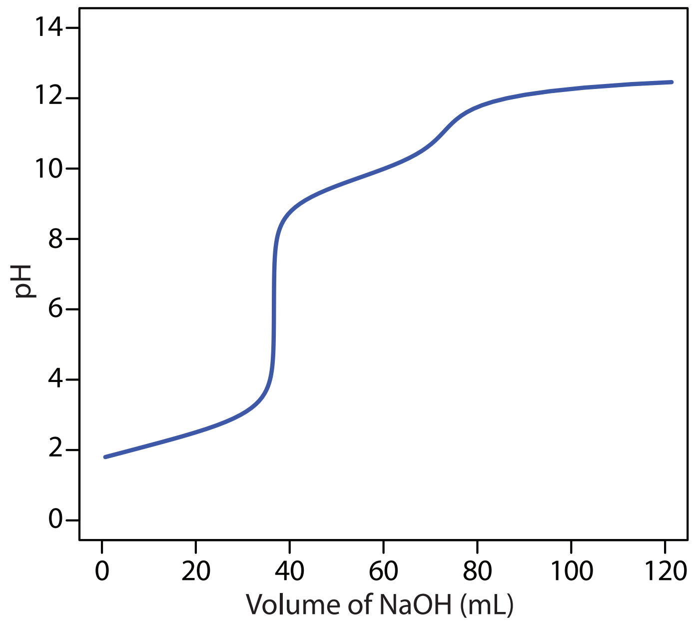


Figure 9.21 Titration curve for Practice Exercise 9.10.

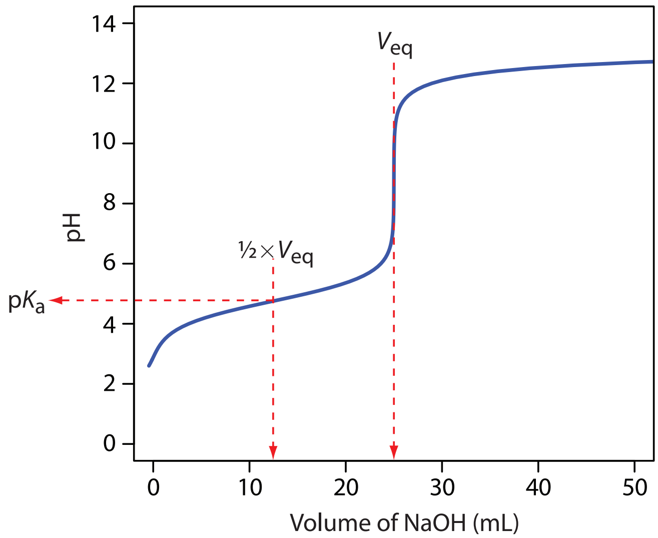


Figure 9.22 Estimating acetic acid's pK_a using its potentiometric titration curve.

Equilibrium Constants

Another application of acid–base titrimetry is the determination of equilibrium constants. Consider, for example, a solution of acetic acid, CH_3COOH, for which the dissociation constant is

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

When the concentrations of CH_3COOH and CH_3COO^- are equal, the K_a expression reduces to $K_a = [H_3O^+]$, or pH = pK_a. If we titrate a solution of acetic acid with NaOH, the pH equals the pK_a when the volume of NaOH is approximately ½V_{eq}. As shown in Figure 9.22, a potentiometric titration curve provides a reasonable estimate of acetic acid's pK_a.

This method provides a reasonable estimate of a weak acid's pK_a if the acid is neither too strong nor too weak. These limitations are easily to appreciate if we consider two limiting cases. For the first case let's assume that the weak acid, HA, is more than 50% dissociated before the titration begins (a relatively large K_a value). The concentration of HA before the equivalence point is always less than the concentration of A^-, and there is no point on the titration curve where $[HA] = [A^-]$. At the other extreme, if the acid is too weak, less than 50% of the weak acid reacts with the titrant at the equivalence point. In this case the concentration of HA before the equivalence point is always greater than that of A^-. Determining the pK_a by the half-equivalence point method overestimates its value if the acid is too strong and underestimates its value if the acid is too weak.

Practice Exercise 9.11

Use the potentiometric titration curve in Figure 9.21 to estimate the pK_a values for the weak acid in Practice Exercise 9.10.

Click here to review your answer to this exercise.

A second approach for determining a weak acid's pK_a is to use a Gran plot. For example, earlier in this chapter we derived the following equation for the titration of a weak acid with a strong base.

$$[H_3O^+] \times V_b = K_a V_{eq} - K_a V_b$$

A plot of $[H_3O^+] \times V_b$ versus V_b, for volumes less than the equivalence point, yields a straight line with a slope of $-K_a$. Other linearizations have been developed which use the entire titration curve, or that require no assumptions.[6] This approach to determining acidity constants has been used to study the acid–base properties of humic acids, which are naturally occurring, large molecular weight organic acids with multiple acidic sites. In one study a humic acid was found to have six titratable sites, three of which were identified as carboxylic acids, two of which were believed to be secondary or tertiary amines, and one of which was identified as a phenolic group.[7]

9B.7 Evaluation of Acid–Base Titrimetry

Scale of Operation

Acid–base titrimetry is an example of a total analysis technique in which the signal is proportional to the absolute amount of analyte. See Chapter 3 for a discussion of the difference between total analysis techniques and concentration techniques.

In an acid–base titration the volume of titrant needed to reach the equivalence point is proportional to the moles of titrand. Because the pH of the titrand or the titrant is a function of its concentration, however, the change in pH at the equivalence point—and thus the feasibility of an acid–base titration—depends on their respective concentrations. Figure 9.23, for example, shows a series of titration curves for the titration of several concentrations of HCl with equimolar solutions NaOH. For titrand and titrant concentrations smaller than 10^{-3} M, the change in pH at the end point may be too small to provide accurate and precise results.

6 (a) Gonzalez, A. G.; Asuero, A. G. *Anal. Chim. Acta* **1992**, *256*, 29–33; (b) Papanastasiou, G.; Ziogas, I.; Kokkindis, G. *Anal. Chim. Acta* **1993**, *277*, 119–135.

7 Alexio, L. M.; Godinho, O. E. S.; da Costa, W. F. *Anal. Chim. Acta* **1992**, *257*, 35–39.

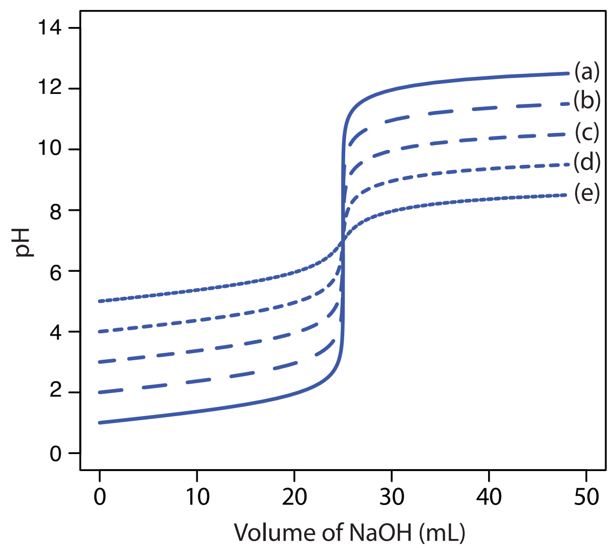


Figure 9.23 Titration curves for 25.0 mL of (a) 10^{-1} M HCl, (b) 10^{-2} M HCl, (c) 10^{-3} M HCl, (d) 10^{-4} M HCl, and (e) 10^{-5} M HCl. In each case the titrant is an equimolar solution of NaOH.

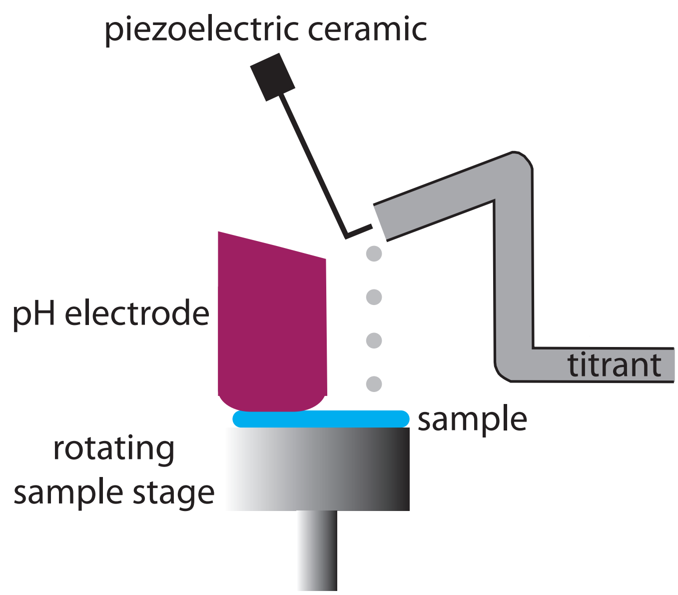


Figure 9.24 Experimental design for a microdroplet titration apparatus.

A minimum concentration of 10^{-3} M places limits on the smallest amount of analyte that we can successfully analyze. For example, suppose our analyte has a formula weight of 120 g/mol. To successfully monitor the titration's end point using an indicator or with a pH probe, the titrand needs an initial volume of approximately 25 mL. If we assume that the analyte's formula weight is 120 g/mol, then each sample must contain at least 3 mg of analyte. For this reason, acid–base titrations are generally limited to major and minor analytes (see Figure 3.6 in Chapter 3). We can extend the analysis of gases to trace analytes by pulling a large volume of the gas through a suitable collection solution.

One goal of analytical chemistry is to extend analyses to smaller samples. Here we describe two interesting approaches to titrating μL and pL samples. In one experimental design (Figure 9.24), samples of 20–100 μL were held by capillary action between a flat-surface pH electrode and a stainless steel sample stage.[8] The titrant was added by using the oscillations of a piezoelectric ceramic device to move an angled glass rod in and out of a tube connected to a reservoir containing the titrant. Each time the glass tube was withdrawn an approximately 2 nL microdroplet of titrant was released. The microdroplets were allowed to fall onto the sample, with mixing accomplished by spinning the sample stage at 120 rpm. A total of 450 microdroplets, with a combined volume of 0.81–0.84 μL, was dispensed between each pH measurement. In this fashion a titration curve was constructed. This method was used to titrate solutions of 0.1 M HCl and 0.1 M CH_3COOH with 0.1 M NaOH. Absolute errors ranged from a minimum of +0.1% to a maximum of –4.1%, with relative standard deviations from 0.15% to 4.7%. Sample as small as 20 μL were successfully titrated.

8 Steele, A.; Hieftje, G. M. *Anal. Chem.* **1984**, *56*, 2884–2888.

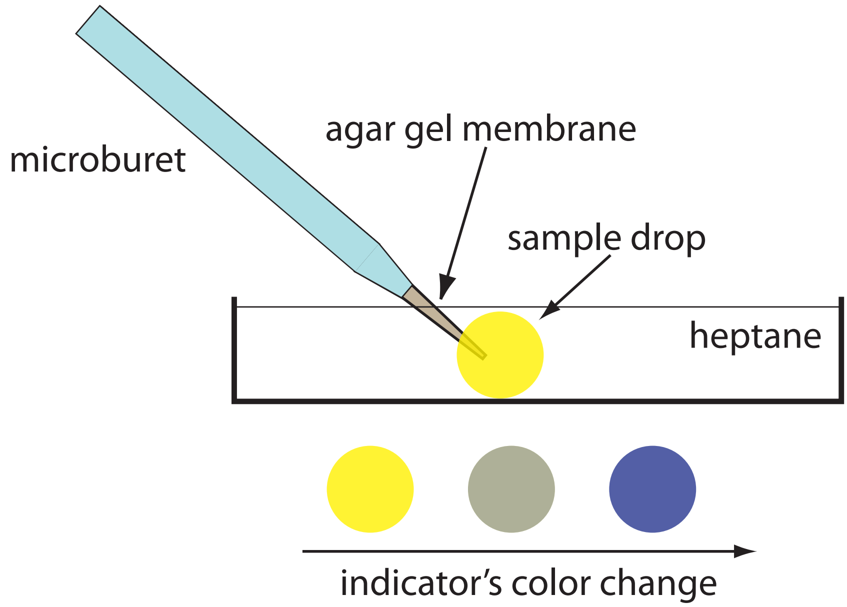


Figure 9.25 Experimental set-up for a diffusional microtitration. The indicator is a mixture of bromothymol blue and bromocresol purple.

Another approach carries out the acid–base titration in a single drop of solution.[9] The titrant is delivered using a microburet fashioned from a glass capillary micropipet (Figure 9.25). The microburet has a 1-2 μm tip filled with an agar gel membrane. The tip of the microburet is placed within a drop of the sample solution, which is suspended in heptane, and the titrant is allowed to diffuse into the sample. The titration's progress is monitored using an acid–base indicator, and the time needed to reach the end point is measured. The rate of the titrant's diffusion from the microburet is determined by a prior calibration. Once calibrated the end point time can be converted to an end point volume. Samples usually consisted of picoliter volumes (10^{-12} liters), with the smallest sample being 0.7 pL. The precision of the titrations was usually about 2%.

Titrations conducted with microliter or picoliter sample volumes require a smaller absolute amount of analyte. For example, diffusional titrations have been successfully conducted on as little as 29 femtomoles (10^{-15} moles) of nitric acid. Nevertheless, the analyte must still be present in the sample at a major or minor level for the titration to be performed accurately and precisely.

Accuracy

See Figure 3.5 in Chapter 3 to review the characteristics of macro–major and macro–minor samples.

When working with a macro–major or a macro–minor sample, an acid–base titration can achieve a relative error of 0.1–0.2%. The principal limitation to accuracy is the difference between the end point and the equivalence point.

9 (a) Gratzl, M.; Yi, C. *Anal. Chem.* **1993**, *65*, 2085–2088; (b) Yi, C.; Gratzl, M. *Anal. Chem.* **1994**, *66*, 1976–1982; (c) Hui, K. Y.; Gratzl, M. *Anal. Chem.* **1997**, *69*, 695–698; (d) Yi, C.; Huang, D.; Gratzl, M. *Anal. Chem.* **1996**, *68*, 1580–1584; (e) Xie, H.; Gratzl, M. *Anal. Chem.* **1996**, *68*, 3665–3669.

Precision

An acid–base titration's relative precision depends primarily on the precision with which we can measure the end point volume and the precision in detecting the end point. Under optimum conditions, an acid–base titration has a relative precision of 0.1–0.2%. We can improve the relative precision by using the largest possible buret and ensuring that we use most of its capacity in reaching the end point. A smaller volume buret is a better choice when using costly reagents, when waste disposal is a concern, or when the titration must be completed quickly to avoid competing chemical reactions. Automatic titrators are particularly useful for titrations requiring small volumes of titrant because they provide significantly better precision (typically about ±0.05% of the buret's volume).

The precision of detecting the end point depends on how it is measured and the slope of the titration curve at the end point. With an indicator the precision of the end point signal is usually ±0.03–0.10 mL. Potentiometric end points usually are more precise.

Sensitivity

For an acid–base titration we can write the following general analytical equation relating the titrant's volume to the absolute amount of titrand

$$\text{volume of titrant} = k \times \text{moles of titrand}$$

where k, the sensitivity, is determined by the stoichiometry between the titrand and the titrant. Consider, for example, the determination of sulfurous acid, H_2SO_3, by titrating with NaOH to the first equivalence point

$$H_2SO_3(aq) + OH^-(aq) \rightarrow H_2O(l) + HSO_3^-(aq)$$

At the equivalence point the relationship between the moles of NaOH and the moles of H_2SO_3 is

$$\text{mol NaOH} = \text{mol } H_2SO_3$$

Substituting the titrant's molarity and volume for the moles of NaOH and rearranging

$$M_{\text{NaOH}} \times V_{\text{NaOH}} = \text{mol } H_2SO_3$$

$$V_{\text{NaOH}} = \frac{1}{M_{\text{NaOH}}} \times \text{mol } H_2SO_3$$

we find that k is

$$k = \frac{1}{M_{\text{NaOH}}}$$

There are two ways in which we can improve a titration's sensitivity. The first, and most obvious, is to decrease the titrant's concentration because it is inversely proportional to the sensitivity, k.

The second approach, which only applies if the titrand is multiprotic, is to titrate to a later equivalence point. If we titrate H_2SO_3 to the second equivalence point

$$H_2SO_3(aq) + 2OH^-(aq) \rightarrow 2H_2O(l) + SO_3^{2-}(aq)$$

then each mole of H_2SO_3 consumes two moles of NaOH

$$\text{mol NaOH} = 2 \times \text{mol } H_2SO_3$$

and the sensitivity becomes

$$k = \frac{2}{M_{\text{NaOH}}}$$

In practice, however, any improvement in sensitivity is offset by a decrease in the end point's precision if the larger volume of titrant requires us to refill the buret. Consequently, standard acid–base titrimetric procedures are written to ensure that titrations require 60–100% of the buret's volume.

Selectivity

Acid–base titrants are not selective. A strong base titrant, for example, reacts with all acids in a sample, regardless of their individual strengths. If the titrand contains an analyte and an interferent, then selectivity depends on their relative acid strengths. Two limiting situations must be considered.

If the analyte is a stronger acid than the interferent, then the titrant will react with the analyte before it begins reacting with the interferent. The feasibility of the analysis depends on whether the titrant's reaction with the interferent affects the accurate location of the analyte's equivalence point. If the acid dissociation constants are substantially different, the end point for the analyte can be accurately determined. Conversely, if the acid dissociation constants for the analyte and interferent are similar, then an accurate end point for the analyte may not be found. In the latter case a quantitative analysis for the analyte is not possible.

In the second limiting situation the analyte is a weaker acid than the interferent. In this case the volume of titrant needed to reach the analyte's equivalence point is determined by the concentration of both the analyte and the interferent. To account for the interferent's contribution to the end point, an end point for the interferent must be present. Again, if the acid dissociation constants for the analyte and interferent are significantly different, then the analyte's determination is possible. If the acid dissociation constants are similar, however, there is only a single equivalence point and the analyte's and interferent's contributions to the equivalence point volume can not be separated.

Time, Cost, and Equipment

Acid–base titrations require less time than most gravimetric procedures, but more time than many instrumental methods of analysis, particularly when analyzing many samples. With an automatic titrator, however, concerns about analysis time are less significant. When performing a titration manually our equipment needs—a buret and, perhaps, a pH meter—are few in number, inexpensive, routinely available, and easy to maintain. Automatic titrators are available for between \$3000 and \$10 000.

9C Complexation Titrations

The earliest examples of metal–ligand COMPLEXATION TITRATIONS are Liebig's determinations, in the 1850s, of cyanide and chloride using, respectively, Ag^+ and Hg^{2+} as the titrant. Practical analytical applications of complexation titrimetry were slow to develop because many metals and ligands form a series of metal–ligand complexes. Liebig's titration of CN^- with Ag^+ was successful because they form a single, stable complex of $Ag(CN)_2^-$, giving a single, easily identified end point. Other metal–ligand complexes, such as CdI_4^{2-}, are not analytically useful because they form a series of metal–ligand complexes (CdI^+, CdI_2*(aq)*, CdI_3^- and CdI_4^{2-}) that produce a sequence of poorly defined end points.

Recall that an acid–base titration curve for a diprotic weak acid has a single end point if its two K_a values are not sufficiently different. See Figure 9.11 for an example.

In 1945, Schwarzenbach introduced aminocarboxylic acids as multidentate ligands. The most widely used of these new ligands—ethylenediaminetetraacetic acid, or EDTA—forms strong 1:1 complexes with many metal ions. The availability of a ligand that gives a single, easily identified end point made complexation titrimetry a practical analytical method.

9C.1 Chemistry and Properties of EDTA

Ethylenediaminetetraacetic acid, or EDTA, is an aminocarboxylic acid. EDTA, which is shown in Figure 9.26a in its fully deprotonated form, is a Lewis acid with six binding sites—four negatively charged carboxylate groups and two tertiary amino groups—that can donate six pairs of electrons to a metal ion. The resulting metal–ligand complex, in which EDTA forms a cage-like structure around the metal ion (Figure 9.26b), is very stable. The actual number of coordination sites depends on the size of the metal ion, however, all metal–EDTA complexes have a 1:1 stoichiometry.

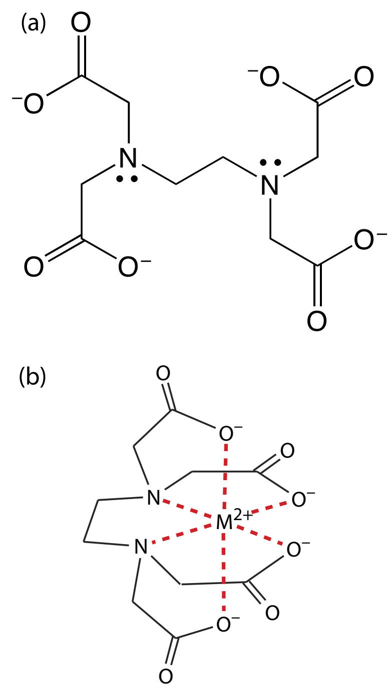


Figure 9.26 Structures of (a) EDTA, in its fully deprotonated form, and (b) in a six-coordinate metal–EDTA complex with a divalent metal ion.

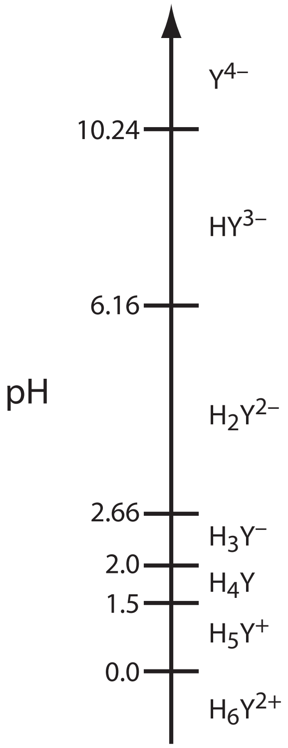


Figure 9.27 Ladder diagram for EDTA.

Metal–EDTA Formation Constants

To illustrate the formation of a metal–EDTA complex, let's consider the reaction between Cd^{2+} and EDTA

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq) \qquad 9.9$$

where Y^{4-} is a shorthand notation for the fully deprotonated form of EDTA shown in Figure 9.26a. Because the reaction's formation constant

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16} \qquad 9.10$$

is large, its equilibrium position lies far to the right. Formation constants for other metal–EDTA complexes are found in Appendix 12.

EDTA is a Weak Acid

In addition to its properties as a ligand, EDTA is also a weak acid. The fully protonated form of EDTA, H_6Y^{2+}, is a hexaprotic weak acid with successive pK_a values of

$$pK_{a1} = 0.0 \qquad pK_{a2} = 1.5 \qquad pK_{a3} = 2.0$$
$$pK_{a4} = 2.66 \qquad pK_{a5} = 6.16 \qquad pK_{a6} = 10.24$$

The first four values are for the carboxylic acid protons and the last two values are for the ammonium protons. Figure 9.27 shows a ladder diagram for EDTA. The specific form of EDTA in reaction 9.9 is the predominate species only at pH levels greater than 10.17.

Conditional Metal–Ligand Formation Constants

The formation constant for CdY^{2-} in equation 9.10 assumes that EDTA is present as Y^{4-}. Because EDTA has many forms, when we prepare a solution of EDTA we know it total concentration, C_{EDTA}, not the concentration of a specific form, such as Y^{4-}. To use equation 9.10, we need to rewrite it in terms of C_{EDTA}.

At any pH a mass balance on EDTA requires that its total concentration equal the combined concentrations of each of its forms.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

To correct the formation constant for EDTA's acid–base properties we need to calculate the fraction, $\alpha_{Y^{4-}}$, of EDTA present as Y^{4-}.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}} \qquad 9.11$$

Table 9.10 Values of $\alpha_{Y^{4-}}$ for Selected pH Levels

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
1	1.9×10^{-18}	8	5.6×10^{-3}
2	3.4×10^{-14}	9	5.4×10^{-2}
3	2.6×10^{-11}	10	0.37
4	3.8×10^{-9}	11	0.85
5	3.7×10^{-7}	12	0.98
6	2.4×10^{-5}	13	1.00
7	5.0×10^{-4}	14	1.00

Table 9.10 provides values of $\alpha_{Y^{4-}}$ for selected pH levels. Solving equation 9.11 for $[Y^{4-}]$ and substituting into equation 9.10 for the CdY^{2-} formation constant

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}} C_{EDTA}}$$

and rearranging gives

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} \qquad 9.12$$

where K_f' is a pH-dependent CONDITIONAL FORMATION CONSTANT. As shown in Table 9.11, the conditional formation constant for CdY^{2-} becomes smaller and the complex becomes less stable at more acidic pHs.

Problem 9.42 from the end of chapter problems asks you to verify the values in Table 9.10 by deriving an equation for $\alpha_{Y^{4-}}$.

EDTA Competes With Other Ligands

To maintain a constant pH during a complexation titration we usually add a buffering agent. If one of the buffer's components is a ligand that binds Cd^{2+}, then EDTA must compete with the ligand for Cd^{2+}. For example, an

Table 9.11 Conditional Formation Constants for CdY^{2-}

pH	K_f'	pH	K_f'
1	5.5×10^{-2}	8	1.6×10^{14}
2	1.0×10^{3}	9	1.6×10^{15}
3	7.7×10^{5}	10	1.1×10^{16}
4	1.1×10^{8}	11	2.5×10^{16}
5	1.1×10^{10}	12	2.9×10^{16}
6	6.8×10^{11}	13	2.9×10^{16}
7	1.5×10^{13}	14	2.9×10^{16}

NH_4^+/NH_3 buffer includes NH_3, which forms several stable Cd^{2+}–NH_3 complexes. Because EDTA forms a stronger complex with Cd^{2+} it will displace NH_3, but the stability of the Cd^{2+}–EDTA complex decreases.

We can account for the effect of an AUXILIARY COMPLEXING AGENT, such as NH_3, in the same way we accounted for the effect of pH. Before adding EDTA, the mass balance on Cd^{2+}, C_{Cd}, is

$$C_{Cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2^{2+}] + [Cd(NH_3)_3^{2+}] + [Cd(NH_3)_4^{2+}]$$

and the fraction of uncomplexed Cd^{2+}, $\alpha_{Cd^{2+}}$, is

The value of $\alpha_{Cd^{2+}}$ depends on the concentration of NH_3. Contrast this with $\alpha_{Y^{4-}}$, which depends on pH.

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd}} \qquad 9.13$$

Solving equation 9.13 for $[Cd^{2+}]$ and substituting into equation 9.12 gives

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[CdY^{2-}]}{\alpha_{Cd^{2+}} C_{Cd} C_{EDTA}}$$

Because the concentration of NH_3 in a buffer is essentially constant, we can rewrite this equation

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{Cd^{2+}} = \frac{[CdY^{2-}]}{C_{Cd} C_{EDTA}} \qquad 9.14$$

to give a conditional formation constant, K_f'', that accounts for both pH and the auxiliary complexing agent's concentration. Table 9.12 provides values of $\alpha_{M^{2+}}$ for several metal ion when NH_3 is the complexing agent.

9C.2 Complexometric EDTA Titration Curves

Now that we know something about EDTA's chemical properties, we are ready to evaluate its usefulness as a titrant. To do so we need to know the

Table 9.12 Values of $\alpha_{M^{2+}}$ for Selected Concentrations of Ammonia

$[NH_3]$ (M)	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$	$\alpha_{Zn^{2+}}$
1	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}	3.95×10^{-10}
0.5	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}	6.27×10^{-9}
0.1	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}	3.68×10^{-6}
0.05	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}	5.45×10^{-5}
0.01	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}	1.82×10^{-2}
0.005	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}	1.27×10^{-1}
0.001	9.99×10^{-1}	6.09×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}	7.48×10^{-1}

shape of a complexometric EDTA titration curve. In section 9B we learned that an acid–base titration curve shows how the titrand's pH changes as we add titrant. The analogous result for a complexation titration shows the change in pM, where M is the metal ion, as a function of the volume of EDTA. In this section we will learn how to calculate a titration curve using the equilibrium calculations from Chapter 6. We also will learn how to quickly sketch a good approximation of any complexation titration curve using a limited number of simple calculations.

Calculating the Titration Curve

Let's calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA. Furthermore, let's assume that the titrand is buffered to a pH of 10 with a buffer that is 0.0100 M in NH_3.

Because the pH is 10, some of the EDTA is present in forms other than Y^{4-}. In addition, EDTA must compete with NH_3 for the Cd^{2+}. To evaluate the titration curve, therefore, we first need to calculate the conditional formation constant for CdY^{2-}. From Table 9.10 and Table 9.11 we find that $\alpha_{Y^{4-}}$ is 0.35 at a pH of 10, and that $\alpha_{Cd^{2+}}$ is 0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, the conditional formation constant is

Step 1: Calculate the conditional formation constant for the metal–EDTA complex.

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{Cd^{2+}} = (2.9 \times 10^{16})(0.37)(0.0881) = 9.5 \times 10^{14}$$

Because K_f'' is so large, we can treat the titration reaction

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightarrow CdY^{2-}(aq)$$

as if it proceeds to completion.

The next task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that

Step 2: Calculate the volume of EDTA needed to reach the equivalence point.

$$\text{moles EDTA} = \text{moles Cd}^{2+}$$
$$M_{EDTA} \times V_{EDTA} = M_{Cd} \times V_{Cd}$$

Substituting in known values, we find that it requires

$$V_{eq} = V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{0.0100\ \text{M}} = 25.0\ \text{mL}$$

of EDTA to reach the equivalence point.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}. Because not all the unreacted Cd^{2+} is free—some is complexed with NH_3—we must account for the presence of NH_3. For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

Step 3: Calculate pM values before the equivalence point by determining the concentration of unreacted metal ions.

$$C_{Cd} = \frac{\text{initial moles Cd}^{2+} - \text{moles EDTA added}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL}) - (0.0100\ \text{M})(5.0\ \text{mL})}{50.0\ \text{mL} + 5.0\ \text{mL}} = 3.64 \times 10^{-3}\ \text{M}$$

To calculate the concentration of free Cd^{2+} we use equation 9.13

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{Cd} = (0.0881)(3.64 \times 10^{-4}\ \text{M}) = 3.21 \times 10^{-4}\ \text{M}$$

which gives a pCd of

$$\text{pCd} = -\log[\text{Cd}^{2+}] = -\log(3.21 \times 10^{-4}) = 3.49$$

Step 4: Calculate pM at the equivalence point using the conditional formation constant.

At the equivalence point all the Cd^{2+} initially in the titrand is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentration of CdY^{2-}.

$$[\text{CdY}^{2-}] = \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 25.0\ \text{mL}} = 3.33 \times 10^{-3}\ \text{M}$$

Next, we solve for the concentration of Cd^{2+} in equilibrium with CdY^{2-}.

At the equivalence point the initial moles of Cd^{2+} and the moles of EDTA added are equal. The total concentrations of Cd^{2+}, C_{Cd}, and the total concentration of EDTA, C_{EDTA}, are equal.

$$K_f'' = \frac{[\text{CdY}^{2-}]}{C_{Cd}C_{EDTA}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 9.5 \times 10^{14}$$

$$x = C_{Cd} = 1.9 \times 10^{-9}\ \text{M}$$

Once again, to find the concentration of uncomplexed Cd^{2+} we must account for the presence of NH_3; thus

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{Cd} = (0.0881)(1.9 \times 10^{-9}\ \text{M}) = 1.70 \times 10^{-10}\ \text{M}$$

and pCd is 9.77 at the equivalence point.

Step 5: Calculate pM after the equivalence point using the conditional formation constant.

After the equivalence point, EDTA is in excess and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentrations of CdY^{2-} and of unreacted EDTA. For example, after adding 30.0 mL of EDTA

$$[\text{CdY}^{2-}] = \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 30.0\ \text{mL}} = 3.13 \times 10^{-3}\ \text{M}$$

$$C_{\text{EDTA}} = \frac{M_{\text{EDTA}}V_{\text{EDTA}} - M_{\text{Cd}}V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$

$$= \frac{(0.0100 \text{ M})(30.0 \text{ mL}) - (5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}}$$

$$= 6.25 \times 10^{-4} \text{ M}$$

Substituting into equation 9.14 and solving for $[Cd^{2+}]$ gives

$$\frac{[\text{CdY}^{2-}]}{C_{\text{Cd}}C_{\text{EDTA}}} = \frac{3.13 \times 10^{-3} \text{ M}}{C_{\text{Cd}}(6.25 \times 10^{-4} \text{ M})} = 9.5 \times 10^{14}$$

$$C_{\text{Cd}} = 5.4 \times 10^{-15} \text{ M}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(5.4 \times 10^{-15} \text{ M}) = 4.8 \times 10^{-16} \text{ M}$$

a pCd of 15.32. Table 9.13 and Figure 9.28 show additional results for this titration.

After the equilibrium point we know the equilibrium concentrations of CdY^{2-} and EDTA. We can solve for the equilibrium concentration of C_{Cd} using K_f'' and then calculate $[Cd^{2+}]$ using $\alpha_{Cd^{2+}}$. Because we use the same conditional formation constant, K_f'', for all calculations, this is the approach shown here.

There is a second method for calculating $[Cd^{2+}]$ after the equivalence point. Because the calculation uses only $[CdY^{2-}]$ and C_{EDTA}, we can use K_f' instead of K_f''; thus

$$\frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}]C_{\text{EDTA}}} = \alpha_{\text{Y}^{4-}} \times K_f$$

$$\frac{3.13 \times 10^{-3} \text{ M}}{[\text{Cd}^{2+}](6.25 \times 10^{-4} \text{ M})} = (0.37)(2.9 \times 10^{16})$$

Solving gives $[Cd^{2+}] = 4.7 \times 10^{-16}$ M and a pCd of 15.33. We will use this approach when learning how to sketch a complexometric titration curve.

Table 9.13 Titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the Presence of 0.0100 M NH_3

Volume of EDTA (mL)	pCd	Volume of EDTA (mL)	pCd
0.00	3.36	27.0	14.95
5.00	3.49	30.0	15.33
10.0	3.66	35.0	15.61
15.0	3.87	40.0	15.76
20.0	4.20	45.0	15.86
23.0	4.62	50.0	15.94
25.0	9.77		

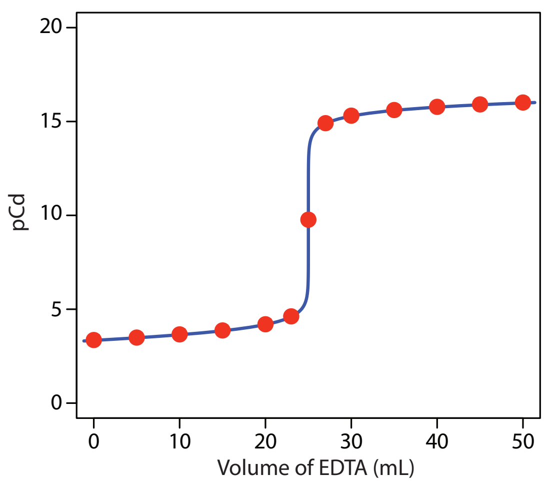


Figure 9.28 Titration curve for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3. The red points correspond to the data in Table 9.13. The blue line shows the complete titration curve.

Practice Exercise 9.12

Calculate titration curves for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7. Neither titration includes an auxiliary complexing agent. Compare your results with Figure 9.28 and comment on the effect of pH and of NH_3 on the titration of Cd^{2+} with EDTA.

Click here to review your answer to this exercise.

Sketching an EDTA Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point, we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a complexation titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA in the presence of 0.0100 M NH_3 to illustrate our approach.

This is the same example that we used in developing the calculations for a complexation titration curve. You can review the results of that calculation in Table 9.13 and Figure 9.28.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next, we draw our axes, placing pCd on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 25.0 mL of EDTA. Figure 9.29a shows the result of the first step in our sketch.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+} . Because not all the unreacted Cd^{2+} is free—some is complexed with NH_3—we must account for the presence of NH_3. The calculations are straightforward, as we saw earlier. Figure 9.29b shows the pCd after adding 5.00 mL and 10.0 mL of EDTA.

See Table 9.13 for the values.

The third step in sketching our titration curve is to add two points after the equivalence point. Here the concentration of Cd^{2+} is controlled by the dissociation of the Cd^{2+}–EDTA complex. Beginning with the conditional formation constant

See the side bar comment on the previous page for an explanation of why we are ignoring the effect of NH_3 on the concentration of Cd^{2+}.

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} = \alpha_{Y^{4-}} \times K_f = (0.37)(2.9 \times 10^{16}) = 1.1 \times 10^{16}$$

we take the log of each side and rearrange, arriving at

$$\log K_f' = -\log[Cd^{2+}] + \log \frac{[CdY^{2-}]}{C_{EDTA}}$$

$$pCd = \log K_f' + \log \frac{C_{EDTA}}{[CdY^{2-}]}$$

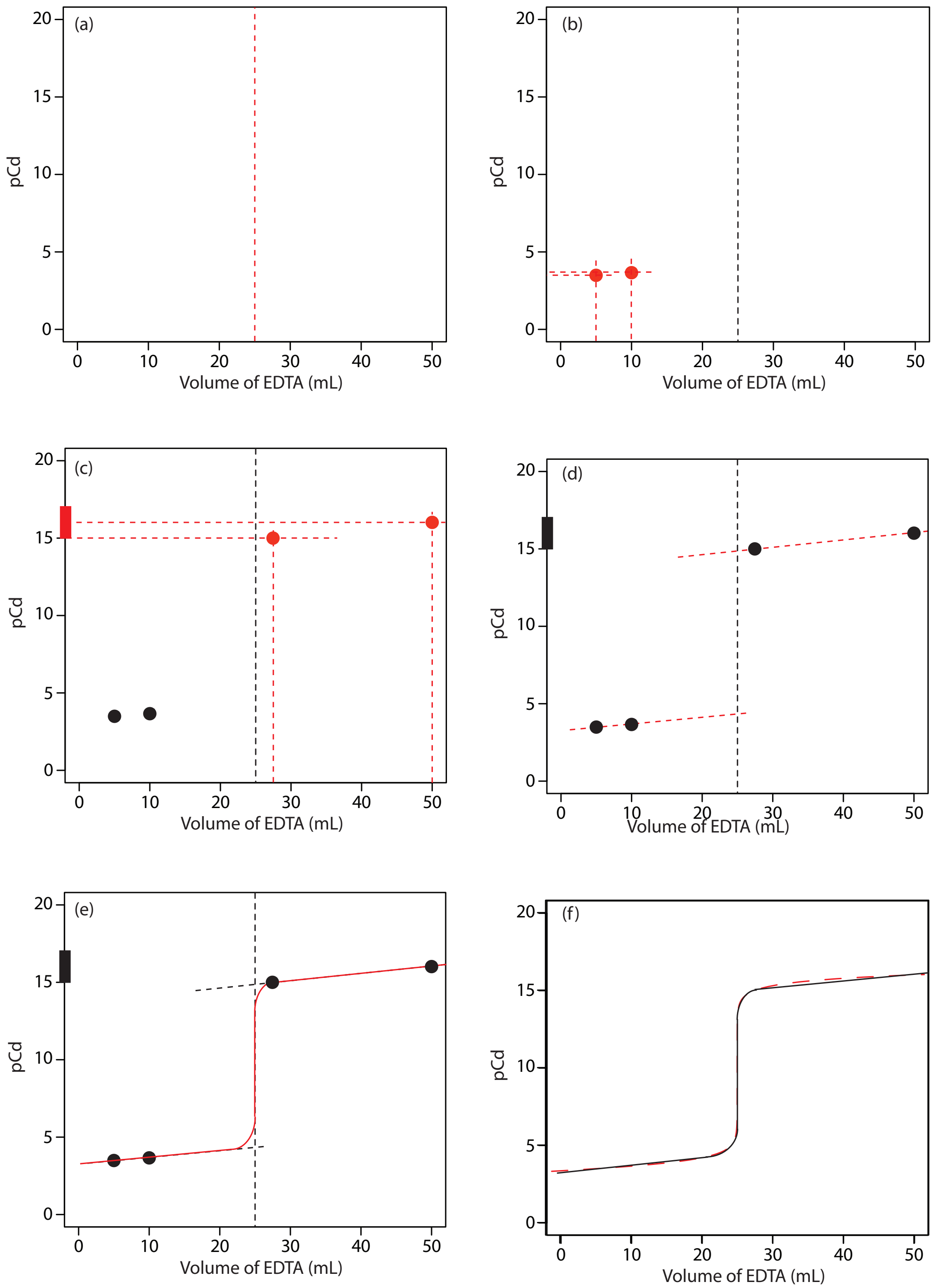


Figure 9.29 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA in the presence of 0.0100 M NH_3: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Note that after the equivalence point, the titrand's solution is a metal–ligand complexation buffer, with pCd determined by C_{EDTA} and $[\text{CdY}^{2-}]$. The buffer is at its lower limit of $\text{pCd} = \log K_f' - 1$ when

$$\frac{C_{\text{EDTA}}}{[\text{CdY}^{2-}]} = \frac{\text{moles EDTA added} - \text{initial moles Cd}^{2+}}{\text{initial moles Cd}^{2+}} = \frac{1}{10}$$

Making appropriate substitutions and solving, we find that

$$\frac{M_{\text{EDTA}}V_{\text{EDTA}} - M_{\text{Cd}}V_{\text{Cd}}}{M_{\text{Cd}}V_{\text{Cd}}} = \frac{1}{10}$$

$$M_{\text{EDTA}}V_{\text{EDTA}} - M_{\text{Cd}}V_{\text{Cd}} = 0.1 \times M_{\text{Cd}}V_{\text{Cd}}$$

$$V_{\text{EDTA}} = \frac{1.1 \times M_{\text{Cd}}V_{\text{Cd}}}{M_{\text{EDTA}}} = 1.1 \times V_{\text{eq}}$$

Our derivation here is general and applies to any complexation titration using EDTA as a titrant.

Thus, when the titration reaches 110% of the equivalence point volume, pCd is $\log K_f' - 1$. A similar calculation should convince you that $\text{pCd} = \log K_f'$ when the volume of EDTA is $2 \times V_{\text{eq}}$.

Figure 9.29c shows the third step in our sketch. First, we add a ladder diagram for the CdY^{2-} complex, including its buffer range, using its $\log K_f'$ value of 16.04. Next, we add points representing pCd at 110% of V_{eq} (a pCd of 15.04 at 27.5 mL) and at 200% of V_{eq} (a pCd of 16.04 at 50.0 mL).

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.29d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.29e). A comparison of our sketch to the exact titration curve (Figure 9.29f) shows that they are in close agreement.

Practice Exercise 9.13

Sketch titration curves for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7. Compare your sketches to the calculated titration curves from Practice Exercise 9.12.

Click here to review your answer to this exercise.

9C.3 Selecting and Evaluating the End point

The equivalence point of a complexation titration occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Finding the End point with an Indicator

Most indicators for complexation titrations are organic dyes—known as metallochromic indicators—that form stable complexes with metal ions. The indicator, In^{m-}, is added to the titrand's solution where it forms a stable complex with the metal ion, MIn^{n-}. As we add EDTA it reacts first with free metal ions, and then displaces the indicator from MIn^{n-}.

$$MIn^{n-} + Y^{4-} \rightarrow MY^{2-} + In^{m-}$$

If MIn^{n-} and In^{m-} have different colors, then the change in color signals the end point.

The accuracy of an indicator's end point depends on the strength of the metal–indicator complex relative to that of the metal–EDTA complex. If the metal–indicator complex is too strong, the change in color occurs after the equivalence point. If the metal–indicator complex is too weak, however, the end point occurs before we reach the equivalence point.

Most metallochromic indicators also are weak acids. One consequence of this is that the conditional formation constant for the metal–indicator complex depends on the titrand's pH. This provides some control over an indicator's titration error because we can adjust the strength of a metal–indicator complex by adjusted the pH at which we carry out the titration. Unfortunately, because the indicator is a weak acid, the color of the uncomplexed indicator also changes with pH. Figure 9.30, for example, shows the color of the indicator calmagite as a function of pH and pMg, where H_2In^-, HIn^{2-}, and In^{3-} are different forms of the uncomplexed indicator, and $MgIn^-$ is the Mg^{2+}–calmagite complex. Because the color of calmagite's metal–indicator complex is red, it use as a metallochromic indicator has a practical pH range of approximately 8.5–11 where the uncomplexed indicator, HIn^{2-}, has a blue color.

Figure 9.30 is essentially a two-variable ladder diagram. The solid lines are equivalent to a step on a conventional ladder diagram, indicating conditions where two (or three) species are equal in concentration.

Table 9.14 provides examples of metallochromic indicators and the metal ions and pH conditions for which they are useful. Even if a suitable indicator does not exist, it is often possible to complete an EDTA titration

Table 9.14 Selected Metallochromic Indicators

Indicator	pH Range	Metal Ions[a]
calmagite	8.5–11	Ba, *Ca*, Mg, Zn
eriochrome Black T	7.5–10.5	Ba, *Ca*, Mg, Zn
eriochrome Blue Black R	8–12	*Ca*, Mg, Zn, Cu
murexide	6–13	Ca, Ni, Cu
PAN	2–11	Cd, Cu, Zn
salicylic acid	2–3	Fe

[a] metal ions in *italic* font have poor end points

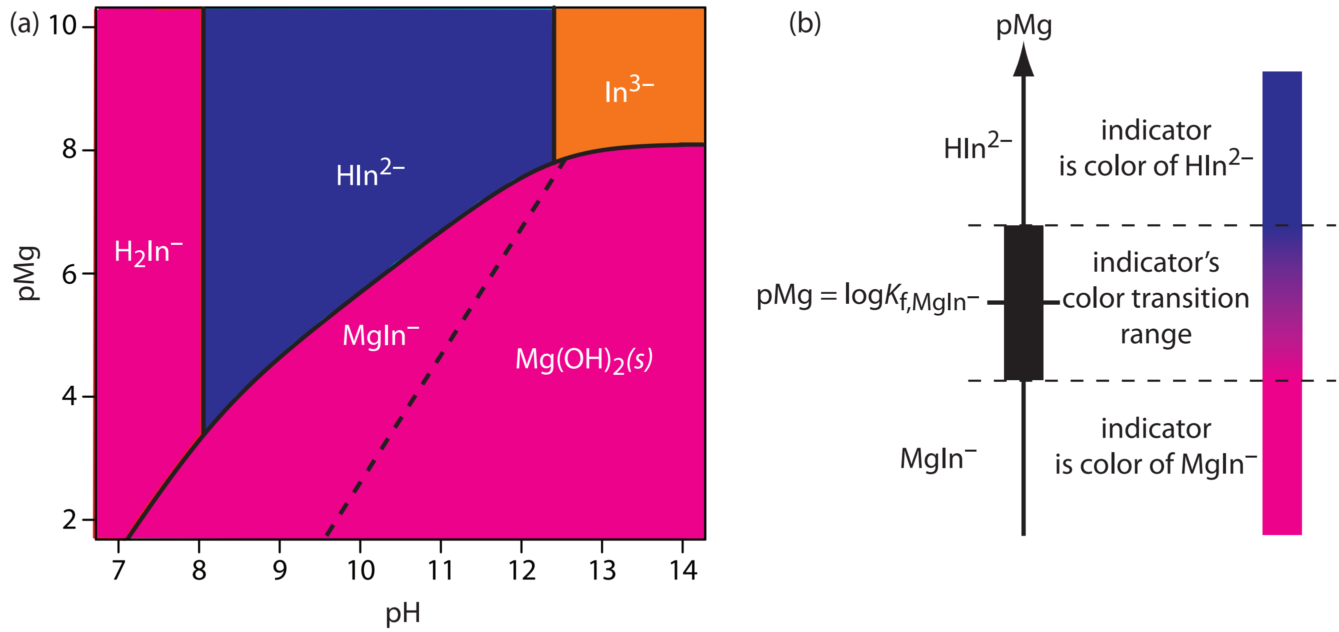


Figure 9.30 (a) Predominance diagram for the metallochromic indicator calmagite showing the most important form and color of calmagite as a function of pH and pMg, where H_2In^-, HIn^{2-}, and In^{3-} are uncomplexed forms of calmagite, and $MgIn^-$ is its complex with Mg^{2+}. Conditions to the right of the dashed line, where Mg^{2+} precipitates as $Mg(OH)_2$, are not analytically useful for a complexation titration. A red to blue end point is possible if we maintain the titrand's pH in the range 8.5–11. (b) Diagram showing the relationship between the concentration of Mg^{2+} (as pMg) and the indicator's color. The ladder diagram defines pMg values where $MgIn^-$ and HIn^- are predominate species. The indicator changes color when pMg is between $\log K_f - 1$ and $\log K_f + 1$.

by introducing a small amount of a secondary metal–EDTA complex, if the secondary metal ion forms a stronger complex with the indicator and a weaker complex with EDTA than the analyte. For example, calmagite gives poor end points when titrating Ca^{2+} with EDTA. Adding a small amount of Mg^{2+}–EDTA to the titrand gives a sharper end point. Because Ca^{2+} forms a stronger complex with EDTA, it displaces Mg^{2+}, which then forms the red-colored Mg^{2+}–calmagite complex. At the titration's end point, EDTA displaces Mg^{2+} from the Mg^{2+}–calmagite complex, signaling the end point by the presence of the uncomplexed indicator's blue form.

Finding the End point by Monitoring Absorbance

Two other methods for finding the end point of a complexation titration are a thermometric titration, in which we monitor the titrand's temperature as we add the titrant, and a potentiometric titration in which we use an ion selective electrode to monitor the metal ion's concentration as we add the titrant. The experimental approach is essentially identical to that described earlier for an acid–base titration, to which you may refer.

See Chapter 11 for more details about ion selective electrodes.

An important limitation when using an indicator is that we must be able to see the indicator's change in color at the end point. This may be difficult if the solution is already colored. For example, when titrating Cu^{2+} with EDTA, ammonia is used to adjust the titrand's pH. The intensely colored $Cu(NH_3)_4^{2+}$ complex obscures the indicator's color, making an accurate determination of the end point difficult. Other absorbing species present within the sample matrix may also interfere. This is often a problem when analyzing clinical samples, such as blood, or environmental samples, such as natural waters.

If at least one species in a complexation titration absorbs electromagnetic radiation, we can identify the end point by monitoring the titrand's absorbance at a carefully selected wavelength. For example, we can identify the end point for a titration of Cu^{2+} with EDTA, in the presence of NH_3 by monitoring the titrand's absorbance at a wavelength of 745 nm, where the $Cu(NH_3)_4^{2+}$ complex absorbs strongly. At the beginning of the titration the absorbance is at a maximum. As we add EDTA, however, the reaction

$$\mathrm{Cu(NH_3)_4^{2+}}(aq) + \mathrm{Y^{4-}}(aq) \rightarrow \mathrm{CuY^{2-}}(aq) + 4\mathrm{NH_3}(aq)$$

decreases the concentration of $Cu(NH_3)_4^{2+}$ and decreases the absorbance until we reach the equivalence point. After the equivalence point the absorbance remains essentially unchanged. The resulting SPECTROPHOTOMETRIC TITRATION CURVE is shown in Figure 9.31a. Note that the titration curve's *y*-axis is not the actual absorbance, *A*, but a corrected absorbance, A_{corr}

$$A_{corr} = A \times \frac{V_{EDTA} + V_{Cu}}{V_{Cu}}$$

where V_{EDTA} and V_{Cu} are, respectively, the volumes of EDTA and Cu. Correcting the absorbance for the titrand's dilution ensures that the spectrophotometric titration curve consists of linear segments that we can extrapolate to find the end point. Other common spectrophotometric titration curves are shown in Figures 9.31b-f.

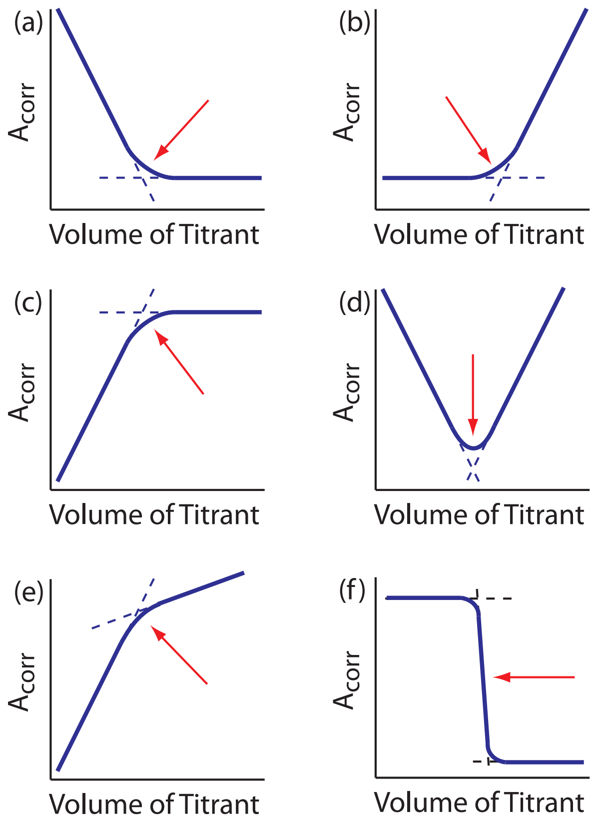


Figure 9.31 Examples of spectrophotometric titration curves: (a) only the titrand absorbs; (b) only the titrant absorbs; (c) only the product of the titration reaction absorbs; (d) both the titrand and the titrant absorb; (e) both the titration reaction's product and the titrant absorb; (f) only the indicator absorbs. The red arrows indicate the end points for each titration curve.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical complexation titrimetric method. Although each method is unique, the following description of the determination of the hardness of water provides an instructive example of a typical procedure. The description here is based on Method 2340C as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.2

Determination of Hardness of Water and Wastewater

Description of the Method

The operational definition of water hardness is the total concentration of cations in a sample capable of forming insoluble complexes with soap. Although most divalent and trivalent metal ions contribute to hardness, the most important are Ca^{2+} and Mg^{2+}. Hardness is determined by titrating with EDTA at a buffered pH of 10. Calmagite is used as an indicator. Hardness is reported as mg $CaCO_3$/L.

Procedure

Select a volume of sample requiring less than 15 mL of titrant to keep the analysis time under 5 minutes and, if necessary, dilute the sample to 50 mL with distilled water. Adjust the sample's pH by adding 1–2 mL of a pH 10 buffer containing a small amount of Mg^{2+}–EDTA. Add 1–2 drops of indicator and titrate with a standard solution of EDTA until the red-to-blue end point is reached (Figure 9.32).

Questions

1. Why is the sample buffered to a pH of 10? What problems might you expect at a higher pH or a lower pH?

   Of the cations contributing to hardness, Mg^{2+} forms the weakest complex with EDTA and is the last cation to be titrated. Calmagite is a useful indicator because it gives a distinct end point when titrating Mg^{2+}. Because of calmagite's acid–base properties, the range of pMg values over which the indicator changes color is pH–dependent (Figure 9.30). Figure 9.33 shows the titration curve for a 50-mL solution of 10^{-3} M Mg^{2+} with 10^{-2} M EDTA at pHs of 9, 10, and 11. Superimposed on each titration curve is the range of conditions for which the average analyst will observe the end point. At a pH of 9 an early end point is possible, leading to a negative determinate error. A

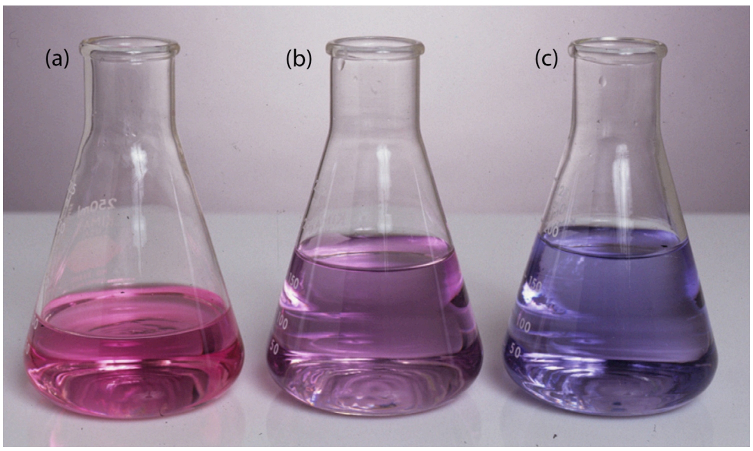


Figure 9.32 End point for the titration of hardness with EDTA using calmagite as an indicator; the indicator is: (a) red prior to the end point due to the presence of the Mg^{2+}–indicator complex; (b) purple at the titration's end point; and (c) blue after the end point due to the presence of uncomplexed indicator.

late end point and a positive determinate error are possible if we use a pH of 11.

2. Why is a small amount of the Mg^{2+}–EDTA complex added to the buffer?

   The titration's end point is signaled by the indicator calmagite. The indicator's end point with Mg^{2+} is distinct, but its change in color when titrating Ca^{2+} does not provide a good end point. If the sample does not contain any Mg^{2+} as a source of hardness, then the titration's end point is poorly defined, leading to inaccurate and imprecise results.

   Adding a small amount of Mg^{2+}–EDTA to the buffer ensures that the titrand includes at least some Mg^{2+}. Because Ca^{2+} forms a stronger complex with EDTA, it displaces Mg^{2+} from the Mg^{2+}–EDTA complex, freeing the Mg^{2+} to bind with the indicator. This displacement is stoichiometric, so the total concentration of hardness cations remains unchanged. The displacement by EDTA of Mg^{2+} from the Mg^{2+}–indicator complex signals the titration's end point.

3. Why does the procedure specify that the titration take no longer than 5 minutes?

   A time limitation suggests that there is a kinetically controlled interference, possibly arising from a competing chemical reaction. In this case the interference is the possible precipitation of $CaCO_3$ at a pH of 10.

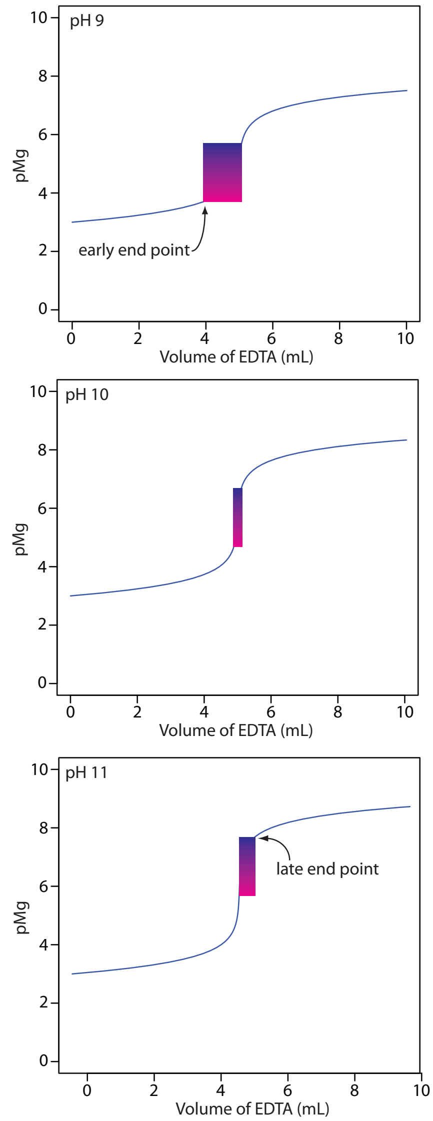


Figure 9.33 Titration curves for 50 mL of 10^{-3} M Mg^{2+} with 10^{-3} M EDTA at pHs 9, 10, and 11 using calmagite as an indicator. The range of pMg and volume of EDTA over which the indicator changes color is shown for each titration curve.

9C.4 Quantitative Applications

Although many quantitative applications of complexation titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In the section we review the general application of complexation titrimetry with an emphasis on applications from the analysis of water and wastewater. First, however, we discuss the selection and standardization of complexation titrants.

Selection and Standardization of Titrants

EDTA is a versatile titrant that can be used to analyze virtually all metal ions. Although EDTA is the usual titrant when the titrand is a metal ion, it cannot be used to titrate anions. In the later case, Ag^+ or Hg^{2+} are suitable titrants.

Solutions of EDTA are prepared from its soluble disodium salt, $Na_2H_2Y{\bullet}2H_2O$ and standardized by titrating against a solution made from the primary standard $CaCO_3$. Solutions of Ag^+ and Hg^{2+} are prepared using $AgNO_3$ and $Hg(NO_3)_2$, both of which are secondary standards. Standardization is accomplished by titrating against a solution prepared from primary standard grade NaCl.

Inorganic Analysis

Complexation titrimetry continues to be listed as a standard method for the determination of hardness, Ca^{2+}, CN^-, and Cl^- in waters and wastewaters. The evaluation of hardness was described earlier in Representative Method 9.2. The determination of Ca^{2+} is complicated by the presence of Mg^{2+}, which also reacts with EDTA. To prevent an interference the pH is adjusted to 12–13, precipitating Mg^{2+} as $Mg(OH)_2$. Titrating with EDTA using murexide or Eriochrome Blue Black R as the indicator gives the concentration of Ca^{2+}.

Cyanide is determined at concentrations greater than 1 mg/L by making the sample alkaline with NaOH and titrating with a standard solution of $AgNO_3$, forming the soluble $Ag(CN)_2^-$ complex. The end point is determined using *p*-dimethylaminobenzalrhodamine as an indicator, with the solution turning from a yellow to a salmon color in the presence of excess Ag^+.

Chloride is determined by titrating with $Hg(NO_3)_2$, forming $HgCl_2(aq)$. The sample is acidified to a pH of 2.3–3.8 and diphenylcarbazone, which forms a colored complex with excess Hg^{2+}, serves as the indicator. A pH indicator—xylene cyanol FF—is added to ensure that the pH is within the desired range. The initial solution is a greenish blue, and the titration is carried out to a purple end point.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. For a titration using EDTA, the stoichiometry is always 1:1.

Note that in this example, the analyte is the titrant.

Example 9.7

The concentration of a solution of EDTA was determined by standardizing against a solution of Ca^{2+} prepared using a primary standard of $CaCO_3$. A 0.4071-g sample of $CaCO_3$ was transferred to a 500-mL volumetric flask, dissolved using a minimum of 6 M HCl, and diluted to volume. After transferring a 50.00-mL portion of this solution to a 250-mL Erlenmeyer flask, the pH was adjusted by adding 5 mL of a pH 10 NH_3–NH_4Cl buffer containing a small amount of Mg^{2+}–EDTA. After adding calmagite as an indicator, the solution was titrated with the EDTA, requiring 42.63 mL to reach the end point. Report the molar concentration of EDTA in the titrant.

Solution

The primary standard of Ca^{2+} has a concentration of

$$\frac{0.4071 \text{ g CaCO}_3}{0.5000 \text{ L}} \times \frac{1 \text{ mol Ca}^{2+}}{100.09 \text{ g CaCO}_3} = 8.135 \times 10^{-3} \text{ M Ca}^{2+}$$

The moles of Ca^{2+} in the titrand is

$$8.135\times10^{-3}\ \text{M Ca}^{2+}\times0.05000\ \text{L Ca}^{2+}=4.068\times10^{-4}\ \text{mol Ca}^{2+}$$

which means that 4.068×10^{-4} moles of EDTA are used in the titration. The molarity of EDTA in the titrant is

$$\frac{4.068\times10^{-4}\ \text{mol EDTA}}{0.04263\ \text{L EDTA}}=9.543\times10^{-3}\ \text{M EDTA}$$

Practice Exercise 9.14

A 100.0-mL sample is analyzed for hardness using the procedure outlined in Representative Method 9.2, requiring 23.63 mL of 0.0109 M EDTA. Report the sample's hardness as mg $CaCO_3$/L.

Click here to review your answer to this exercise.

As shown in the following example, we can easily extended this calculation to complexation reactions using other titrants.

Example 9.8

The concentration of Cl^- in a 100.0-mL sample of water from a freshwater aquifer was tested for the encroachment of sea water by titrating with 0.0516 M $Hg(NO_3)_2$. The sample was acidified and titrated to the diphenylcarbazone end point, requiring 6.18 mL of the titrant. Report the concentration of Cl^-, in mg/L, in the aquifer.

Solution

The reaction between Cl^- and Hg^{2+} produces a metal–ligand complex of $HgCl_2(aq)$. Each mole of Hg^{2+} reacts with 2 moles of Cl^-; thus

$$\frac{0.0516\ \text{mol Hg(NO}_3)_2}{\text{L}}\times0.00618\ \text{L Hg(NO}_3)_2\times\frac{2\ \text{mol Cl}^-}{\text{mol Hg(NO}_3)_2}\times\frac{35.453\ \text{g Cl}^-}{\text{mol Cl}^-}=0.0226\ \text{g Cl}^-$$

are in the sample. The concentration of Cl^- in the sample is

$$\frac{0.0226\ \text{g Cl}^-}{0.1000\ \text{L}}\times\frac{1000\ \text{mg}}{\text{g}}=226\ \text{mg / L}$$

Practice Exercise 9.15

A 0.4482-g sample of impure NaCN is titrated with 0.1018 M $AgNO_3$, requi i iring 39.68 mL to reach the end point. Report the purity of the sample as %w/w NaCN.

Click here to review your answer to this exercise.

Finally, complex titrations involving multiple analytes or back titrations are possible.

Example 9.9

An alloy of chromel containing Ni, Fe, and Cr was analyzed by a complexation titration using EDTA as the titrant. A 0.7176-g sample of the alloy was dissolved in HNO_3 and diluted to 250 mL in a volumetric flask. A 50.00-mL aliquot of the sample, treated with pyrophosphate to mask the Fe and Cr, required 26.14 mL of 0.05831 M EDTA to reach the murexide end point. A second 50.00-mL aliquot was treated with hexamethylenetetramine to mask the Cr. Titrating with 0.05831 M EDTA required 35.43 mL to reach the murexide end point. Finally, a third 50.00-mL aliquot was treated with 50.00 mL of 0.05831 M EDTA, and back titrated to the murexide end point with 6.21 mL of 0.06316 M Cu^{2+}. Report the weight percents of Ni, Fe, and Cr in the alloy.

Solution

The stoichiometry between EDTA and each metal ion is 1:1. For each of the three titrations, therefore, we can easily equate the moles of EDTA to the moles of metal ions that are titrated.

Titration 1: moles Ni = moles EDTA

Titration 2: moles Ni + moles Fe = moles EDTA

Titration 3: moles Ni + moles Fe + moles Cr + moles Cu = moles EDTA

We can use the first titration to determine the moles of Ni in our 50.00-mL portion of the dissolved alloy. The titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.02614 \text{ L EDTA} = 1.524 \times 10^{-3} \text{ mol EDTA}$$

which means the sample contains 1.524×10^{-3} mol Ni.

Having determined the moles of EDTA reacting with Ni, we can use the second titration to determine the amount of Fe in the sample. The second titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.03543 \text{ L EDTA} = 2.066 \times 10^{-3} \text{ mol EDTA}$$

of which 1.524×10^{-3} mol are used to titrate Ni. This leaves 5.42×10^{-4} mol of EDTA to react with Fe; thus, the sample contains 5.42×10^{-4} mol of Fe.

Finally, we can use the third titration to determine the amount of Cr in the alloy. The third titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.05000 \text{ L EDTA} = 2.916 \times 10^{-3} \text{ mol EDTA}$$

of which 1.524×10^{-3} mol are used to titrate Ni and 5.42×10^{-4} mol are used to titrate Fe. This leaves 8.50×10^{-4} mol of EDTA to react with Cu and Cr. The amount of EDTA reacting with Cu is

$$\frac{0.06316 \text{ mol Cu}^{2+}}{\text{L}} \times 0.00621 \text{ L Cu}^{2+} \times \frac{1 \text{ mol EDTA}}{\text{mol Cu}^{2+}} = 3.92 \times 10^{-4} \text{ mol EDTA}$$

leaving 4.58×10^{-4} mol of EDTA to react with Cr. The sample, therefore, contains 4.58×10^{-4} mol of Cr.

Having determined the moles of Ni, Fe, and Cr in a 50.00-mL portion of the dissolved alloy, we can calculate the %w/w of each analyte in the alloy.

$$\frac{1.524 \times 10^{-3} \text{ mol Ni}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{58.69 \text{ g Ni}}{\text{mol Ni}} = 0.4472 \text{ g Ni}$$

$$\frac{0.4472 \text{ g Ni}}{0.7176 \text{ g sample}} \times 100 = 62.32\% \text{ w/w Ni}$$

$$\frac{5.42 \times 10^{-4} \text{ mol Fe}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{55.847 \text{ g Fe}}{\text{mol Fe}} = 0.151 \text{ g Fe}$$

$$\frac{0.151 \text{ g Fe}}{0.7176 \text{ g sample}} \times 100 = 21.0\% \text{ w/w Fe}$$

$$\frac{4.58 \times 10^{-4} \text{ mol Cr}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{51.996 \text{ g Cr}}{\text{mol Cr}} = 0.119 \text{ g Cr}$$

$$\frac{0.119 \text{ g Cr}}{0.7176 \text{ g sample}} \times 100 = 16.6\% \text{ w/w Fe}$$

Practice Exercise 9.16

A indirect complexation titration with EDTA can be used to determine the concentration of sulfate, SO_4^{2-}, in a sample. A 0.1557-g sample is dissolved in water, any sulfate present is precipitated as $BaSO_4$ by adding $Ba(NO_3)_2$. After filtering and rinsing the precipitate, it is dissolved in 25.00 mL of 0.02011 M EDTA. The excess EDTA is then titrated w iith 0.01113 M Mg^{2+}, requiring 4.23 mL to reach the end point. Calculate the %w/w Na_2SO_4 in the sample.

Click here to review your answer to this exercise.

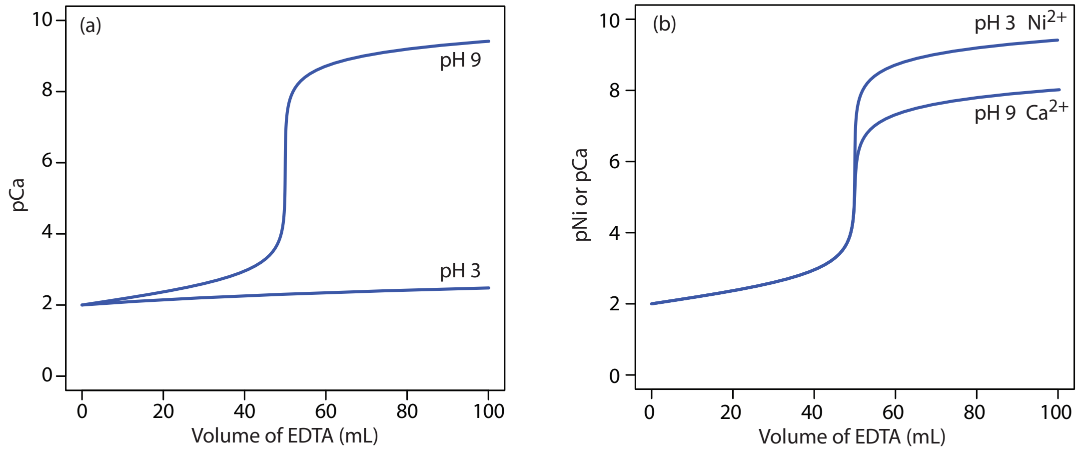


Figure 9.34 Titration curves illustrating how we can use the titrand's pH to control EDTA's selectivity. (a) Titration of 50.0 mL of 0.010 M Ca^{2+} at a pH of 3 and a pH of 9 using 0.010 M EDTA. At a pH of 3 the CaY^{2-} complex is too weak to successfully titrate. (b) Titration of a 50.0 mL mixture of 0.010 M Ca^{2+} and 0.010 M Ni^{2+} at a pH of 3 and a pH of 9 using 0.010 M EDTA. At a pH of 3 EDTA reacts only with Ni^{2+}. When the titration is complete, raising the pH to 9 allows for the titration of Ca^{2+}.

9C.5 Evaluation of Complexation Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a complexation titration are similar to those described earlier for acid–base titrations. Complexation titrations, however, are more selective. Although EDTA forms strong complexes with most metal ion, by carefully controlling the titrand's pH we can analyze samples containing two or more analytes. The reason we can use pH to provide selectivity is shown in Figure 9.34a. A titration of Ca^{2+} at a pH of 9 gives a distinct break in the titration curve because the conditional formation constant for CaY^{2-} of 2.6×10^9 is large enough to ensure that the reaction of Ca^{2+} and EDTA goes to completion. At a pH of 3, however, the conditional formation constant of 1.23 is so small that very little Ca^{2+} reacts with the EDTA.

Suppose we need to analyze a mixture of Ni^{2+} and Ca^{2+}. Both analytes react with EDTA, but their conditional formation constants differ significantly. If we adjust the pH to 3 we can titrate Ni^{2+} with EDTA without titrating Ca^{2+} (Figure 9.34b). When the titration is complete, we adjust the titrand's pH to 9 and titrate the Ca^{2+} with EDTA.

A spectrophotometric titration is a particularly useful approach for analyzing a mixture of analytes. For example, as shown in Figure 9.35, we can determine the concentration of a two metal ions if there is a difference between the absorbance of the two metal-ligand complexes.

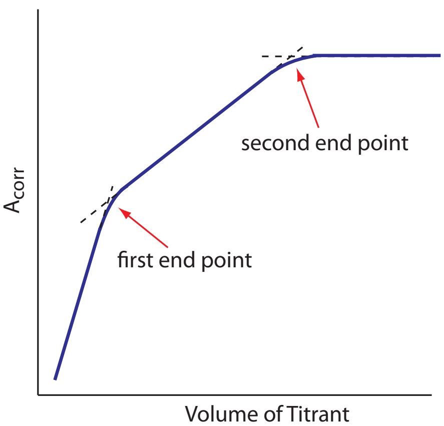


Figure 9.35 Spectrophotometric titration curve for the complexation titration of a mixture of two analytes. The red arrows indicate the end points for each analyte.

9D Redox Titrations

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest REDOX TITRATION took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

9D.1 Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{B_{ox}/B_{red}} - E_{A_{ox}/A_{red}}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{B_{ox}/B_{red}} = E_{A_{ox}/A_{red}}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{rxn} = E^{o}_{A_{ox}/A_{red}} - \frac{RT}{nF}\ln\frac{[A_{red}]}{[A_{ox}]}$$

Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent FORMAL POTENTIAL often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^{o}_{B_{ox}/B_{red}} - \frac{RT}{nF}\ln\frac{[B_{red}]}{[B_{ox}]}$$

CALCULATING THE TITRATION CURVE

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \qquad 9.15$$

Because the equilibrium constant for reaction 9.15 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

$$\text{moles } Fe^{2+} = \text{moles } Ce^{4+}$$

$$M_{Fe} \times V_{Fe} = M_{Ce} \times V_{Ce}$$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 50.0\text{ mL}$$

Step 2: Calculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = \\ +0.767\text{V} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad 9.16$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[\mathrm{Fe^{2+}}] = \frac{\text{initial moles Fe}^{2+} - \text{moles Ce}^{4+}\text{ added}}{\text{total volume}} = \frac{M_{\mathrm{Fe}}V_{\mathrm{Fe}} - M_{\mathrm{Ce}}V_{\mathrm{Ce}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 6.67 \times 10^{-2}\ \mathrm{M}$$

$$[\mathrm{Fe^{3+}}] = \frac{\text{moles Ce}^{4+}\text{ added}}{\text{total volume}} = \frac{M_{\mathrm{Ce}}V_{\mathrm{Ce}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 1.67 \times 10^{-2}\ \mathrm{M}$$

Substituting these concentrations into equation 9.16 gives a potential of

$$E = +0.767\ \mathrm{V} - 0.05916 \log \frac{6.67 \times 10^{-2}\ \mathrm{M}}{1.67 \times 10^{-2}\ \mathrm{M}} = +0.731\ \mathrm{V}$$

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

Step 3: Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

$$E = E^{\circ}_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF} \log \frac{[\mathrm{Ce^{3+}}]}{[\mathrm{Ce^{4+}}]} = \\ +1.70\ \mathrm{V} - 0.05916 \log \frac{[\mathrm{Ce^{3+}}]}{[\mathrm{Ce^{4+}}]} \qquad 9.17$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[\mathrm{Ce^{3+}}] = \frac{\text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{\mathrm{Fe}}V_{\mathrm{Fe}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 60.0\ \mathrm{mL}} = 4.55 \times 10^{-3}\ \mathrm{M}$$

$$[\mathrm{Ce^{4+}}] = \frac{\text{moles Ce}^{4+}\text{ added} - \text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{\mathrm{Ce}}V_{\mathrm{Ce}} - M_{\mathrm{Fe}}V_{\mathrm{Fe}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(60.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 60.0\ \mathrm{mL}} = 9.09 \times 10^{-3}\ \mathrm{M}$$

Substituting these concentrations into equation 9.17 gives a potential of

$$E = +1.70\ \mathrm{V} - 0.05916 \log \frac{4.55 \times 10^{-2}\ \mathrm{M}}{9.09 \times 10^{-3}\ \mathrm{M}} = +1.66\ \mathrm{V}$$

At the titration's equivalence point, the potential, E_{eq}, in equation 9.16 and equation 9.17 are identical. Adding the equations together to gives

Step 4: Calculate the potential at the equivalence point.

Table 9.15 Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}

Volume of Ce^{4+} (mL)	E (V)	Volume Ce^{4+} (mL)	E (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

$$2E_{\text{eq}} = E^{\text{o}}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^{\text{o}}_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}$$

Because $[Fe^{2+}]=[Ce^{4+}]$ and $[Ce^{3+}]=[Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{\text{eq}} = \frac{E^{\text{o}}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^{\text{o}}_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\text{ V} + 1.70\text{ V}}{2} = 1.23\text{ V}$$

Additional results for this titration curve are shown in Table 9.15 and Figure 9.36.

Practice Exercise 9.17

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$\text{Sn}^{2+}(aq) + \text{Tl}^{3+}(aq) \longrightarrow \text{Sn}^{4+}(aq) + \text{Tl}^{+}(aq)$$

Click here to review your answer to this exercise.

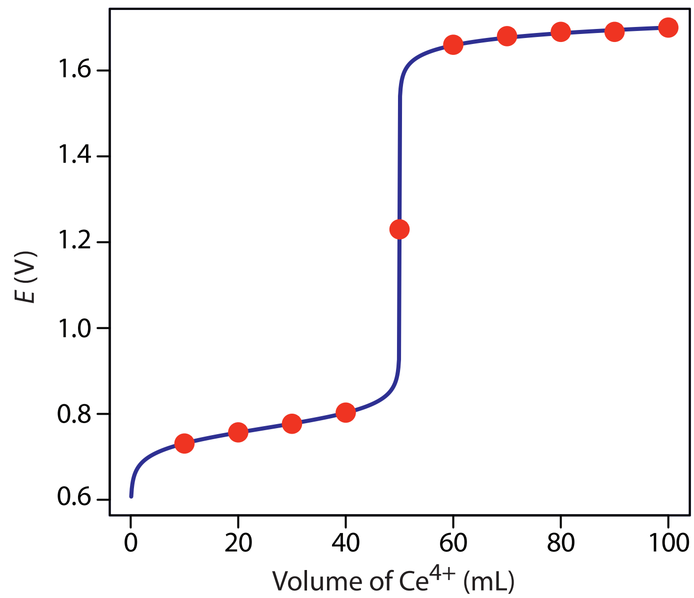


Figure 9.36 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 9.15. The blue line shows the complete titration curve.

Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 9.15 and Figure 9.36.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, E, on the y-axis and the titrant's volume on the x-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure 9.37a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately $\pm(0.05916/n)$ unit on either side of $E^{o}_{Fe^{3+}/Fe^{2+}}$. The potential is at the buffer's lower limit

$$\mathrm{E} = E^{o}_{Fe^{3+}/Fe^{2+}} - 0.05916$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$\mathrm{E} = E^{o}_{Fe^{3+}/Fe^{2+}} + 0.05916$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure 9.37b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the y-axis, using its $E^{o}_{Fe^{3+}/Fe^{2+}}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.

The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}. The redox buffer is at its lower limit of $\mathrm{E} = E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^{o}_{Ce^{4+}/Ce^{3+}}$ when the volume of Ce^{4+} is $2\times V_{eq}$.

Figure 9.37c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$ value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.

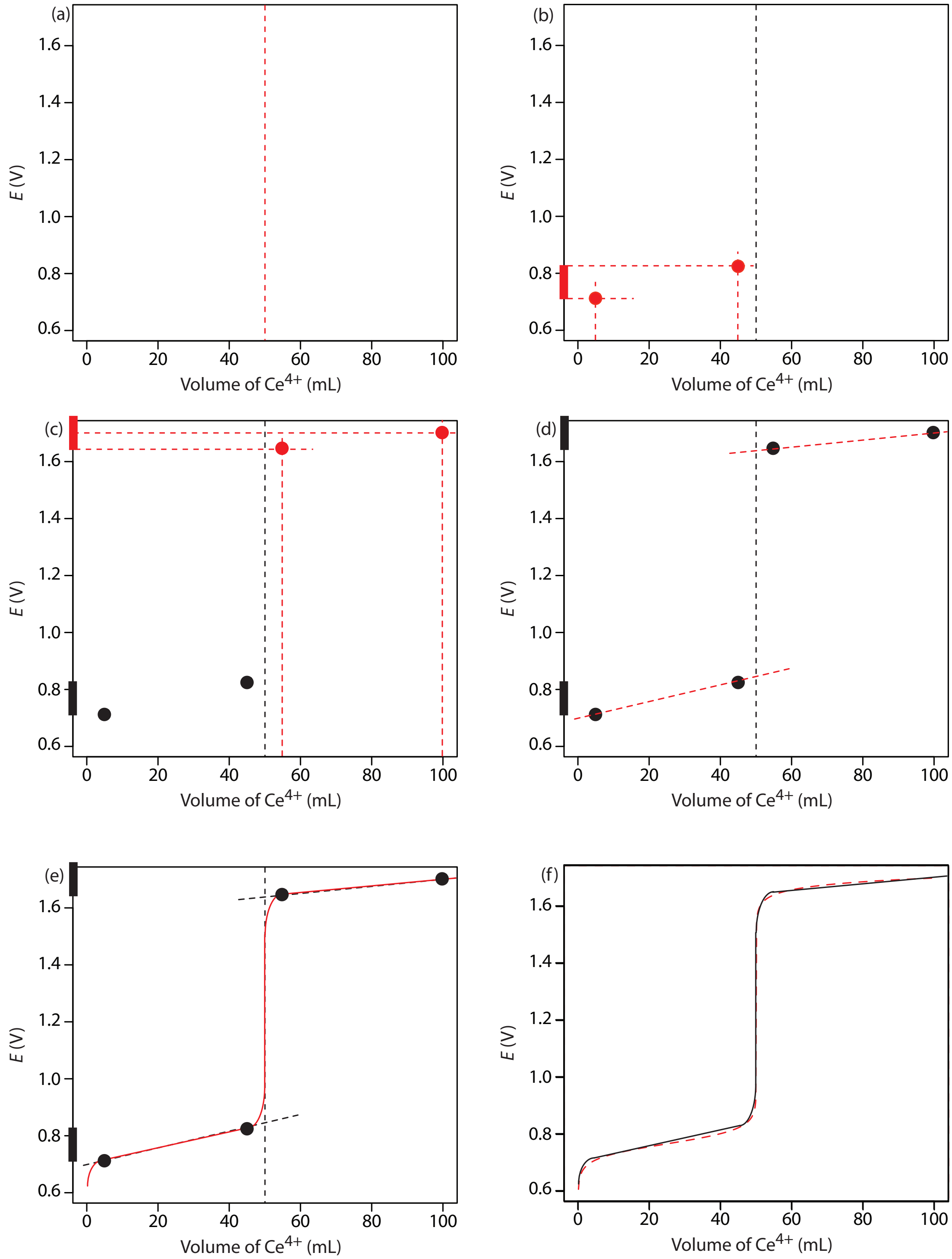


Figure 9.37 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.37d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.37e). A comparison of our sketch to the exact titration curve (Figure 9.37f) shows that they are in close agreement.

Practice Exercise 9.18

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq)$$

Compare your sketch to your calculated titration curve from Practice Exercise 9.17.

Click here to review your answer to this exercise.

9D.2 Selecting and Evaluating the End point

A redox titration's equivalence point occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base and complexation titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Where is the Equivalence Point?

For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at Figure 9.7 and Figure 9.28, you will see that the inflection point is in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves. We call this a SYMMETRIC EQUIVALENCE POINT. If the stoichiometry of a redox titration is symmetric—one mole of titrant reacts with each mole of titrand—then the equivalence point is symmetric. If the titration reaction's stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve's sharp rise. In this case we have an ASYMMETRIC EQUIVALENCE POINT.

Example 9.10

Derive a general equation for the equivalence point's potential when titrating Fe^{2+} with MnO_4^-.

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$$

We often use H^+ instead of H_3O^+ when writing a redox reaction.

SOLUTION

The half-reactions for Fe^{2+} and MnO_4^- are

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

for which the Nernst equations are

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E = E^\circ_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Before adding these two equations together we must multiply the second equation by 5 so that we can combine the log terms; thus

$$6E = E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}} - 0.05916\log\frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H^+]^8}$$

At the equivalence point we know that

$$[Fe^{2+}] = 5\times[MnO_4^-]$$

$$[Fe^{3+}] = 5\times[Mn^{2+}]$$

Substituting these equalities into the previous equation and rearranging gives us a general equation for the potential at the equivalence point.

$$6E_{eq} = E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}} - 0.05916\log\frac{5[MnO_4^-][Mn^{2+}]}{5[Mn^{2+}][MnO_4^-][H^+]^8}$$

$$E_{eq} = \frac{E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}}}{6} - \frac{0.05916}{6}\log\frac{1}{[H^+]^8}$$

$$E_{eq} = \frac{E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}}}{6} + \frac{0.05916\times 8}{6}\log[H^+]$$

$$E_{eq} = \frac{E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}}}{6} - 0.07888\text{pH}$$

Our equation for the equivalence point has two terms. The first term is a weighted average of the titrand's and the titrant's standard state potentials, in which the weighting factors are the number of electrons in their respective half-reactions. The second term shows that E_{eq} for this titration

Instead of standard state potentials, you can use formal potentials.

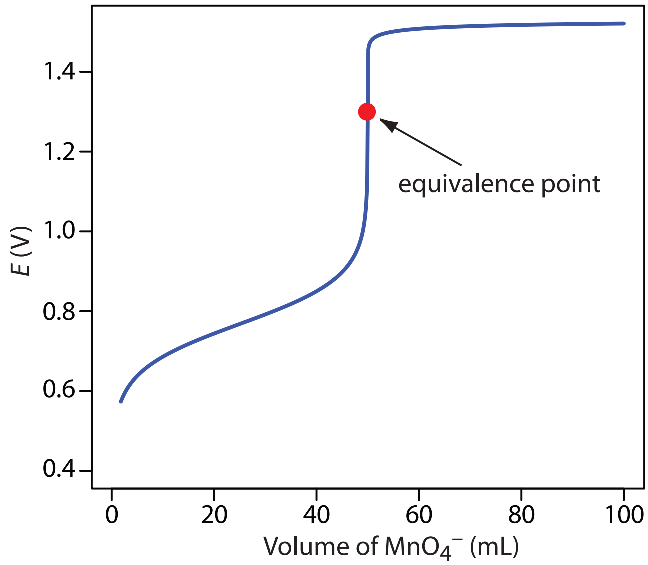


Figure 9.38 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.0200 M MnO_4^- at a fixed pH of 1 (using H_2SO_4). The equivalence point is shown by the red dot.

is pH-dependent. At a pH of 1 (in H_2SO_4), for example, the equivalence point has a potential of

$$E_{eq} = \frac{0.768 + 5 \times 1.51}{6} - 0.07888 \times 1 = 1.31 \text{ V}$$

Figure 9.38 shows a typical titration curve for titration of Fe^{2+} with MnO_4^-. Note that the titration's equivalence point is asymmetrical.

Practice Exercise 9.19

Derive a general equation for the equivalence point's potential for the titration of U^{4+} with Ce^{4+}. The unbalanced reaction is

$$Ce^{4+}(aq) + U^{4+}(aq) \rightarrow UO_2^{2+}(aq) + Ce^{3+}(aq)$$

What is the equivalence point's potential if the pH is 1?

Click here to review your answer to this exercise.

Finding the End point with an Indicator

Three types of indicators are used to signal a redox titration's end point. The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When using MnO_4^- as a titrant, the titrand's solution remains colorless until the equivalence point. The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the titrand. Starch, for example, forms a dark blue complex with I_3^-. We can use this distinct color to signal the presence of excess I_3^- as a titrant—a change in color from colorless to blue—or the completion of a reaction consuming I_3^- as the titrand—a change in color from blue to colorless. Another example of a specific indicator is thiocyanate, SCN^-, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with Fe^{3+}.

The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When we add a REDOX INDICATOR to the titrand, the indicator imparts a color that depends on the solution's potential. As the solution's potential changes with the addition of titrant, the indicator changes oxidation state and changes color, signaling the end point.

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

For simplicity, In_{ox} and In_{red} are shown without specific charges. Because there is a change in oxidation state, In_{ox} and In_{red} cannot both be neutral.

$$\mathrm{In_{ox}} + ne^- \rightleftharpoons \mathrm{In_{red}}$$

where In_{ox} and In_{red} are, respectively, the indicator's oxidized and reduced forms. The Nernst equation for this half-reaction is

$$E = E^{\circ}_{\mathrm{In_{ox}/In_{red}}} - \frac{0.05916}{n}\log\frac{[\mathrm{In_{red}}]}{[\mathrm{In_{ox}}]}$$

This is the same approach we took in considering acid–base indicators and complexation indicators.

As shown in Figure 9.39, if we assume that the indicator's color changes from that of In_{ox} to that of In_{red} when the ratio $[In_{red}]/[In_{ox}]$ changes from 0.1 to 10, then the end point occurs when the solution's potential is within the range

$$E = E^{\circ}_{\mathrm{In_{ox}/In_{red}}} \pm \frac{0.05916}{n}$$

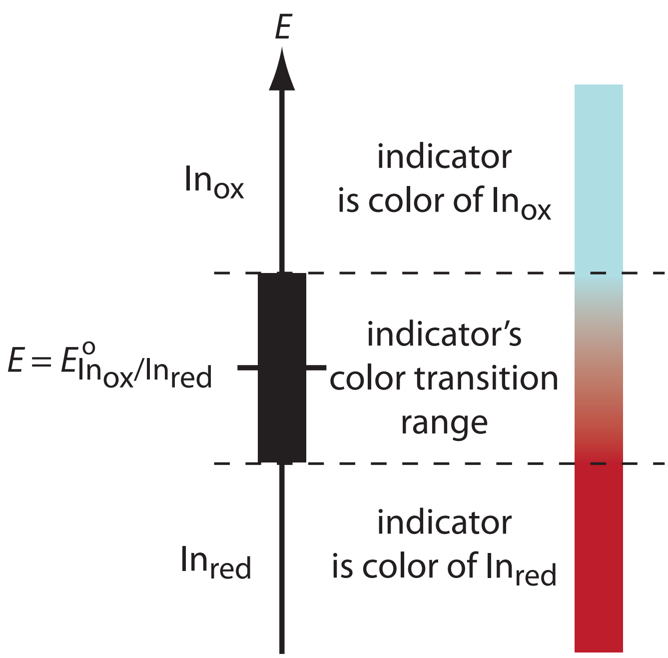


Figure 9.39 Diagram showing the relationship between E and an indicator's color. The ladder diagram defines potentials where In_{red} and In_{ox} are the predominate species. The indicator changes color when E is within the range

$$E = E^{\circ}_{\mathrm{In_{ox}/In_{red}}} \pm \frac{0.05916}{n}$$

Table 9.16 Selected Examples of Redox Indicators

Indicator	Color of In_{ox}	Color of In_{red}	$E^{o}_{In_{ox}/In_{red}}$
indigo tetrasulfate	blue	colorless	0.36
methylene blue	blue	colorless	0.53
diphenylamine	violet	colorless	0.75
diphenylamine sulfonic acid	red-violet	colorless	0.85
tris(2,2´-bipyridine)iron	pale blue	red	1.120
ferroin	pale blue	red	1.147
tris(5-nitro-1,10-phenanthroline)iron	pale blue	red-violet	1.25

A partial list of redox indicators is shown in Table 9.16. Examples of appropriate and inappropriate indicators for the titration of Fe^{2+} with Ce^{4+} are shown in Figure 9.40.

Other Methods for Finding the End point

Another method for locating a redox titration's end point is a potentiometric titration in which we monitor the change in potential while adding the titrant to the titrand. The end point is found by visually examining the titration curve. The simplest experimental design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand's or titrant's redox half-reaction, and a reference electrode that has a fixed potential. A further discussion of potentiometry is found in Chapter 11. Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

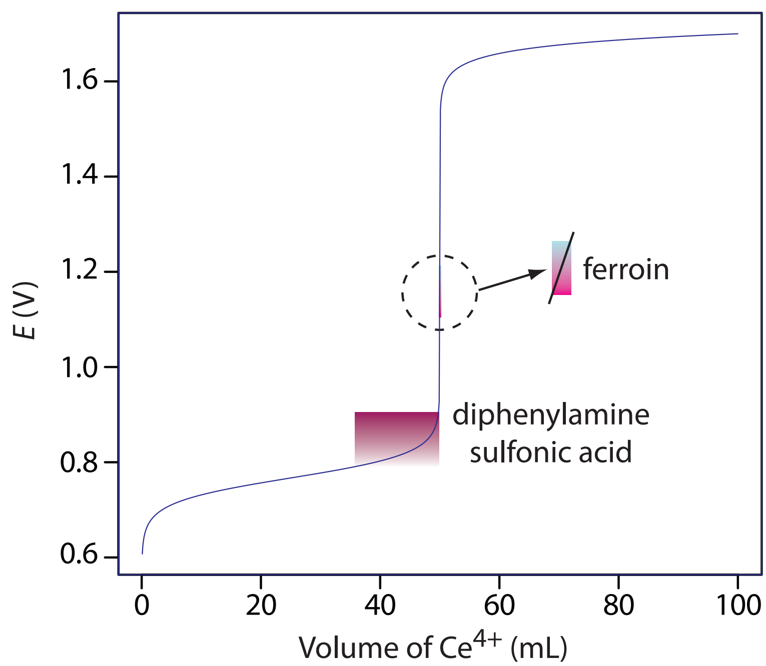


Figure 9.40 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve. Because the transition for ferroin is too small to see on the scale of the *x*-axis—it requires only 1–2 drops of titrant—the color change is expanded to the right.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical redox titrimetric method. Although each method is unique, the following description of the determination of the total chlorine residual in water provides an instructive example of a typical procedure. The description here is based on Method 4500-Cl B as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.3

Determination of Total Chlorine Residual

Description of the Method

The chlorination of public water supplies produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states, including the free residual chlorine, consisting of Cl_2, HOCl and OCl^-, and the combined chlorine residual, consisting of NH_2Cl, $NHCl_2$, and NCl_3. The total chlorine residual is determined by using the oxidizing power of chlorine to convert I^- to I_3^-. The amount of I_3^- formed is then determined by titrating with $Na_2S_2O_3$ using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if Cl_2 is the only source of chlorine, and is reported as mg Cl/L.

Procedure

Select a volume of sample requiring less than 20 mL of $Na_2S_2O_3$ to reach the end point. Using glacial acetic acid, acidify the sample to a pH of 3–4, and add about 1 gram of KI. Titrate with $Na_2S_2O_3$ until the yellow color of I_3^- begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch–I_3^- complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

Questions

1. Is this an example of a direct or an indirect analysis?

   This is an indirect analysis because the chlorine-containing species do not react with the titrant. Instead, the total chlorine residual oxidizes I^- to I_3^-, and the amount of I_3^- is determined by titrating with $Na_2S_2O_3$.

2. Why does the procedure rely on an indirect analysis instead of directly titrating the chlorine-containing species using KI as a titrant?

   Because the total chlorine residual consists of six different species, a titration with I^- does not have a single, well-defined equivalence

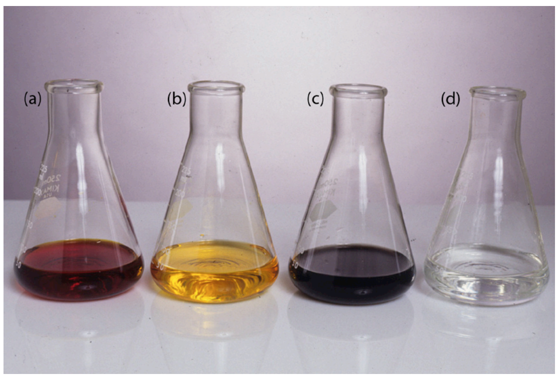


Figure 9.41 Endpoint for the determination of the total chlorine residual. (a) Acidifying the sample and adding KI forms a brown solution of I_3^-. (b) Titrating with $Na_2S_2O_3$ converts I_3^- to I^- with the solution fading to a pale yellow color as we approach the end point. (c) Adding starch forms the deep purple starch–I_3^- complex. (d) As the titration continues, the end point is a sharp transition from a purple to a colorless solution. The change in color from (c) to (d) typically takes 1–2 drops of titrant.

point. By converting the chlorine residual to an equivalent amount of I_3^-, the indirect titration with $Na_2S_2O_3$ has a single, useful equivalence point.

Even if the total chlorine residual is from a single species, such as HOCl, a direct titration with KI is impractical. Because the product of the titration, I_3^-, imparts a yellow color, the titrand's color would change with each addition of titrant, making it difficult to find a suitable indicator.

3. Both oxidizing and reducing agents can interfere with this analysis. Explain the effect of each type of interferent has on the total chlorine residual.

An interferent that is an oxidizing agent converts additional I^- to I_3^-. Because this extra I_3^- requires an additional volume of $Na_2S_2O_3$ to reach the end point, we overestimate the total chlorine residual. If the interferent is a reducing agent, it reduces back to I^- some of the I_3^- produced by the reaction between the total chlorine residual and iodide. As a result. we underestimate the total chlorine residual.

9D.3 Quantitative Applications

Although many quantitative applications of redox titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In this section we review the general application of redox titrimetry with an emphasis on environmental, pharmaceutical, and industrial applications. We begin, however, with a brief discussion of selecting and characterizing redox titrants, and methods for controlling the titrand's oxidation state.

Adjusting the Titrand's Oxidation State

If a redox titration is to be used in a quantitative analysis, the titrand must initially be present in a single oxidation state. For example, iron can be determined by a redox titration in which Ce^{4+} oxidizes Fe^{2+} to Fe^{3+}. Depending on the sample and the method of sample preparation, iron may initially be present in both the +2 and +3 oxidation states. Before titrating, we must reduce any Fe^{3+} to Fe^{2+}. This type of pretreatment can be accomplished using an auxiliary reducing agent or oxidizing agent.

A metal that is easy to oxidize—such as Zn, Al, and Ag—can serve as an auxiliary reducing agent. The metal, as a coiled wire or powder, is added to the sample where it reduces the titrand. Because any unreacted auxiliary reducing agent will react with the titrant, it must be removed before beginning the titration. This can be accomplished by simply removing the coiled wire, or by filtering.

An alternative method for using an auxiliary reducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finally divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suction. The length of the reduction column and the flow rate are selected to ensure the analyte's complete reduction.

Two common reduction columns are used. In the JONES REDUCTOR the column is filled with amalgamated zinc, Zn(Hg), prepared by briefly placing Zn granules in a solution of $HgCl_2$. Oxidation of zinc

$$\mathrm{Zn(Hg)}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Hg}(l) + 2e^-$$

provides the electrons for reducing the titrand. In the WALDEN REDUCTOR the column is filled with granular Ag metal. The solution containing the titrand is acidified with HCl and passed through the column where the oxidation of silver

$$\mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \rightarrow \mathrm{AgCl}(s) + e^-$$

provides the necessary electrons for reducing the titrand. Table 9.17 provides a summary of several applications of reduction columns.

Several reagents are commonly used as AUXILIARY OXIDIZING AGENTS, including ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, and hydrogen peroxide, H_2O_2. Peroxydisulfate is a powerful oxidizing agent

$$\mathrm{S_2O_8^{2-}}(aq) + 2e^- \rightarrow 2\mathrm{SO_4^{2-}}(aq)$$

Table 9.17 Examples of Reactions For Reducing a Titrand's Oxidation State Using a Reduction Column

Oxidized Titrand	Walden Reductor	Jones Reductor
Cr^{3+}	—	$\mathrm{Cr^{3+}}(aq) + e^- \rightarrow \mathrm{Cr^{2+}}(aq)$
Cu^{2+}	$\mathrm{Cu^{2+}}(aq) + e^- \rightarrow \mathrm{Cu^{+}}(aq)$	$\mathrm{Cu^{2+}}(aq) + 2e^- \rightarrow \mathrm{Cr}(s)$
Fe^{3+}	$\mathrm{Fe^{3+}}(aq) + e^- \rightarrow \mathrm{Fe^{2+}}(aq)$	$\mathrm{Fe^{3+}}(aq) + e^- \rightarrow \mathrm{Fe^{2+}}(aq)$
TiO^{2+}	—	$\mathrm{TiO^{2+}}(aq) + 2\mathrm{H^+}(aq) + e^- \rightarrow \mathrm{Ti^{3+}}(aq) + \mathrm{H_2O}(l)$
$MoO_2{}^{2+}$	$\mathrm{MoO_2^{2+}}(aq) + e^- \rightarrow \mathrm{MoO_2^{+}}(aq)$	$\mathrm{MoO_2^{2+}}(aq) + 4\mathrm{H^+}(aq) + 3e^- \rightarrow \mathrm{Mo^{3+}}(aq) + 2\mathrm{H_2O}(l)$
$VO_2{}^{+}$	$\mathrm{VO_2^{+}}(aq) + 2\mathrm{H^+}(aq) + e^- \rightarrow \mathrm{VO^{2+}}(aq) + \mathrm{H_2O}(l)$	$\mathrm{VO_2^{+}}(aq) + 4\mathrm{H^+}(aq) + 3e^- \rightarrow \mathrm{V^{2+}}(aq) + 2\mathrm{H_2O}(l)$

capable of oxidizing Mn^{2+} to MnO_4^-, Cr^{3+} to $Cr_2O_7^{2-}$, and Ce^{3+} to Ce^{4+}. Excess peroxydisulfate is easily destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in acidic solution

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

provides another method for oxidizing a titrand. Excess H_2O_2 is destroyed by briefly boiling the solution.

Selecting and Standardizing a Titrant

If it is to be used quantitatively, the titrant's concentration must remain stable during the analysis. Because a titrant in a reduced state is susceptible to air oxidation, most redox titrations use an oxidizing agent as the titrant. There are several common oxidizing titrants, including MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-. Which titrant is used often depends on how easy it is to oxidize the titrand. A titrand that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point.

The two strongest oxidizing titrants are MnO_4^- and Ce^{4+}, for which the reduction half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$$

Solutions of Ce^{4+} usually are prepared from the primary standard cerium ammonium nitrate, $Ce(NO_3)_4{\bullet}2NH_4NO_3$, in 1 M H_2SO_4. When prepared using a reagent grade material, such as $Ce(OH)_4$, the solution is standardized against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire) using ferroin as an indicator. Despite its availability as a primary standard and its ease of preparation, Ce^{4+} is not as frequently used as MnO_4^- because it is more expensive.

The standardization reactions are

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

$$2Ce^{4+}(aq) + H_2C_2O_4(aq) \rightarrow 2Ce^{3+}(aq) + 2CO_2(g) + 2H^+(aq)$$

Solutions of MnO_4^- are prepared from $KMnO_4$, which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water.

$$4MnO_4^-(aq) + 2H_2O(l) \rightleftharpoons 4MnO_2(s) + 3O_2(g) + 4OH^-(aq)$$

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. A moderately stable solution of permanganate can be prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid MnO_2 that precipitates. Standardization is accomplished against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire), with the pink color of excess MnO_4^- signaling the end point. A solution of MnO_4^- prepared in this fashion is stable for 1–2 weeks, although the standardization should be rechecked periodically.

The standardization reactions are

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO_4^- or Ce^{4+}, which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$$

Although a solution of $Cr_2O_7^{2-}$ is orange and a solution of Cr^{3+} is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with $Cr_2O_7^{2-}$.

Iodine is another important oxidizing titrant. Because it is a weaker oxidizing agent than MnO_4^-, Ce^{4+}, and $Cr_2O_7^{2-}$, it is useful only when the titrand is a stronger reducing agent. This apparent limitation, however, makes I_2 a more selective titrant for the analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for I_2 is

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$$

Because iodine is not very soluble in water, solutions are prepared by adding an excess of I^-. The complexation reaction

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

increases the solubility of I_2 by forming the more soluble triiodide ion, I_3^-. Even though iodine is present as I_3^- instead of I_2, the number of electrons in the reduction half-reaction is unaffected.

$$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq)$$

The standardization reaction is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq)$$

Solutions of I_3^- are normally standardized against $Na_2S_2O_3$ using starch as a specific indicator for I_3^-.

An oxidizing titrant such as MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-, is used when the titrand is in a reduced state. If the titrand is in an oxidized state, we can first reduce it with an auxiliary reducing agent and then complete the titration using an oxidizing titrant. Alternatively, we can titrate it using a reducing titrant. Iodide is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I^- is susceptible to the air-oxidation of I^- to I_3^-.

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of I_3^-.

$$3I^-(aq) \rightleftharpoons I_3^-(aq) + 2e^-$$

Instead, adding an excess of KI reduces the titrand, releasing a stoichiometric amount of I_3^-. The amount of I_3^- produced is then determined by a back titration using thiosulfate, $S_2O_3^{2-}$, as a reducing titrant.

$$2S_2O_3^{2-}(aq) \rightleftharpoons 2S_4O_6^{2-}(aq) + 2e^-$$

Solutions of $S_2O_3^{2-}$ are prepared using $Na_2S_2O_3 \bullet 5H_2O$, and must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard KIO_3 in an acidic solution containing an excess of KI. The reaction between IO_3^- and I^-

$$IO_3^-(aq) + 8I^-(aq) + 6H^+(aq) \rightarrow 3I_3^-(aq) + 3H_2O(l)$$

liberates a stoichiometric amount of I_3^-. By titrating this I_3^- with thiosulfate, using starch as a visual indicator, we can determine the concentration of $S_2O_3^{2-}$ in the titrant.

The standardization titration is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq)$$

which is the same reaction used to standardize solutions of I_3^-. This approach to standardizing solutions of $S_2O_3^{2-}$ is similar to the determination of the total chlorine residual outlined in Representative Method 9.3.

Although thiosulfate is one of the few reducing titrants that is not readily oxidized by contact with air, it is subject to a slow decomposition to bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as HgI_2 to the solution.

Another useful reducing titrant is ferrous ammonium sulfate, $Fe(NH_4)_2(SO4)_2 \bullet 6H_2O$, in which iron is present in the +2 oxidation state. A solution of Fe^{2+} is susceptible to air-oxidation, but when prepared in 0.5 M H_2SO_4 it remains stable for as long as a month. Periodic restandardization with $K_2Cr_2O_7$ is advisable. The titrant can be used to directly titrate the titrand by oxidizing Fe^{2+} to Fe^{3+}. Alternatively, ferrous ammonium sulfate is added to the titrand in excess and the quantity of Fe^{3+} produced determined by back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

Inorganic Analysis

One of the most important applications of redox titrimetry is evaluating the chlorination of public water supplies. Representative Method 9.3, for example, describes an approach for determining the total chlorine residual by using the oxidizing power of chlorine to oxidize I^- to I_3^-. The amount of I_3^- is determined by back titrating with $S_2O_3^{2-}$.

The efficiency of chlorination depends on the form of the chlorinating species. There are two contributions to the total chlorine residual—the free chlorine residual and the combined chlorine residual. The free chlorine residual includes forms of chlorine that are available for disinfecting the water supply. Examples of species contributing to the free chlorine residual include Cl_2, HOCl and OCl^-. The combined chlorine residual includes those species in which chlorine is in its reduced form and, therefore, no longer capable of providing disinfection. Species contributing to the combined chlorine residual are NH_2Cl, $NHCl_2$ and NCl_3.

When a sample of iodide-free chlorinated water is mixed with an excess of the indicator *N*,*N*-diethyl-*p*-phenylenediamine (DPD), the free chlorine oxidizes a stoichiometric portion of DPD to its red-colored form. The oxidized DPD is then back titrated to its colorless form using ferrous ammonium sulfate as the titrant. The volume of titrant is proportional to the free residual chlorine.

Having determined the free chlorine residual in the water sample, a small amount of KI is added, catalyzing the reduction monochloramine, NH_2Cl, and oxidizing a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of NH_2Cl in the sample. The amount of dichloramine and trichloramine are determined in a similar fashion.

The methods described above for determining the total, free, or combined chlorine residual also are used to establish a water supply's chlorine demand. Chlorine demand is defined as the quantity of chlorine needed to completely react with any substance that can be oxidized by chlorine, while also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, such as lakes and rivers, the level of dissolved O_2 is important for two reasons: it is the most readily available oxidant for the biological oxidation of inorganic and organic pollutants; and it is necessary for the support of aquatic life. In a wastewater treatment plant dissolved O_2 is essential for the aerobic oxidation of waste materials. If the concentration of dissolved O_2 falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases, such as CH_4 and H_2S.

One standard method for determining the dissolved O_2 content of natural waters and wastewaters is the Winkler method. A sample of water is collected without exposing it to the atmosphere, which might change the concentration of dissolved O_2. The sample is first treated with a solution of $MnSO_4$, and then with a solution of NaOH and KI. Under these alkaline conditions the dissolved oxygen oxidizes Mn^{2+} to MnO_2.

$$2Mn^{2+}(aq) + 4OH^-(aq) + O_2(g) \rightarrow 2MnO_2(s) + 2H_2O(l)$$

After the reaction is complete, the solution is acidified with H_2SO_4. Under the now acidic conditions I^- is oxidized to I_3^- by MnO_2.

$$MnO_2(s) + 3I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+} + I_3^-(aq) + 2H_2O(l)$$

The amount of I_3^- formed is determined by titrating with $S_2O_3^{2-}$ using starch as an indicator. The Winkler method is subject to a variety of interferences, and several modifications to the original procedure have been proposed. For example, NO_2^- interferes because it can reduce I_3^- to I^- under acidic conditions. This interference is eliminated by adding sodium azide, NaN_3, reducing NO_2^- to N_2. Other reducing agents, such as Fe^{2+}, are eliminated by pretreating the sample with $KMnO_4$, and destroying the excess permanganate with $K_2C_2O_4$.

Another important example of redox titrimetry is the determination of water in nonaqueous solvents. The titrant for this analysis is known as the Karl Fischer reagent and consists of a mixture of iodine, sulfur dioxide, pyridine, and methanol. Because the concentration of pyridine is sufficiently large, I_2 and SO_2 react with pyridine (py) to form the complexes py•I_2 and py•SO_2. When added to a sample containing water, I_2 is reduced to I^- and SO_2 is oxidized to SO_3.

$$\text{py} \bullet \text{I}_2 + \text{py} \bullet \text{SO}_2 + \text{py} + \text{H}_2\text{O} \rightarrow 2\text{py} \bullet \text{HI} + \text{py} \bullet \text{SO}_3$$

Methanol is included to prevent the further reaction of py•SO_3 with water. The titration's end point is signaled when the solution changes from the product's yellow color to the brown color of the Karl Fischer reagent.

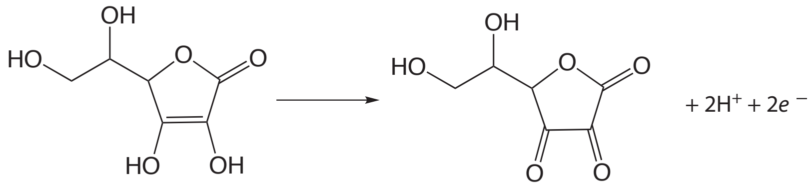
Organic Analysis

Redox titrimetry also is used for the analysis of organic analytes. One important example is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters. The COD provides a measure of the quantity of oxygen necessary to completely oxidize all the organic matter in a sample to CO_2 and H_2O. Because no attempt is made to correct for organic matter that can not be decomposed biologically, or for slow decomposition kinetics, the COD always overestimates a sample's true oxygen demand. The determination of COD is particularly important in managing industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or the environment.

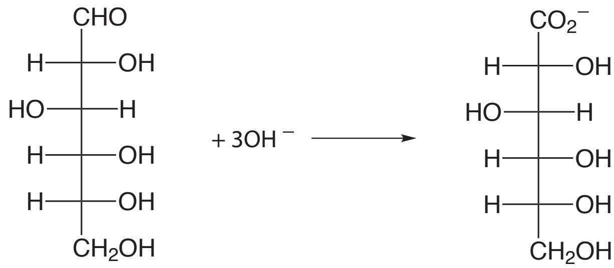
A sample's COD is determined by refluxing it in the presence of excess $K_2Cr_2O_7$, which serves as the oxidizing agent. The solution is acidified with H_2SO_4 using Ag_2SO_4 to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate, $HgSO_4$, is added to complex any chloride that is present, preventing the precipitation of the Ag^+ catalyst as AgCl. Under these conditions, the efficiency for oxidizing organic matter is 95–100%. After refluxing for two hours, the solution is cooled to room temperature and the excess $Cr_2O_7^{2-}$ is determined by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to completely remove all traces of organic matter from the reagents, a blank titration must be performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of $S_2O_3^{2-}$

with I_3^- produces the tetrathionate ion, $S_4O_6^{2-}$. The tetrathionate ion is actually a dimer consisting of two thiosulfate ions connected through a disulfide (–S–S–) linkage. In the same fashion, I_3^- can be used to titrate mercaptans of the general formula RSH, forming the dimer RSSR as a product. The amino acid cysteine also can be titrated with I_3^-. The product of this titration is cystine, which is a dimer of cysteine. Triiodide also can be used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone



and for the analysis of reducing sugars, such as glucose, by oxidizing the aldehyde functional group to a carboxylate ion in a basic solution.



An organic compound containing a hydroxyl, a carbonyl, or an amine functional group adjacent to an hydoxyl or a carbonyl group can be oxidized using metaperiodate, IO_4^-, as an oxidizing titrant.

$$IO_4^-(aq) + H_2O(l) + 2e^- \rightleftharpoons IO_3^-(aq) + 2OH^-(aq)$$

A two-electron oxidation cleaves the C–C bond between the two functional groups, with hydroxyl groups being oxidized to aldehydes or ketones, carbonyl functional groups being oxidized to carboxylic acids, and amines being oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of IO_4^- to the solution containing the analyte, and allowing the oxidation to take place for approximately one hour at room temperature. When the oxidation is complete, an excess of KI is added, which converts any unreacted IO_4^- to IO_3^- and I_3^-.

$$IO_4^-(aq) + 3I^-(aq) + H_2O(l) \rightarrow IO_3^-(aq) + I_3^-(aq) + 2OH^-(aq)$$

The I_3^- is then determined by titrating with $S_2O_3^{2-}$ using starch as an indicator.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry by remembering that the electrons in a redox reaction must be conserved.

Example 9.11

The amount of Fe in a 0.4891-g sample of an ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore's iron content as %w/w Fe_2O_3.

Solution

Because we have not been provided with the titration reaction, let's use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from Fe^{2+} to Fe^{3+}, and the titrant is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}. Oxidizing Fe^{2+} to Fe^{3+} requires only a single electron. Reducing $Cr_2O_7^{2-}$, in which each chromium is in the +6 oxidation state, to Cr^{3+} requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of $K_2Cr_2O_7$ reacts with six moles of Fe^{2+}.

The moles of $K_2Cr_2O_7$ used in reaching the end point is

$$(0.02153\text{ M } K_2Cr_2O_7) \times (0.03692\text{ L } K_2Cr_2O_7) = 7.949 \times 10^{-4}\text{ mol } K_2Cr_2O_7$$

which means that the sample contains

$$7.949 \times 10^{-4}\text{ mol } K_2Cr_2O_7 \times \frac{6\text{ mol } Fe^{2+}}{\text{mol } K_2Cr_2O_7} = 4.769 \times 10^{-3}\text{ mol } Fe^{2+}$$

Thus, the %w/w Fe_2O_3 in the sample of ore is

$$4.769 \times 10^{-3}\text{ mol } Fe^{2+} \times \frac{1\text{ mol } Fe_2O_3}{2\text{ mol } Fe^{2+}} \times \frac{159.69\text{ g } Fe_2O_3}{\text{mol } Fe_2O_3} = 0.3808\text{ g } Fe_2O_3$$

$$\frac{0.3808\text{ g } Fe_2O_3}{0.4891\text{ g sample}} \times 100 = 77.86\%\text{ w/w } Fe_2O_3$$

Although we can deduce the stoichiometry between the titrant and the titrand without balancing the titration reaction, the balanced reaction

$$K_2Cr_2O_7(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 2K^+(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

does provide useful information. For example, the presence of H^+ reminds us that the reaction's feasibility is pH-dependent.

Practice Exercise 9.20

The purity of a sample of sodium oxalate, $Na_2C_2O_4$, is determined by titrating with a standard solution of $KMnO_4$. If a 0.5116-g sample requires 35.62 mL of 0.0400 M $KMnO_4$ to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

Click here to review your answer to this exercise.

As shown in the following two examples, we can easily extend this approach to an analysis that requires an indirect analysis or a back titration.

Example 9.12

A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 mL to reach the starch indicator end point. Report the %w/v NaOCl in the sample of bleach.

Solution

To determine the stoichiometry between the analyte, NaOCl, and the titrant, $Na_2S_2O_3$, we need to consider both the reaction between OCl^- and I^-, and the titration of I_3^- with $Na_2S_2O_3$.

First, in reducing OCl^- to Cl^-, the oxidation state of chlorine changes from +1 to –1, requiring two electrons. The oxidation of three I^- to form I_3^- releases two electrons as the oxidation state of each iodine changes from –1 in I^- to –⅓ in I_3^-. A conservation of electrons, therefore, requires that each mole of OCl^- produces one mole of I_3^-.

Second, in the titration reaction, I_3^- is reduced to I^- and $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$. Reducing I_3^- to $3I^-$ requires two elections as each iodine changes from an oxidation state of –⅓ to –1. In oxidizing $S_2O_3^{2-}$ to $S_4O_6^{2-}$, each sulfur changes its oxidation state from +2 to +2.5, releasing one electron for each $S_2O_3^{2-}$. A conservation of electrons, therefore, requires that each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$.

The balanced reactions for this analysis are:

$$OCl^-(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + Cl^-(aq) + H_2O(l)$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq)$$

Finally, because each mole of OCl^- produces one mole of I_3^-, and each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$, we know that every mole of NaOCl in the sample ultimately results in the consumption of two moles of $Na_2S_2O_3$.

The moles of $Na_2S_2O_3$ used in reaching the titration's end point is

$$(0.09892 \text{ M } Na_2S_2O_3) \times (0.00896 \text{ L } Na_2S_2O_3) = 8.86 \times 10^{-4} \text{ mol } Na_2S_2O_3$$

which means the sample contains

$$8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3 \times \frac{1 \text{ mol NaOCl}}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{74.44 \text{ g NaOCl}}{\text{mol NaOCl}} = 0.03299 \text{ g NaOCl}$$

Thus, the %w/v NaOCl in the diluted sample is

$$\frac{0.03299 \text{ g NaOCl}}{25.00 \text{ mL}} \times 100 = 1.32\% \text{ w/v NaOCl}$$

Because the bleach was diluted by a factor of 40 (25 mL to 1000 mL), the concentration of NaOCl in the bleach is 5.28% (w/v).

Example 9.13

The amount of ascorbic acid, $C_6H_8O_6$, in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, with a known amount of I_3^-, and back titrating the excess I_3^- with $Na_2S_2O_3$. A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of 0.01023 M I_3^-. After the oxidation was complete, 13.82 mL of 0.07203 M $Na_2S_2O_3$ was needed to reach the starch indicator end point. Report the concentration ascorbic acid in mg/100 mL.

Solution

For a back titration we need to determine the stoichiometry between I_3^- and the analyte, $C_6H_8O_6$, and between I_3^- and the titrant, $Na_2S_2O_3$. The later is easy because we know from Example 9.12 that each mole of I_3^- reacts with two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$C_6H_8O_6(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + C_6H_6O_6(aq) + 2H^+(aq)$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq)$$

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from +⅔ in $C_6H_8O_6$ to +1 in $C_6H_6O_6$. Each carbon releases ⅓ of an electron, or a total of two electrons per ascorbic acid. As we learned in Example 9.12, reducing I_3^- requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of I_3^-.

The total moles of I_3^- reacting with $C_6H_8O_6$ and with $Na_2S_2O_3$ is

$$(0.01023 \text{ M I}_3^-) \times (0.05000 \text{ L I}_3^-) = 5.115 \times 10^{-4} \text{ mol I}_3^-$$

The back titration consumes

$$0.01382 \text{ L Na}_2\text{S}_2\text{O}_3 \times \frac{0.07203 \text{ mol Na}_2\text{S}_2\text{O}_3}{\text{L Na}_2\text{S}_2\text{O}_3} \times \frac{1 \text{ mol I}_3^-}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} = 4.977 \times 10^{-4} \text{ mol I}_3^-$$

Subtracting the moles of I_3^- reacting with $Na_2S_2O_3$ from the total moles of I_3^- gives the moles reacting with ascorbic acid.

$$5.115 \times 10^{-4} \text{ mol } I_3^- - 4.977 \times 10^{-4} \text{ mol } I_3^- = 1.38 \times 10^{-5} \text{ mol } I_3^-$$

The grams of ascorbic acid in the 5.00-mL sample of orange juice is

$$1.38 \times 10^{-5} \text{ mol } I_3^- \times \frac{1 \text{ mol } C_6H_8O_6}{\text{mol } I_3^-} \times \frac{176.13 \text{ g } C_6H_8O_6}{\text{mol } C_6H_8O_6} = 2.43 \times 10^{-3} \text{ g } C_6H_8O_6$$

There are 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg per 100 mL of orange juice.

Practice Exercise 9.21

A quantitative analysis for ethanol, C_2H_6O, can be accomplished by a redox back titration. Ethanol is oxidized to acetic acid, $C_2H_4O_2$, using excess dichromate, $Cr_2O_7^{2-}$, which is reduced to Cr^{3+}. The excess dichromate is titrated with Fe^{2+}, giving Cr^{3+} and Fe^{3+} as products. In a typical analysis, a 5.00-mL sample of a brandy is diluted to 500 mL in a volumetric flask. A 10.00-mL sample is taken and the ethanol is removed by distillation and collected in 50.00 mL of an acidified solution of 0.0200 M $K_2Cr_2O_7$. A back titration of the unreacted $Cr_2O_7^{2-}$ requires 21.48 mL of 0.1014 M Fe^{2+}. Calculate the %w/v ethanol in the brandy.

Click here to review your answer to this exercise.

9D.4 Evaluation of Redox Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a redox titration are similar to those described earlier in this chapter for acid–base or a complexation titration. As with acid–base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials. Figure 9.42 shows an example of the titration curve for a mixture of Fe^{2+} and Sn^{2+} using Ce^{4+} as the titrant. A titration of a mixture of analytes is possible if their standard state potentials or formal potentials differ by at least 200 mV.

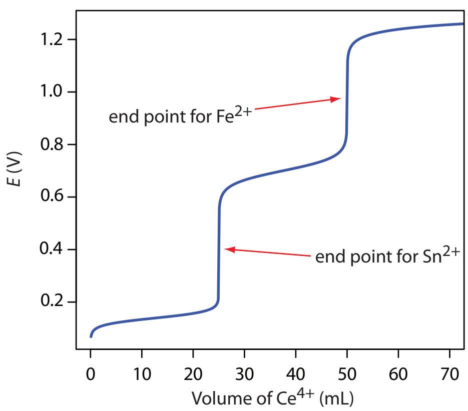


Figure 9.42 Titration curve for the titration of 50.0 mL of 0.0125 M Sn^{2+} and 0.0250 M Fe^{2+} with 0.050 M Ce^{4+}. Both the titrand and the titrant are 1M in HCl.

9E Precipitation Titrations

Thus far we have examined titrimetric methods based on acid–base, complexation, and redox reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can serve as the basis for a titration. We call this type of titration a PRECIPITATION TITRATION.

One of the earliest precipitation titrations—developed at the end of the eighteenth century—was the analysis of K_2CO_3 and K_2SO_4 in potash.

Calcium nitrate, $Ca(NO_3)_2$, was used as the titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$. The titration's end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

9E.1 Titration Curves

A precipitation titration curve follows the change in either the titrand's or the titrant's concentration as a function of the titrant's volume. As we have done with other titrations, we first show how to calculate the titration curve and then demonstrate how we can quickly sketch a reasonable approximation of the titration curve.

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$. The reaction in this case is

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Because the reaction's equilibrium constant is so large

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

we may assume that Ag^+ and Cl^- react completely.

By now you are familiar with our approach to calculating a titration curve. The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that

Step 1: Calculate the volume of $AgNO_3$ needed to reach the equivalence point.

$$\text{moles Ag}^+ = \text{moles Cl}^-$$

$$M_{Ag} \times V_{Ag} = M_{Cl} \times V_{Cl}$$

Solving for the volume of Ag^+

$$V_{eq} = V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.0500\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 25.0\text{ mL}$$

shows that we need 25.0 mL of Ag^+ to reach the equivalence point.

Before the equivalence point the titrand, Cl^-, is in excess. The concentration of unreacted Cl^- after adding 10.0 mL of Ag^+, for example, is

Step 2: Calculate pCl before the equivalence point by determining the concentration of unreacted NaCl.

$$[Cl^-] = \frac{\text{initial moles Cl}^- - \text{moles Ag}^+\text{ added}}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.0500\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 2.50 \times 10^{-2}\text{ M}$$

Table 9.18 Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

Volume of $AgNO_3$ (mL)	pCl	Volume of $AgNO_3$ (mL)	pCl
0.00	1.30	30.0	7.54
5.00	1.44	35.0	7.82
10.0	1.60	40.0	7.97
15.0	1.81	45.0	8.07
20.0	2.15	50.0	8.14
25.0	4.89		

which corresponds to a pCl of 1.60.

Step 3: Calculate pCl at the equivalence point using the K_{sp} for AgCl to calculate the concentration of Cl^-.

At the titration's equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. To calculate the concentration of Cl^- we use the K_{sp} expression for AgCl; thus

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = 1.8 \times 10^{-10}$$

Solving for x gives $[Cl^-]$ as 1.3×10^{-5} M, or a pCl of 4.89.

Step 4: Calculate pCl after the equivalence point by first calculating the concentration of excess $AgNO_3$ and then calculating the concentration of Cl^- using the K_{sp} for AgCl.

After the equivalence point, the titrant is in excess. We first calculate the concentration of excess Ag^+ and then use the K_{sp} expression to calculate the concentration of Cl^-. For example, after adding 35.0 mL of titrant

$$[Ag^+] = \frac{\text{moles Ag}^+ \text{ added} - \text{initial moles Cl}^-}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} = 1.18 \times 10^{-2} \text{ M}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$

or a pCl of 7.81. Additional results for the titration curve are shown in Table 9.18 and Figure 9.43.

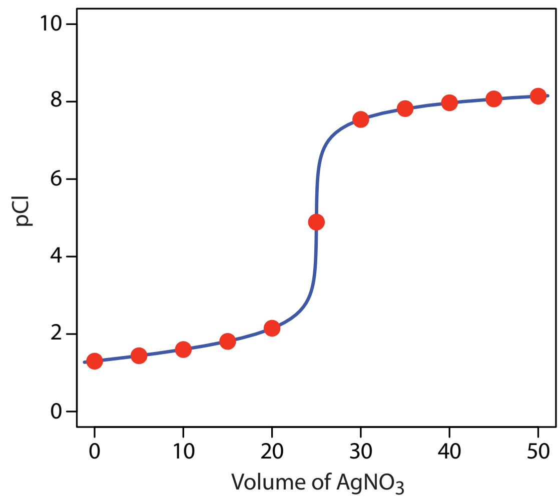


Figure 9.43 Titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$. The red points corresponds to the data in Table 9.18. The blue line shows the complete titration curve.

Practice Exercise 9.22

When calculating a precipitation titration curve, you can choose to follow the change in the titrant's concentration or the change in the titrand's concentration. Calculate the titration curve for the titration of 50.0 mL of 0.0500 M $AgNO_3$ with 0.100 M NaCl as pAg versus V_{NaCl}, and as pCl versus V_{NaCl}.

Click here to review your answer to this exercise.

Sketching the Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a precipitation titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$.

This is the same example that we used in developing the calculations for a precipitation titration curve. You can review the results of that calculation in Table 9.18 and Figure 9.43.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pCl on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 25.0 mL of AgNO3. Figure 9.44a shows the result of this first step in our sketch.

Before the equivalence point, Cl^- is present in excess and pCl is determined by the concentration of unreacted Cl^-. As we learned earlier, the calculations are straightforward. Figure 9.44b shows pCl after adding 10.0 mL and 20.0 mL of $AgNO_3$.

See Table 9.18 for the values.

After the equivalence point, Ag^+ is in excess and the concentration of Cl^- is determined by the solubility of AgCl. Again, the calculations are straightforward. Figure 4.43c shows pCl after adding 30.0 mL and 40.0 mL of $AgNO_3$.

See Table 9.18 for the values.

Next, we draw a straight line through each pair of points, extending them through the vertical line representing the equivalence point's volume (Figure 9.44d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.44e). A comparison of our sketch to the exact titration curve (Figure 9.44f) shows that they are in close agreement.

9E.2 Selecting and Evaluating the End point

At the beginning of this section we noted that the first precipitation titration used the cessation of precipitation to signal the end point. At best, this is a cumbersome method for detecting a titration's end point. Before precipitation titrimetry became practical, better methods for identifying the end point were necessary.

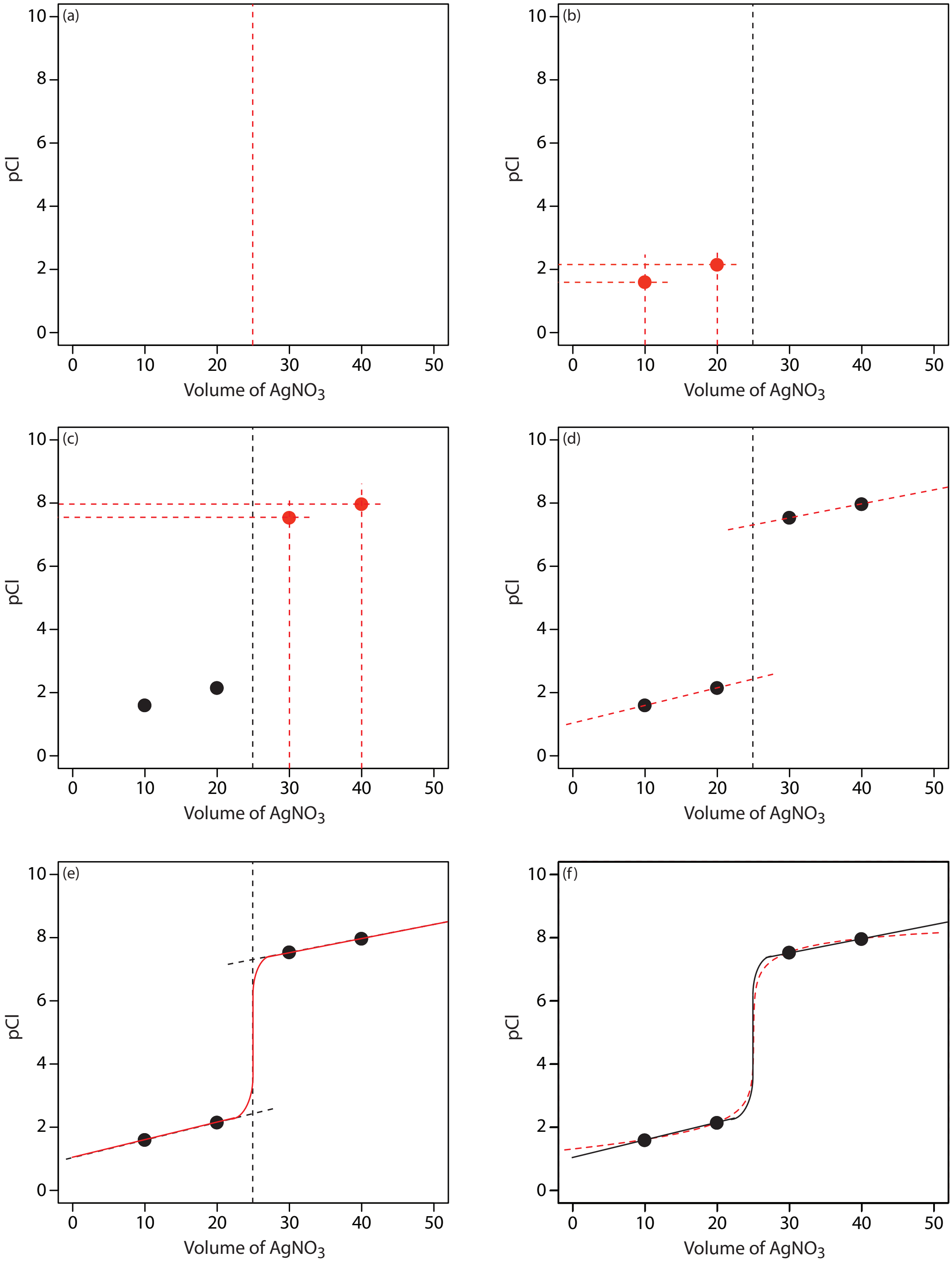


Figure 9.44 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details. A better fit is possible if the two points before the equivalence point are further apart—for example, 0 mL and 20 mL— and the two points after the equivalence point are further apart.

Finding the End point With an Indicator

There are three general types of indicators for precipitation titrations, each of which changes color at or near the titration's equivalence point. The first type of indicator is a species that forms a precipitate with the titrant. In the Mohr method for Cl^- using Ag^+ as a titrant, for example, a small amount of K_2CrO_4 is added to the titrand's solution. The titration's end point is the formation of a reddish-brown precipitate of Ag_2CrO_4.

The Mohr method was first published in 1855 by Karl Friedrich Mohr.

Because CrO_4^{2-} imparts a yellow color to the solution, which might obscure the end point, only a small amount of K_2CrO_4 is added. As a result, the end point is always later than the equivalence point. To compensate for this positive determinate error, an analyte-free reagent blank is analyzed to determine the volume of titrant needed to affect a change in the indicator's color. Subtracting the end point for the reagent blank from the titrand's end point gives the titration's end point. Because CrO_4^{2-} is a weak base, the titrand's solution is made slightly alkaline. If the pH is too acidic, chromate is present as $HCrO_4^-$ instead of CrO_4^{2-}, and the Ag_2CrO_4 end point is delayed. The pH also must be less than 10 to avoid the precipitation of silver hydroxide.

A second type of indicator uses a species that forms a colored complex with the titrant or the titrand. In the Volhard method for Ag^+ using KSCN as the titrant, for example, a small amount of Fe^{3+} is added to the titrand's solution. The titration's end point is the formation of the reddish-colored $Fe(SCN)^{2+}$ complex. The titration must be carried out in an acidic solution to prevent the precipitation of Fe^{3+} as $Fe(OH)_3$.

The Volhard method was first published in 1874 by Jacob Volhard.

The third type of end point uses a species that changes color when it adsorbs to the precipitate. In the Fajans method for Cl^- using Ag^+ as a titrant, for example, the anionic dye dichlorofluoroscein is added to the titrand's solution. Before the end point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess Cl^-. Because dichlorofluoroscein also carries a negative charge, it is repelled by the precipitate and remains in solution where it has a greenish-yellow color. After the end point, the surface of the precipitate carries a positive surface charge due to the adsorption of excess Ag^+. Dichlorofluoroscein now adsorbs to the precipitate's surface where its color is pink. This change in the indicator's color signals the end point.

The Fajans method was first published in the 1920s by Kasimir Fajans.

Finding the End point Potentiometrically

Another method for locating the end point is a potentiometric titration in which we monitor the change in the titrant's or the titrand's concentration using an ion-selective electrode. The end point is found by visually examining the titration curve. A further discussion of potentiometry is found in Chapter 11.

Table 9.19 Representative Examples of Precipitation Titrations

Titrand	Titrant[a]	End Point[b]
AsO_4^{3-}	$AgNO_3$, KSCN	Volhard
Br^-	$AgNO_3$ $AgNO_3$, KSCN	Mohr or Fajans Volhard
Cl^-	$AgNO_3$ $AgNO_3$, KSCN	Mohr or Fajans Volhard*
CO_3^{2-}	$AgNO_3$, KSCN	Volhard*
$C_2O_4^{2-}$	$AgNO_3$, KSCN	Volhard*
CrO_4^{2-}	$AgNO_3$, KSCN	Volhard*
I^-	$AgNO_3$ $AgNO_3$, KSCN	Fajans Volhard
PO_4^{3-}	$AgNO_3$, KSCN	Volhard*
S^{2-}	$AgNO_3$, KSCN	Volhard*
SCN^-	$AgNO_3$, KSCN	Volhard*

[a] When two reagents are listed, the analysis is by a back titration. The first reagent is added in excess and the second reagent used to back titrate the excess.
[b] For those Volhard methods identified with an asterisk (*) the precipitated silver salt must be removed before carrying out the back titration.

9E.3 Quantitative Applications

Although precipitation titrimetry is rarely listed as a standard method of analysis, it may still be useful as a secondary analytical method for verifying other analytical methods. Most precipitation titrations use Ag^+ as either the titrand or the titration. A titration in which Ag^+ is the titrant is called an ARGENTOMETRIC TITRATION. Table 9.19 provides a list of several typical precipitation titrations.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry from the precipitate's formula. For example, in forming a precipitate of Ag_2CrO_4, each mole of CrO_4^{2-} reacts with two moles of Ag^+.

Example 9.14

A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172-g sample is dissolved in 50 mL of water and titrated to the Ag_2CrO_4 end point, requiring 36.85 mL of 0.1120 M $AgNO_3$. A blank titration requires 0.71 mL of titrant to reach the same end point. Report the %w/w KCl in the sample.

Solution

To find the moles of titrant reacting with the sample, we first need to correct for the reagent blank; thus

$$V_{Ag} = 36.85 \text{ mL} - 0.71 \text{ mL} = 36.14 \text{ mL}$$

$$(0.1120 \text{ M AgNO}_3) \times (0.03614 \text{ L AgNO}_3) = 4.048 \times 10^{-3} \text{ mol AgNO}_3$$

Titrating with $AgNO_3$ produces a precipitate of AgCl and AgBr. In forming the precipitates, each mole of KCl consumes one mole of $AgNO_3$ and each mole of NaBr consumes one mole of $AgNO_3$; thus

$$\text{moles KCl} + \text{moles NaBr} = 4.048 \times 10^{-3}$$

We are interested in finding the mass of KCl, so let's rewrite this equation in terms of mass. We know that

$$\text{moles KCl} = \frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}}$$

$$\text{moles NaBr} = \frac{\text{g NaBr}}{102.89 \text{ g NaBr/mol NaBr}}$$

which we substitute back into the previous equation

$$\frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}} + \frac{\text{g NaBr}}{102.89 \text{ g NaBr/mol NaBr}} = 4.048 \times 10^{-3}$$

Because this equation has two unknowns—g KCl and g NaBr—we need another equation that includes both unknowns. A simple equation takes advantage of the fact that the sample contains only KCl and NaBr; thus,

$$\text{g NaBr} = 0.3172 \text{ g} - \text{g KCl}$$

$$\frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}} + \frac{0.3172 \text{ g} - \text{g KCl}}{102.89 \text{ g NaBr/mol NaBr}} = 4.048 \times 10^{-3}$$

$$1.341 \times 10^{-2}(\text{g KCl}) + 3.083 \times 10^{-3} - 9.719 \times 10^{-3}(\text{g KCl}) = 4.048 \times 10^{-3}$$

$$3.69 \times 10^{-3}(\text{g KCl}) = 9.65 \times 10^{-4}$$

The sample contains 0.262 g of KCl and the %w/w KCl in the sample is

$$\frac{0.262 \text{ g KCl}}{0.3172 \text{ g sample}} \times 100 = 82.6\% \text{ w/w KCl}$$

The analysis for I^- using the Volhard method requires a back titration. A typical calculation is shown in the following example.

Example 9.15

The %w/w I^- in a 0.6712-g sample was determined by a Volhard titration. After adding 50.00 mL of 0.05619 M $AgNO_3$ and allowing the precipitate to form, the remaining silver was back titrated with 0.05322 M KSCN, requiring 35.14 mL to reach the end point. Report the %w/w I^- in the sample.

Solution

There are two precipitates in this analysis: $AgNO_3$ and I^- form a precipitate of AgI, and $AgNO_3$ and KSCN form a precipitate of AgSCN. Each mole of I^- consumes one mole of $AgNO_3$, and each mole of KSCN consumes one mole of $AgNO_3$; thus

$$\text{moles AgNO}_3 = \text{moles I}^- + \text{moles KSCN}$$

Solving for the moles of I^- we find

$$\text{moles I}^- = \text{moles AgNO}_3 - \text{moles KSCN}$$

$$\text{moles I}^- = M_{\text{Ag}} \times V_{\text{Ag}} - M_{\text{KSCN}} \times V_{\text{KSCN}}$$

$$\text{moles I}^- = (0.05619\ \text{M AgNO}_3) \times (0.05000\ \text{L AgNO}_3) - (0.05322\ \text{M KSCN}) \times (0.03514\ \text{L KSCN})$$

that there are 9.393×10^{-4} moles of I^- in the sample. The %w/w I^- in the sample is

$$\frac{(9.393 \times 10^{-4}\ \text{mol I}^-) \times \frac{126.9\ \text{g I}^-}{\text{mol I}^-}}{0.6712\ \text{g sample}} \times 100 = 17.76\%\ \text{w/w I}^-$$

Practice Exercise 9.23

A 1.963-g sample of an alloy is dissolved in HNO3 and diluted to volume in a 100-mL volumetric flask. Titrating a 25.00-mL portion with 0.1078 M KSCN requires 27.19 mL to reach the end point. Calculate the %w/w Ag in the alloy.

Click here to review your answer to this exercise.

9E.4 Evaluation of Precipitation Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a precipitation titration is similar to those described elsewhere in this chapter for acid–base, complexation, and redox titrations. Precipitation titrations also can be extended to the analysis of mixtures provided that there is a sig-

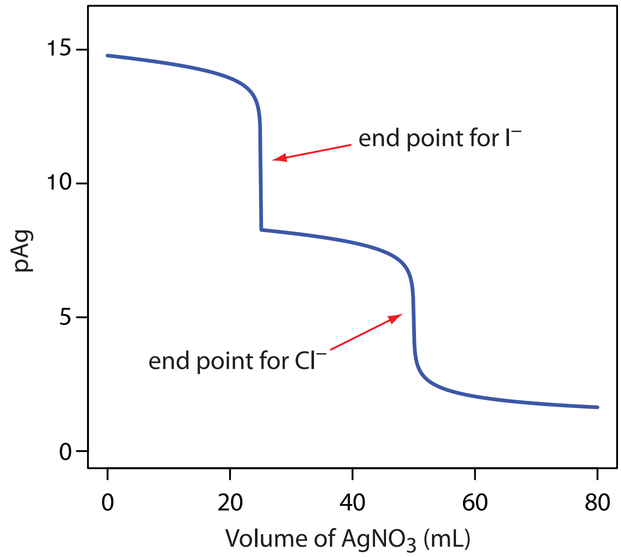


Figure 9.45 Titration curve for the titration of a 50.0 mL mixture of 0.0500 M I^- and 0.0500 M Cl^- using 0.100 M Ag^+ as a titrant. The red arrows show the end points. Note that the end point for I^- is earlier than the end point for Cl^- because AgI is less soluble than AgCl.

nificant difference in the solubilities of the precipitates. Figure 9.45 shows an example of a titration curve for a mixture of I^- and Cl^- using Ag^+ as a titrant.

9F Key Terms

As you review this chapter, try to define a key term in your own words. Check your answer by clicking on the key term, which will take you to the page where it was first introduced. Clicking on the KEY TERM there, will bring you back to this page so that you can continue with another key term.

acid–base titration	acidity	alkalinity
argentometric titration	asymmetric equivalence point	auxiliary complexing agent
auxiliary oxidizing agent	auxiliary reducing agent	back titration
buret	complexation titration	conditional formation constant
direct titration	displacement titration	end point
equivalence point	Fajans method	formal potential
Gran plot	indicator	Jones reductor
Kjeldahl analysis	leveling	metallochromic indicator
Mohr method	potentiometric titration	precipitation titration
redox indicator	redox titration	spectrophotometric titration
symmetric equivalence point	thermometric titration	titrand
titrant	titration curve	titration error
titrimetry	Volhard method	Walden reductor

9G Chapter Summary

In a titrimetric method of analysis, the volume of titrant reacting stoichiometrically with a titrand provides quantitative information about the amount of analyte in a sample. The volume of titrant corresponding to this stoichiometric reaction is called the equivalence point. Experimentally we determine the titration's end point using an indicator that changes color near the equivalence point. Alternatively, we can locate the end point by continuously monitoring a property of the titrand's solution—absorbance, potential, and temperature are typical examples—that changes as the titration progresses. In either case, an accurate result requires that the end point closely match the equivalence point. Knowing the shape of a titration curve is critical to evaluating the feasibility of a titrimetric method.

Many titrations are direct, in which the analyte participates in the titration as the titrand or the titrant. Other titration strategies may be used when a direct reaction between the analyte and titrant is not feasible. In a back titration a reagent is added in excess to a solution containing the analyte. When the reaction between the reagent and the analyte is complete, the amount of excess reagent is determined by a titration. In a displacement titration the analyte displaces a reagent, usually from a complex, and the amount of displaced reagent is determined by an appropriate titration.

Titrimetric methods have been developed using acid–base, complexation, redox, and precipitation reactions. Acid–base titrations use a strong acid or a strong base as a titrant. The most common titrant for a complexation titration is EDTA. Because of their stability against air oxidation, most redox titrations use an oxidizing agent as a titrant. Titrations with reducing agents also are possible. Precipitation titrations often involve Ag^+ as either the analyte or titrant.

9H Problems

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

Appendix 10: Solubility Products

Appendix 11: Acid Dissociation Constants

Appendix 12: Metal-Ligand Formation Constants

Appendix 13: Standard State Reduction Potentials

1. Calculate or sketch titration curves for the following acid–base titrations.
   a. 25.0 mL of 0.100 M NaOH with 0.0500 M HCl
   b. 50.0 mL of 0.0500 M HCOOH with 0.100 M NaOH
   c. 50.0 mL of 0.100 M NH_3 with 0.100 M HCl
   d. 50.0 mL of 0.0500 M ethylenediamine with 0.100 M HCl
   e. 50.0 mL of 0.0400 M citric acid with 0.120 M NaOH
   f. 50.0 mL of 0.0400 M H_3PO_4 with 0.120 M NaOH
2. Locate the equivalence point for each titration curve in problem 1. What is the stoichiometric relationship between the moles of acid and the moles of base at each of these equivalence points?
3. Suggest an appropriate visual indicator for each of the titrations in problem 1.
4. In sketching the titration curve for a weak acid we approximate the pH at 10% of the equivalence point volume as $pK_a - 1$, and the pH at 90% of the equivalence point volume as $pK_a + 1$. Show that these assumptions are reasonable.

5. Tartaric acid, $H_2C_4H_4O_6$, is a diprotic weak acid with a pK_{a1} of 3.0 and a pK_{a2} of 4.4. Suppose you have a sample of impure tartaric acid (purity > 80%), and that you plan to determine its purity by titrating with a solution of 0.1 M NaOH using an indicator to signal the end point. Describe how you will carry out the analysis, paying particular attention to how much sample to use, the desired pH range for the indicator, and how you will calculate the %w/w tartaric acid.

6. The following data for the titration of a monoprotic weak acid with a strong base were collected using an automatic titrator. Prepare normal, first derivative, second derivative, and Gran plot titration curves for this data, and locate the equivalence point for each.

Volume of NaOH (ml)	pH	Volume of NaOH (mL)	pH
0.25	3.0	49.95	7.8
0.86	3.2	49.97	8.0
1.63	3.4	49.98	8.2
2.72	3.6	49.99	8.4
4.29	3.8	50.00	8.7
6.54	4.0	50.01	9.1
9.67	4.2	50.02	9.4
13.79	4.4	50.04	9.6
18.83	4.6	50.06	9.8
24.47	4.8	50.10	10.0
30.15	5.0	50.16	10.2
35.33	5.2	50.25	10.4
39.62	5.4	50.40	10.6
42.91	5.6	50.63	10.8
45.28	5.8	51.01	11.0
46.91	6.0	51.61	11.2
48.01	6.2	52.58	11.4
48.72	6.4	54.15	11.6
49.19	6.6	56.73	11.8
49.48	6.8	61.11	12.0
49.67	7.0	68.83	12.2
49.79	7.2	83.54	12.4
49.78	7.4	116.14	12.6
49.92	7.6		

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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7. Schwartz published the following simulated data for the titration of a 1.02×10^{-4} M solution of a monoprotic weak acid (pK_a = 8.16) with

1.004×10^{-3} M NaOH.[10] The simulation assumes that a 50-mL pipet is used to transfer a portion of the weak acid solution to the titration vessel. A calibration of the pipet shows that it delivers a volume of only 49.94 mL. Prepare normal, first derivative, second derivative, and Gran plot titration curves for this data, and determine the equivalence point for each. How do these equivalence points compare to the expected equivalence point? Comment on the utility of each titration curve for the analysis of very dilute solutions of very weak acids.

mL of NaOH	pH	mL of NaOH	pH
0.03	6.212	4.79	8.858
0.09	6.504	4.99	8.926
0.29	6.936	5.21	8.994
0.72	7.367	5.41	9.056
1.06	7.567	5.61	9.118
1.32	7.685	5.85	9.180
1.53	7.776	6.05	9.231
1.76	7.863	6.28	9.283
1.97	7.938	6.47	9.327
2.18	8.009	6.71	9.374
2.38	8.077	6.92	9.414
2.60	8.146	7.15	9.451
2.79	8.208	7.36	9.484
3.01	8.273	7.56	9.514
3.41	8.332	7.79	9.545
3.60	8.458	8.21	9.572
3.80	8.521	8.44	9.599
3.99	8.584	8.64	9.645
4.18	8.650	8.84	9.666
4.40	8.720	9.07	9.688
4.57	8.784	9.27	9.706

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8. Calculate or sketch the titration curve for a 50.0 mL solution of a 0.100 M monoprotic weak acid (pK_a = 8) with 0.1 M strong base in a nonaqueous solvent with $K_s = 10^{-20}$. You may assume that the change in solvent does not affect the weak acid's pK_a. Compare your titration curve to the titration curve when water is the solvent.

9. The titration of a mixture of *p*-nitrophenol (pK_a = 7.0) and *m*-nitrophenol (pK_a = 8.3) can be followed spectrophotometrically. Neither acid absorbs at a wavelength of 545 nm, but their respective conjugate bases

10 Schwartz, L. M. *J. Chem. Educ.* **1992**, *69*, 879–883.

do absorb at this wavelength. The *m*-nitrophenolate ion has a greater absorbance than an equimolar solution of the *p*-nitrophenolate ion. Sketch the spectrophotometric titration curve for a 50.00-mL mixture consisting of 0.0500 M *p*-nitrophenol and 0.0500 M *m*-nitrophenol with 0.100 M NaOH. Compare your result to the expected potentiometric titration curves.

10. The quantitative analysis for aniline ($C_6H_5NH_2$, $K_b = 3.94 \times 10^{-10}$) can be carried out by an acid–base titration using glacial acetic acid as the solvent and $HClO_4$ as the titrant. A known volume of sample containing 3–4 mmol of aniline is transferred to a 250-mL Erlenmeyer flask and diluted to approximately 75 mL with glacial acetic acid. Two drops of a methyl violet indicator are added, and the solution is titrated with previously standardized 0.1000 M $HClO_4$ (prepared in glacial acetic acid using anhydrous $HClO_4$) until the end point is reached. Results are reported as parts per million aniline.
    (a) Explain why this titration is conducted using glacial acetic acid as the solvent instead of water.
    (b) One problem with using glacial acetic acid as solvent is its relatively high coefficient of thermal expansion of 0.11%/°C. For example, 100.00 mL of glacial acetic acid at 25 °C occupies 100.22 mL at 27 °C. What is the effect on the reported concentration of aniline if the standardization of $HClO_4$ is conducted at a temperature that is lower than that for the analysis of the unknown?
    (c) The procedure calls for a sample containing 3–4 mmoles of aniline. Why is this requirement necessary?

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11. Using a ladder diagram, explain why the presence of dissolved CO_2 leads to a determinate error for the standardization of NaOH if the end point's pH falls between 6–10, but no determinate error if the end point's pH is less than 6.

12. A water sample's acidity is determined by titrating to fixed end point pHs of 3.7 and 8.3, with the former providing a measure of the concentration of strong acid, and the later a measure of the combined concentrations of strong acid and weak acid. Sketch a titration curve for a mixture of 0.10 M HCl and 0.10 M H_2CO_3 with 0.20 M strong base, and use it to justify the choice of these end points.

13. Ethylenediaminetetraacetic acid, H_4Y, is a weak acid with successive acid dissociation constants of 0.010, 2.19×10^{-3}, 6.92×10^{-7}, and 5.75×10^{-11}. Figure 9.46 shows a titration curve for H_4Y with NaOH. What is the stoichiometric relationship between H_4Y and NaOH at the equivalence point marked with the red arrow?

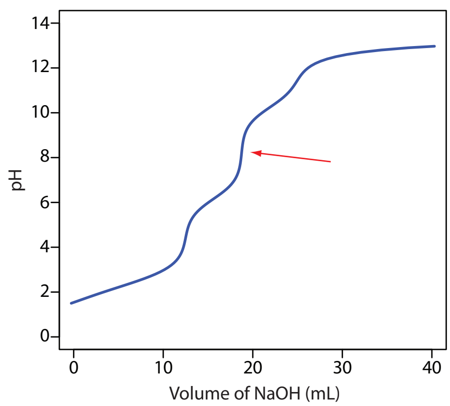

Figure 9.46 Titration curve for Problem 9.13.

14. A Gran plot method has been described for the quantitative analysis of a mixture consisting of a strong acid and a monoprotic weak acid.[11] A 50.00-mL mixture of HCl and CH_3COOH is transferred to an Erlenmeyer flask and titrated by using a digital pipet to add successive 1.00-mL aliquots of 0.09186 M NaOH. The progress of the titration is monitored by recording the pH after each addition of titrant. Using the two papers listed in the footnote as a reference, prepare a Gran plot for the following data, and determine the concentrations of HCl and CH_3COOH.

Volume of NaOH (ml)	pH	Volume of NaOH (mL)	pH	Volume of NaOH (ml)	pH
1.00	1.83	24.00	4.45	47.00	12.14
2.00	1.86	25.00	4.53	48.00	12.17
3.00	1.89	26.00	4.61	49.00	12.20
4.00	1.92	27.00	4.69	50.00	12.23
5.00	1.95	28.00	4.76	51.00	12.26
6.00	1.99	29.00	4.84	52.00	12.28
7.00	2.03	30.00	4.93	53.00	12.30
8.00	2.10	31.00	5.02	54.00	12.32
9.00	2.18	32.00	5.13	55.00	12.34
10.00	2.31	33.00	5.23	56.00	12.36
11.00	2.51	34.00	5.37	57.00	12.38
12.00	2.81	35.00	5.52	58.00	12.39
13.00	3.16	36.00	5.75	59.00	12.40
14.00	3.36	37.00	6.14	60.00	12.42
15.00	3.54	38.00	10.30	61.00	12.43
16.00	3.69	39.00	11.31	62.00	12.44
17.00	3.81	40.00	11.58	63.00	12.45
18.00	3.93	41.00	11.74	64.00	12.47
19.00	4.02	42.00	11.85	65.00	12.48
20.00	4.14	43.00	11.93	66.00	12.49
21.00	4.22	44.00	12.00	67.00	12.50
22.00	4.30	45.00	12.05	68.00	12.51
23.00	4.38	46.00	12.10	69.00	12.52

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15. Explain why it is not possible for a sample of water to simultaneously have OH^- and HCO_3^- as sources of alkalinity.

16. For each of the following, determine the sources of alkalinity (OH^-, HCO_3^-, CO_3^{2-}) and their respective concentrations in parts per mil-

11 (a) Boiani, J. A. *J. Chem. Educ.* **1986**, *63*, 724–726; (b) Castillo, C. A.; Jaramillo, A. *J. Chem. Educ.* **1989**, *66*, 341.

lion In each case a 25.00-mL sample is titrated with 0.1198 M HCl to the bromocresol green and the phenolphthalein end points.

	Volume of HCl (mL) to the phenolphthalein end point	Volume of HCl (mL) to the bromocresol green end point
a	21.36	21.38
b	5.67	21.13
c	0.00	14.28
d	17.12	34.26
e	21.36	25.69

17. A sample may contain any of the following: HCl, NaOH, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}. The composition of a sample is determined by titrating a 25.00-mL portion with 0.1198 M HCl or 0.1198 M NaOH to the phenolphthalein and the methyl orange end points. For each of the following, determine which species are present in the sample, and their respective molar concentrations.

	Titrant	Phenolphthalein end point volume (mL)	methyl orange end point volume (mL)
a	HCl	11.54	35.29
b	NaOH	19.79	9.89
c	HCl	22.76	22.78
d	NaOH	39.42	17.48

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18. The protein in a 1.2846-g sample of an oat cereal is determined by a Kjeldahl analysis. The sample is digested with H_2SO_4, the resulting solution made basic with NaOH, and the NH_3 distilled into 50.00 mL of 0.09552 M HCl. The excess HCl is back titrated using 37.84 mL of 0.05992 M NaOH. Given that the proteins in grains average 17.54% w/w N, report the %w/w protein in the sample.

19. The concentration of SO_2 in air is determined by bubbling a sample of air through a trap containing H_2O_2. Oxidation of SO_2 by H_2O_2 results in the formation of H_2SO_4, which is then determined by titrating with NaOH. In a typical analysis, a sample of air was passed through the peroxide trap at a rate of 12.5 L/min for 60 min and required 10.08 mL of 0.0244 M NaOH to reach the phenolphthalein end point. Calculate the μL/L SO_2 in the sample of air. The density of SO_2 at the temperature of the air sample is 2.86 mg/mL.

20. The concentration of CO_2 in air is determined by an indirect acid–base titration. A sample of air is bubbled through a solution containing an excess of $Ba(OH)_2$, precipitating $BaCO_3$. The excess $Ba(OH)_2$ is back titrated with HCl. In a typical analysis a 3.5-L sample of air was bubbled through 50.00 mL of 0.0200 M $Ba(OH)_2$. Back titrating with

0.0316 M HCl required 38.58 mL to reach the end point. Determine the ppm CO_2 in the sample of air given that the density of CO_2 at the temperature of the sample is 1.98 g/L.

21. The purity of a synthetic preparation of methylethyl ketone, C_3H_8O, is determined by reacting it with hydroxylamine hydrochloride, liberating HCl (see reaction in Table 9.8). In a typical analysis a 3.00-mL sample was diluted to 50.00 mL and treated with an excess of hydroxylamine hydrochloride. The liberated HCl was titrated with 0.9989 M NaOH, requiring 32.68 mL to reach the end point. Report the percent purity of the sample given that the density of methylethyl ketone is 0.805 g/mL.

22. Animal fats and vegetable oils are triesters formed from the reaction between glycerol (1,2,3-propanetriol) and three long-chain fatty acids. One of the methods used to characterize a fat or an oil is a determination of its saponification number. When treated with boiling aqueous KOH, an ester saponifies into the parent alcohol and fatty acids (as carboxylate ions). The saponification number is the number of milligrams of KOH required to saponify 1.000 gram of the fat or the oil. In a typical analysis a 2.085-g sample of butter is added to 25.00 mL of 0.5131 M KOH. After saponification is complete the excess KOH is back titrated with 10.26 mL of 0.5000 M HCl. What is the saponification number for this sample of butter?

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23. A 250.0-mg sample of an organic weak acid is dissolved in an appropriate solvent and titrated with 0.0556 M NaOH, requiring 32.58 mL to reach the end point. Determine the compound's equivalent weight.

24. Figure 9.47 shows a potentiometric titration curve for a 0.4300-g sample of a purified amino acid that was dissolved in 50.00 mL of water and titrated with 0.1036 M NaOH. Identify the amino acid from the possibilities listed in the following table.

amino acid	formula weight (g/mol)	K_a
alanine	89.1	1.36×10^{-10}
glycine	75.1	1.67×10^{-10}
methionine	149.2	8.9×10^{-10}
taurine	125.2	1.8×10^{-9}
asparagine	150	1.9×10^{-9}
leucine	131.2	1.79×10^{-10}
phenylalanine	166.2	4.9×10^{-10}
valine	117.2	1.91×10^{-10}

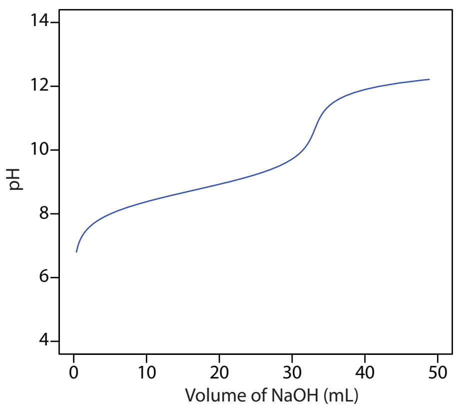

Figure 9.47 Titration curve for Problem 9.24.

25. Using its titration curve, determine the acid dissociation constant for the weak acid in problem 9.6.

26. Where in the scale of operations do the microtitration techniques discussed in section 9B.7 belong?

27. An acid–base titration may be used to determine an analyte's gram equivalent weight, but it can not be used to determine its gram formula weight. Explain why.

28. Commercial washing soda is approximately 30–40% w/w Na_2CO_3. One procedure for the quantitative analysis of washing soda contains the following instructions:

> Transfer an approximately 4-g sample of the washing soda to a 250-mL volumetric flask. Dissolve the sample in about 100 mL of H_2O and then dilute to the mark. Using a pipet, transfer a 25-mL aliquot of this solution to a 125-mL Erlenmeyer flask, and add 25-mL of H_2O and 2 drops of bromocresol green indicator. Titrate the sample with 0.1 M HCl to the indicator's end point.

What modifications, if any, are necessary if you want to adapt this procedure to evaluate the purity of commercial Na_2CO_3 that is >98% pure?

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29. A variety of systematic and random errors are possible when standardizing a solution of NaOH against the primary weak acid standard potassium hydrogen phthalate (KHP). Identify, with justification, whether the following are systematic or random sources of error, or if they have no effect. If the error is systematic, then indicate whether the experimentally determined molarity for NaOH is too high or too low. The standardization reaction is

$$C_8H_5O_4^-(aq) + OH^-(aq) \rightarrow C_8H_4O_4^{2-}(aq) + H_2O(l)$$

(a) The balance used to weigh KHP is not properly calibrated and always reads 0.15 g too low.

(b) The indicator for the titration changes color between a pH of 3–4.

(c) An air bubble, which is lodged in the buret's tip at the beginning of the analysis, dislodges during the titration.

(d) Samples of KHP are weighed into separate Erlenmeyer flasks, but the balance is only tarred with the first flask.

(e) The KHP is not dried before it was used.

(f) The NaOH is not dried before it was used.

(g) The procedure states that the sample of KHP should be dissolved in 25 mL of water, but it is accidentally dissolved in 35 mL of water.

30. The concentration of *o*-phthalic acid in an organic solvent, such as *n*-butanol, is determined by an acid–base titration using aqueous NaOH as the titrant. As the titrant is added, the *o*-phthalic acid is extracted into the aqueous solution where it reacts with the titrant. The titrant must be added slowly to allow sufficient time for the extraction to take place.

    (a) What type of error do you expect if the titration is carried out too quickly?

    (b) Propose an alternative acid–base titrimetric method that allows for a more rapid determination of the concentration of *o*-phthalic acid in *n*-butanol.

31. Calculate or sketch titration curves for 50.00 mL of 0.0500 Mg^{2+} with 0.0500 M EDTA at a pH of 7 and 10. Locate the equivalence point for each titration curve.

32. Calculate or sketch titration curves for 25.0 mL of 0.0500 M Cu^{2+} with 0.025 M EDTA at a pH of 10, and in the presence of 10^{-3} M and 10^{-1} M NH_3. Locate the equivalence point for each titration curve.

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33. Sketch the spectrophotometric titration curve for the titration of a mixture of 5.00×10^{-3} M Bi^{3+} and 5.00×10^{-3} M Cu^{2+} with 0.0100 M EDTA. Assume that only the Cu^{2+}–EDTA complex absorbs at the selected wavelength.

34. The EDTA titration of mixtures of Ca^{2+} and Mg^{2+} can be followed thermometrically because the formation of the Ca^{2+}–EDTA complex is exothermic and the formation of the Mg^{2+}–EDTA complex is endothermic. Sketch the thermometric titration curve for a mixture of 5.00×10^{-3} M Ca^{2+} and 5.00×10^{-3} M Mg^{2+} with 0.0100 M EDTA. The heats of formation for CaY^{2-} and MgY^{2-} are, respectively, –23.9 kJ/mole and 23.0 kJ/mole.

35. EDTA is one member of a class of aminocarboxylate ligands that form very stable 1:1 complexes with metal ions. The following table provides $\log K_f$ values for the complexes of six such ligands with Ca^{2+} and Mg^{2+}. Which ligand is the best choice for the direct titration of Ca^{2+} in the presence of Mg^{2+}?

		Mg^{2+}	Ca^{2+}
EDTA	ethylenediaminetetraacetic acid	8.7	10.7
HEDTA	N-hydroxyethylenediaminetriacetic acid	7.0	8.0

		Mg^{2+}	Ca^{2+}
EEDTA	ethyletherdiaminetetraacetic acid	8.3	10.0
DGTA	ethyleneglycol-bis(β-aminoethylether)-N,N′-tetraacetic acid	5.4	10.9
DTPA	diethylenetriaminepentaacetic acid	9.0	10.7
CyDTA	cyclohexanediaminetetraacetic acid	10.3	12.3

36. The amount of calcium in physiological fluids can be determined by a complexometric titration with EDTA. In one such analysis a 0.100-mL sample of a blood serum was made basic by adding 2 drops of NaOH and titrated with 0.00119 M EDTA, requiring 0.268 mL to reach the end point. Report the concentration of calcium in the sample as milligrams Ca per 100 mL.

37. After removing the membranes from an eggshell, the shell is dried and its mass recorded as 5.613 g. The eggshell is transferred to a 250-mL beaker and dissolved in 25 mL of 6 M HCl. After filtering, the solution containing the dissolved eggshell is diluted to 250 mL in a volumetric flask. A 10.00-mL aliquot is placed in a 125-mL Erlenmeyer flask and buffered to a pH of 10. Titrating with 0.04988 M EDTA requires 44.11 mL to reach the end point. Determine the amount of calcium in the eggshell as %w/w $CaCO_3$.

38. The concentration of cyanide, CN^-, in a copper electroplating bath can be determined by a complexometric titration with Ag^+, forming the soluble $Ag(CN)_2^-$ complex. In a typical analysis a 5.00-mL sample from an electroplating bath is transferred to a 250-mL Erlenmeyer flask, and treated with 100 mL of H_2O, 5 mL of 20% w/v NaOH and 5 mL of 10% w/v KI. The sample is titrated with 0.1012 M $AgNO_3$, requiring 27.36 mL to reach the end point as signaled by the formation of a yellow precipitate of AgI. Report the concentration of cyanide as parts per million of NaCN.

39. Before the introduction of EDTA most complexation titrations used Ag^+ or CN^- as the titrant. The analysis for Cd^{2+}, for example, was accomplished indirectly by adding an excess of KCN to form $Cd(CN)_4^{2-}$, and back titrating the excess CN^- with Ag^+, forming $Ag(CN)_2^-$. In one such analysis a 0.3000-g sample of an ore was dissolved and treated with 20.00 mL of 0.5000 M KCN. The excess CN^- required 13.98 mL of 0.1518 M $AgNO^3$ to reach the end point. Determine the %w/w Cd in the ore.

40. Solutions containing both Fe^{3+} and Al^{3+} can be selectively analyzed for Fe^{3+} by buffering to a pH of 2 and titrating with EDTA. The pH of the solution is then raised to 5 and an excess of EDTA added, resulting in

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the formation of the Al^{3+}–EDTA complex. The excess EDTA is back-titrated using a standard solution of Fe^{3+}, providing an indirect analysis for Al^{3+}.

(a) At a pH of 2, verify that the formation of the Fe^{3+}–EDTA complex is favorable, and that the formation of the Al^{3+}–EDTA complex is not favorable.

(b) A 50.00-mL aliquot of a sample containing Fe^{3+} and Al^{3+} is transferred to a 250-mL Erlenmeyer flask and buffered to a pH of 2. A small amount of salicylic acid is added, forming the soluble red-colored Fe^{3+}–salicylic acid complex. The solution is titrated with 0.05002 M EDTA, requiring 24.82 mL to reach the end point as signaled by the disappearance of the Fe^{3+}–salicylic acid complex's red color. The solution is buffered to a pH of 5 and 50.00 mL of 0.05002 M EDTA is added. After ensuring that the formation of the Al^{3+}–EDTA complex is complete, the excess EDTA was back titrated with 0.04109 M Fe^{3+}, requiring 17.84 mL to reach the end point as signaled by the reappearance of the red-colored Fe^{3+}–salicylic acid complex. Report the molar concentrations of Fe^{3+} and Al^{3+} in the sample.

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41. Prada and colleagues described an indirect method for determining sulfate in natural samples, such as seawater and industrial effluents.[12] The method consists of three steps: precipitating the sulfate as $PbSO_4$; dissolving the $PbSO_4$ in an ammonical solution of excess EDTA to form the soluble PbY^{2-} complex; and titrating the excess EDTA with a standard solution of Mg^{2+}. The following reactions and equilibrium constants are known

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = 1.6 \times 10^{-8}$$

$$Pb^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons PbY^{2-}(aq) \qquad K_f = 1.1 \times 10^{18}$$

$$Mg^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons MgY^{2-}(aq) \qquad K_f = 4.9 \times 10^{8}$$

$$Zn^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons ZnY^{2-}(aq) \qquad K_f = 3.2 \times 10^{16}$$

(a) Verify that a precipitate of $PbSO_4$ dissolves in a solution of Y^{4-}.

(b) Sporek proposed a similar method using Zn^{2+} as a titrant and found that the accuracy was frequently poor.[13] One explanation is that Zn^{2+} might react with the PbY^{2-} complex, forming ZnY^{2-}. Show that this might be a problem when using Zn^{2+} as a titrant, but that it is not a problem when using Mg^{2+} as a titrant. Would such a

12 Prada, S.; Guekezian, M.; Suarez-Iha, M. E. V. *Anal. Chim. Acta* **1996**, *329*, 197–202.
13 Sporek, K. F. *Anal. Chem.* **1958**, *30*, 1030–1032.

displacement of Pb^{2+} by Zn^{2+} lead to the reporting of too much or too little sulfate?

(c) In a typical analysis, a 25.00-mL sample of an industrial effluent was carried through the procedure using 50.00 mL of 0.05000 M EDTA. Titrating the excess EDTA required 12.42 mL of 0.1000 M Mg^{2+}. Report the molar concentration of SO_4^{2-} in the sample of effluent.

42. Table 9.10 provides values for the fraction of EDTA present as Y^{4-}, α_{Y4-}. Values of α_{Y4-} are calculated using the equation

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

where $[Y^{4-}]$ is the concentration of the fully deprotonated EDTA and C_{EDTA} is the total concentration of EDTA in all of its forms

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

Using the following equilibria

$$H_6Y^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + H_5Y^{+}(aq) \qquad K_{a1}$$

$$H_5Y^{+}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + H_4Y(aq) \qquad K_{a2}$$

$$H_4Y(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + H_3Y^{-}(aq) \qquad K_{a3}$$

$$H_3Y^{-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + H_2Y^{2-}(aq) \qquad K_{a4}$$

$$H_2Y^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + HY^{3-}(aq) \qquad K_{a5}$$

$$HY^{3-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + Y^{4-}(aq) \qquad K_{a6}$$

show that

$$\alpha_{Y^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}{d}$$

where

$$d = [H^+]^6 + [H^+]^5 K_{a1} + [H^+]^4 K_{a1}K_{a2} + [H^+]^3 K_{a1}K_{a2}K_{a3} + [H^+]^2 K_{a1}K_{a2}K_{a3}K_{a4} + [H^+]^1 K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$$

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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43. Calculate or sketch titration curves for the following (unbalanced) redox titration reactions at 25 °C. Assume the analyte is initially present at a concentration of 0.0100 M and that a 25.0-mL sample is taken for analysis. The titrant, which is the underlined species in each reaction, is 0.0100 M.

(a) $V^{2+}(aq) + \underline{Ce^{4+}}(aq) \rightarrow V^{3+}(aq) + Ce^{3+}(aq)$

(b) $Ti^{2+}(aq) + \underline{Fe^{3+}}(aq) \rightarrow Ti^{3+}(aq) + Fe^{2+}(aq)$

(c) $Fe^{2+}(aq) + \underline{MnO_4^-}(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$ (at pH = 1)

44. What is the equivalence point for each titration in problem 43?

45. Suggest an appropriate indicator for each titration in problem 43.

46. The iron content of an ore can be determined by a redox titration using $K_2Cr_2O_7$ as the titrant. A sample of the ore is dissolved in concentrated HCl using Sn^{2+} to speed its dissolution by reducing Fe^{3+} to Fe^{2+}. After the sample is dissolved, Fe^{2+} and any excess Sn^{2+} are oxidized to Fe^{3+} and Sn^{4+} using MnO_4^-. The iron is then carefully reduced to Fe^{2+} by adding a 2–3 drop excess of Sn^{2+}. A solution of $HgCl_2$ is added and, if a white precipitate of Hg_2Cl_2 forms, the analysis is continued by titrating with $K_2Cr_2O_7$. The sample is discarded without completing the analysis if a precipitate of Hg_2Cl_2 does not form, or if a gray precipitate (due to Hg) forms.

(a) Explain why the analysis is not completed if a white precipitate of Hg_2Cl_2 forms, or if a gray precipitate forms.

(b) Is a determinate error introduced if the analyst forgets to add Sn^{2+} in the step where the iron ore is dissolved?

(c) Is a determinate error introduced if the iron is not quantitatively oxidized back to Fe^{3+} by the MnO_4^-?

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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47. The amount of Cr^{3+} in an inorganic salt can be determined by a redox titration. A portion of sample containing approximately 0.25 g of Cr^{3+} is accurately weighed and dissolved in <u>50 mL of H_2O</u>. The Cr^{3+} is oxidized to $Cr_2O_7^{2-}$ by adding <u>20 mL of 0.1 M $AgNO_3$</u>, which serves as a catalyst, and <u>50 mL of 10%w/v $(NH_4)_2S_2O_8$</u>, which serves as the oxidizing agent. After the reaction is complete the resulting solution is boiled for 20 minutes to destroy the excess $S_2O_8^{2-}$, cooled to room temperature, and diluted to 250 mL in a volumetric flask. A <u>50-mL portion of the resulting solution</u> is transferred to an Erlenmeyer flask, treated with <u>50 mL of a standard solution of Fe^{2+}</u>, and acidified with <u>200 mL of 1 M H_2SO_4</u>, reducing the $Cr_2O_7^{2-}$ to Cr^{3+}. The excess Fe^{2+} is then determined by a back titration with a standard solution

of $K_2Cr_2O_7$ using an appropriate indicator. The results are reported as %w/w Cr^{3+}.

(a) There are several places in the procedure where a reagent's volume is specified (see underlined text). Which of these measurements must be made using a volumetric pipet.

(b) Excess peroxydisulfate, $S_2O_8^{2-}$ is destroyed by boiling the solution. What is the effect on the reported %w/w Cr^{3+} if some of the $S_2O_8^{2-}$ is not destroyed during this step?

(c) Solutions of Fe^{2+} undergo slow air oxidation to Fe^{3+}. What is the effect on the reported %w/w Cr^{3+} if the standard solution of Fe^{2+} is inadvertently allowed to be partially oxidized?

48. The exact concentration of H_2O_2 in a solution that is nominally 6% w/v H_2O_2 can be determined by a redox titration with MnO_4^-. A 25-mL aliquot of the sample is transferred to a 250-mL volumetric flask and diluted to volume with distilled water. A 25-mL aliquot of the diluted sample is added to an Erlenmeyer flask, diluted with 200 mL of distilled water, and acidified with 20 mL of 25% v/v H_2SO_4. The resulting solution is titrated with a standard solution of $KMnO_4$ until a faint pink color persists for 30 s. The results are reported as %w/v H_2O_2.

(a) Many commercially available solutions of H_2O_2 contain an inorganic or organic stabilizer to prevent the autodecomposition of the peroxide to H_2O and O_2. What effect does the presence of this stabilizer have on the reported %w/v H_2O_2 if it also reacts with MnO_4^-?

(b) Laboratory distilled water often contains traces of dissolved organic material that may react with MnO_4^-. Describe a simple method to correct for this potential interference.

(c) What modifications to the procedure, if any, are need if the sample has a nominal concentration of 30% w/v H_2O_2.

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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49. The amount of iron in a meteorite was determined by a redox titration using $KMnO_4$ as the titrant. A 0.4185-g sample was dissolved in acid and the liberated Fe^{3+} quantitatively reduced to Fe^{2+} using a Walden reductor. Titrating with 0.02500 M $KMnO_4$ requires 41.27 mL to reach the end point. Determine the %w/w Fe_2O_3 in the sample of meteorite.

50. Under basic conditions, MnO_4^- can be used as a titrant for the analysis of Mn^{2+}, with both the analyte and the titrant forming MnO_2. In the analysis of a mineral sample for manganese, a 0.5165-g sample is dissolved and the manganese reduced to Mn^{2+}. The solution is made basic

and titrated with 0.03358 M $KMnO_4$, requiring 34.88 mL to reach the end point. Calculate the %w/w Mn in the mineral sample.

51. The amount of uranium in an ore can be determined by a redox back titration. The analysis is accomplished by dissolving the ore in sulfuric acid and reducing the resulting UO_2^{2+} to U^{4+} with a Walden reductor. The resulting solution is treated with an excess of Fe^{3+}, forming Fe^{2+} and U^{6+}. The Fe^{2+} is titrated with a standard solution of $K_2Cr_2O_7$. In a typical analysis a 0.315-g sample of ore is passed through the Walden reductor and treated with 50.00 mL of 0.0125 M Fe^{3+}. Back titrating with 0.00987 M $K_2Cr_2O_7$ requires 10.52 mL. What is the %w/w U in the sample?

52. The thickness of the chromium plate on an auto fender was determined by dissolving a 30.0-cm^2 section in acid, and oxidizing the liberated Cr^{3+} to $Cr_2O_7^{2-}$ with peroxydisulfate. After removing the excess peroxydisulfate by boiling, 500.0 mg of $Fe(NH_4)_2(SO_4)_2{\bullet}6H_2O$ was added, reducing the $Cr_2O_7^{2-}$ to Cr^{3+}. The excess Fe^{2+} was back titrated, requiring 18.29 mL of 0.00389 M $K_2Cr_2O_7$ to reach the end point. Determine the average thickness of the chromium plate given that the density of Cr is 7.20 g/cm^3.

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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53. The concentration of CO in air can be determined by passing a known volume of air through a tube containing I_2O_5, forming CO_2 and I_2. The I_2 is removed from the tube by distilling it into a solution containing an excess of KI, producing I_3^-. The I_3^- is titrated with a standard solution of $Na_2S_2O_3$. In a typical analysis a 4.79-L sample of air was sampled as described here, requiring 7.17 mL of 0.00329 M $Na_2S_2O_3$ to reach the end point. If the air has a density of 1.23×10^{-3} g/mL, determine the parts per million CO in the air.

54. The level of dissolved oxygen in a water sample can be determined by the Winkler method. In a typical analysis a 100.0-mL sample is made basic and treated with a solution of $MnSO_4$, resulting in the formation of MnO_2. An excess of KI is added and the solution is acidified, resulting in the formation of Mn^{2+} and I_2. The liberated I_2 is titrated with a solution of 0.00870 M $Na_2S_2O_3$, requiring 8.90 mL to reach the starch indicator end point. Calculate the concentration of dissolved oxygen as parts per million O_2.

55. The analysis for Cl^- using the Volhard method requires a back titration. A known amount of $AgNO_3$ is added, precipitating AgCl. The unreacted Ag^+ is determined by back titrating with KSCN. There is a complication, however, because AgCl is more soluble than AgSCN.

(a) Why do the relative solubilities of AgCl and AgSCN lead to a titration error?

(b) Is the resulting titration error a positive or a negative determinate error?

(c) How might you modify the procedure to prevent this eliminate this source of determinate error?

(d) Will this source of determinate error be of concern when using the Volhard method to determine Br^-?

56. Voncina and co-workers suggest that a precipitation titration can be monitored by measuring pH as a function of the volume of titrant if the titrant is a weak base.[14] For example, when titrating Pb^{2+} with CrO_4^{2-} the solution containing the analyte is initially acidified to a pH of 3.50 using HNO_3. Before the equivalence point the concentration of CrO_4^{2-} is controlled by the solubility product of $PbCrO_4$. After the equivalence point the concentration of CrO_4^{2-} is determined by the amount of excess titrant. Considering the reactions controlling the concentration of CrO_4^{2-}, sketch the expected titration curve of pH versus volume of titrant.

Some of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants

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57. Calculate or sketch the titration curve for the titration of 50.0 mL of 0.0250 M KI with 0.0500 M $AgNO_3$. Prepare separate titration curve using pAg and pI on the *y*-axis.

58. Calculate or sketch the titration curve for the titration of 25.0 mL mixture of 0.0500 M KI and 0.0500 M KSCN with 0.0500 M $AgNO_3$.

59. A 0.5131-g sample containing KBr is dissolved in 50 mL of distilled water. Titrating with 0.04614 M $AgNO_3$ requires 25.13 mL to reach the Mohr end point. A blank titration requires 0.65 mL to reach the same end point. Report the %w/w KBr in the sample.

60. A 0.1093-g sample of impure Na_2CO_3 was analyzed by the Volhard method. After adding 50.00 mL of 0.06911 M $AgNO_3$, the sample was back titrated with 0.05781 M KSCN, requiring 27.36 mL to reach the end point. Report the purity of the Na_2CO_3 sample.

61. A 0.1036-g sample containing only $BaCl_2$ and NaCl is dissolved in 50 mL of distilled water. Titrating with 0.07916 M $AgNO_3$ requires 19.46 mL to reach the Fajans end point. Report the %w/w $BaCl_2$ in the sample.

14 Vončina, D. B.; Dobčnik, D.; Gomišček, S. *Anal. Chim. Acta* **1992**, *263*, 147–153.

9I Solutions to Practice Exercises

Practice Exercise 9.1

The volume of HCl needed to reach the equivalence point is

$$V_{eq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125\text{ M})(25.0\text{ mL})}{0.0625\text{ M}} = 50.0\text{ mL}$$

Before the equivalence point, NaOH is present in excess and the pH is determined by the concentration of unreacted OH^-. For example, after adding 10.0 mL of HCl

$$[OH^-] = \frac{(0.125\text{ M})(25.0\text{ mL}) - (0.0625\text{ M})(10.0\text{ mL})}{25.0\text{ mL} + 10.0\text{ mL}} = 0.0714\text{ M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00\times10^{-14}}{0.0714\text{ M}} = 1.40\times10^{-13}\text{ M}$$

the pH is 12.85.

For the titration of a strong base with a strong acid the pH at the equivalence point is 7.00.

For volumes of HCl greater than the equivalence point, the pH is determined by the concentration of excess HCl. For example, after adding 70.0 mL of titrant the concentration of HCl is

$$[HCl] = \frac{(0.0625\text{ M})(70.0\text{ mL}) - (0.125\text{ M})(25.0\text{ mL})}{70.0\text{ mL} + 25.0\text{ mL}} = 0.0132\text{ M}$$

giving a pH of 1.88. Some additional results are shown here.

Volume of HCl (mL)	pH	Volume of HCl (mL)	pH
0	13.10	60	2.13
10	12.85	70	1.88
20	12.62	80	1.75
30	12.36	90	1.66
40	11.98	100	1.60
50	7.00		

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Practice Exercise 9.2

The volume of HCl needed to reach the equivalence point is

$$V_{eq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125\text{ M})(25.0\text{ mL})}{0.0625\text{ M}} = 50.0\text{ mL}$$

Before adding HCl the pH is that for a solution of 0.100 M NH_3.

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = \frac{(x)(x)}{0.125 - x} = 1.75 \times 10^{-5}$$

$$x = [OH^-] = 1.47 \times 10^{-3} \text{ M}$$

The pH at the beginning of the titration, therefore, is 11.17.

Before the equivalence point the pH is determined by an NH_3/NH_4^+ buffer. For example, after adding 10.0 mL of HCl

$$[NH_3] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$[NH_4^+] = \frac{(0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0179 \text{ M}$$

$$\text{pH} = 9.244 + \log\frac{0.0714 \text{ M}}{0.0179 \text{ M}} = 9.84$$

At the equivalence point the predominate ion in solution is NH_4^+. To calculate the pH we first determine the concentration of NH_4^+

$$[NH_4^+] = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 50.0 \text{ mL}} = 0.0417 \text{ M}$$

and then calculate the pH

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.0417 - x} = 5.70 \times 10^{-10}$$

$$x = [H_3O^+] = 4.88 \times 10^{-6} \text{ M}$$

obtaining a value of 5.31.

After the equivalence point, the pH is determined by the excess HCl. For example, after adding 70.0 mL of HCl

$$[HCl] = \frac{(0.0625 \text{ M})(70.0 \text{ mL}) - (0.125 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 70.0 \text{ mL}} = 0.0132 \text{ M}$$

and the pH is 1.88. Some additional results are shown here.

Volume of HCl (mL)	pH	Volume of HCl (mL)	pH
0	11.17	60	2.13
10	9.84	70	1.88
20	9.42	80	1.75
30	9.07	90	1.66
40	8.64	100	1.60
50	5.31		

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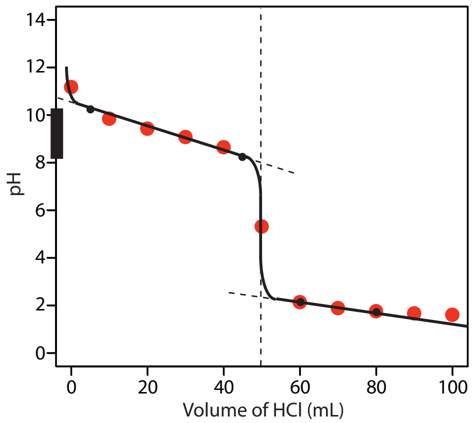

Figure 9.48 Titration curve for Practice Exercise 9.3. The black dots and curve are the approximate sketch of the titration curve. The points in red are the calculations from Practice Exercise 9.2.

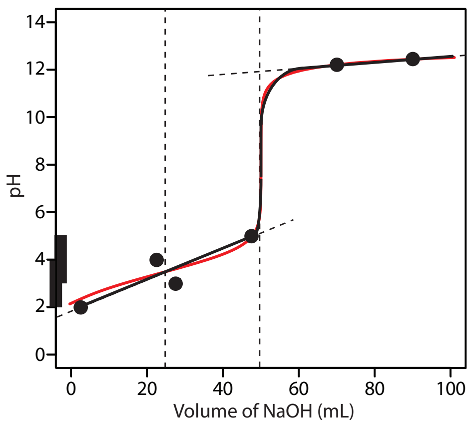

Figure 9.49 Titration curve for Practice Exercise 9.4. The black points and curve are the approximate titration curve, and the red curve is the exact titration curve.

Practice Exercise 9.3

Figure 9.48 shows a sketch of the titration curve. The two points before the equivalence point ($V_{HCl}=5$ mL, pH = 10.24 and $V_{HCl}=45$ mL, pH = 8.24) are plotted using the pK_a of 9.244 for NH_4^+. The two points after the equivalence point ($V_{HCl}=60$ mL, pH = 2.13 and $V_{HCl}=80$ mL, pH = 1.75) are from the answer to Practice Exercise 9.2.

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Practice Exercise 9.4

Figure 9.49 shows a sketch of the titration curve. The titration curve has two equivalence points, one at 25.0 mL ($H_2A \rightarrow HA^-$) and one at 50.0 mL ($HA^- \rightarrow A^{2-}$). In sketching the curve, we plot two points before the first equivalence point using the pK_a of 3 for H_2A

$$V_{HCl}=2.5 \text{ mL, pH}=2 \text{ and } V_{HCl}=22.5 \text{ mL, pH}=4$$

two points between the equivalence points using the pK_a of 5 for HA^-

$$V_{HCl}=27.5 \text{ mL, pH}=3\text{, and } V_{HCl}=47.5 \text{ mL, pH}=5$$

and two points after the second equivalence point

$$V_{HCl}=70 \text{ mL, pH}=12.22 \text{ and } V_{HCl}=90 \text{ mL, pH}=12.46)$$

Drawing a smooth curve through these points presents us with the following dilemma—the pH appears to increase as the titrant's volume approaches the first equivalence point and then appears to decrease as it passes through the first equivalence point. This is, of course, absurd; as we add NaOH the pH cannot decrease. Instead, we model the titration curve before the second equivalence point by drawing a straight line from the first point ($V_{HCl}=2.5$ mL, pH = 2) to the fourth ($V_{HCl}=47.5$ mL, pH = 5), ignoring the second and third points. The results is a reasonable approximation of the exact titration curve.

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Practice Exercise 9.5

The pH at the equivalence point is 5.31 (see Practice Exercise 9.2) and the sharp part of the titration curve extends from a pH of approximately 7 to a pH of approximately 4. Of the indicators in Table 9.4, methyl red is the best choice because it pK_a value of 5.0 is closest to the equivalence point's pH and because the pH range of 4.2–6.3 for its change in color will not produce a significant titration error.

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Practice Exercise 9.6

Because salicylic acid is a diprotic weak acid, we must first determine to which equivalence point it is being titrated. Using salicylic acid's pK_a

values as a guide, the pH at the first equivalence point is between a pH of 2.97 and 13.74, and the second equivalence points is at a pH greater than 13.74. From Table 9.4, phenolphthalein's end point falls in the pH range 8.3–10.0. The titration, therefore, is to the first equivalence point for which the moles of NaOH equal the moles of salicylic acid; thus

$$\frac{0.1354 \text{ mol NaOH}}{\text{L}} \times 0.02192 \text{ L} = 2.968 \times 10^{-3} \text{ mol NaOH}$$

$$2.968 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol } C_7H_6O_3}{\text{mol NaOH}} \times \frac{138.12 \text{ g } C_7H_6O_3}{\text{mol } C_7H_6O_3} = 0.4099 \text{ g } C_7H_6O_3$$

$$\frac{0.4099 \text{ g } C_7H_6O_3}{0.4208 \text{ g sample}} \times 100 = 97.41\% \text{ w/w } C_7H_6O_3$$

Because the purity of the sample is less than 99%, we reject the shipment.

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Practice Exercise 9.7

The moles of HNO_3 produced by pulling the air sample through the solution of H_2O_2 is

$$\frac{0.01012 \text{ mol NaOH}}{\text{L}} \times 0.00914 \text{ L} \times \frac{1 \text{ mol } HNO_3}{\text{mol NaOH}} = 9.25 \times 10^{-5} \text{ mol } HNO_3$$

A conservation of mass on nitrogen requires that each mole of NO_2 in the sample of air produces one mole of HNO_3; thus, the mass of NO_2 in the sample is

$$9.25 \times 10^{-5} \text{ mol } HNO_3 \times \frac{1 \text{ mol } NO_2}{\text{mol } HNO_3} \times \frac{46.01 \text{ g } NO_2}{\text{mol } NO_2} = 4.26 \times 10^{-3} \text{ g } NO_2$$

and the concentration of NO_2 is

$$\frac{4.26 \times 10^{-3} \text{ g } NO_2}{5 \text{ L air}} \times \frac{1000 \text{ mg}}{\text{g}} = 0.852 \text{ mg } NO_2/\text{L air}$$

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Practice Exercise 9.8

The total moles of HCl used in this analysis is

$$\frac{1.396 \text{ mol NaOH}}{\text{L}} \times 0.01000 \text{ L} = 1.396 \times 10^{-2} \text{ mol HCl}$$

Of this,

$$\frac{0.1004 \text{ mol NaOH}}{\text{L}} \times 0.03996 \text{ L} \times \frac{1 \text{ mol HCl}}{\text{mol NaOH}} = 4.012 \times 10^{-3} \text{ mol HCl}$$

are consumed in the back titration with NaOH, which means that

$$1.396 \times 10^{-2} \text{ mol HCl} - 4.012 \times 10^{-3} \text{ mol HCl} = 9.95 \times 10^{-3} \text{ mol HCl}$$

react with the $CaCO_3$. Because CO_3^{2-} is dibasic, each mole of $CaCO_3$ consumes two moles of HCl; thus

$$9.95 \times 10^{-3} \text{ mol HCl} \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol HCl}} \times \frac{100.09 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.498 \text{ g CaCO}_3$$

$$\frac{0.498 \text{ g CaCO}_3}{0.5143 \text{ g sample}} \times 100 = 96.8\% \text{ w/w CaCO}_3$$

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Practice Exercise 9.9

Of the two analytes, 2-methylanilinium is the stronger acid and is the first to react with the titrant. Titrating to the bromocresol purple end point, therefore, provides information about the amount of 2-methylanilinium in the sample.

$$\frac{0.200 \text{ mol NaOH}}{\text{L}} \times 0.01965 \text{ L} \times \frac{1 \text{ mol C}_7\text{H}_{10}\text{NCl}}{\text{mol NaOH}} \times \frac{143.61 \text{ g C}_7\text{H}_{10}\text{NCl}}{\text{mol C}_7\text{H}_{10}\text{NCl}} = 0.564 \text{ g C}_7\text{H}_{10}\text{NCl}$$

$$\frac{0.564 \text{ g C}_7\text{H}_{10}\text{NCl}}{2.006 \text{ g sample}} \times 100 = 28.1\% \text{ w/w C}_7\text{H}_{10}\text{NCl}$$

Titrating from the bromocresol purple end point to the phenolphthalein end point, a total of 48.41 mL – 19.65 mL, or 28.76 mL, gives the amount of NaOH reacting with 3-nitrophenol. The amount of 3-nitrophenol in the sample, therefore, is

$$\frac{0.200 \text{ mol NaOH}}{\text{L}} \times 0.02876 \text{ L} \times \frac{1 \text{ mol } C_6H_5NO_3}{\text{mol NaOH}} \times \frac{139.11 \text{ g } C_6H_5NO_3}{\text{mol } C_6H_5NO_3} = 0.800 \text{ g } C_6H_5NO_3$$

$$\frac{0.800 \text{ g } C_6H_5NO_3}{2.006 \text{ g sample}} \times 100 = 38.8\% \text{ w/w } C_6H_5NO_3$$

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Practice Exercise 9.10

The first of the two visible end points is approximately 37 mL of NaOH. The analyte's equivalent weight, therefore, is

$$\frac{0.1032 \text{ mol NaOH}}{\text{L}} \times 0.037 \text{ L} \times \frac{1 \text{ equivalent}}{\text{mol NaOH}} = 3.8 \times 10^{-3} \text{ equivalents}$$

$$EW = \frac{0.5000 \text{ g}}{3.8 \times 10^{-3} \text{ equivalents}} = 1.3 \times 10^{2} \text{ g/equivalent}$$

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Practice Exercise 9.11

At ½V_{eq}, or approximately 18.5 mL, the pH is approximately 2.2; thus, we estimate that the analyte's pK_a is 2.2.

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Practice Exercise 9.12

Let's begin with the calculations at a pH of 10. Ata pH of 10 some of the EDTA is present in forms other than Y^{4-}. To evaluate the titration curve, therefore, we need the conditional formation constant for CdY^{2-}, which, from Table 9.11 is $K_f' = 1.1 \times 10^{16}$. Note that the conditional formation constant is larger in the absence of an auxiliary complexing agent.

The titration's equivalence point requires

$$V_{eq} = V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{0.0100 \text{ M}} = 25.0 \text{ mL}$$

of EDTA.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}. For example, after adding 5.00 mL of EDTA, the total concentration of Cd^{2+} is

$$[Cd^{2+}] = \frac{(5.00 \times 10^{-3}\text{ M})(50.0\text{ mL}) - (0.0100\text{ M})(5.00\text{ mL})}{50.0\text{ mL} + 5.00\text{ mL}}$$
$$= 3.64 \times 10^{-3}\text{ M}$$

which gives a pCd of 2.43.

At the equivalence point all the Cd^{2+} initially in the titrand is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentration of CdY^{2-}.

$$[CdY^{2-}] = \frac{(5.00 \times 10^{-3}\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 25.0\text{ mL}} = 3.33 \times 10^{-3}\text{ M}$$

Next, we solve for the concentration of Cd^{2+} in equilibrium with CdY^{2-}.

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 1.1 \times 10^{16}$$

Solving gives $[Cd^{2+}]$ as 5.50×10^{-10} M, or a pCd of 9.26 at the equivalence point.

After the equivalence point, EDTA is in excess and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentrations of CdY^{2-} and of unreacted EDTA. For example, after adding 30.0 mL of EDTA

$$[CdY^{2-}] = \frac{(5.00 \times 10^{-3}\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 30.0\text{ mL}} = 3.13 \times 10^{-3}\text{ M}$$

$$C_{EDTA} = \frac{(0.0100\text{ M})(30.0\text{ mL}) - (5.00 \times 10^{-3}\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 30.0\text{ mL}}$$
$$= 6.25 \times 10^{-4}\text{ M}$$

Substituting into the equation for the conditional formation constant and solving for $[Cd^{2+}]$ gives

$$\frac{3.13 \times 10^{-3}\text{ M}}{[Cd^{2+}](6.25 \times 10^{-4}\text{ M})} = 1.1 \times 10^{16}$$

$[Cd^{2+}]$ as 4.55×10^{-16} M, or a pCd of 15.34.

The calculations at a pH of 7 are identical, except the conditional formation constant for CdY^{2-} is 1.5×10^{13} instead of 1.1×10^{16}. The following table summarizes results for these two titrations as well as the results from Table 9.13 for the titration of Cd^{2+} at a pH of 10 in the presence of 0.0100 M NH_3 as an auxiliary complexing agent.

Volume of EDTA (mL)	pCd at pH 10	pCd at pH 10 w/ 0.0100 M NH_3	pCd at pH 7
0	2.30	3.36	2.30
5.00	2.43	3.49	2.43
10.0	2.60	3.66	2.60
15.0	2.81	3.87	2.81
20.0	3.15	4.20	3.15
23.0	3.56	4.62	3.56
25.0	9.26	9.77	7.83
27.0	14.94	14.95	12.08
30.0	15.34	15.33	12.48
35.0	15.61	15.61	12.78
40.0	15.76	15.76	12.95
45.0	15.86	15.86	13.08
50.0	15.94	15.94	13.18

Examining these results allows us to draw several conclusions. First, in the absence of an auxiliary complexing agent the titration curve before the equivalence point is independent of pH (compare columns 2 and 4). Second, for any pH, the titration curve after the equivalence point is the same regardless of whether or not an auxiliary complexing agent is present (compare columns 2 and 3). Third, the largest change in pH through the equivalence point occurs at higher pHs and in the absence of an auxiliary complexing agent. For example, from 23.0 mL to 27.0 mL of EDTA the change in pCd is 11.38 at a pH of 10, 10.33 at a pH of 10 and in the presence of 0.0100 M NH_3, and 8.52 at a pH of 7.

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Practice Exercise 9.13

Figure 9.50 shows a sketch of the titration curves. The two points before the equivalence point ($V_{EDTA} = 5$ mL, pCd = 2.43 and $V_{EDTA} = 15$ mL, pCd = 2.81) are the same for both pHs and are taken from the results of Practice Exercise 9.12. The two points after the equivalence point for a pH of 7 ($V_{EDTA} = 27.5$ mL, pCd = 12.2 and $V_{EDTA} = 50$ mL, pCd = 13.2) are plotted using the $\log K_f'$ of 13.2 for CdY^{2-}. The two points after the equivalence point for a pH of 10 ($V_{EDTA} = 27.5$ mL, pCd = 15.0 and $V_{EDTA} = 50$ mL, pCd = 16.0) are plotted using the $\log K_f'$ of 16.0 for CdY^{2-}.

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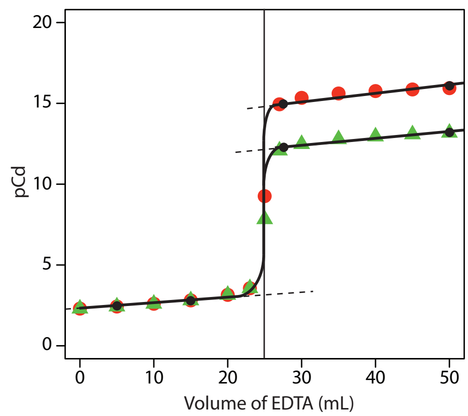

Figure 9.50 Titration curve for Practice Exercise 9.13. The black dots and curve are the approximate sketches of the two titration curves. The points in red are the calculations from Practice Exercise 9.12 for a pH of 10, and the points in green are the calculations from Practice Exercise 9.12 for a pH of 7.

Practice Exercise 9.14

In an analysis for hardness we treat the sample as if Ca^{2+} is the only metal ion reacting with EDTA. The grams of Ca^{2+} in the sample, therefore, is

$$\frac{0.0109 \text{ mol EDTA}}{\text{L}} \times 0.02363 \text{ L} \times \frac{1 \text{ mol Ca}^{2+}}{\text{mol EDTA}} = 2.58 \times 10^{-4} \text{ mol Ca}^{2+}$$

$$2.58 \times 10^{-4} \text{ mol Ca}^{2+} \times \frac{1 \text{ mol CaCO}_3}{\text{mol Ca}^{2+}} \times \frac{100.09 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.0258 \text{ g CaCO}_3$$

and the sample's hardness is

$$\frac{0.0258 \text{ g CaCO}_3}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 258 \text{ mg CaCO}_3\text{/L}$$

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Practice Exercise 9.15

The titration of CN^- with Ag^+ produces a metal-ligand complex of $Ag(CN)_2^{2-}$; thus, each mole of $AgNO_3$ reacts with two moles of NaCN. The grams of NaCN in the sample is

$$\frac{0.1018 \text{ mol AgNO}_3}{\text{L}} \times 0.03968 \text{ L} \times \frac{2 \text{ mol NaCN}}{\text{mol AgNO}_3} \times \frac{49.01 \text{ g NaCN}}{\text{mol NaCN}} = 0.3959 \text{ g NaCN}$$

and the purity of the sample is

$$\frac{0.3959 \text{ g NaCN}}{0.4482 \text{ g sample}} \times 100 = 88.33\% \text{ w/w NaCN}$$

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Practice Exercise 9.16

The total moles of EDTA used in this analysis is

$$\frac{0.02011 \text{ mol EDTA}}{\text{L}} \times 0.02500 \text{ L} = 5.028 \times 10^{-4} \text{ mol EDTA}$$

Of this,

$$\frac{0.01113 \text{ mol Mg}^{2+}}{\text{L}} \times 0.00423 \text{ L} \times \frac{1 \text{ mol EDTA}}{\text{mol Mg}^{2+}} = 4.708 \times 10^{-5} \text{ mol EDTA}$$

are consumed in the back titration with Mg^{2+}, which means that

$$5.028 \times 10^{-4} \text{ mol EDTA} - 4.708 \times 10^{-5} \text{ mol EDTA} = 4.557 \times 10^{-4} \text{ mol EDTA}$$

react with the $BaSO_4$. Each mole of $BaSO_4$ reacts with one mole of EDTA; thus

$$4.557 \times 10^{-4} \text{ mol EDTA} \times \frac{1 \text{ mol BaSO}_4}{\text{mol EDTA}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{\text{mol BaSO}_4} \times \frac{142.04 \text{ g Na}_2\text{SO}_4}{\text{mol Na}_2\text{SO}_4} = 0.06473 \text{ g Na}_2\text{SO}_4$$

$$\frac{0.06473 \text{ g Na}_2\text{SO}_4}{0.1557 \text{ g sample}} \times 100 = 41.23\% \text{ w/w Na}_2\text{SO}_4$$

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Practice Exercise 9.17

The volume of Tl^{3+} needed to reach the equivalence point is

$$V_{eq} = V_{Tl} = \frac{M_{Sn}V_{Sn}}{M_{Tl}} = \frac{(0.050 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, the concentration of unreacted Sn^{2+} and the concentration of Sn^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Sn^{4+}/Sn^{2+} half-reaction. For example, the concentrations of Sn^{2+} and Sn^{4+} after adding 10.0 mL of titrant are

$$[\text{Sn}^{2+}] = \frac{(0.050 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0250 \text{ M}$$

$$[\text{Sn}^{4+}] = \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0167 \text{ M}$$

and the potential is

$$E = +0.139 \text{ V} - \frac{0.05916}{2} \log \frac{0.0250 \text{ M}}{0.0167 \text{ M}} = +0.134 \text{ V}$$

After the equivalence point, the concentration of Tl^{+} and the concentration of excess Tl^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Tl^{3+}/Tl^{+} half-reaction. For example, after adding 40.0 mL of titrant, the concentrations of Tl^{+} and Tl^{3+} are

$$[\text{Tl}^{+}] = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 40.0 \text{ mL}} = 0.0278 \text{ M}$$

$$[\mathrm{Tl}^{3+}] = \frac{(0.100\ \mathrm{M})(40.0\ \mathrm{mL}) - (0.0500\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 40.0\ \mathrm{mL}} = 0.0167\ \mathrm{M}$$

and the potential is

$$E = +0.77\ \mathrm{V} - \frac{0.05916}{2}\log\frac{0.0278\ \mathrm{M}}{0.0167\ \mathrm{M}} = +0.76\ \mathrm{V}$$

At the titration's equivalence point, the potential, E_{eq}, potential is

$$E_{eq} = \frac{0.139\ \mathrm{V} + 0.77\ \mathrm{V}}{2} = 0.45\ \mathrm{V}$$

Some additional results are shown here.

Volume of Tl^{3+} (mL)	E (V)	Volume of Tl^{3+} (mL)	E (V)
5	0.121	30	0.75
10	0.134	35	0.75
15	0.144	40	0.76
20	0.157	45	0.76
25	0.45	50	0.76

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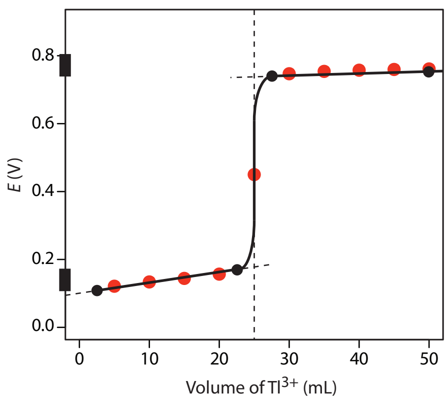

Figure 9.51 Titration curve for Practice Exercise 9.18. The black dots and curve are the approximate sketch of the titration curve. The points in red are the calculations from Practice Exercise 9.17.

Practice Exercise 9.18

Figure 9.51 shows a sketch of the titration curve. The two points before the equivalence point

$$V_{\mathrm{Tl}} = 2.5\ \mathrm{mL},\ E = +0.109\ \mathrm{V}\ \text{and}\ V_{\mathrm{Tl}} = 22.5\ \mathrm{mL},\ E = +0.169\ \mathrm{V}$$

are plotted using the redox buffer for Sn^{4+}/Sn^{2+}, which spans a potential range of $+0.139 \pm 0.5916/2$. The two points after the equivalence point

$$V_{\mathrm{Tl}} = 27.5\ \mathrm{mL},\ E = +0.74\ \mathrm{V}\ \text{and}\ V_{\mathrm{EDTA}} = 50\ \mathrm{mL},\ E = +0.77\ \mathrm{V}$$

are plotted using the redox buffer for Tl^{3+}/Tl^{+}, which spans the potential range of $+0.139 \pm 0.5916/2$.

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Practice Exercise 9.19

The two half reactions are

$$\mathrm{Ce}^{4+}(aq) + e^- \rightarrow \mathrm{Ce}^{3+}(aq)$$

$$\mathrm{U}^{4+}(aq) + 2\mathrm{H_2O} \rightarrow \mathrm{UO_2^{2+}}(aq) + 4\mathrm{H}^+(aq) + 2e^-$$

for which the Nernst equations are

$$E = E^{\circ}_{\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}} - \frac{0.05916}{1}\log\frac{[\mathrm{Ce}^{3+}]}{[\mathrm{Ce}^{4+}]}$$

$$E = E^{\circ}_{UO_2^{2+}/U^{4+}} - \frac{0.05916}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

Before adding these two equations together we must multiply the second equation by 2 so that we can combine the log terms; thus

$$3E = E^{\circ}_{Ce^{4+}/Ce^{3+}} + 2E^{\circ}_{UO_2^{2+}/U^{4+}} - 0.05916\log\frac{[Ce^{3+}][U^{4+}]}{[Ce^{4+}][UO_2^{2+}][H^+]^4}$$

At the equivalence point we know that

$$[Ce^{3+}] = 2\times[UO_2^{2+}]$$
$$[Ce^{4+}] = 2\times[U^{4+}]$$

Substituting these equalities into the previous equation and rearranging gives us a general equation for the potential at the equivalence point.

$$3E = E^{\circ}_{Ce^{4+}/Ce^{3+}} + 2E^{\circ}_{UO_2^{2+}/U^{4+}} - 0.05916\log\frac{2[UO_2^{2+}][U^{4+}]}{2[U^{4+}][UO_2^{2+}][H^+]^4}$$

$$E = \frac{E^{\circ}_{Ce^{4+}/Ce^{3+}} + 2E^{\circ}_{UO_2^{2+}/U^{4+}}}{3} - \frac{0.05916}{3}\log\frac{1}{[H^+]^4}$$

$$E = \frac{E^{\circ}_{Ce^{4+}/Ce^{3+}} + 2E^{\circ}_{UO_2^{2+}/U^{4+}}}{3} + \frac{0.05916\times 4}{3}\log[H^+]$$

$$E = \frac{E^{\circ}_{Ce^{4+}/Ce^{3+}} + 2E^{\circ}_{UO_2^{2+}/U^{4+}}}{3} - 0.07888\text{pH}$$

At a pH of 1 the equivalence point has a potential of

$$E_{eq} = \frac{1.72 + 2\times 0.327}{3} - 0.07888\times 1 = 0.712\text{ V}$$

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Practice Exercise 9.20

Because we have not been provided with a balanced reaction, let's use a conservation of electrons to deduce the stoichiometry. Oxidizing $C_2O_4^{2-}$, in which each carbon has a +3 oxidation state, to CO_2, in which carbon has an oxidation state of +4, requires one electron per carbon, or a total of two electrons for each mole of $C_2O_4^{2-}$. Reducing MnO_4^-, in which each manganese is in the +7 oxidation state, to Mn^{2+} requires five electrons. A conservation of electrons for the titration, therefore, requires that two moles of $KMnO_4$ (10 moles of e^-) reacts with five moles of $Na_2C_2O_4$ (10 moles of e^-).

The moles of $KMnO_4$ used in reaching the end point is

$$(0.0400 \text{ M KMnO}_4) \times (0.03562 \text{ L KMnO}_4) = 1.42 \times 10^{-3} \text{ mol KMnO}_4$$

which means that the sample contains

$$1.42 \times 10^{-3} \text{ mol KMnO}_4 \times \frac{5 \text{ mol Na}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} = 3.55 \times 10^{-3} \text{ mol Na}_2\text{C}_2\text{O}_4$$

Thus, the %w/w $Na_2C_2O_4$ in the sample of ore is

$$3.55 \times 10^{-3} \text{ mol Na}_2\text{C}_2\text{O}_4 \times \frac{134.00 \text{ g Na}_2\text{C}_2\text{O}_4}{\text{mol Na}_2\text{C}_2\text{O}_4} = 0.476 \text{ g Na}_2\text{C}_2\text{O}_4$$

$$\frac{0.476 \text{ g Na}_2\text{C}_2\text{O}_4}{0.5116 \text{ g sample}} \times 100 = 93.0\% \text{ w/w Na}_2\text{C}_2\text{O}_4$$

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Practice Exercise 9.21

For a back titration we need to determine the stoichiometry between $Cr_2O_7^{2-}$ and the analyte, C_2H_6O, and between $Cr_2O_7^{2-}$ and the titrant, Fe^{2+}. In oxidizing ethanol to acetic acid, the oxidation state of carbon changes from –2 in C_2H_6O to 0 in $C_2H_4O_2$. Each carbon releases two electrons, or a total of four electrons per C_2H_6O. In reducing $Cr_2O_7^{2-}$, in which each chromium has an oxidation state of +6, to Cr^{3+}, each chromium loses three electrons, for a total of six electrons per $Cr_2O_7^{2-}$. Oxidation of Fe^{2+} to Fe^{3+} requires one electron. A conservation of electrons requires that each mole of $K_2Cr_2O_7$ (6 moles of e^-) reacts with six moles of Fe^{2+} (6 moles of e^-), and that four moles of $K_2Cr_2O_7$ (24 moles of e^-) react with six moles of C_2H_6O (24 moles of e^-).

The total moles of $K_2Cr_2O_7$ reacting with C_2H_6O and with Fe^{2+} is

$$(0.0200 \text{ M K}_2\text{Cr}_2\text{O}_7) \times (0.05000 \text{ L I}_3^-) = 1.00 \times 10^{-3} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

The back titration with Fe^{2+} consumes

$$0.02148 \text{ L Fe}^{2+} \times \frac{0.1014 \text{ mol Fe}^{2+}}{\text{L Fe}^{2+}} \times \frac{1 \text{ mol K}_2\text{Cr}_2\text{O}_7}{6 \text{ mol Fe}^{2+}} = 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

Subtracting the moles of $K_2Cr_2O_7$ reacting with Fe^{2+} from the total moles of $K_2Cr_2O_7$ gives the moles reacting with the analyte.

$$1.00 \times 10^{-3} \text{ K}_2\text{Cr}_2\text{O}_7 - 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 = 6.37 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

The grams of ethanol in the 10.00-mL sample of diluted brandy is

$$6.37\times10^{-4}\ \text{mol}\ K_2Cr_2O_7 \times \frac{6\ \text{mol}\ C_2H_6O}{4\ \text{mol}\ K_2Cr_2O_7} \times \frac{46.50\ \text{g}\ C_2H_6O}{\text{mol}\ C_2H_6O} = 0.0444\ \text{g}\ C_2H_6O$$

The %w/v C_2H_6O in the brandy is

$$\frac{0.0444\ \text{g}\ C_2H_6O}{10.00\ \text{mL dilute brandy}} \times \frac{500.0\ \text{mL dilute brandy}}{5.00\ \text{mL brandy}} \times 100 = 44.4\%\ \text{w/v}\ C_2H_6O$$

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Practice Exercise 9.22

The first task is to calculate the volume of NaCl needed to reach the equivalence point; thus

$$V_{eq} = V_{NaCl} = \frac{M_{Ag}V_{Ag}}{M_{NaCl}} = \frac{(0.0500\ \text{M})(50.0\ \text{mL})}{(0.100\ \text{M})} = 25.0\ \text{mL}$$

Before the equivalence point the titrand, Ag^+, is in excess. The concentration of unreacted Ag^+ after adding 10.0 mL of NaCl, for example, is

$$[Ag^+] = \frac{(0.0500\ \text{M})(50.0\ \text{mL}) - (0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}} = 2.50\times10^{-2}\ \text{M}$$

which corresponds to a pAg of 1.60. To find the concentration of Cl^- we use the K_{sp} for AgCl; thus

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8\times10^{-10}}{2.50\times10^{-2}} = 7.2\times10^{-9}\ \text{M}$$

or a pCl of 8.14.

At the titration's equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. To calculate their concentrations we use the K_{sp} expression for AgCl; thus

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = 1.8\times10^{-10}$$

Solving for x gives a concentration of Ag^+ and the concentration of Cl^- as 1.3×10^{-5} M, or a pAg and a pCl of 4.89.

After the equivalence point, the titrant is in excess. For example, after adding 35.0 mL of titrant

$$[Cl^-] = \frac{(0.100\ \text{M})(35.0\ \text{mL}) - (0.0500\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 35.0\ \text{mL}} = 1.18\times10^{-2}\ \text{M}$$

or a pCl of 1.93. To find the concentration of Ag^+ we use the K_{sp} for AgCl; thus

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$

or a pAg of 7.82. The following table summarizes additional results for this titration.

Volume of NaCl (mL)	pAg	pCl
0	1.30	–
5.00	1.44	8.31
10.0	1.60	8.14
15.0	1.81	7.93
20.0	2.15	7.60
25.0	4.89	4.89
30.0	7.54	2.20
35.0	7.82	1.93
40.0	7.97	1.78
45.0	8.07	1.68
50.0	8.14	1.60

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Practice Exercise 9.23

The titration uses

$$\frac{0.1078 \text{ M KSCN}}{\text{L}} \times 0.02719 \text{ L} = 2.931 \times 10^{-3} \text{ mol KSCN}$$

The stoichiometry between SCN^- and Ag^+ is 1:1; thus, there are

$$2.931 \times 10^{-3} \text{ mol Ag}^+ \times \frac{107.87 \text{ g Ag}}{\text{mol Ag}} = 0.3162 \text{ g Ag}$$

in the 25.00 mL sample. Because this represents ¼ of the total solution, there are 0.3162 × 4 or 1.265 g Ag in the alloy. The %w/w Ag in the alloy is

$$\frac{1.265 \text{ g Ag}}{1.963 \text{ g sample}} \times 100 = 64.44\% \text{ w/w Ag}$$

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