

# Chapter 9

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## Titrimetric Methods

### Chapter Overview

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**T**itrimetry, in which volume serves as the analytical signal, first appears 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 that era include titrimetric methods of analysis.

Precipitation gravimetry first developed as an analytical method without a general theory of precipitation. An empirical relationship between a precipitate's mass and the mass of analyte in a sample—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.

We will deliberately avoid 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. Later, when we discuss specific titrimetric methods, we will use the term analyte where appropriate.

## 9A Overview of Titrimetry

In **TITRIMETRY** we add a reagent, called the **TITRANT**, to a solution that contains another reagent, called the **TITRAND**, and allow them to react. The type of reaction provides us with a simple way to divide titrimetry into 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, which are 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 their 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 the 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 give an accurate result we must combine the titrand and the titrant in stoichiometrically equivalent amounts. 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 that react with the titrand.

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

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

Unfortunately, for most titration reactions there is no obvious sign when we reach the equivalence point. Instead, we stop adding the titrant 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's volume and the equivalence point's volume is a determinate **TITRATION ERROR**. If the end point and the equivalence point volumes coincide closely, then this error is insignificant and is safely ignored. Clearly, selecting an appropriate end point is of critical importance.

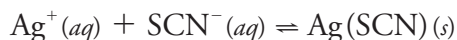
### 9A.2 Volume as a Signal

Almost any chemical reaction can serve as a titrimetric method provided that 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 used to reach

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

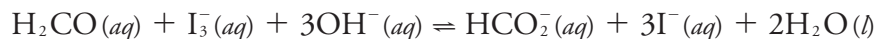
the end point to the moles of titrand in our sample. Second, the titration reaction effectively must proceed to completion; that is, the stoichiometric mixing of the titrant and the titrand must result in their complete reaction. Third, the titration reaction must occur rapidly. If we add the titrant faster than it can react with the titrand, then the end point and the equivalence point will differ significantly. Finally, we must have a suitable method for accurately determining the end point. These are significant limitations and, for this reason, there are several common titration strategies.

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

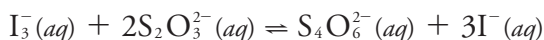


This reaction occurs quickly and with a known stoichiometry, which satisfies two of our requirements. To indicate the titration's end point, we add a small amount of  $\text{Fe}^{3+}$  to the analyte's solution before we begin the titration. When the reaction between  $\text{Ag}^+$  and  $\text{SCN}^-$  is complete, formation of the red-colored  $\text{Fe}(\text{SCN})^{2+}$  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,  $\text{H}_2\text{CO}$ , in an aqueous solution. The oxidation of  $\text{H}_2\text{CO}$  by  $\text{I}_3^-$

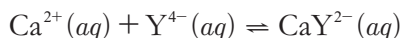


is a useful reaction, but it is too slow for a titration. If we add a known excess of  $\text{I}_3^-$  and allow its reaction with  $\text{H}_2\text{CO}$  to go to completion, we can titrate the unreacted  $\text{I}_3^-$  with thiosulfate,  $\text{S}_2\text{O}_3^{2-}$ .

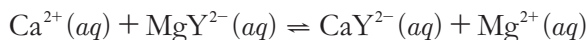


The difference between the initial amount of  $\text{I}_3^-$  and the amount in excess gives us the amount of  $\text{I}_3^-$  that reacts with the formaldehyde. This is an example of a **BACK TITRATION**.

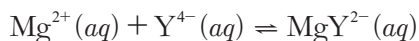
Calcium ions play an important role in many environmental systems. A direct analysis for  $\text{Ca}^{2+}$  might take advantage of its reaction with the ligand ethylenediaminetetraacetic acid (EDTA), which we represent here as  $\text{Y}^{4-}$ .



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



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



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.

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

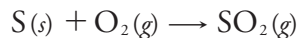
This is an example of a redox titration. You will find more information about redox titrations in Section 9D.

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

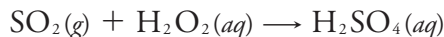
This is an example of a complexation titration. You will find more information about complexation titrations in Section 9C.

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  $\text{Ca}^{2+}$  in the original sample. Because the species we are titrating was displaced by the analyte, we call this a **DISPLACEMENT TITRATION**.

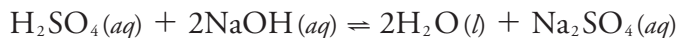
If a suitable reaction with the analyte does not exist it may be possible to generate a species that we can titrate. For example, we can determine the sulfur content of coal by using a combustion reaction to convert sulfur to sulfur dioxide



and then convert the  $\text{SO}_2$  to sulfuric acid,  $\text{H}_2\text{SO}_4$ , by bubbling it through an aqueous solution of hydrogen peroxide,  $\text{H}_2\text{O}_2$ .



Titration of  $\text{H}_2\text{SO}_4$  with NaOH



provides an indirect determination of sulfur.

### 9A.3 Titration Curves

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

A **TITRATION CURVE** provides 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.

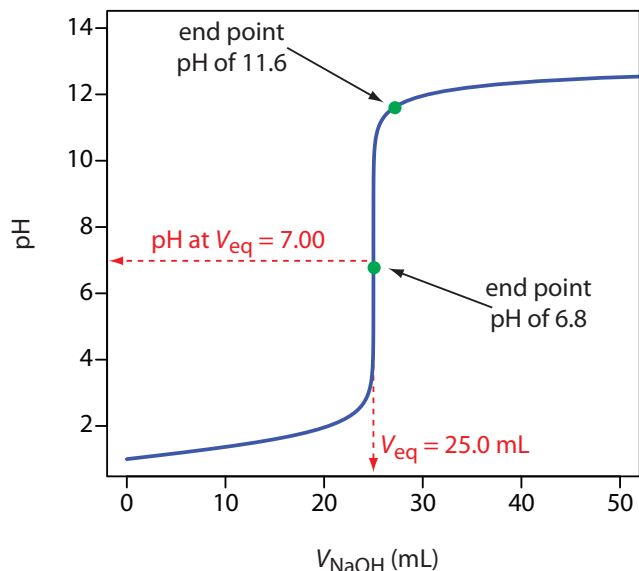
The shape of the titration curve in [Figure 9.1](#) is not unique to an acid–base titration. Any titration curve that follows the change in concentration of a species in the titration reaction (plotted logarithmically) as a function of the titrant's volume has the same general sigmoidal shape. Several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

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

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

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  $-2.00 \times 10^{-4}\%$  relative to the equivalence point of 25.00 mL. Typically, we can read the volume only 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.

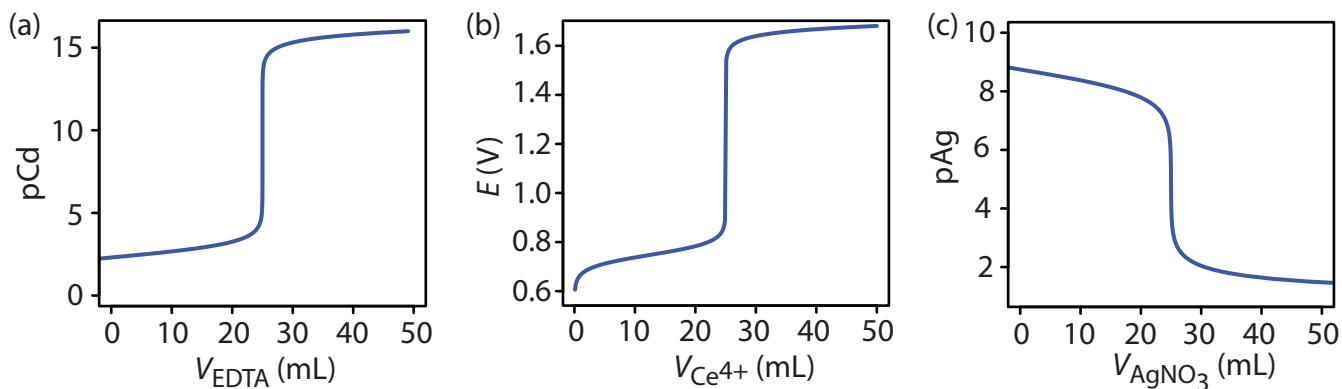


**Figure 9.1** Typical acid–base titration curve showing how the titrand’s pH changes with the addition of titrant. The titrand is a 25.0 mL solution of 0.100 M HCl and the titrant is 0.100 M NaOH. The titration curve is the solid blue line, and the equivalence point volume (25.0 mL) and pH (7.00) are 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.

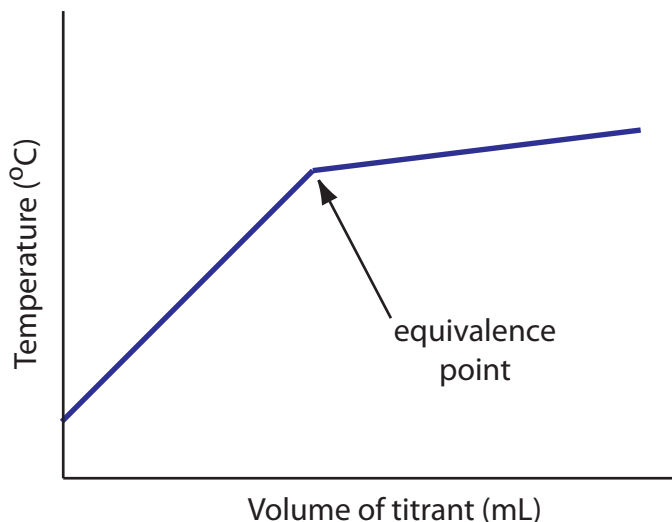
The titrand’s or the titrant’s concentration is not the only property we can use to record a titration curve. Other parameters, such as the temperature or absorbance of the titrand’s solution, may provide a useful end point signal. Many acid–base titration reactions, for example, are exothermic. As the titrant and the titrand react, the temperature of the titrand’s solution 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** where the intersection of the two linear segments indicates the equivalence point.

#### 9A.4 The Buret

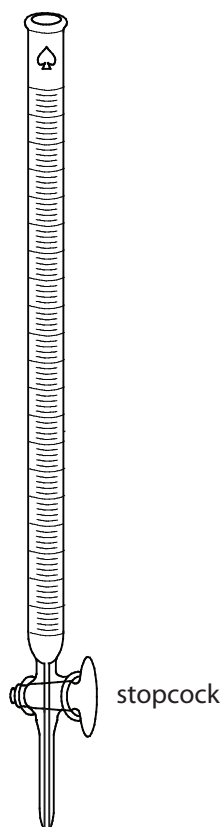
The only essential equipment for an acid–base titration is a means for delivering the titrant to the titrand’s solution. The most common method for delivering titrant is a **BURET** ([Figure 9.4](#)), which is a long, narrow tube



**Figure 9.2** Additional examples of titration curves. (a) Complexation titration of 25.0 mL of 1.0 mM  $\text{Cd}^{2+}$  with 1.0 mM EDTA at a pH of 10. The  $y$ -axis displays the titrand’s equilibrium concentration as  $\text{pCd}$ . (b) Redox titration of 25.0 mL of 0.050 M  $\text{Fe}^{2+}$  with 0.050 M  $\text{Ce}^{4+}$  in 1 M  $\text{HClO}_4$ . 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  $\text{AgNO}_3$ . The  $y$ -axis displays the titrant’s equilibrium concentration as  $\text{pAg}$ .



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



**Figure 9.4** A typical volumetric buret. The stopcock is shown here in the open position, which allows the titrant to flow into the titrand's solution. Rotating the stopcock controls the titrant's flow rate.

with graduated markings and equipped with a stopcock for dispensing the titrant. The buret's small internal diameter provides a better defined meniscus, making it easier to read precisely the titrant's volume. 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.

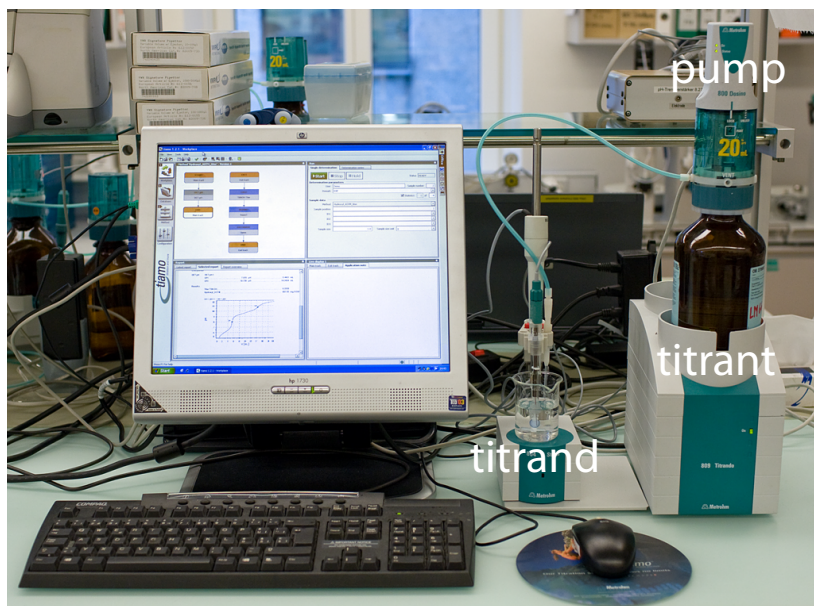
An automated titration uses a pump to deliver the titrant at a constant flow rate (Figure 9.5). Automated titrations offer the additional advantage of using a microcomputer for data storage and analysis.

## 9B Acid–Base Titrations

Before 1800, most **ACID–BASE TITRATIONS** used  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , or  $\text{HNO}_3$  as acidic titrants, and  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  as basic titrants. A titration's end

**Table 9.1** Specifications for Volumetric Burets

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



**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).

point was determined using litmus as an indicator, which is red in acidic solutions and blue in basic solutions, or by the cessation of  $\text{CO}_2$  effervescence when neutralizing  $\text{CO}_3^{2-}$ . Early examples of acid–base titrimetry include determining the acidity or alkalinity of solutions, and determining the purity of carbonates and alkaline earth oxides.

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 increased 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. Sørensen’s establishment of the pH scale in 1909 provided a rigorous means to compare 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, making acid–base titrimetry a useful alternative to gravimetry.

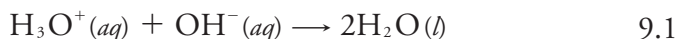
The determination of acidity and alkalinity continue to be important applications of acid–base titrimetry. We will take a closer look at these applications later in this section.

## 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 titrand's 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 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



The first task 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

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

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

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

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

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 the pH is

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

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

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

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

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.

$$K_w = 1.00 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2$$

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7}$$

Thus, the pH at the equivalence point is 7.00.

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  $(K_w)^{-1}$  or  $1.00 \times 10^{14}$ —we can treat reaction 9.1 as though it goes to completion.

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

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

$$\text{pH} = -\log(0.0500) = 1.30$$

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



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

$$[\text{OH}^-] = \frac{(\text{mol NaOH})_{\text{added}} - (\text{mol HCl})_{\text{initial}}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b}$$

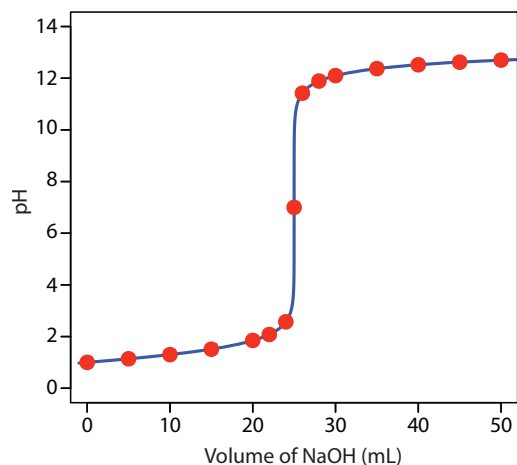
$$[\text{OH}^-] = \frac{(0.200 \text{ M})(30.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{30.0 \text{ mL} + 50.0 \text{ mL}} = 0.0125 \text{ M}$$

To find the concentration of  $\text{H}_3\text{O}^+$  we use the  $K_w$  expression

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13} \text{ M}$$

to find that the pH is 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.

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



**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.

### 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		

**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,  $\text{CH}_3\text{COOH}$ , with 0.200 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

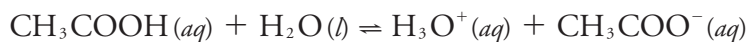
$$\text{mol CH}_3\text{COOH} = \text{mol NaOH}$$

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

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

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

Before we begin the titration 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

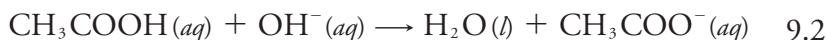


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 1.32 \times 10^{-3} \text{ M}$$

finding that the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base,  $\text{CH}_3\text{COO}^-$ .



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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Before the equivalence point the concentration of unreacted acetic acid is

$$\begin{aligned} [\text{CH}_3\text{COOH}] &= \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}} - (\text{mol NaOH})_{\text{added}}}{\text{total volume}} \\ &= \frac{M_a V_a - M_b V_b}{V_a + V_b} \end{aligned}$$

and the concentration of acetate is

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are

$$\begin{aligned} [\text{CH}_3\text{COOH}] &= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} \\ &= 0.0500 \text{ M} \end{aligned}$$

$$[\text{CH}_3\text{COO}^-] = \frac{(0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0333 \text{ M}$$

which gives us a pH of

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.

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

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

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  $\text{CH}_3\text{COO}^-$ , which is a weak base. To calculate the pH we first determine the concentration of  $\text{CH}_3\text{COO}^-$

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{(0.200 \text{ M})(25.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}$$

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

$$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{CH}_3\text{COOH}(aq)$$

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{0.0667 - x} = 5.71 \times 10^{-10}$$

$$x = [\text{OH}^-] = 6.17 \times 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{6.17 \times 10^{-6}} = 1.62 \times 10^{-9} \text{ M}$$

finding that the pH at the equivalence point is 8.79.

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  $\text{OH}^-$  is

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13} \text{ M}$$

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.

We can extend this approach for calculating a weak acid–strong base titration curve to reactions that involve 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,

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

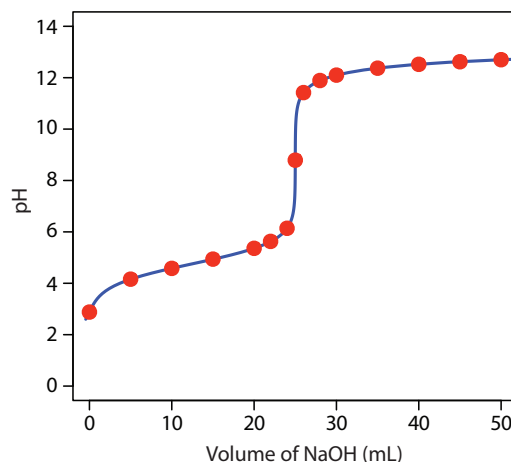
$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}}}{\text{total volume}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}$$

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

### Practice Exercise 9.2

Construct a titration curve for the titration of 25.0 mL of 0.125 M  $\text{NH}_3$  with 0.0625 M HCl.

Click [here](#) to review your answer to this exercise.



**Figure 9.7** Titration curve for the titration of 50.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$  with 0.200 M NaOH. The **red** points correspond to the data in Table 9.3. The **blue** line shows the complete titration curve.

**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		

a variety of algebraic<sup>1</sup> and computer spreadsheet<sup>2</sup> approaches are available to aid in constructing titration curves.

### SKETCHING AN ACID–BASE 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 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  $\text{CH}_3\text{COOH}$  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

- (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.
- (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.

This is the same example that we used to develop 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.

the  $y$ -axis and the titrant's volume on the  $x$ -axis. To indicate the equivalence point volume, we draw a vertical line that intersects the  $x$ -axis at 25.0 mL of NaOH. [Figure 9.8a](#) shows the first step in our sketch.

Before the equivalence point the titrand's pH is determined by a buffer of acetic acid,  $\text{CH}_3\text{COOH}$ , and acetate,  $\text{CH}_3\text{COO}^-$ . Although we can 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 that extends approximately  $\pm 1$  pH unit on either side of the weak acid's  $\text{p}K_a$  value. The pH is at the lower end of this range,  $\text{pH} = \text{p}K_a - 1$ , when the weak acid's concentration is  $10\times$  greater than that of its conjugate weak base. The buffer reaches its upper pH limit,  $\text{pH} = \text{p}K_a + 1$ , when the weak acid's concentration is  $10\times$  smaller than that of its conjugate weak base. When we titrate 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  $\text{p}K_a$  value of 4.76. Next, we add two points, one for the pH at 10% of the equivalence point volume (a pH of 3.76 at 2.5 mL) and one for the pH at 90% of the equivalence point volume (a pH of 5.76 at 22.5 mL).

The third step 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 saw earlier. [Figure 9.8c](#) includes points for the pH after adding 30.0 mL and after adding 40.0 mL of NaOH.

Next, we draw a straight line through each pair of points, extending each line through the vertical line that represents 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.

As shown in the following example, we can adapt this approach to any acid–base titration, including those where exact calculations are more challenging, including the titration of polyprotic weak acids and bases, and the titration of mixtures of weak acids or weak bases.

### Example 9.1

Sketch titration curves for the following two systems: (a) the titration of 50.0 mL of 0.050 M  $\text{H}_2\text{A}$ , a diprotic weak acid with a  $\text{p}K_{a1}$  of 3 and a  $\text{p}K_{a2}$  of 7; and (b) the titration of a 50.0 mL mixture that contains 0.075 M HA, a weak acid with a  $\text{p}K_a$  of 3, and 0.025 M HB, a weak acid with a  $\text{p}K_a$  of 7. For both titrations, assume that the titrant is 0.10 M NaOH.

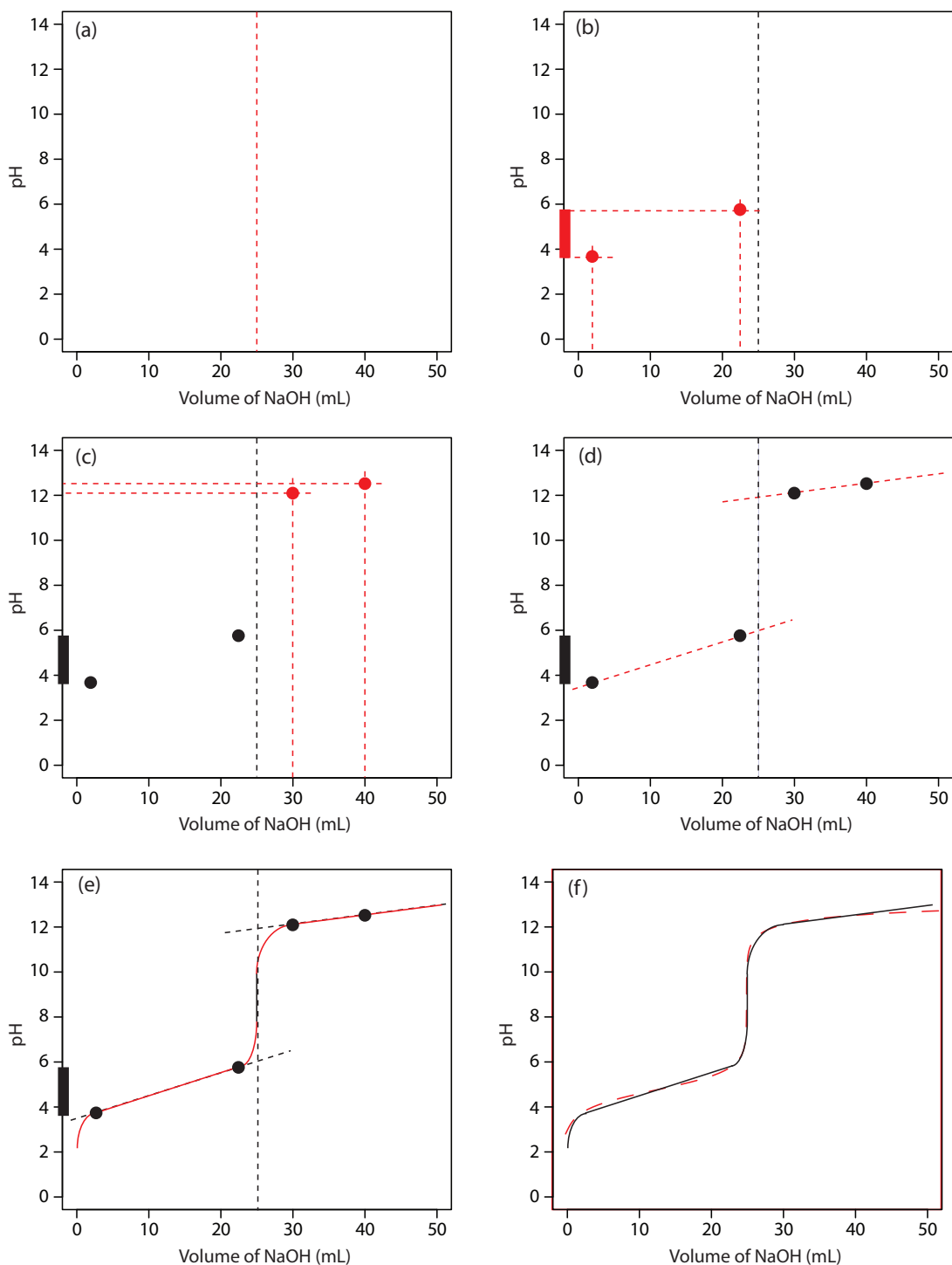
The actual values are 9.09% and 90.9%, but for our purpose, using 10% and 90% is more convenient; that is, after all, one advantage of an approximation! [Problem 9.4](#) in the end-of-chapter problems asks you to verify these percentages.

See [Table 9.3](#) for the values.

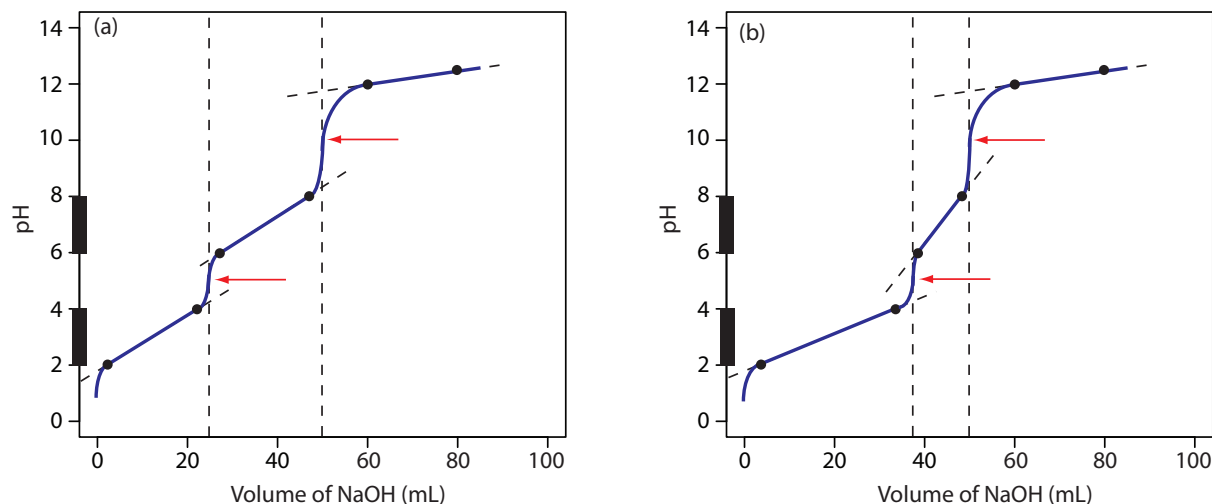
### Practice Exercise 9.3

Sketch a titration curve for the titration of 25.0 mL of 0.125 M  $\text{NH}_3$  with 0.0625 M HCl and compare to the result from [Practice Exercise 9.2](#).

Click [here](#) to review your answer to this exercise.



**Figure 9.8** Illustrations showing the steps used to sketch an approximate titration curve for the titration of 50.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$  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.



**Figure 9.9** Titration curves for Example 9.1. The solid **black** dots show the points used to sketch the titration curves (shown in **blue**) and the **red** arrows show the locations of the equivalence points.

### SOLUTION

Figure 9.9a shows the titration curve for H<sub>2</sub>A, including the ladder diagram for H<sub>2</sub>A on the *y*-axis, the two equivalence points at 25.0 mL and at 50.0 mL, two points before each equivalence point, two points after the last equivalence point, and the straight-lines used to sketch the final titration curve. Before the first equivalence point the pH is controlled by a buffer of H<sub>2</sub>A and HA<sup>-</sup>. An HA<sup>-</sup>/A<sup>2-</sup> 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; however, in this case the equivalence points are not equally spaced because the concentration of HA is greater than that for HB. Because 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 of HA and A<sup>-</sup>. Between the two equivalence points the pH reflects the titration of HB and is determined by a buffer of HB and B<sup>-</sup>. After the second equivalence point excess NaOH determines the pH.

### Practice Exercise 9.4

Sketch the titration curve for 50.0 mL of 0.050 M H<sub>2</sub>A, 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.

For an Excel spreadsheet that simulates acid–base titrations, see [CurTiPot](#).

## 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 that represents our best estimate of the equivalence point. Any difference between a titration's equivalence point and its corresponding end point is a source of determinate error.

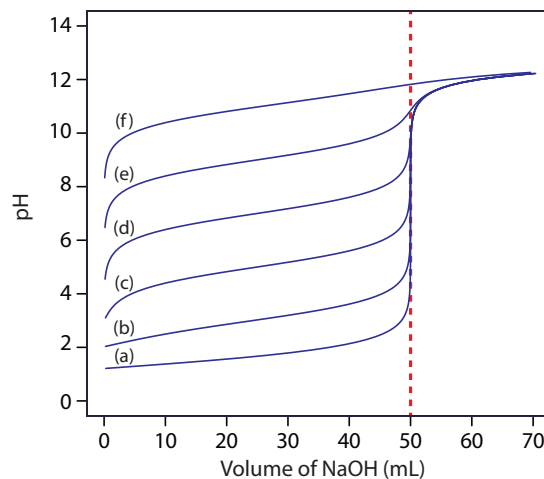
### WHERE IS THE EQUIVALENCE POINT?

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 how to 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, often is yes!

For most acid–base titration the inflection point—the point on a titration curve that has the greatest slope—very nearly coincides with the titration's equivalence point. The red arrows in [Figure 9.9](#), for example, identify the equivalence points for the titration curves in [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 and weak bases with dissociation constants smaller than  $10^{-9}$ , or for very dilute solutions.<sup>3</sup>

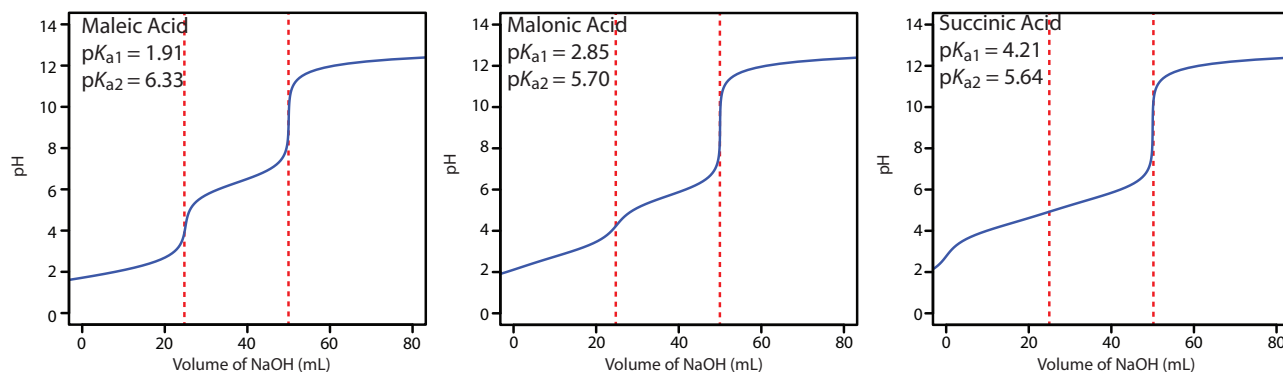
The principal limitation of an inflection point is that it must be present and easy to identify. For some titrations the inflection point is missing or difficult to find. [Figure 9.10](#), for example, demonstrates the affect of a weak acid's dissociation constant,  $K_a$ , on the shape of its titration 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  $10^{-11}$ .

<sup>3</sup> 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. The dashed red line shows the equivalence point, which is 50.0 mL for all six analytes.





**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 as the titrant. Although each titration curve has equivalence points at 25.0 mL and 50.0 mL of NaOH (shown by the dashed red lines), the titration curve for succinic acid shows only one inflection point.

An inflection point also may be missing or difficult to see 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.



To see two distinct inflection points, reaction 9.3 must essentially be 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  $20\,000\times$  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 the second. Finally, the titration curve for succinic acid, for which the two  $K_a$  values differ by a factor of only  $27\times$ , has only a single inflection point that corresponds 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  $\Delta pK_a$  of at least 2.7).

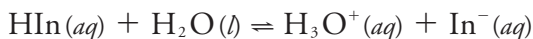
The same holds true for mixtures of weak acids or mixtures of weak bases. To detect separate inflection points when titrating a mixture of weak acids, their  $pK_a$  values must differ by at least a factor of 500.

### 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 its pH and its 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.

As an example, let's consider an indicator for which the acid form,  $HIn$ , is yellow and the base form,  $In^-$ , is red. The color of the indicator's solution

depends on the relative concentrations of HIn and  $\text{In}^-$ . To understand the relationship between pH and color we use the indicator's acid dissociation reaction



and its equilibrium constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad 9.5$$

Taking the negative log of each side of equation 9.5, and rearranging to solve for pH leaves us with a equation that relates the solution's pH to the relative concentrations of HIn and  $\text{In}^-$ .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad 9.6$$

If we can detect HIn and  $\text{In}^-$  with equal ease, then the transition from yellow-to-red (or from red-to-yellow) reaches its midpoint, which is orange, when the concentrations of HIn and  $\text{In}^-$  are equal, or when the pH is equal to the indicator's  $\text{p}K_a$ . If the indicator's  $\text{p}K_a$  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  $\text{In}^-$  are equal is difficult if the indicator's change in color is subtle.

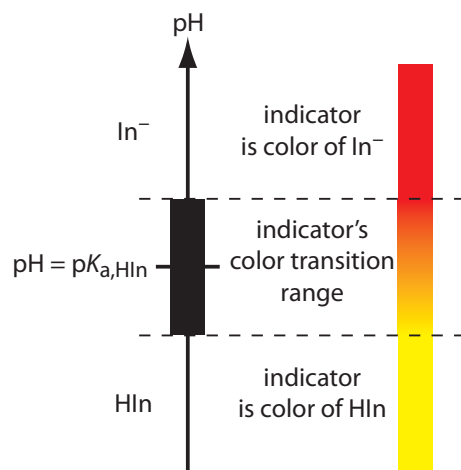
We can establish the range of pHs over which the average analyst observes a change in the indicator's color by making two assumptions: that the indicator's color is yellow if the concentration of HIn is  $10\times$  greater than that of  $\text{In}^-$  and that its color is red if the concentration of HIn is  $10\times$  smaller than that of  $\text{In}^-$ . Substituting these inequalities into equation 9.6

$$\text{pH} = \text{p}K_a + \log \frac{1}{10} = \text{p}K_a - 1$$

$$\text{pH} = \text{p}K_a + \log \frac{10}{1} = \text{p}K_a + 1$$

shows that the indicator changes color over a pH range that extends  $\pm 1$  unit on either side of its  $\text{p}K_a$ . As shown in [Figure 9.12](#), the indicator is yellow when the pH is less than  $\text{p}K_a - 1$  and it is red when the pH is greater than  $\text{p}K_a + 1$ . For pH values between  $\text{p}K_a - 1$  and  $\text{p}K_a + 1$  the indicator's color passes through various shades of orange. The properties of several common acid–base indicators are listed in [Table 9.4](#).

The relatively broad range of pHs over which an indicator changes color places additional limitations on its ability to signal a titration's end point. To minimize a determinate titration error, the indicator's entire pH range must fall within the rapid change in pH near 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 well before the initial sharp rise in pH,



**Figure 9.12** Diagram showing the relationship between pH and an indicator's color. The ladder diagram defines pH values where  $\text{HIn}$  and  $\text{In}^-$  are the predominate species. The indicator changes color when the pH is between  $\text{p}K_a - 1$  and  $\text{p}K_a + 1$ .

and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining an inaccurate result, and the range of possible end point volumes increases the probability of obtaining imprecise results.

### Practice Exercise 9.5

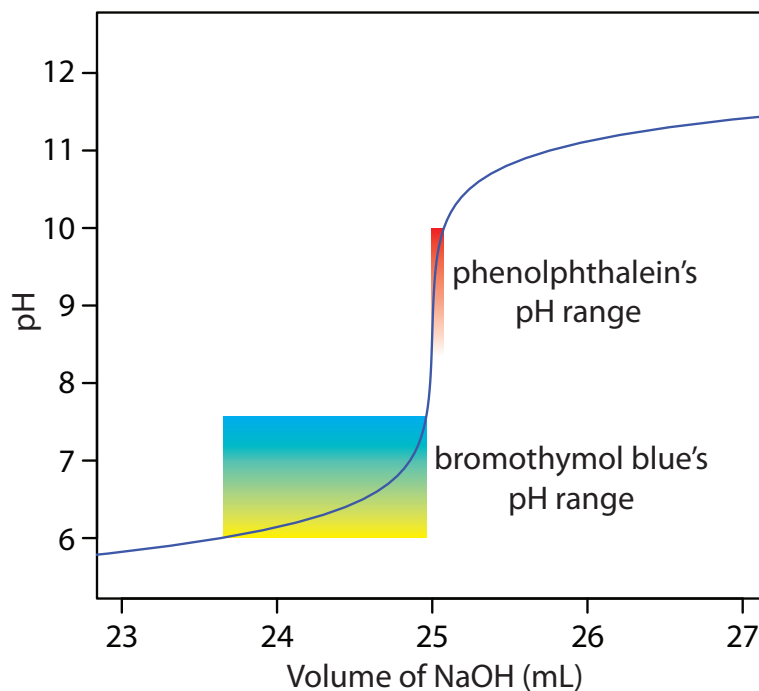
Suggest a suitable indicator for the titration of 25.0 mL of 0.125 M  $\text{NH}_3$  with 0.0625 M NaOH. You constructed a titration curve for this titration in [Practice Exercise 9.2](#) and [Practice Exercise 9.3](#).

Click [here](#) to review your answer to this exercise.

**Table 9.4** Properties of Selected Acid–Base Indicators

Indicator	Acid Color	Base Color	pH Range	$\text{p}K_a$
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  $\text{p}K_a$  value. The explanation is simple. Figure 9.12 presents an idealized view 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.



**Figure 9.13** Portion of the titration curve for 50.0 mL of 0.050 M  $\text{CH}_3\text{COOH}$  with 0.10 M NaOH, highlighting the region that contains 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

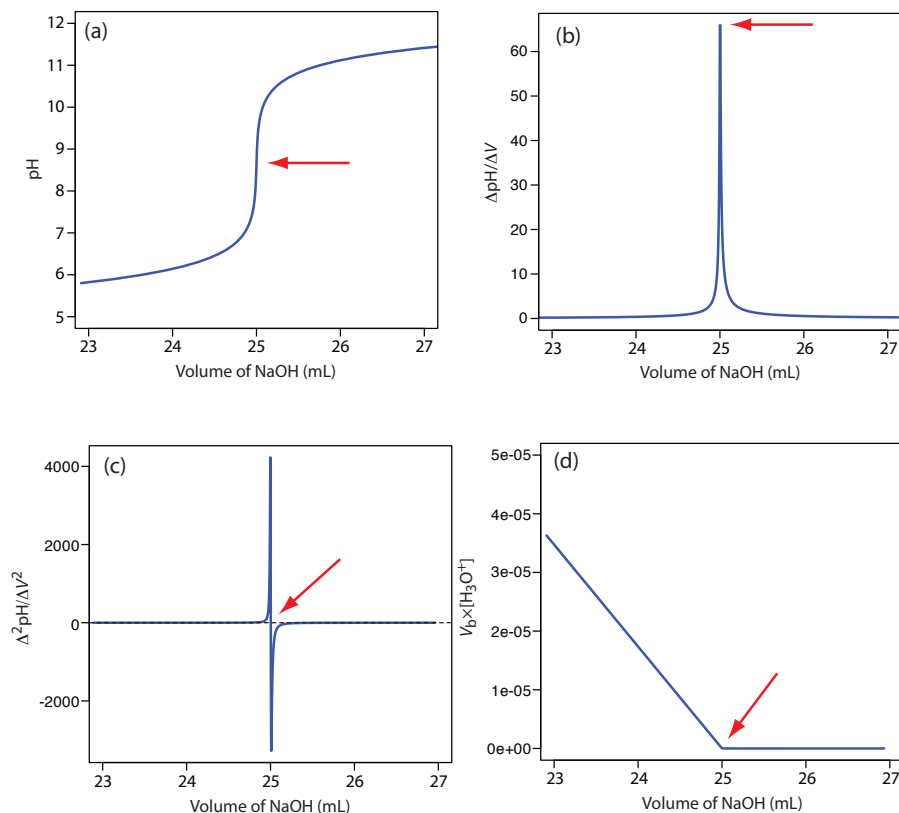
An alternative approach for locating a titration's end point is to monitor the titration's progress using a sensor whose signal is a function of the analyte's concentration. The result is a plot of the entire titration curve, which we can use to locate the end point with a minimal error.

A pH electrode is the obvious sensor for monitoring an acid–base titration 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  $\text{CH}_3\text{COOH}$  with 0.10 M NaOH, which focuses on the region that contains the equivalence point. The simplest method for finding the end point is to locate the titration curve's inflection point, which is shown by the arrow. This is also the least accurate method, particularly if the titration curve has a shallow slope at the equivalence point.

Another method for locating the end point is to plot the first derivative of the titration curve, which gives its 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 can 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

See Chapter 11 for more details about pH electrodes.

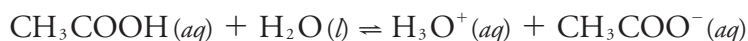


**Figure 9.14** Titration curves for the titration of 50.0 mL of 0.050 M  $\text{CH}_3\text{COOH}$  with 0.10 M NaOH: (a) normal titration curve; (b) first derivative titration curve; (c) second derivative titration curve; (d) Gran plot. The red arrows show the location of each titration's end point.

so that we can see the change in color for each end point. 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 that has 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 usually is not a problem if we use an automatic titrator, such as the one seen earlier in [Figure 9.5](#). Because the pH changes so rapidly near the equivalence point—a change of several pH units over a span 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,  $\text{CH}_3\text{COOH}$ , with NaOH. At any point during the titration acetic acid is in equilibrium with  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{COO}^-$



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  $\Delta\text{pH}/\Delta V$ , where  $\Delta\text{pH}$  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)	$\Delta\text{pH}/\Delta V$
23.78	0.385
24.02	0.455

We can approximate the second derivative as  $\Delta(\Delta\text{pH}/\Delta V)/\Delta V$ , or  $\Delta^2\text{pH}/\Delta V^2$ . Using the two points from our calculation of the first derivative, the second derivative is

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

which we assign to the average of the two volumes, or 23.90 mL.

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.

for which the equilibrium constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Before the equivalence point the concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are

$$\begin{aligned} [\text{CH}_3\text{COOH}] &= \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}} - (\text{mol NaOH})_{\text{added}}}{\text{total volume}} \\ &= \frac{M_a V_a - M_b V_b}{V_a + V_b} \end{aligned}$$

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+](M_b V_b) / (V_a + V_b)}{\{M_a V_a - M_b V_b\} / (V_a + V_b)}$$

$$K_a M_a V_a - K_a M_b V_b = [\text{H}_3\text{O}^+](M_b V_b)$$

$$\frac{K_a M_a V_a}{M_b} - K_a V_b = [\text{H}_3\text{O}^+] V_b$$

Finally, recognizing that the equivalence point volume is

$$V_{eq} = \frac{M_a V_a}{M_b}$$

leaves us with the following equation.

$$[\text{H}_3\text{O}^+] \times V_b = K_a V_{eq} - K_a V_b$$

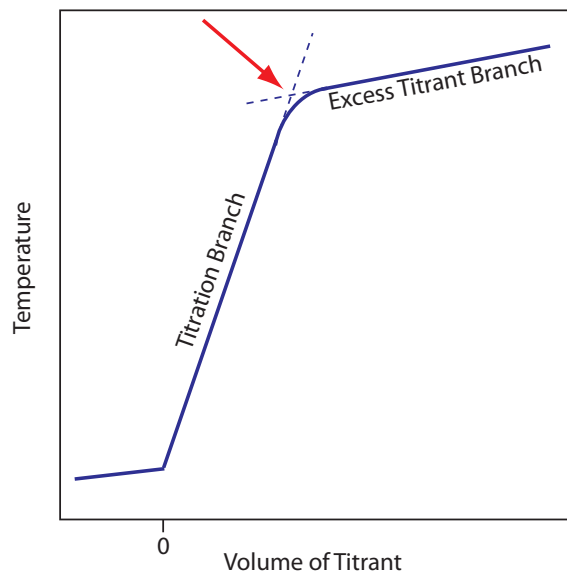
For volumes of titrant before the equivalence point, a plot of  $V_b \times [\text{H}_3\text{O}^+]$  versus  $V_b$  is a straight-line with an  $x$ -intercept of  $V_{eq}$  and a slope of  $-K_a$ . [Figure 9.14d](#) shows a typical result. This method of data analysis, which converts a portion of a titration 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, which increases 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 we add the 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 and increases the titrand's temperature. This part of a thermometric titration curve is called the titration 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,

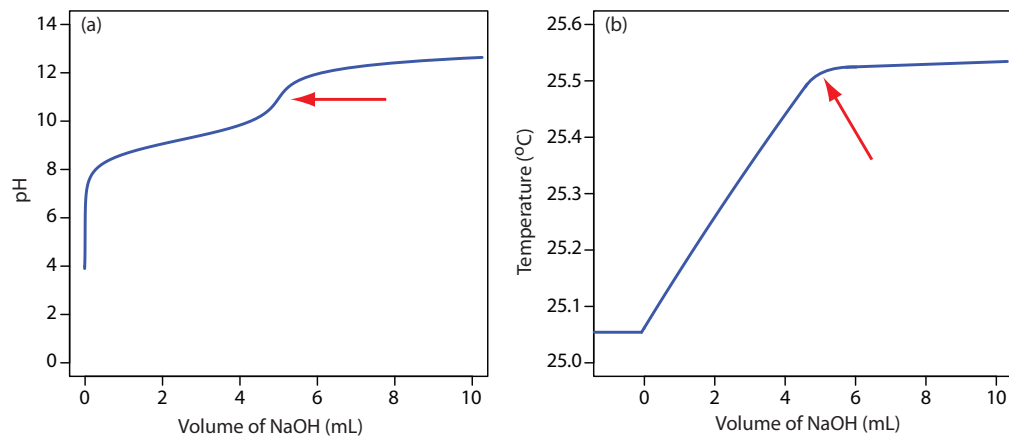
Values of  $K_a$  determined by this method may have a substantial error if the effect of activity is ignored. See Chapter 6I for a discussion of activity.



**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.

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 common method for monitoring an acid–base titration, 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,  $\text{H}_3\text{BO}_3$ , with  $\text{NaOH}$  does not provide a sharp end point when monitoring pH because boric acid's  $K_a$  of  $5.8 \times 10^{-10}$  is too small (Figure 9.16a). Because boric acid's enthalpy of neutralization is fairly large,  $-42.7$  kJ/mole, its thermometric titration curve provides a useful endpoint (Figure 9.16b).



**Figure 9.16** Titration curves for the titration of 50.0 mL of 0.050 M  $\text{H}_3\text{BO}_3$  with 0.50 M  $\text{NaOH}$  obtained by monitoring (a) pH and (b) temperature. The red arrows show the end points for the titrations.

### 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 for 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,  $\text{SH}_2^+$ , to its deprotonated form,  $\text{S}^-$



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

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  $1.0 \times 10^{-4}$  M HCl using  $1.0 \times 10^{-4}$  M NaOH as the titrant. 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  $\text{H}_3\text{O}^+$  is

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{M_a V_a - M_b V_b}{V_a + V_b} \\ &= \frac{(1.0 \times 10^{-4} \text{ M})(50.0 \text{ mL}) - (1.0 \times 10^{-4} \text{ M})(45.0 \text{ mL})}{50.0 \text{ mL} + 45.0 \text{ mL}} \\ &= 5.3 \times 10^{-6} \text{ M} \end{aligned}$$

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

$$\begin{aligned} [\text{OH}^-] &= \frac{M_b V_b - M_a V_a}{V_a + V_b} \\ &= \frac{(1.0 \times 10^{-4} \text{ M})(55.0 \text{ mL}) - (1.0 \times 10^{-4} \text{ M})(50.0 \text{ mL})}{55.0 \text{ mL} + 50.0 \text{ mL}} \\ &= 4.8 \times 10^{-6} \text{ M} \end{aligned}$$

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

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.0 - 5.3 = 8.7$$

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

$$\Delta\text{pH} = 8.7 - 5.3 = 3.4$$

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

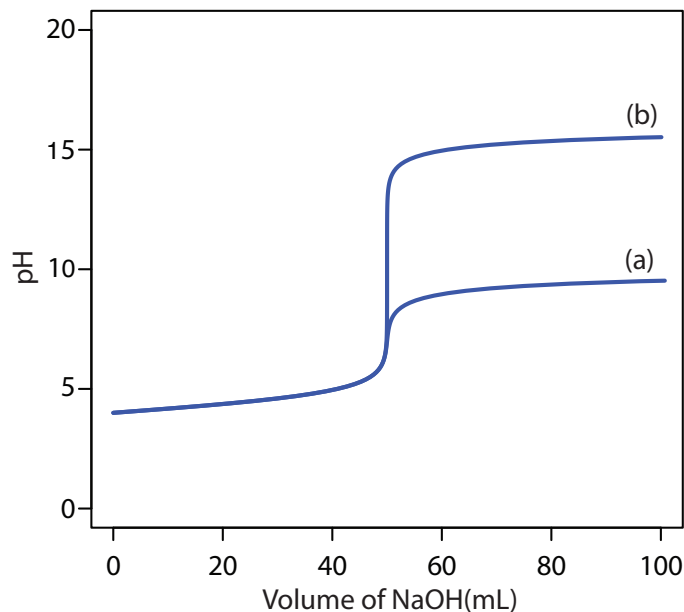
$$\text{pH} = \text{p}K_s - \text{pOH} = 20.0 - 5.3 = 14.7$$

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

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

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





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

In this case the change in pH

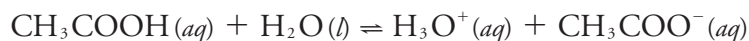
$$\Delta\text{pH} = 14.7 - 5.3 = 9.4$$

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.

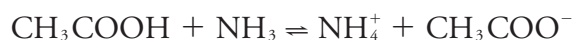
Another parameter that affects the feasibility of an acid–base titration is the titrand’s dissociation constant. Here, too, the solvent plays an important role. The strength of an acid or a base is a relative measure of how easy it is to transfer a proton from the acid to the solvent or from the solvent to the base. For example, HF, with a  $K_a$  of  $6.8 \times 10^{-4}$ , is a better proton donor than  $\text{CH}_3\text{COOH}$ , for which  $K_a$  is  $1.75 \times 10^{-5}$ .

The strongest acid that can exist in water is the hydronium ion,  $\text{H}_3\text{O}^+$ . HCl and  $\text{HNO}_3$  are strong acids because they are better proton donors than  $\text{H}_3\text{O}^+$  and essentially donate all their protons to  $\text{H}_2\text{O}$ , **LEVELING** their acid strength to that of  $\text{H}_3\text{O}^+$ . In a different solvent HCl and  $\text{HNO}_3$  may not behave as strong acids.

If we place acetic acid in water the dissociation reaction



does not proceed to a significant extent because  $\text{CH}_3\text{COO}^-$  is a stronger base than  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  is a stronger acid than  $\text{CH}_3\text{COOH}$ . If we place acetic acid in a solvent that is a stronger base than water, such as ammonia, then the reaction



proceeds to a greater extent. In fact, both HCl and  $\text{CH}_3\text{COOH}$  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  $\text{NH}_3$  is 4.75 in water and it is 6.40 in the more acidic glacial acetic acid. In contradiction to our expectations,  $\text{NH}_3$  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 the 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*

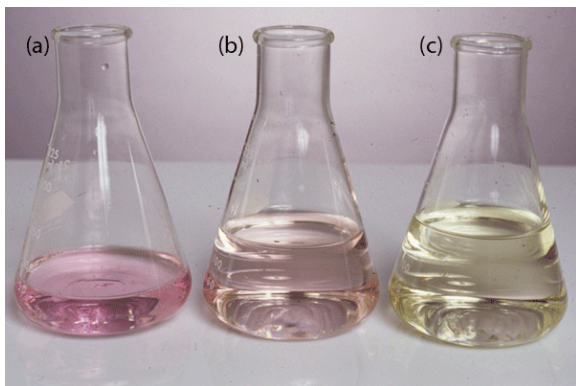
This method is based on a determination of %w/w nitrogen using the Kjeldahl method. The protein in a sample of bread is oxidized to  $\text{NH}_4^+$  using hot concentrated  $\text{H}_2\text{SO}_4$ . After making the solution alkaline, which converts  $\text{NH}_4^+$  to  $\text{NH}_3$ , the ammonia is distilled into a flask that contains a known amount of HCl. The amount of unreacted HCl is determined by a back titration using a standard strong base titrant. Because different cereal proteins contain similar amounts of nitrogen—on average there are 5.7 g protein for every gram of nitrogen—we multiply the experimentally determined %w/w N by a factor of 5.7 gives the %w/w protein in the sample.

#### *PROCEDURE*

Transfer a 2.0-g sample of bread, which previously has 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  $\text{K}_2\text{SO}_4$ , and 25 mL of concentrated  $\text{H}_2\text{SO}_4$ . 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  $\text{Hg}^{2+}$  catalyst by adding 200 mL of  $\text{H}_2\text{O}$  and 25 mL of 4% w/v  $\text{K}_2\text{S}$ . 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  $\text{NH}_3$  into a collecting flask that contains 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  $\text{NH}_4^+$ . Why is the amount of nitrogen not determined by directly titrating the  $\text{NH}_4^+$  with a strong base?



**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.

There are two reasons for not directly titrating the ammonium ion. First, because  $\text{NH}_4^+$  is a very weak acid (its  $K_a$  is  $5.6 \times 10^{-10}$ ), its titration with NaOH has a poorly-defined end point. Second, even if we can determine the end point with acceptable accuracy and precision, the solution also contains a substantial concentration of unreacted  $\text{H}_2\text{SO}_4$ . 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  $\text{H}_2\text{SO}_4$ , then the equivalence point volume for the titration of  $\text{NH}_4^+$  is too small to measure reliably. On the other hand, if the titrant's concentration is similar to that of  $\text{NH}_4^+$ , the volume needed to neutralize the  $\text{H}_2\text{SO}_4$  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  $\text{NH}_3$  is loss of nitrogen and, therefore, a loss of protein. The result is a negative determinate error.

3. Identify the steps in this procedure that minimize the determinate error from the possible loss of  $\text{NH}_3$ .

Three specific steps minimize the loss of ammonia: (1) the solution is cooled below room temperature before we add NaOH; (2) after we add NaOH, the digestion flask is quickly connected to the distillation apparatus; and (3) we place the condenser's tip below the surface of the HCl to ensure that the  $\text{NH}_3$  reacts with the HCl before it is lost through volatilization.

4. How does  $\text{K}_2\text{S}$  remove  $\text{Hg}^{2+}$ , and why is its removal important?

Adding sulfide precipitates  $\text{Hg}^{2+}$  as  $\text{HgS}$ . This is important because  $\text{NH}_3$  forms stable complexes with many metal ions, including  $\text{Hg}^{2+}$ . Any  $\text{NH}_3$  that reacts with  $\text{Hg}^{2+}$  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 find use. 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

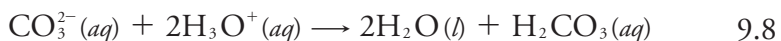
The most common strong acid titrants are HCl, HClO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>. Solutions of these titrants usually are prepared by diluting a commercially available concentrated stock solution. Because the concentration of a concentrated acid is known only approximately, the titrant's concentration is determined by standardizing against one of the primary standard weak bases listed in [Table 9.5](#).

The most common strong base titrant is NaOH, which is available both as an impure solid and as an approximately 50% w/v solution. Solutions of NaOH are 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 dissolved CO<sub>2</sub> and OH<sup>−</sup>.



During the titration, NaOH reacts both with the titrand and with CO<sub>2</sub>, which increases the volume of NaOH needed to reach the titration's end point. This is not a problem if the end point pH is less than 6. Below this pH the CO<sub>3</sub><sup>2−</sup> from reaction 9.7 reacts with H<sub>3</sub>O<sup>+</sup> to form carbonic acid.

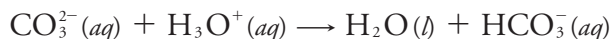


Combining reaction 9.7 and reaction 9.8 gives an overall reaction that does not include OH<sup>−</sup>.

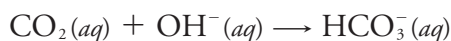


Under these conditions the presence of CO<sub>2</sub> does not affect the quantity of OH<sup>−</sup> used in the titration and is not a source of determinate error.

If the end point pH is between 6 and 10, however, the neutralization of CO<sub>3</sub><sup>2−</sup> requires one proton



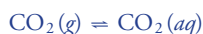
and the net reaction between CO<sub>2</sub> and OH<sup>−</sup> is



Under these conditions some OH<sup>−</sup> is consumed in neutralizing CO<sub>2</sub>, which results in a determinate error. We can avoid the determinate error if we use

The nominal concentrations of the concentrated stock solutions are 12.1 M HCl, 11.7 M HClO<sub>4</sub>, and 18.0 M H<sub>2</sub>SO<sub>4</sub>. The actual concentrations of these acids are given as %w/v and vary slightly from lot-to-lot.

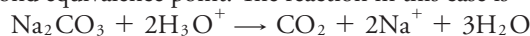
Any solution in contact with the atmosphere contains a small amount of CO<sub>2</sub>(aq) from the equilibrium



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

Standardization of Acidic Titrants		
Primary Standard	Titration Reaction	Comment
$\text{Na}_2\text{CO}_3$	$\text{Na}_2\text{CO}_3 + 2\text{H}_3\text{O}^+ \longrightarrow \text{H}_2\text{CO}_3 + 2\text{Na}^+ + 2\text{H}_2\text{O}$	a
$(\text{HOCH}_2)_3\text{CNH}_2$	$(\text{HOCH}_2)_3\text{CNH}_2 + \text{H}_3\text{O}^+ \longrightarrow (\text{HOCH}_2)_3\text{CNH}_3^+ + \text{H}_2\text{O}$	b
$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} \longrightarrow 2\text{Na}^+ + 4\text{H}_3\text{BO}_3$	
Standardization of Basic Titrants		
Primary Standard	Titration Reaction	Comment
$\text{KHC}_8\text{H}_4\text{O}_4$	$\text{KHC}_8\text{H}_4\text{O}_4 + \text{OH}^- \longrightarrow \text{K}^+ + \text{C}_8\text{H}_4\text{O}_4^- + \text{H}_2\text{O}$	c
$\text{C}_6\text{H}_5\text{COOH}$	$\text{C}_6\text{H}_5\text{COOH} + \text{OH}^- \longrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O}$	d
$\text{KH}(\text{IO}_3)_2$	$\text{KH}(\text{IO}_3)_2 + \text{OH}^- \longrightarrow \text{K}^+ + 2\text{IO}_3^- + \text{H}_2\text{O}$	

<sup>a</sup> The end point for this titration is improved by titrating to the second equivalence point, boiling the solution to expel  $\text{CO}_2$ , and retitrating to the second equivalence point. The reaction in this case is



<sup>b</sup> *Tris*-(hydroxymethyl)aminomethane often goes by the shorter name of TRIS or THAM.

<sup>c</sup> Potassium hydrogen phthalate often goes by the shorter name of KHP.

<sup>d</sup> Because it is not very soluble in water, dissolve benzoic acid in a small amount of ethanol before diluting with water.

the same end point pH for both the standardization of NaOH and the analysis of our analyte, although this is not always practical.

Solid NaOH is always contaminated with carbonate due to its contact with the atmosphere, and we cannot use it to prepare a carbonate-free solution of NaOH. Solutions of carbonate-free NaOH are prepared from 50% w/v NaOH because  $\text{Na}_2\text{CO}_3$  is insoluble in concentrated NaOH. When  $\text{CO}_2$  is absorbed,  $\text{Na}_2\text{CO}_3$  precipitates and settles to the bottom of the container, which allow access to the carbonate-free NaOH. When preparing a solution of NaOH, be sure to use water that is free from dissolved  $\text{CO}_2$ . Briefly boiling the water expels  $\text{CO}_2$ ; after it cools, the water is used to prepare carbonate-free solutions of NaOH. A solution of carbonate-free NaOH is relatively stable if we limit its contact with the atmosphere. Standard solutions of sodium hydroxide are not stored in glass bottles as NaOH reacts with glass to form silicate; instead, store such solutions in polyethylene bottles.

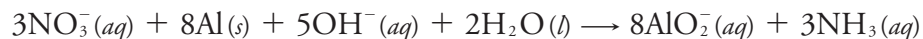
## INORGANIC ANALYSIS

Acid–base titrimetry is a standard method for the quantitative analysis of many inorganic acids and bases. A standard solution of NaOH is used to determine the concentration of inorganic acids, such as  $\text{H}_3\text{PO}_4$  or  $\text{H}_3\text{AsO}_4$ , and inorganic bases, such as  $\text{Na}_2\text{CO}_3$  are analyzed using a standard solution of HCl.

Figure 9.16a shows a typical result for the titration of  $\text{H}_3\text{BO}_3$  with  $\text{NaOH}$ .

If an inorganic acid or base that is too weak to be analyzed by an aqueous acid–base titration, it may be possible to complete the analysis by adjusting the solvent or by an indirect analysis. For example, when analyzing boric acid,  $\text{H}_3\text{BO}_3$ , by titrating with  $\text{NaOH}$ , accuracy is limited by boric acid's small acid dissociation constant of  $5.8 \times 10^{-10}$ . Boric acid's  $K_a$  value increases to  $1.5 \times 10^{-4}$  in the presence of mannitol, because it forms a stable complex with the borate ion, which results in a sharper end point and a more accurate titration. Similarly, the analysis of ammonium salts is limited by the ammonium ion's small acid dissociation constant of  $5.7 \times 10^{-10}$ . We can determine  $\text{NH}_4^+$  indirectly by using a strong base to convert it to  $\text{NH}_3$ , which is removed by distillation and titrated with  $\text{HCl}$ . Because  $\text{NH}_3$  is a stronger weak base than  $\text{NH}_4^+$  is a weak acid (its  $K_b$  is  $1.58 \times 10^{-5}$ ), the titration has a sharper end point.

We can analyze a neutral inorganic analyte if we can first convert it into an acid or a base. For example, we can determine the concentration of  $\text{NO}_3^-$  by reducing it to  $\text{NH}_3$  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.



The  $\text{NH}_3$  is removed by distillation and titrated with  $\text{HCl}$ . Alternatively, we can titrate  $\text{NO}_3^-$  as a weak base by placing it in an acidic nonaqueous solvent, such as anhydrous acetic acid, and using  $\text{HClO}_4$  as a titrant.

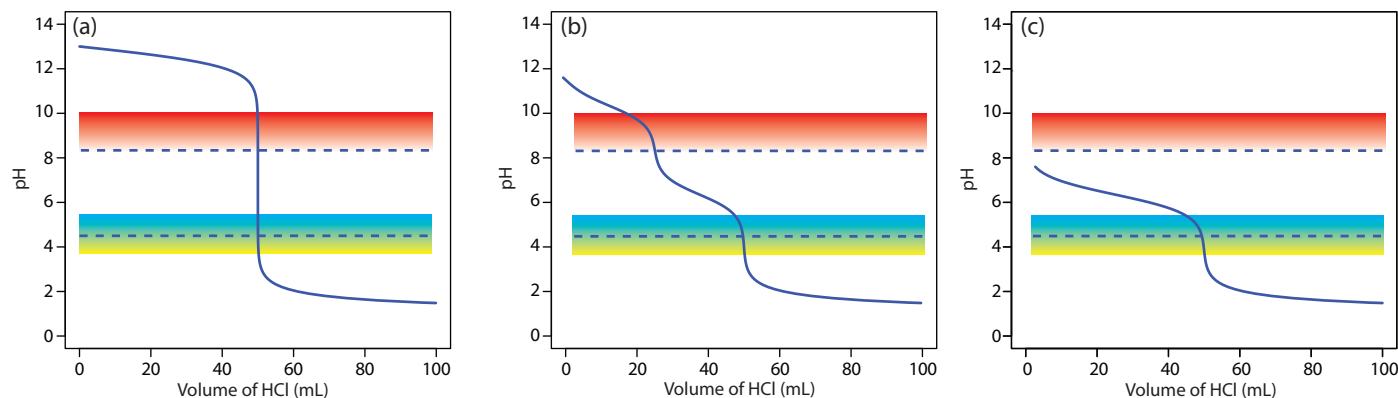
Acid–base titrimetry continues to be listed as a standard method for the determination of alkalinity, acidity, and free  $\text{CO}_2$  in waters and wastewaters. **ALKALINITY** is a measure of a sample's capacity to neutralize acids. The most important sources of alkalinity are  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , 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  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . Results are reported as mg  $\text{CaCO}_3/\text{L}$ .

When the sources of alkalinity are limited to  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , 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  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  are shown in Figure 9.19. For a solution that contains  $\text{OH}^-$  alkalinity only, the volume of strong acid needed to reach each of the two end points is identical (Figure 9.19a). When the only source of alkalinity is  $\text{CO}_3^{2-}$ , 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  $\text{HCO}_3^-$  alkalinity only, 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).

A mixture of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  or a mixture of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  also is possible. Consider, for example, a mixture of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . The volume of strong acid to titrate  $\text{OH}^-$  is the same whether we titrate to a pH of 8.3

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  $\text{CaCO}_3$  is the only source provides a means for comparing the acid-neutralizing capacities of different samples.

A mixture of  $\text{OH}^-$  and  $\text{HCO}_3^-$  is unstable with respect to the formation of  $\text{CO}_3^{2-}$ . Problem 9.15 in the end chapter problems asks you to explain why this is true.



**Figure 9.19** Titration curves for 50.0 mL of (a) 0.10 M NaOH, (b) 0.050 M  $\text{Na}_2\text{CO}_3$ , and (c) 0.10 M  $\text{NaHCO}_3$  using 0.10 M HCl as a titrant. The dashed lines indicate the fixed pH end points of 8.3 and 4.5. The color gradients show the phenolphthalein (red  $\rightarrow$  colorless) and the bromocresol green (blue  $\rightarrow$  green) endpoints. When titrating to the phenolphthalein endpoint, the titration continues until the last trace of red is lost.

or a pH of 4.5. Titrating  $\text{CO}_3^{2-}$  to a pH of 4.5, however, requires twice as much strong acid as titrating to a pH of 8.3. Consequently, when we titrate a mixture of these two ions, the volume of strong acid needed to reach a pH of 4.5 is less than twice that needed to reach a pH of 8.3. For a mixture of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  the volume of strong acid needed to reach a pH of 4.5 is more than twice that needed 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 to neutralize base and is divided into strong acid and weak acid acidity. Strong acid acidity from inorganic acids such as HCl,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  is common in industrial effluents and in acid mine drainage. Weak acid acidity usually is dominated by the formation of  $\text{H}_2\text{CO}_3$  from dissolved  $\text{CO}_2$ , but also includes contributions from hydrolyzable metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Mn}^{2+}$ . In addition, weak acid acidity may include a contribution from organic acids.

Acidity is determined by titrating with a standard solution of NaOH to a fixed pH of 3.7 (or the bromothymol blue end point) and to a fixed pH of 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

**Table 9.6** Relationship Between End Point Volumes and Sources of Alkalinity

Source of Alkalinity	Relationship Between End Point Volumes
$\text{OH}^-$	$V_{\text{pH } 4.5} = V_{\text{pH } 8.3}$
$\text{CO}_3^{2-}$	$V_{\text{pH } 4.5} = 2 \times V_{\text{pH } 8.3}$
$\text{HCO}_3^-$	$V_{\text{pH } 4.5} > 0; V_{\text{pH } 8.3} = 0$
$\text{OH}^-$ and $\text{CO}_3^{2-}$	$V_{\text{pH } 4.5} < 2 \times V_{\text{pH } 8.3}$
$\text{CO}_3^{2-}$ and $\text{HCO}_3^-$	$V_{\text{pH } 4.5} > 2 \times V_{\text{pH } 8.3}$

As is the case with alkalinity, acidity is reported as mg CaCO<sub>3</sub>/L.

Free CO<sub>2</sub> is the same thing as CO<sub>2</sub>(aq).

a measure of total acidity. Weak acid acidity is the difference between the total acidity and the strong acid acidity. Results are expressed as the amount of CaCO<sub>3</sub> 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.<sup>4</sup>

Water in contact with either the atmosphere or with carbonate-bearing sediments contains free CO<sub>2</sub> in equilibrium with CO<sub>2</sub>(g) and with aqueous H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The concentration of free CO<sub>2</sub> 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<sub>2</sub>/L. This analysis essentially is the same as that for the determination of total acidity and is used only for water samples that do not contain strong acid acidity.

### 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 oxidized quantitatively to NH<sub>4</sub><sup>+</sup>. 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 as nitro and azo nitrogens, are oxidized to N<sub>2</sub>, which results 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 converted quantitatively into a titratable acid or base.

<sup>4</sup> 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 <sup>a</sup>	Titration Details
N	NH <sub>3</sub> (g)	NH <sub>3</sub> (aq) + <b>HCl</b> (aq) → NH <sub>4</sub> <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)	add HCl in excess and back titrate with NaOH
S	SO <sub>2</sub> (g)	SO <sub>2</sub> (g) + H <sub>2</sub> O <sub>2</sub> (aq) → <b>H<sub>2</sub>SO<sub>4</sub></b> (aq)	titrate H <sub>2</sub> SO <sub>4</sub> with NaOH
C	CO <sub>2</sub> (g)	CO <sub>2</sub> (g) + <b>Ba(OH)<sub>2</sub></b> (aq) → BaCO <sub>3</sub> (s) + H <sub>2</sub> O(l)	add excess Ba(OH) <sub>2</sub> and back titrate with HCl
Cl	<b>HCl</b> (g)	—	titrate HCl with NaOH
F	SiF <sub>4</sub> (g)	3SiF <sub>4</sub> (aq) + 2H <sub>2</sub> O(l) → <b>2H<sub>2</sub>SiF<sub>6</sub></b> (aq) + SiO <sub>2</sub> (s)	titrate H <sub>2</sub> SiF <sub>4</sub> with NaOH

<sup>a</sup> The species that is titrated is shown in **bold**.



**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 <sup>a</sup>	Titration Details
ester	$\text{RCOOR}'(aq) + \mathbf{OH}^-(aq) \rightarrow \text{RCOO}^-(aq) + \text{HOR}'(aq)$	titrate $\text{OH}^-$ with HCl
carbonyl	$\text{R}_2\text{CO}(aq) + \text{NH}_2\text{OH} \cdot \text{HCl}(aq) \rightarrow \text{R}_2\text{CNOH}(aq) + \mathbf{HCl}(aq) + \text{H}_2\text{O}(l)$	titrate HCl with NaOH
alcohol <sup>b</sup>	[1] $(\text{CH}_3\text{CO})_2\text{O} + \text{ROH} \rightarrow \text{CH}_3\text{COOR} + \mathbf{CH}_3\text{COOH}$ [2] $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \rightarrow 2\mathbf{CH}_3\text{COOH}$	titrate $\text{CH}_3\text{COOH}$ with NaOH; a blank titration of acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$ , corrects for the contribution of reaction [2]

<sup>a</sup> The species that is titrated is shown in **bold**.

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

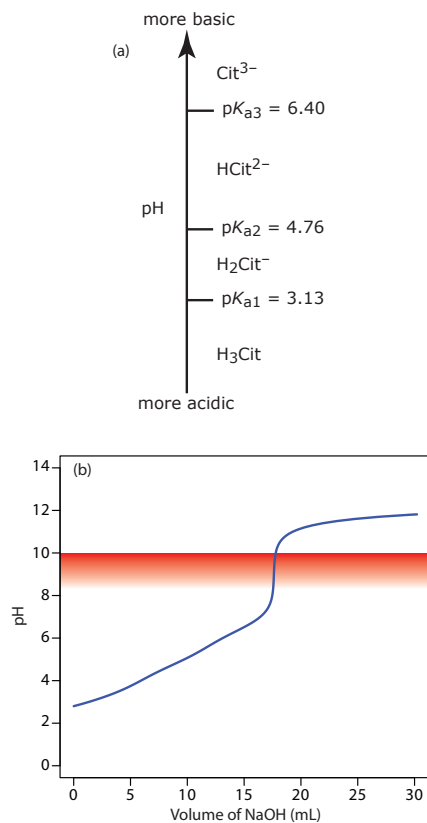
Several organic functional groups are weak acids or weak bases. Carboxylic ( $-\text{COOH}$ ), sulfonic ( $-\text{SO}_3\text{H}$ ) and phenolic ( $-\text{C}_6\text{H}_5\text{OH}$ ) functional groups are weak acids that are titrated successfully in either aqueous or non-aqueous solvents. Sodium hydroxide is the titrant of choice for aqueous solutions. Nonaqueous titrations often are carried out in a basic solvent, such as ethylenediamine, using tetrabutylammonium hydroxide,  $(\text{C}_4\text{H}_9)_4\text{NOH}$ , as the titrant. Aliphatic and aromatic amines are weak bases that are titrated using HCl in aqueous solutions, or  $\text{HClO}_4$  in glacial acetic acid. Other functional groups are 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 weak bases that are analyzed by an aqueous or a nonaqueous acid–base titration; examples include salicylic acid, phenobarbital, caffeine, and sulfanilamide. Amino acids and proteins are analyzed in glacial acetic acid using  $\text{HClO}_4$  as the titrant. For example, a procedure for determining the amount of nutritionally available protein uses an acid–base titration of lysine residues.<sup>5</sup>

### QUANTITATIVE CALCULATIONS

The quantitative relationship between the titrand and the titrant is determined by the titration reaction's stoichiometry. 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.



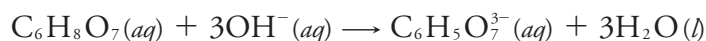
**Figure 9.20** (a) Ladder diagram for citric acid; (b) Titration curve for the sample in Example 9.2 showing phenolphthalein's pH transition region.

### 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<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, per 100 mL.

#### SOLUTION

Because citric acid is a triprotic weak acid, we first must 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 must proceed to the third equivalence point and the titration reaction is



To reach the equivalence point, each mole of citric acid consumes three moles of NaOH; thus

$$(0.04166 \text{ M NaOH})(0.01762 \text{ L NaOH}) = 7.3405 \times 10^{-4} \text{ mol NaOH}$$

$$7.3405 \times 10^{-4} \text{ mol NaOH} \times \frac{1 \text{ mol C}_6\text{H}_8\text{O}_7}{3 \text{ mol NaOH}} = 2.4468 \times 10^{-4} \text{ mol C}_6\text{H}_8\text{O}_7$$

$$2.4468 \times 10^{-4} \text{ mol C}_6\text{H}_8\text{O}_7 \times \frac{192.1 \text{ g C}_6\text{H}_8\text{O}_7}{\text{mol C}_6\text{H}_8\text{O}_7} = 0.04700 \text{ g C}_6\text{H}_8\text{O}_7$$

Because this is the amount of citric acid in a 50.00 mL sample, the concentration of citric acid in the citrus drink is 0.09400 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<sub>7</sub>H<sub>6</sub>O<sub>3</sub>, for use in the production of acetylsalicylic acid (aspirin). You can accept the shipment only if the salicylic acid is more than 99% pure. To evaluate the shipment's purity, you dissolve a 0.4208-g sample in water and titrate to the phenolphthalein end point, using 21.92 mL of 0.1354 M NaOH. Report the shipment's purity as %w/w C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>. Salicylic acid is a diprotic weak acid with pK<sub>a</sub> values of 2.97 and 13.74.

Click [here](#) to review your answer to this exercise.

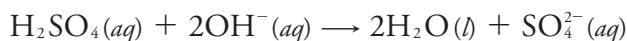
In an indirect analysis the analyte participates in one or more preliminary reactions, one of which produces or consumes acid or base. Despite the additional complexity, the calculations are straightforward.

### Example 9.3

The purity of a pharmaceutical preparation of sulfanilamide,  $\text{C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$ , is determined by oxidizing the sulfur to  $\text{SO}_2$  and bubbling it through  $\text{H}_2\text{O}_2$  to produce  $\text{H}_2\text{SO}_4$ . The acid is titrated to the bromothymol blue end point using a standard solution of  $\text{NaOH}$ . Calculate the purity of the preparation given that a 0.5136-g sample requires 48.13 mL of 0.1251 M  $\text{NaOH}$ .

#### SOLUTION

The bromothymol blue end point has a pH range of 6.0–7.6. Sulfuric acid is a diprotic acid, with a  $\text{p}K_{\text{a}2}$  of 1.99 (the first  $K_{\text{a}}$  value is very large and the acid dissociation reaction goes to completion, which is why  $\text{H}_2\text{SO}_4$  is a strong acid). The titration, therefore, proceeds to the second equivalence point and the titration reaction is



Using the titration results, there are

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

$$6.012 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 3.010 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

produced when the  $\text{SO}_2$  is bubbled through  $\text{H}_2\text{O}_2$ . Because all the sulfur in  $\text{H}_2\text{SO}_4$  comes from the sulfanilamide, we can use a conservation of mass to determine the amount of sulfanilamide in the sample.

$$3.010 \times 10^{-3} \text{ mol H}_2\text{SO}_4 \times \frac{1 \text{ mol S}}{\text{mol H}_2\text{SO}_4} \times \frac{1 \text{ mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol S}} \times \frac{168.17 \text{ g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}} = 0.5062 \text{ g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$$

$$\frac{0.5062 \text{ g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{0.5136 \text{ g sample}} \times 100 = 98.56\% \text{ w/w C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$$

### Practice Exercise 9.7

The concentration of  $\text{NO}_2$  in air is determined by passing the sample through a solution of  $\text{H}_2\text{O}_2$ , which oxidizes  $\text{NO}_2$  to  $\text{HNO}_3$ , and titrating the  $\text{HNO}_3$  with  $\text{NaOH}$ . What is the concentration of  $\text{NO}_2$ , in mg/L, if a 5.0 L sample of air requires 9.14 mL of 0.01012 M  $\text{NaOH}$  to reach the methyl red end point

Click [here](#) to review your answer to this exercise.

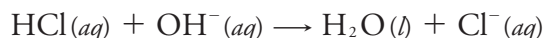
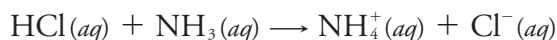
For a back titration we must consider two acid–base reactions. Again, the calculations are straightforward.

### 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  $\text{NH}_4^+$ , converted to  $\text{NH}_3$  with NaOH, and the  $\text{NH}_3$  distilled into a collection flask that contains 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 there are 6.38 grams of protein for every gram of nitrogen in most dairy products.

#### SOLUTION

The HCl in the collection flask reacts with two bases



The collection flask originally contains

$$(0.1047 \text{ M HCl})(0.05000 \text{ L HCl}) = 5.235 \times 10^{-3} \text{ mol HCl}$$

of which

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

react with NaOH. The difference between the total moles of HCl and the moles of HCl that react with NaOH is the moles of HCl that react with  $\text{NH}_3$ .

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

Because all the nitrogen in  $\text{NH}_3$  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

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

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.

#### Practice Exercise 9.8

Limestone consists mainly of  $\text{CaCO}_3$ , 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  $\text{CO}_2$ , 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  $\text{CaCO}_3$ .

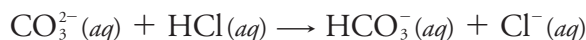
Click [here](#) to review your answer to this exercise.

### Example 9.5

The alkalinity of natural waters usually is controlled by  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , present singularly or in combination. Titrating a 100.0-mL sample to a pH of 8.3 requires 18.67 mL of 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  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . Titrating to a pH of 8.3 neutralizes  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$

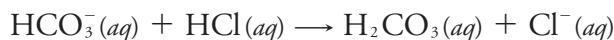


but there is no reaction between the titrant and  $\text{HCO}_3^-$  (see [Figure 9.19](#)). The concentration of  $\text{CO}_3^{2-}$  in the sample, therefore, is

$$(0.02812 \text{ M HCl})(0.01867 \text{ L HCl}) \times \frac{1 \text{ mol CO}_3^{2-}}{\text{mol HCl}} = 5.250 \times 10^{-4} \text{ mol CO}_3^{2-}$$

$$\frac{5.250 \times 10^{-4} \text{ mol CO}_3^{2-}}{0.1000 \text{ L}} \times \frac{60.01 \text{ g CO}_3^{2-}}{\text{mol CO}_3^{2-}} \times \frac{1000 \text{ mg}}{\text{g}} = 315.1 \text{ mg/L}$$

Titrating to a pH of 4.5 neutralizes  $\text{CO}_3^{2-}$  to  $\text{H}_2\text{CO}_3$  and neutralizes  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$  (see [Figure 9.19](#)).



Because we know how many moles of  $\text{CO}_3^{2-}$  are in the sample, we can calculate the volume of HCl it consumes.

$$5.250 \times 10^{-4} \text{ mol CO}_3^{2-} \times \frac{2 \text{ mol HCl}}{\text{mol CO}_3^{2-}} \times \frac{1 \text{ L HCl}}{0.02812 \text{ mol HCl}} \times \frac{1000 \text{ mL}}{\text{L}} = 37.34 \text{ mL HCl}$$

This leaves 48.12 mL–37.34 mL, or 10.78 mL of HCl to react with  $\text{HCO}_3^-$ . The amount of  $\text{HCO}_3^-$  in the sample is

$$(0.02812 \text{ M HCl})(0.01078 \text{ L HCl}) \times \frac{1 \text{ mol HCO}_3^-}{\text{mol HCl}} = 3.031 \times 10^{-4} \text{ mol HCO}_3^-$$

$$\frac{3.031 \times 10^{-4} \text{ mol HCO}_3^-}{0.1000 \text{ L}} \times \frac{61.02 \text{ g HCO}_3^-}{\text{mol HCO}_3^-} \times \frac{1000 \text{ mg}}{\text{g}} = 185.0 \text{ mg/L}$$

The sample contains 315.1 mg  $\text{CO}_3^{2-}$ /L and 185.0 mg  $\text{HCO}_3^-$ /L

### Practice Exercise 9.9

Samples that contain a mixture of 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 determine the forms of alkalinity in waters and their concentrations. We can extend this approach to other systems. For example, if we titrate a sample to the methyl orange end point and the phenolphthalein end point using either a strong acid or a strong base, we can determine which of the following species are present and their concentrations:  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ , 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. Note that mixtures containing three or more these species are not possible.

Use a ladder diagram to convince yourself that mixtures containing three or more of these species are unstable.

**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 <sup>a</sup>	Relationship Between End Point Volumes With Strong Acid Titrant <sup>a</sup>
$H_3PO_4$	$V_{PH} = 2 \times V_{MO}$	— <sup>b</sup>
$H_2PO_4^-$	$V_{PH} > 0$ ; $V_{MO} = 0$	—
$HPO_4^{2-}$	—	$V_{MO} > 0$ ; $V_{PH} = 0$
$PO_4^{3-}$	—	$V_{MO} = 2 \times V_{PH}$
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	—	$V_{MO} < 2 \times V_{PH}$

<sup>a</sup>  $V_{PH}$  and  $V_{MO}$  are, respectively, the volume of titrant at the phenolphthalein and methyl orange end points.

<sup>b</sup> When no information is provided, the volume of titrant to each end point is zero.

## 9B.6 Characterization Applications

In addition to a quantitative analysis and a qualitative analysis, we also can use an acid–base titration to characterize the chemical and physical properties of matter. Two useful characterization applications are the determination of a compound's equivalent weight and the determination of its acid dissociation constant or its base dissociation constant.

### EQUIVALENT WEIGHTS

Suppose we titrate a sample of an impure weak acid to a well-defined end point using a monoprotic strong base as the titrant. If we assume 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

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

where  $FW$  is the analyte's formula weight.

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

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

where

$$FW = n \times EW$$

### 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

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

The equivalents of weak acid are the same as the moles of NaOH used in the titration; thus, the analyte's equivalent weight is

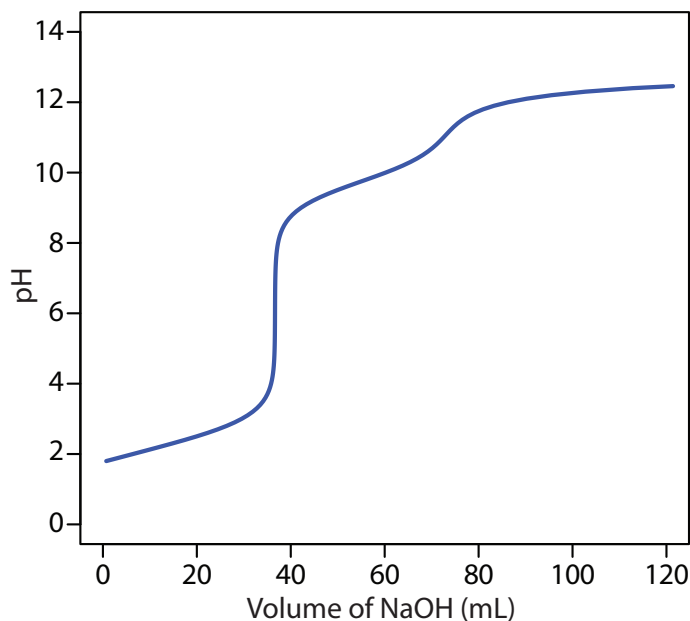
$$EW = \frac{0.2521 \text{ g}}{4.289 \times 10^{-3} \text{ equivalents}} = 58.78 \text{ g/equivalent}$$

The possible formula weights for the weak acid are 58.78 g/mol ( $n=1$ ), 117.6 g/mol ( $n=2$ ), and 176.3 g/mol ( $n=3$ ). 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 weak acid was titrated to its first or its 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**

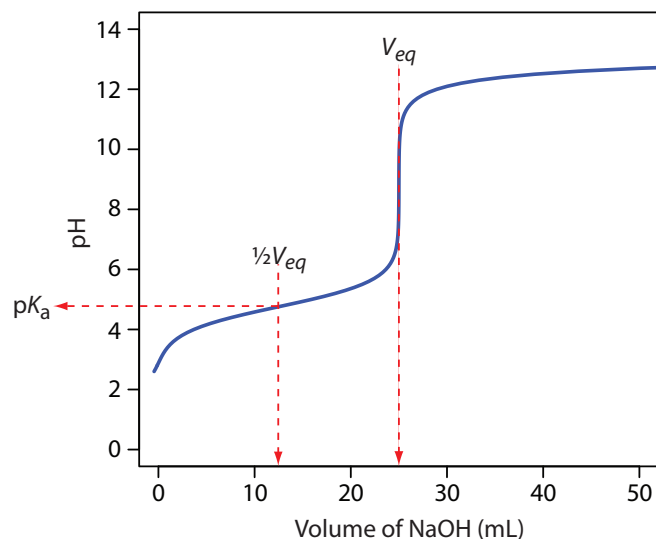
Figure 9.21 shows the potentiometric titration curve for the titration of a 0.500-g sample of an unknown weak acid. The titrant is 0.1032 M NaOH. What is the weak acid's equivalent weight?

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 a weak acid's or a weak base's dissociation constant. Consider, for example, a solution of acetic acid,  $\text{CH}_3\text{COOH}$ , for which the dissociation constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

When the concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are equal, the  $K_a$  expression reduces to  $K_a = [\text{H}_3\text{O}^+]$ , or  $\text{pH} = \text{p}K_a$ . If we titrate a solution of acetic acid with  $\text{NaOH}$ , the  $\text{pH}$  equals the  $\text{p}K_a$  when the volume of  $\text{NaOH}$  is approximately  $\frac{1}{2}V_{eq}$ . As shown in Figure 9.22, a potentiometric titration curve provides a reasonable estimate of acetic acid's  $\text{p}K_a$ .

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

Recall that  $\text{pH} = \text{p}K_a$  is a step on a ladder diagram, which divides the  $\text{pH}$  axis into two regions, one where the weak acid is the predominate species, and one where its conjugate weak base is the predominate species.

#### Practice Exercise 9.11

Use the potentiometric titration curve in [Figure 9.21](#) to estimate the  $\text{p}K_a$  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.

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

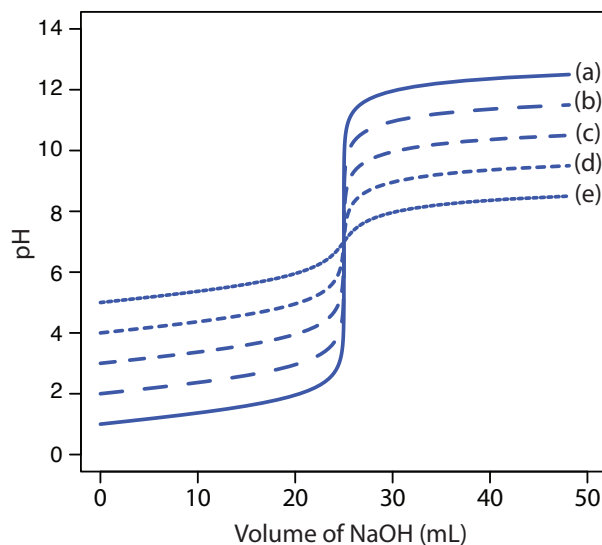
A plot of  $[H_3O^+] \times V_b$  versus  $V_b$  for volumes less than the equivalence point yields a straight line with a slope of  $-K_a$ . Other linearizations have been developed that use the entire titration curve or that require no assumptions.<sup>6</sup> This approach to determining an acidity constant 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 which were identified as carboxylic acids, two which were believed to be secondary or tertiary amines, and one which was identified as a phenolic group.<sup>7</sup>

## 9B.7 Evaluation of Acid–Base Titrimetry

### SCALE OF OPERATION

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, 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 is too small to provide an accurate and a precise result.

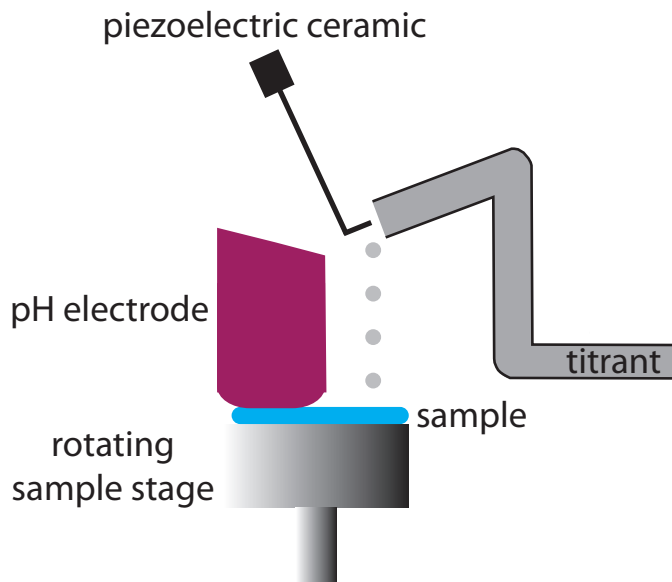
- 6 (a) Gonzalez, A. G.; Asuero, A. G. *Anal. Chim. Acta* **1992**, 256, 29–33; (b) Papanastasiou, G.; Ziogas, I.; Kokkindis, G. *Anal. Chim. Acta* **1993**, 277, 119–135.  
7 Alexio, L. M.; Godinho, O. E. S.; da Costa, W. F. *Anal. Chim. Acta* **1992**, 257, 35–39.



**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.

Values of  $K_a$  determined by this method may have a substantial error if the effect of activity is ignored. See Chapter 6I for a discussion of activity.

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.



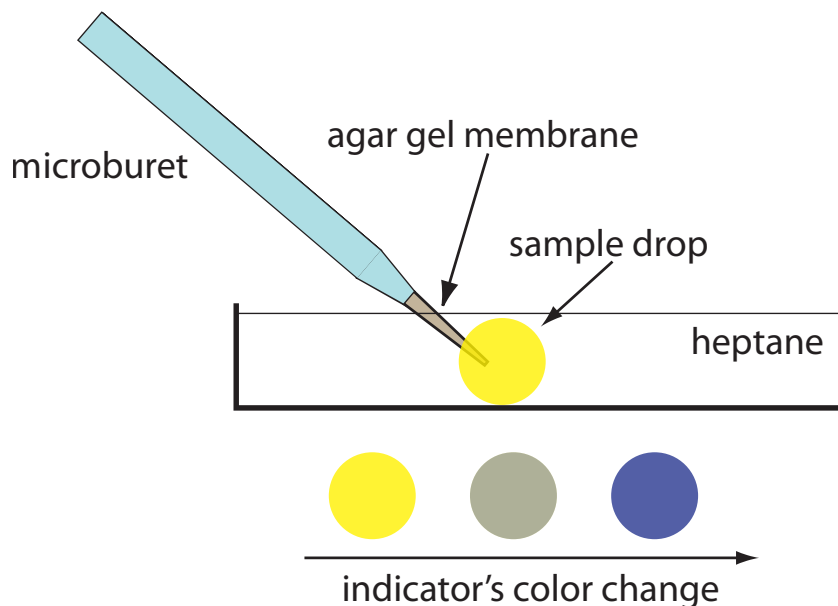
**Figure 9.24** Experimental design for a microdroplet titration apparatus.

A minimum concentration of  $10^{-3}$  M places limits on the smallest amount of analyte we can analyze successfully. 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 a pH probe, the titrand needs an initial volume of approximately 25 mL. If we assume 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 generally are limited to major and minor analytes (see [Figure 3.5](#) 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  $\mu\text{L}$  and  $\text{pL}$  samples. In one experimental design (Figure 9.24), samples of 20–100  $\mu\text{L}$  are held by capillary action between a flat-surface pH electrode and a stainless steel sample stage.<sup>8</sup> The titrant is added using the oscillations of a piezoelectric ceramic device to move an angled glass rod in and out of a tube connected to a reservoir that contains the titrant. Each time the glass tube is withdrawn an approximately 2 nL microdroplet of titrant is released. The microdroplets are 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  $\mu\text{L}$ , is dispensed between each pH measurement. In this fashion a titration curve is constructed. This method has been used to titrate solutions of 0.1 M HCl and 0.1 M  $\text{CH}_3\text{COOH}$  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%. Samples as small as 20  $\mu\text{L}$  were titrated successfully.

We need a volume of titrand sufficient to cover the tip of the pH probe or to allow for an easy observation of the indicator's color. A volume of 25 mL is not an unreasonable estimate of the minimum volume.

<sup>8</sup> 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.<sup>9</sup> The titrant is delivered using a microburet fashioned from a glass capillary micropipet (Figure 9.25). The microburet has a 1–2  $\mu\text{m}$  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 is converted to an end point volume. Samples usually consist of picoliter volumes ( $10^{-12}$  liters), with the smallest sample being 0.7 pL. The precision of the titrations is about 2%.

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

### ACCURACY

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.

<sup>9</sup> (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 by ensuring 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 we must complete the titration quickly to avoid competing chemical reactions. An automatic titrator is particularly useful for titrations that require small volumes of titrant because it provides significantly better precision (typically about  $\pm 0.05\%$  of the buret’s volume).

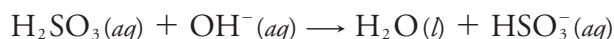
The precision of detecting the end point depends on how it is measured and the slope of the titration curve at the end point. With an indicator the precision of the end point signal usually is  $\pm 0.03$ – $0.10$  mL. Potentiometric end points usually are more precise.

**SENSITIVITY**

For an acid–base titration we can write the following general analytical equation to express the titrant’s volume in terms of the 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,  $\text{H}_2\text{SO}_3$ , by titrating with  $\text{NaOH}$  to the first equivalence point



At the equivalence point the relationship between the moles of  $\text{NaOH}$  and the moles of  $\text{H}_2\text{SO}_3$  is

$$\text{mol NaOH} = \text{mol H}_2\text{SO}_3$$

Substituting the titrant’s molarity and volume for the moles of  $\text{NaOH}$  and rearranging

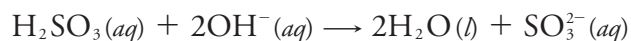
$$\begin{aligned} M_{\text{NaOH}} \times V_{\text{NaOH}} &= \text{mol H}_2\text{SO}_3 \\ V_{\text{NaOH}} &= \frac{1}{M_{\text{NaOH}}} \times \text{mol H}_2\text{SO}_3 \end{aligned}$$

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 applies only if the titrand is multiprotic, is to titrate to a later equivalence point. If we titrate  $\text{H}_2\text{SO}_3$  to its second equivalence point



then each mole of  $\text{H}_2\text{SO}_3$  consumes two moles of NaOH

$$\text{mol NaOH} = 2 \times \text{mol H}_2\text{SO}_3$$

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 a larger volume of titrant requires us to refill the buret. For this reason, standard acid–base titrimetric procedures are written to ensure that a titration uses 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. Let's consider two limiting situations.

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 determined accurately. Conversely, if the acid dissociation constants for the analyte and interferent are similar, then there may not be an accurate end point for the analyte. 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 available. 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 we cannot separate the analyte's and the interferent's contributions to the equivalence point volume.

### 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,  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  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  $\text{CN}^-$  with  $\text{Ag}^+$  was successful because they form a single, stable complex of  $\text{Ag}(\text{CN})_2^-$ , which results in a single, easily identified end point. Other metal–ligand complexes, such as  $\text{CdI}_4^{2-}$ , are not analytically useful because they form a series of metal–ligand complexes ( $\text{CdI}^+$ ,  $\text{CdI}_2(\text{aq})$ ,  $\text{CdI}_3^-$  and  $\text{CdI}_4^{2-}$ ) that produce a sequence of poorly defined end points.

In 1945, Schwarzenbach introduced aminocarboxylic acids as multidentate ligands. The most widely used of these new ligands—ethylenediaminetetraacetic acid, or EDTA—forms a strong 1:1 complex 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, the structure of which is shown in Figure 9.26a in its fully deprotonated form, is a Lewis acid with six binding sites—the four negatively charged carboxylate groups and the two tertiary amino groups—that can donate up to 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.

#### METAL–EDTA FORMATION CONSTANTS

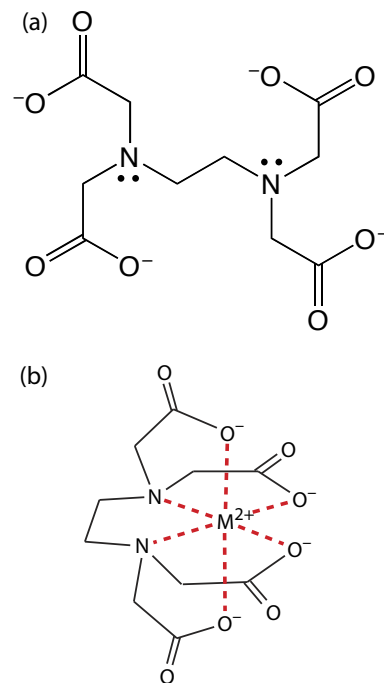
To illustrate the formation of a metal–EDTA complex, let's consider the reaction between  $\text{Cd}^{2+}$  and EDTA



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

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

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.



**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.

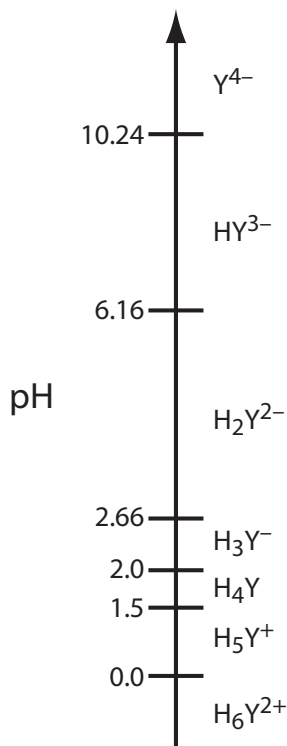


Figure 9.27 Ladder diagram for EDTA.

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<sub>6</sub>Y<sup>2+</sup>, is a hexaprotic weak acid with successive pK<sub>a</sub> values of

$$\begin{aligned} pK_{a1} &= 0.0 & pK_{a2} &= 1.5 & pK_{a3} &= 2.0 \\ pK_{a4} &= 2.66 & pK_{a5} &= 6.16 & pK_{a6} &= 10.24 \end{aligned}$$

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 when the pH is more basic than 10.24.

### CONDITIONAL METAL–LIGAND FORMATION CONSTANTS

The formation constant for CdY<sup>2-</sup> in [equation 9.10](#) assumes that EDTA is present as Y<sup>4-</sup>. Because EDTA has many forms, when we prepare a solution of EDTA we know its total concentration, C<sub>EDTA</sub>, not the concentration of a specific form, such as Y<sup>4-</sup>. To use [equation 9.10](#), we need to rewrite it in terms of C<sub>EDTA</sub>.

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

$$C_{\text{EDTA}} = [\text{H}_6\text{Y}^{2+}] + [\text{H}_5\text{Y}^+] + [\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^-] + [\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}] + [\text{Y}^{4-}]$$

To correct the formation constant for EDTA's acid–base properties we need to calculate the fraction, α<sub>Y<sup>4-</sup></sub>, of EDTA that is present as Y<sup>4-</sup>.

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

[Table 9.10](#) provides values of α<sub>Y<sup>4-</sup></sub> for selected pH levels. Solving [equation 9.11](#) for [Y<sup>4-</sup>] and substituting into [equation 9.10](#) for the CdY<sup>2-</sup> formation constant

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

and rearranging gives

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

where K'<sub>f</sub> is a pH-dependent **CONDITIONAL FORMATION CONSTANT**. As shown in [Table 9.11](#), the conditional formation constant for CdY<sup>2-</sup> 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 α<sub>Y<sup>4-</sup></sub>.



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

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
1	$1.94 \times 10^{-18}$	8	$5.68 \times 10^{-3}$
2	$3.47 \times 10^{-14}$	9	$5.47 \times 10^{-2}$
3	$2.66 \times 10^{-11}$	10	0.367
4	$3.80 \times 10^{-9}$	11	0.853
5	$3.73 \times 10^{-7}$	12	0.983
6	$2.37 \times 10^{-5}$	13	0.988
7	$5.06 \times 10^{-4}$	14	1.00

### 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 with  $\text{Cd}^{2+}$ , then EDTA must compete with the ligand for  $\text{Cd}^{2+}$ . For example, an  $\text{NH}_4^+/\text{NH}_3$  buffer includes  $\text{NH}_3$ , which forms several stable  $\text{Cd}^{2+}\text{-NH}_3$  complexes. Because EDTA forms a stronger complex with  $\text{Cd}^{2+}$  than does  $\text{NH}_3$ , it displaces  $\text{NH}_3$ ; however, the stability of the  $\text{Cd}^{2+}\text{-EDTA}$  complex decreases.

We can account for the effect of an **AUXILIARY COMPLEXING AGENT**, such as  $\text{NH}_3$ , in the same way we accounted for the effect of pH. Before adding EDTA, the mass balance on  $\text{Cd}^{2+}$ ,  $C_{\text{Cd}}$ , is

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

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

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

Solving equation 9.13 for  $[\text{Cd}^{2+}]$  and substituting into [equation 9.12](#) gives

The value of  $\alpha_{\text{Cd}^{2+}}$  depends on the concentration of  $\text{NH}_3$ . Contrast this with  $\alpha_{Y^{4-}}$ , which depends on pH.

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

pH	$K_f'$	pH	$K_f'$
1	$5.6 \times 10^{-2}$	8	$1.6 \times 10^{14}$
2	$1.0 \times 10^3$	9	$1.6 \times 10^{15}$
3	$7.7 \times 10^5$	10	$1.1 \times 10^{16}$
4	$1.1 \times 10^8$	11	$2.5 \times 10^{16}$
5	$1.1 \times 10^{10}$	12	$2.9 \times 10^{16}$
6	$6.9 \times 10^{11}$	13	$2.9 \times 10^{16}$
7	$1.5 \times 10^{13}$	14	$2.9 \times 10^{16}$

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

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

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

Because the concentration of NH<sub>3</sub> in a buffer essentially is constant, we can rewrite this equation

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

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<sub>3</sub> 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 shape of a complexometric 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's concentration, 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 sketch a good approximation of any complexation titration curve using a limited number of simple calculations.

$$pM = -\log[M^{2+}]$$

### CALCULATING THE TITRATION CURVE

Let's calculate the titration curve for 50.0 mL of  $5.00 \times 10^{-3}$  M Cd<sup>2+</sup> using a titrant of 0.0100 M EDTA. Furthermore, let's assume the titrand is buffered to a pH of 10 using a buffer that is 0.0100 M in NH<sub>3</sub>.

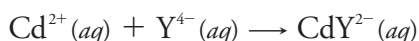
Because the pH is 10, some of the EDTA is present in forms other than Y<sup>4-</sup>. In addition, EDTA will compete with NH<sub>3</sub> for the Cd<sup>2+</sup>. To evaluate the titration curve, therefore, we first need to calculate the conditional formation constant for CdY<sup>2-</sup>. From [Table 9.10](#) and Table 9.12 we find that  $\alpha_{Y^{4-}}$  is 0.367 at a pH of 10, and that  $\alpha_{Cd^{2+}}$  is 0.0881 when the

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

concentration of  $\text{NH}_3$  is 0.0100 M. Using these values, the conditional formation constant is

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{\text{Cd}^{2+}} = (2.9 \times 10^{16})(0.367)(0.0881) = 9.4 \times 10^{14}$$

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



as if it proceeds to completion.

The next task is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that the moles of EDTA added must equal the moles of  $\text{Cd}^{2+}$  in our sample; thus

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

Substituting in known values, we find that it requires

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

of EDTA to reach the equivalence point.

Before the equivalence point,  $\text{Cd}^{2+}$  is present in excess and pCd is determined by the concentration of unreacted  $\text{Cd}^{2+}$ . Because not all unreacted  $\text{Cd}^{2+}$  is free—some is complexed with  $\text{NH}_3$ —we must account for the presence of  $\text{NH}_3$ . For example, after adding 5.0 mL of EDTA, the total concentration of  $\text{Cd}^{2+}$  is

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

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

$$C_{\text{Cd}} = 3.64 \times 10^{-3} \text{ M}$$

To calculate the concentration of free  $\text{Cd}^{2+}$  we use [equation 9.13](#)

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(3.64 \times 10^{-3} \text{ M}) = 3.21 \times 10^{-4} \text{ M}$$

which gives a pCd of

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

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

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

$$[\text{CdY}^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 3.33 \times 10^{-3} \text{ M}$$

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

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

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

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

In calculating that  $[\text{CdY}^{2-}]$  at the equivalence point is  $3.33 \times 10^{-3} \text{ M}$ , we assumed the reaction between  $\text{Cd}^{2+}$  and EDTA went to completion. Here we let the system relax back to equilibrium, increasing  $C_{\text{Cd}}$  and  $C_{\text{EDTA}}$  from 0 to  $x$ , and decreasing the concentration of  $\text{CdY}^{2-}$  by  $x$ .

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

$$x = C_{\text{Cd}} = 1.87 \times 10^{-9} \text{ M}$$

Once again, to find the concentration of uncomplexed  $\text{Cd}^{2+}$  we must account for the presence of  $\text{NH}_3$ ; thus

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(1.87 \times 10^{-9} \text{ M}) = 1.64 \times 10^{-10} \text{ M}$$

and pCd is 9.78 at the equivalence point.

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

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

$$[\text{CdY}^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 3.12 \times 10^{-3} \text{ M}$$

and the concentration of EDTA is

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

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

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

Substituting into [equation 9.14](#) and solving for  $[\text{Cd}^{2+}]$  gives

$$\frac{[\text{CdY}^{2-}]}{C_{\text{Cd}} C_{\text{EDTA}}} = \frac{3.12 \times 10^{-3} \text{ M}}{C_{\text{Cd}}(6.25 \times 10^{-4} \text{ M})} = 9.5 \times 10^{14}$$

$$C_{\text{Cd}} = 5.27 \times 10^{-15} \text{ M}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(5.27 \times 10^{-15} \text{ M}) = 4.64 \times 10^{-16} \text{ M}$$

a pCd of 15.33. [Table 9.13](#) and [Figure 9.28](#) show additional results for this titration.

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

After the equilibrium point we know the equilibrium concentrations of  $\text{CdY}^{2-}$  and of EDTA in all its forms,  $C_{\text{EDTA}}$ . We can solve for  $C_{\text{Cd}}$  using  $K_f''$  and then calculate  $[\text{Cd}^{2+}]$  using  $\alpha_{\text{Cd}^{2+}}$ . Because we used the same conditional formation constant,  $K_f''$ , for other calculations in this section, this is the approach used here as well.

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

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

$$\frac{3.13 \times 10^{-3} \text{ M}}{[\text{Cd}^{2+}](6.25 \times 10^{-4})} = (0.367)(2.9 \times 10^{16})$$

Solving gives  $[\text{Cd}^{2+}] = 4.71 \times 10^{-16} \text{ M}$  and a pCd of 15.33. We will use this approach when we learn how to sketch a complexometric titration curve.

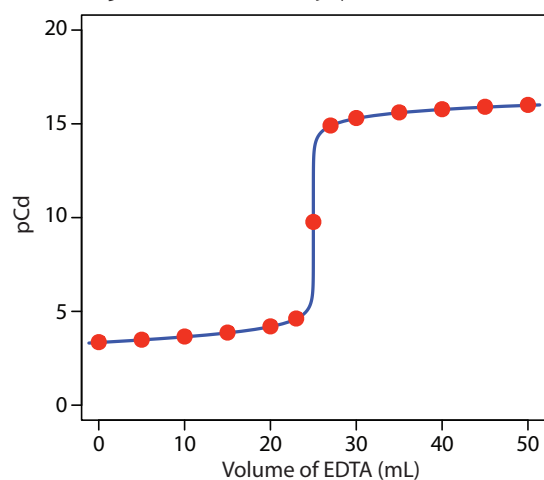
### Practice Exercise 9.12

Calculate titration curves for the titration of 50.0 mL of  $5.00 \times 10^{-3} \text{ M}$   $\text{Cd}^{2+}$  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 on the titration of  $\text{Cd}^{2+}$  with EDTA.

Click [here](#) to review your answer to this exercise.

**Table 9.13** Titration of 50.0 mL of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA at a pH of 10 and in the Presence of 0.0100 M  $\text{NH}_3$

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	9.78		



**Figure 9.28** Titration curve for the titration of 50.0 mL of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M  $\text{NH}_3$ . The red points correspond to the data in Table 9.13. The blue line shows the complete titration curve.

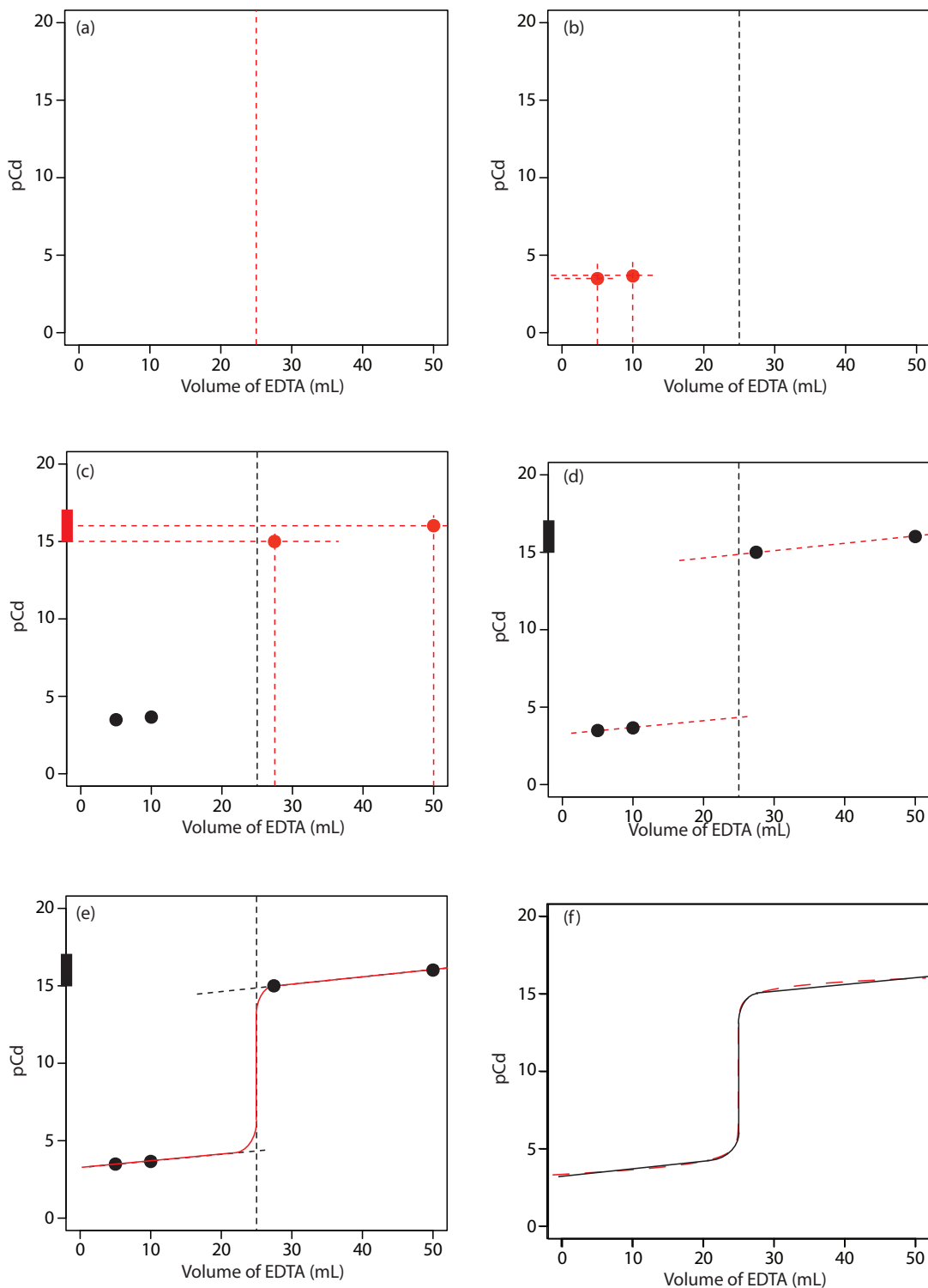
### SKETCHING AN EDTA TITRATION CURVE

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  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA in the presence of 0.0100 M  $\text{NH}_3$  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 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 that intersects the  $x$ -axis at 25.0 mL of EDTA. [Figure 9.29a](#) shows the result of the first step in our sketch.

Before the equivalence point,  $\text{Cd}^{2+}$  is present in excess and pCd is determined by the concentration of unreacted  $\text{Cd}^{2+}$ . Because not all unreacted  $\text{Cd}^{2+}$  is free—some is complexed with  $\text{NH}_3$ —we must account for

This is the same example 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](#).



**Figure 9.29** Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA in the presence of 0.0100 M  $\text{NH}_3$ : (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.

the presence of  $\text{NH}_3$ . 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.

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

$$K_f' = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}]C_{\text{EDTA}}} = \alpha_{\text{Y}^{4-}} \times K_f = (0.367)(2.9 \times 10^{16}) = 1.1 \times 10^{16}$$

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

$$\begin{aligned} \log K_f' &= -\log[\text{Cd}^{2+}] + \log \frac{[\text{CdY}^{2-}]}{C_{\text{EDTA}}} \\ \text{pCd} &= \log K_f' + \log \frac{C_{\text{EDTA}}}{[\text{CdY}^{2-}]} \end{aligned}$$

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

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

Making appropriate substitutions and solving, we find that

$$\begin{aligned} \frac{M_{\text{EDTA}} V_{\text{EDTA}} - M_{\text{Cd}} V_{\text{Cd}}}{M_{\text{Cd}} V_{\text{Cd}}} &= \frac{1}{10} \\ M_{\text{EDTA}} V_{\text{EDTA}} - M_{\text{Cd}} V_{\text{Cd}} &= 0.1 \times M_{\text{Cd}} V_{\text{Cd}} \\ V_{\text{EDTA}} &= \frac{1.1 \times M_{\text{Cd}} V_{\text{Cd}}}{M_{\text{EDTA}}} = 1.1 \times V_{\text{eq}} \end{aligned}$$

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  $\text{CdY}^{2-}$  complex, including its buffer range, using its  $\log K_f'$  value of 16.04. Next, we add two points, one for pCd at 110% of  $V_{\text{eq}}$  (a pCd of 15.04 at 27.5 mL) and one for pCd at 200% of  $V_{\text{eq}}$  (a pCd of 16.04 at 50.0 mL).

Next, we draw a straight line through each pair of points, extending each line through the vertical line that indicates 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.

### 9C.3 Selecting and Evaluating the End point

The equivalence point of a complexation titration occurs when we react stoichiometrically equivalent amounts of the titrand and titrant. As is the case for an acid–base titration, we estimate the equivalence point for a com-

See [Table 9.13](#) for the values.

Recall that we can use either of our two possible conditional formation constants,  $K_f'$  or  $K_f''$ , to determine the composition of the system at equilibrium.

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

#### Practice Exercise 9.13

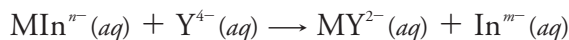
Sketch titration curves for the titration of 50.0 mL of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7. Compare your sketches to the calculated titration curves from [Practice Exercise 9.12](#).

Click [here](#) to review your answer to this exercise.

plexation 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,  $\text{In}^{m-}$ , is added to the titrand's solution where it forms a stable complex with the metal ion,  $\text{MIn}^{n-}$ . As we add EDTA it reacts first with free metal ions, and then displaces the indicator from  $\text{MIn}^{n-}$ .



If  $\text{MIn}^{n-}$  and  $\text{In}^{m-}$  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 the strength 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 may change with pH. [Figure 9.30](#), for example, shows the color of the indicator calmagite as a function of pH and pMg, where  $\text{H}_2\text{In}^-$ ,  $\text{HIn}^{2-}$ , and  $\text{In}^{3-}$  are different forms of the uncomplexed indicator, and  $\text{MgIn}^-$  is the  $\text{Mg}^{2+}$ –calmagite complex. Because the color of calmagite's metal–indicator complex is red, its use as a metallochromic indicator has a practical pH range of approximately 8.5–11 where the uncomplexed indicator,  $\text{HIn}^{2-}$ , has a blue color.

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 often is possible to complete an EDTA titration 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

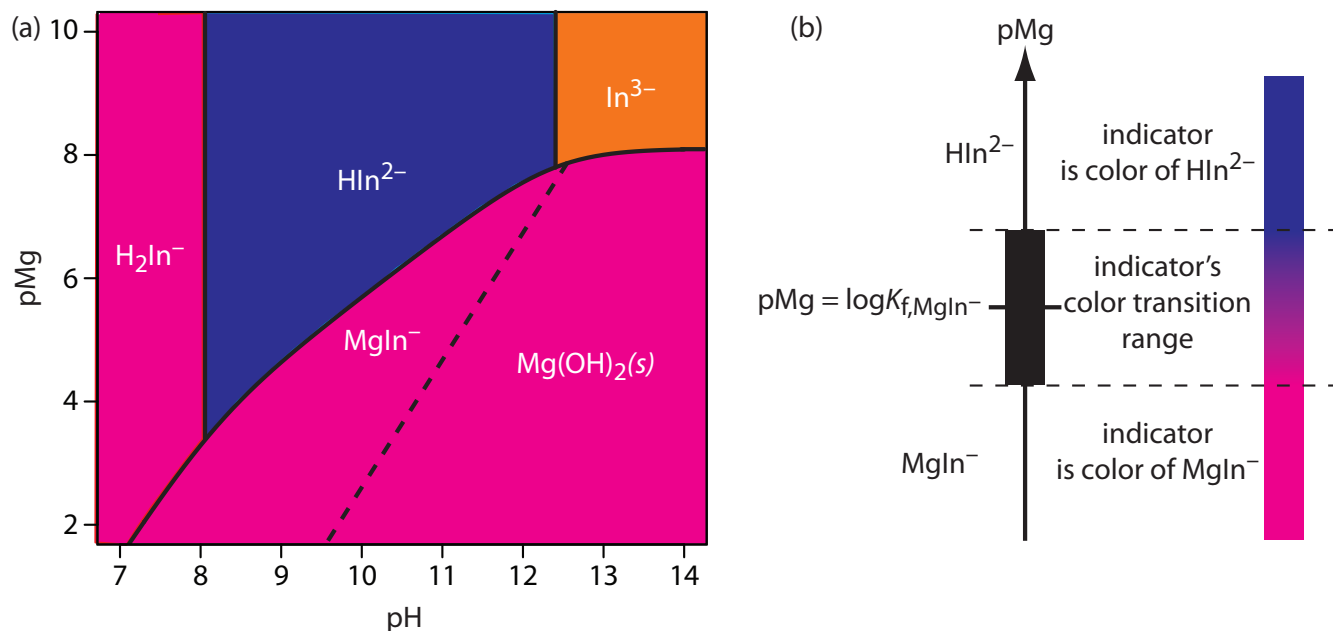
[Figure 9.30](#) is essentially a two-variable ladder diagram. The solid lines are equivalent to a step on a conventional ladder diagram, indicating conditions where two (or three) species are equal in concentration.

**Table 9.14 Selected Metallochromic Indicators**

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

<sup>a</sup> all metal ions carry a +2 charge except for iron, which is +3; metal ions in *italic* font have poor end points





**Figure 9.30** (a) Predominance diagram for the metallochromic indicator calmagite showing the most important forms and colors 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  $\log K_f + 1$ .

weaker complex with EDTA than the analyte. For example, calmagite has a poor end point 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

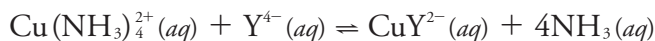
An important limitation when using a metallochromic indicator is that we must be able to see the indicator's change in color at the end point. This may be difficult if the solution is already colored. For example, when titrating  $Cu^{2+}$  with EDTA, ammonia is used to adjust the titrand's pH. The intensely 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 often is 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, then we can identify the end point by monitoring the titrand's absorbance at a carefully selected wavelength. For example, we can identify

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 essentially is 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.

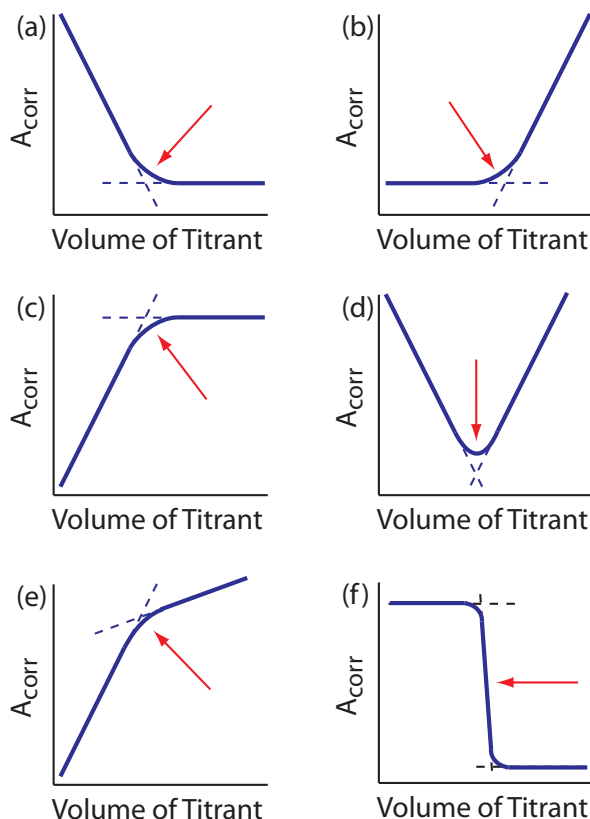
the end point for a titration of  $\text{Cu}^{2+}$  with EDTA in the presence of  $\text{NH}_3$  by monitoring the titrand's absorbance at a wavelength of 745 nm, where the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex absorbs strongly. At the beginning of the titration the absorbance is at a maximum. As we add EDTA, however, the reaction



decreases the concentration of  $\text{Cu}(\text{NH}_3)_4^{2+}$  and decreases the absorbance until we reach the equivalence point. After the equivalence point the absorbance essentially remains unchanged. The resulting **SPECTROPHOTOMETRIC TITRATION CURVE** is shown in Figure 9.31a. Note that the titration curve's  $y$ -axis is not the measured absorbance,  $A_{\text{meas}}$ , but a corrected absorbance,  $A_{\text{corr}}$

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

where  $V_{\text{EDTA}}$  and  $V_{\text{Cu}}$  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.

See Chapter 10 for a discussion of spectrophotometry.

## 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 that can form an insoluble complex with soap. Although most divalent and trivalent metal ions contribute to hardness, the two most important metal ions are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Hardness is determined by titrating with EDTA at a buffered pH of 10. Calmagite is used as an indicator. Hardness is reported as mg  $\text{CaCO}_3/\text{L}$ .

#### PROCEDURE

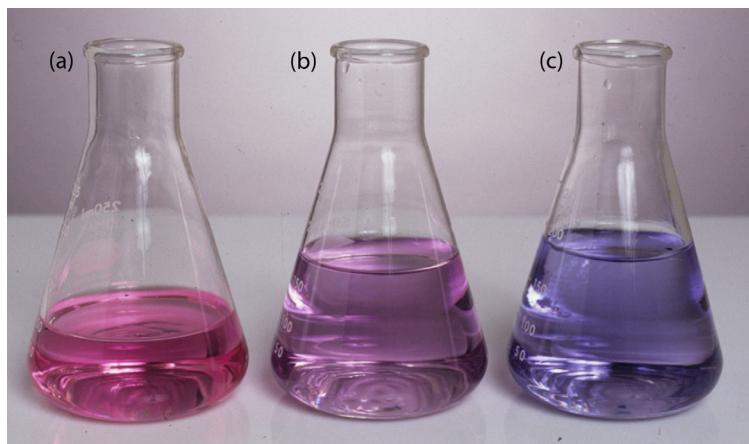
Select a volume of sample that requires less than 15 mL of titrant to keep the analysis time under 5 minutes and, if necessary, dilute the sample to 50 mL with distilled water. Adjust the sample's pH by adding 1–2 mL of a pH 10 buffer that contains a small amount of  $\text{Mg}^{2+}$ -EDTA. Add 1–2 drops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

#### QUESTIONS

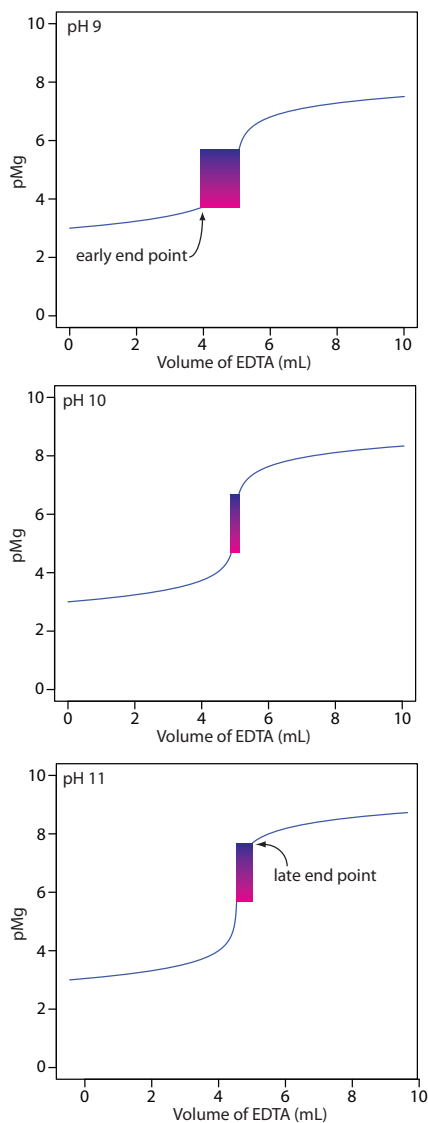
1. Why is the sample buffered to a pH of 10? What problems might you expect at a higher pH or a lower pH?

Of the two primary cations that contribute to hardness,  $\text{Mg}^{2+}$  forms the weaker complex with EDTA and is the last cation to react with the titrant. Calmagite is a useful indicator because it gives a distinct end point when titrating  $\text{Mg}^{2+}$  (see [Table 9.14](#)). Because of calmagite's acid–base properties, the range of pMg values over which the indicator changes color depends on the titrand's pH ([Figure 9.30](#)). [Figure 9.33](#) shows the titration curve for a 50-mL solution of  $10^{-3}$  M  $\text{Mg}^{2+}$  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

The best way to appreciate the theoretical and the 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.



**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  $\text{Mg}^{2+}$ -indicator complex; (b) purple at the titration's end point; and (c) blue after the end point due to the presence of uncomplexed indicator.



**Figure 9.33** Titration curves for 50 mL of  $10^{-3}$  M  $\text{Mg}^{2+}$  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.

is possible, which results in a negative determinate error. A late end point and a positive determinate error are possible if the pH is 11.

- Why is a small amount of the  $\text{Mg}^{2+}$ -EDTA complex added to the buffer?

The titration's end point is signaled by the indicator calmagite. The indicator's end point with  $\text{Mg}^{2+}$  is distinct, but its change in color when titrating  $\text{Ca}^{2+}$  does not provide a good end point (see [Table 9.14](#)). If the sample does not contain any  $\text{Mg}^{2+}$  as a source of hardness, then the titration's end point is poorly defined, which leads to an inaccurate and imprecise result.

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

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

A time limitation suggests there is a kinetically-controlled interference, possibly arising from a competing chemical reaction. In this case the interference is the possible precipitation of  $\text{CaCO}_3$  at a pH of 10.

## 9C.4 Quantitative Applications

Although many quantitative applications of complexation titrimetry have been replaced by other analytical methods, a few important applications continue to find relevance. 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, for which  $\text{Ag}^+$  or  $\text{Hg}^{2+}$  are suitable titrants.

Solutions of EDTA are prepared from its soluble disodium salt,  $\text{Na}_2\text{H}_2\text{Y}\cdot 2\text{H}_2\text{O}$ , and standardized by titrating against a solution made from the primary standard  $\text{CaCO}_3$ . Solutions of  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  are prepared using  $\text{AgNO}_3$  and  $\text{Hg}(\text{NO}_3)_2$ , 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,  $\text{Ca}^{2+}$ ,  $\text{CN}^-$ , and  $\text{Cl}^-$  in waters and wastewaters. The evaluation of hardness was described earlier in [Representative Method 9.2](#). The determination of  $\text{Ca}^{2+}$  is complicated by the presence of  $\text{Mg}^{2+}$ , which also reacts with EDTA. To prevent an interference the pH is adjusted to 12–13, which precipitates  $\text{Mg}^{2+}$  as  $\text{Mg}(\text{OH})_2$ . Titrating with EDTA using murexide or Eriochrome Blue Black R as the indicator gives the concentration of  $\text{Ca}^{2+}$ .

Cyanide is determined at concentrations greater than 1 mg/L by making the sample alkaline with NaOH and titrating with a standard solution of  $\text{AgNO}_3$  to form the soluble  $\text{Ag}(\text{CN})_2^-$  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  $\text{Ag}^+$ .

Chloride is determined by titrating with  $\text{Hg}(\text{NO}_3)_2$ , forming  $\text{HgCl}_2(\text{aq})$ . The sample is acidified to a pH of 2.3–3.8 and diphenylcarbazone, which forms a colored complex with excess  $\text{Hg}^{2+}$ , serves as the indicator. The 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 titration reaction's stoichiometry. For a titration using EDTA, the stoichiometry is always 1:1.

**Example 9.7**

The concentration of a solution of EDTA is determined by standardizing against a solution of  $\text{Ca}^{2+}$  prepared using a primary standard of  $\text{CaCO}_3$ . A 0.4071-g sample of  $\text{CaCO}_3$  is 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 is adjusted by adding 5 mL of a pH 10  $\text{NH}_3\text{--NH}_4\text{Cl}$  buffer that contains a small amount of  $\text{Mg}^{2+}$ –EDTA. After adding calmagite as an indicator, the solution is titrated with the EDTA, requiring 42.63 mL to reach the end point. Report the molar concentration of EDTA in the titrant.

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

**SOLUTION**

The primary standard of  $\text{Ca}^{2+}$  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  $\text{Ca}^{2+}$  in the titrand is

$$8.135 \times 10^{-3} \text{ M} \times 0.05000 \text{ L} = 4.068 \times 10^{-4} \text{ mol Ca}^{2+}$$

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

$$\frac{4.068 \times 10^{-4} \text{ mol EDTA}}{0.04263 \text{ L}} = 9.543 \times 10^{-3} \text{ M EDTA}$$

### 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  $\text{CaCO}_3/\text{L}$ .

Click [here](#) to review your answer to this exercise.

As shown in the following example, we can extend this calculation to complexation reactions that use other titrants.

### Example 9.8

The concentration of  $\text{Cl}^-$  in a 100.0-mL sample of water from a freshwater aquifer is tested for the encroachment of sea water by titrating with 0.0516 M  $\text{Hg}(\text{NO}_3)_2$ . The sample is acidified and titrated to the diphenylcarbazone end point, requiring 6.18 mL of the titrant. Report the concentration of  $\text{Cl}^-$ , in mg/L, in the aquifer.

#### SOLUTION

The reaction between  $\text{Cl}^-$  and  $\text{Hg}^{2+}$  produces a metal–ligand complex of  $\text{HgCl}_2(\text{aq})$ . Each mole of  $\text{Hg}^{2+}$  reacts with 2 moles of  $\text{Cl}^-$ ; thus

$$\frac{0.0516 \text{ mol Hg}(\text{NO}_3)_2}{\text{L}} \times 0.00618 \text{ L} \times \frac{2 \text{ mol Cl}^-}{\text{mol Hg}(\text{NO}_3)_2} \times \frac{35.453 \text{ g Cl}^-}{\text{mol Cl}^-} = 0.0226 \text{ g Cl}^-$$

are in the sample. The concentration of  $\text{Cl}^-$  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  $\text{AgNO}_3$ , requiring 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 that contains Ni, Fe, and Cr is analyzed by a complexation titration using EDTA as the titrant. A 0.7176-g sample of the alloy is dissolved in  $\text{HNO}_3$  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, requires 26.14 mL of 0.05831 M EDTA to reach the murexide end point. A second 50.00-mL aliquot is treated with hexamethylenetetramine to mask the Cr. Titrating with 0.05831 M EDTA requires 35.43 mL to reach the murexide end point. Finally, a third 50.00-mL aliquot is 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  $\text{Cu}^{2+}$ . 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 write an equation that relates the moles of EDTA to the moles of metal ions that are titrated.

$$\text{titration 1: mol Ni} = \text{mol EDTA}$$

$$\text{titration 2: mol Ni} + \text{mol Fe} = \text{mol EDTA}$$

$$\text{titration 3: mol Ni} + \text{mol Fe} + \text{mol Cr} + \text{mol Cu} = \text{mol EDTA}$$

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

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

which means the sample contains  $1.524 \times 10^{-3}$  mol Ni.

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

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

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

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

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

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

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

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

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

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

$$\frac{5.42 \times 10^{-4} \text{ mol Fe}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{55.845 \text{ g Fe}}{\text{mol Fe}} = 0.151 \text{ g Fe}$$

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

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

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

### Practice Exercise 9.16

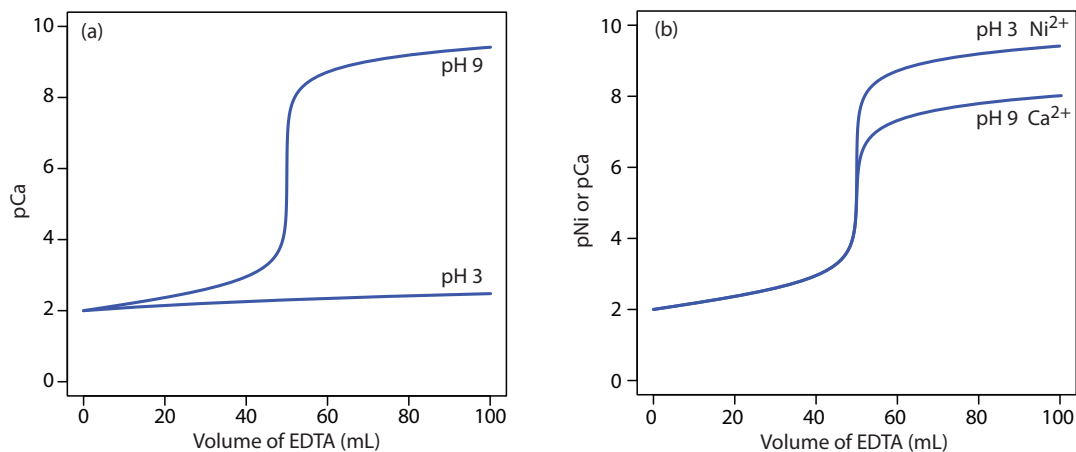
An indirect complexation titration with EDTA can be used to determine the concentration of sulfate,  $\text{SO}_4^{2-}$ , in a sample. A 0.1557-g sample is dissolved in water and any sulfate present is precipitated as  $\text{BaSO}_4$  by adding  $\text{Ba}(\text{NO}_3)_2$ . After filtering and rinsing the precipitate, it is dissolved in 25.00 mL of 0.02011 M EDTA. The excess EDTA is titrated with 0.01113 M  $\text{Mg}^{2+}$ , requiring 4.23 mL to reach the end point. Calculate the %w/w  $\text{Na}_2\text{SO}_4$  in the sample.

Click [here](#) to review your answer to this exercise.

## 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 that contain two or more analytes. The reason we can use pH to provide selectivity is shown in [Figure 9.34a](#). A titration of  $\text{Ca}^{2+}$  at a pH of 9 has a distinct break in the titration curve because the conditional formation constant for  $\text{CaY}^{2-}$  of  $2.6 \times 10^9$  is large enough to ensure that the reaction of  $\text{Ca}^{2+}$  and EDTA goes to



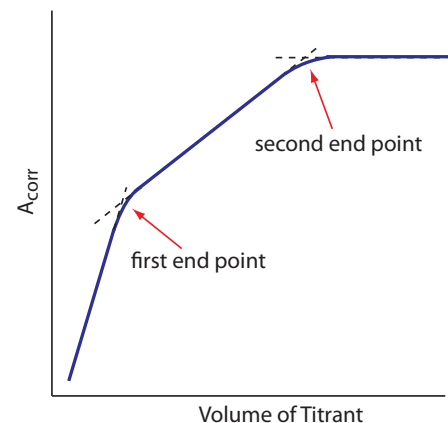


**Figure 9.34** Titration curves illustrating how we can use the titrand's pH to control EDTA's selectivity. (a) Titration of 50.0 mL of 0.010 M Ca<sup>2+</sup> at a pH of 3 and a pH of 9 using 0.010 M EDTA. At a pH of 3 the CaY<sup>2-</sup> complex is too weak to titrate successfully. (b) Titration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

completion. At a pH of 3, however, the conditional formation constant of 1.23 is so small that very little Ca<sup>2+</sup> reacts with the EDTA.

Suppose we need to analyze a mixture of Ni<sup>2+</sup> and Ca<sup>2+</sup>. Both analytes react with EDTA, but their conditional formation constants differ significantly. If we adjust the pH to 3 we can titrate Ni<sup>2+</sup> with EDTA without titrating Ca<sup>2+</sup> (Figure 9.34b). When the titration is complete, we adjust the titrand's pH to 9 and titrate the Ca<sup>2+</sup> 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 oxidation–reduction reactions were introduced shortly after the development of acid–base titrimetry. The earliest **REDOX TITRATION** took advantage of chlorine's oxidizing power. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl<sub>2</sub>, 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 to determine 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.

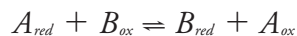
The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, and I<sub>2</sub> as oxidizing titrants, and of Fe<sup>2+</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> as reducing titrants. Even with 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 its reduced forms differ significantly in color. For example, the intensely purple  $\text{MnO}_4^-$  ion serves as its own indicator since its reduced form,  $\text{Mn}^{2+}$ , 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  $\text{H}_3\text{O}^+$  (as pH) or  $\text{M}^{n+}$  (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 that participate 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,  $B_{ox}$ .



where  $A_{ox}$  is the titrand's oxidized form,  $B_{red}$  is the titrant's reduced form, and the stoichiometry between the two is 1:1. The reaction's potential,  $E_{\text{rxn}}$ , is the difference between the reduction potentials for each half-reaction.

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

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 as it allows us to 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

$$E_{\text{rxn}} = E_{A_{ox}/A_{red}}^{\circ} - \frac{RT}{nF} \ln \frac{[A_{red}]}{[A_{ox}]}$$

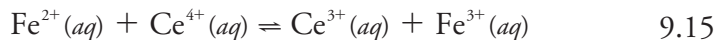
After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{\text{rxn}} = E_{B_{ox}/B_{red}}^{\circ} - \frac{RT}{nF} \ln \frac{[B_{red}]}{[B_{ox}]}$$

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.

**CALCULATING THE TITRATION CURVE**

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M  $\text{Fe}^{2+}$  with 0.100 M  $\text{Ce}^{4+}$  in a matrix of 1 M  $\text{HClO}_4$ . The reaction in this case is



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

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

$$\text{mol Fe}^{2+} = M_{\text{Fe}} \times V_{\text{Fe}} = M_{\text{Ce}} \times V_{\text{Ce}} = \text{mol Ce}^{4+}$$

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

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

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

$$E = +0.767 \text{ V} - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad 9.16$$

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

$$[\text{Fe}^{2+}] = \frac{(\text{mol Fe}^{2+})_{\text{initial}} - (\text{mol Ce}^{4+})_{\text{added}}}{\text{total volume}} = \frac{M_{\text{Fe}} V_{\text{Fe}} - M_{\text{Ce}} V_{\text{Ce}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

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

$$[\text{Fe}^{3+}] = \frac{(\text{mol Ce}^{4+})_{\text{added}}}{\text{total volume}} = \frac{M_{\text{Ce}} V_{\text{Ce}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

$$[\text{Fe}^{3+}] = \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 1.67 \times 10^{-2} \text{ M}$$

Substituting these concentrations into equation 9.16 gives the potential as

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

After the equivalence point, the concentration of  $\text{Ce}^{3+}$  and the concentration of excess  $\text{Ce}^{4+}$  are easy to calculate. For this reason we find the potential using the Nernst equation for the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  half-reaction in a manner similar to that used above to calculate potentials before the equivalence point.

$$E = +1.70 \text{ V} - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \quad 9.17$$

In 1 M  $\text{HClO}_4$ , the formal potential for the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is +0.767 V, and the formal potential for the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  is +1.70 V.

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

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.

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.

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

Volume of $\text{Ce}^{4+}$ (mL)	$E$ (V)	Volume $\text{Ce}^{4+}$ (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

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

$$[\text{Ce}^{3+}] = \frac{(\text{mol Fe}^{2+})_{\text{initial}}}{\text{total volume}} = \frac{M_{\text{Fe}} V_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

$$[\text{Ce}^{3+}] = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}} = 4.55 \times 10^{-2} \text{ M}$$

$$[\text{Ce}^{4+}] = \frac{(\text{mol Ce}^{4+})_{\text{added}} - (\text{mol Fe}^{2+})_{\text{initial}}}{\text{total volume}} = \frac{M_{\text{Ce}} V_{\text{Ce}} - M_{\text{Fe}} V_{\text{Fe}}}{V_{\text{Ce}} + V_{\text{Fe}}}$$

$$[\text{Ce}^{4+}] = \frac{(0.100 \text{ M})(60.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}} = 9.09 \times 10^{-3} \text{ M}$$

Substituting these concentrations into [equation 9.17](#) gives a potential of

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

Step 4: Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential,  $E_{\text{eq}}$ , in [equation 9.16](#) and [equation 9.17](#) are identical. Adding the equations together to gives

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

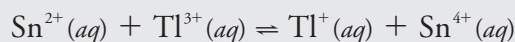
Because  $[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$  and  $[\text{Ce}^{3+}] = [\text{Fe}^{3+}]$  at the equivalence point, the log term has a value of zero and the equivalence point's potential is

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

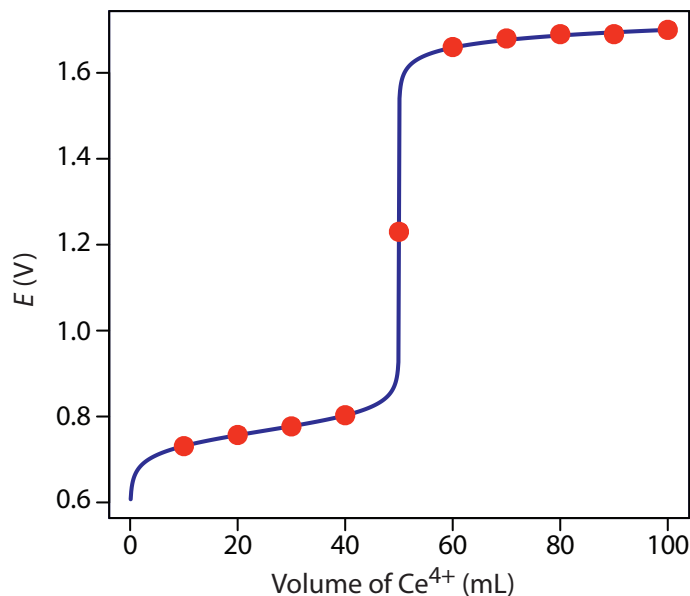
Additional results for this titration curve are shown in [Table 9.15](#) and [Figure 9.36](#).

### Practice Exercise 9.17

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



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  $\text{Fe}^{2+}$  with 0.100 M  $\text{Ce}^{4+}$ . 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  $\text{Fe}^{2+}$  with 0.100 M  $\text{Ce}^{4+}$  in a matrix of 1 M  $\text{HClO}_4$ .

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 that intersects the  $x$ -axis at 50.0 mL of  $\text{Ce}^{4+}$ . [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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Although we can calculate the potential using the Nernst equation, we can avoid this calculation if we make 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  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$ . The potential at the buffer's lower limit is

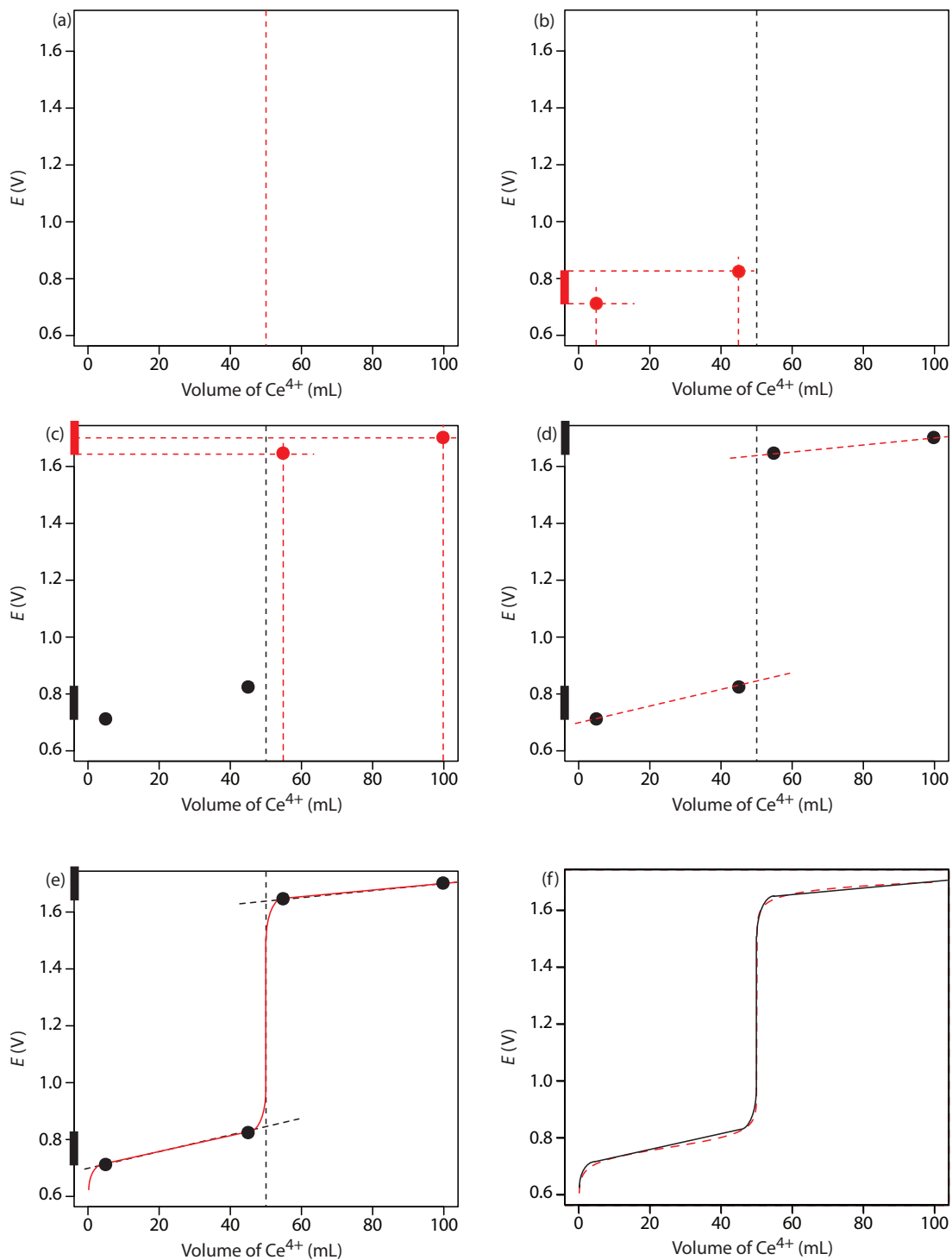
$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.05916$$

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

$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 0.05916$$

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

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](#).



**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<sup>2+</sup> with 0.100 M Ce<sup>4+</sup> in 1 M HClO<sub>4</sub>: (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.

[Figure 9.37b](#) shows the second step in our sketch. First, we superimpose a ladder diagram for  $\text{Fe}^{2+}$  on the  $y$ -axis, using its  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ}$  value of 0.767 V and including the buffer's range of potentials. Next, we add points for the potential at 10% of  $V_{eq}$  (a potential of 0.708 V at 5.0 mL) and for the potential at 90% of  $V_{eq}$  (a potential of 0.826 V at 45.0 mL).

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  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ . The redox buffer is at its lower limit of

$$E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - 0.05916$$

when the titrant reaches 110% of the equivalence point volume and the potential is  $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ}$  when the volume of  $\text{Ce}^{4+}$  is  $2 \times V_{eq}$ .

[Figure 9.37c](#) shows the third step in our sketch. First, we superimpose a ladder diagram for  $\text{Ce}^{4+}$  on the  $y$ -axis, using its  $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ}$  value of 1.70 V and including the buffer's range. 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).

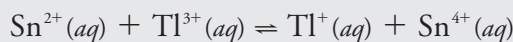
Next, we draw a straight line through each pair of points, extending the line through the vertical line that indicates the equivalence point's volume ([Figure 9.37d](#)). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments ([Figure 9.37e](#)). A comparison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

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

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

### Practice Exercise 9.18

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



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

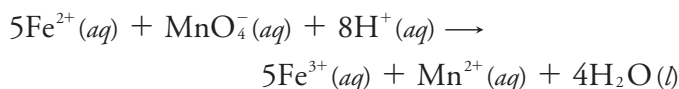
A redox titration's equivalence point occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case for acid–base titrations and complexation titrations, we estimate the equivalence point of a redox titration using an experimental end point. A variety of methods are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

**WHERE IS THE EQUIVALENCE POINT?**

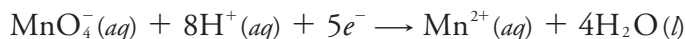
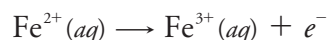
For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at [Figure 9.7](#) and [Figure 9.28](#), you will see that the inflection point is in the middle of this steep 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 1:1—that is, 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 the 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  $\text{Fe}^{2+}$  with  $\text{MnO}_4^-$ .

**SOLUTION**

The half-reactions for the oxidation of  $\text{Fe}^{2+}$  and the reduction of  $\text{MnO}_4^-$  are



for which the Nernst equations are

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

$$E = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} - \frac{0.05916}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

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

$$6E_{eq} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} - 0.05916 \log \frac{[\text{Fe}^{2+}][\text{Mn}^{2+}]}{[\text{Fe}^{3+}][\text{MnO}_4^-][\text{H}^+]^8}$$

At the equivalence point we know that

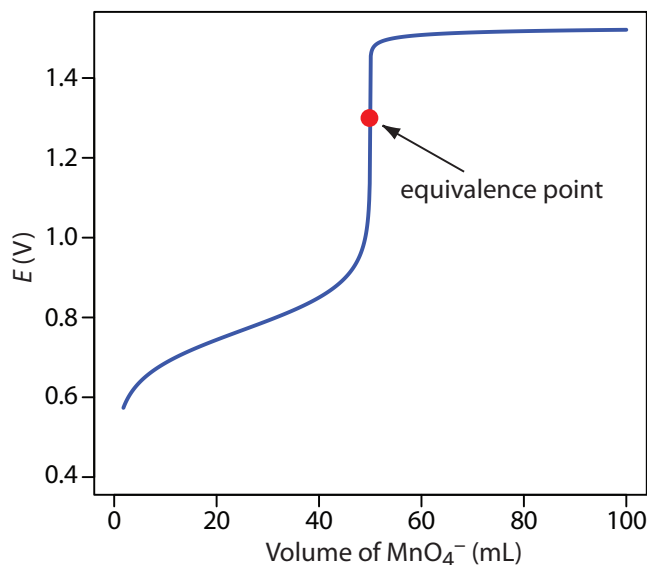
$$[\text{Fe}^{2+}] = 5 \times [\text{MnO}_4^-] \quad \text{and} \quad [\text{Fe}^{3+}] = 5 \times [\text{Mn}^{2+}]$$

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

$$6E_{eq} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} - 0.05916 \log \frac{5[\text{MnO}_4^-][\text{Mn}^{2+}]}{5[\text{Mn}^{2+}][\text{MnO}_4^-][\text{H}^+]^8}$$

We often use  $\text{H}^+$  instead of  $\text{H}_3\text{O}^+$  when writing a redox reaction.





**Figure 9.38** Titration curve for the titration of 50.0 mL of 0.100 M  $\text{Fe}^{2+}$  with 0.0200 M  $\text{MnO}_4^-$  at a fixed pH of 1 (using  $\text{H}_2\text{SO}_4$ ). The equivalence point is shown by the red dot.

$$E_{eq} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}}{6} - \frac{0.05916}{6} \log \frac{1}{[\text{H}^+]^8}$$

$$E_{eq} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}}{6} + \frac{0.05916 \times 8}{6} \log [\text{H}^+]$$

$$E_{eq} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}}{6} - 0.07888 \text{pH}$$

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 is pH-dependent. At a pH of 1 (in  $\text{H}_2\text{SO}_4$ ), for example, the equivalence point has a potential of

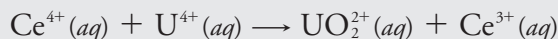
$$E_{eq} = \frac{0.768 + 5 \times 1.51}{6} - 0.07888 \times 1 = 1.31 \text{ V}$$

Figure 9.38 shows a typical titration curve for titration of  $\text{Fe}^{2+}$  with  $\text{MnO}_4^-$ . Note that the titration's equivalence point is asymmetrical.

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

### Practice Exercise 9.19

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



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  $\text{MnO}_4^-$ , have different colors. A solution of  $\text{MnO}_4^-$  is intensely purple. In an acidic solution, however, permanganate's reduced form,  $\text{Mn}^{2+}$ , is nearly colorless. When using  $\text{MnO}_4^-$  as a titrant, the titrand's solution remains colorless until the equivalence point. The first drop of excess  $\text{MnO}_4^-$  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 purple complex with  $\text{I}_3^-$ . We can use this distinct color to signal the presence of excess  $\text{I}_3^-$  as a titrant—a change in color from colorless to purple—or the completion of a reaction that consumes  $\text{I}_3^-$  as the titrand—a change in color from purple to colorless. Another example of a specific indicator is thiocyanate,  $\text{SCN}^-$ , which forms the soluble red-colored complex of  $\text{Fe}(\text{SCN})^{2+}$  in the presence of  $\text{Fe}^{3+}$ .

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 eventually 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



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

$$E = E_{\text{In}_{\text{ox}}/\text{In}_{\text{red}}}^{\circ} - \frac{0.05916}{n} \log \frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]}$$

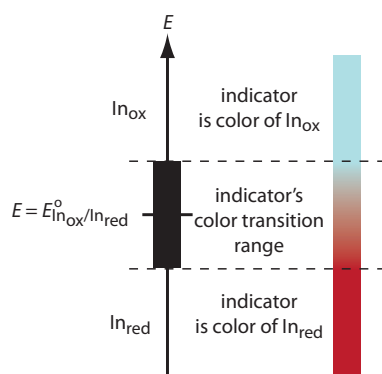
As shown in Figure 9.39, if we assume the indicator's color changes from that of  $\text{In}_{\text{ox}}$  to that of  $\text{In}_{\text{red}}$  when the ratio  $[\text{In}_{\text{red}}]/[\text{In}_{\text{ox}}]$  changes from 0.1 to 10, then the end point occurs when the solution's potential is within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

$$E = E_{\text{In}_{\text{ox}}/\text{In}_{\text{red}}}^{\circ} \pm \frac{0.05916}{n}$$

A partial list of redox indicators is shown in [Table 9.16](#). Examples of an appropriate and an inappropriate indicator for the titration of  $\text{Fe}^{2+}$  with  $\text{Ce}^{4+}$  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 we add the titrant to the titrand. The end point is found by examining visually the



**Figure 9.39** Diagram showing the relationship between  $E$  and an indicator's color. The ladder diagram defines potentials where  $\text{In}_{\text{red}}$  and  $\text{In}_{\text{ox}}$  are the predominate species.

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

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

Table 9.16 Selected Examples of Redox Indicators

Indicator	Color of In <sub>ox</sub>	Color of In <sub>red</sub>	$E^\circ$
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

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 the titrant's redox half-reaction, and a reference electrode that has a fixed potential. Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

You will a further discussion of potentiometry in Chapter 11.

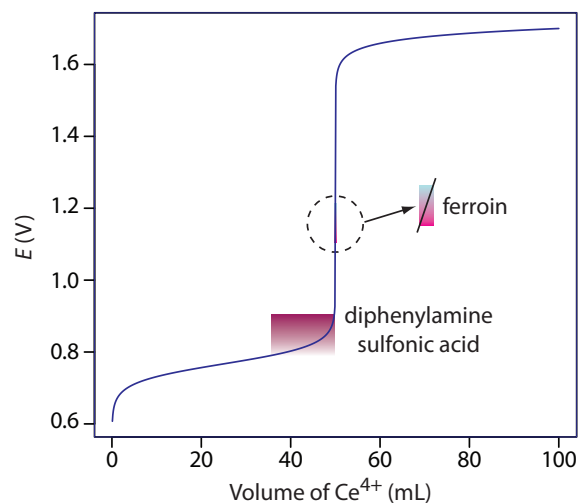
### Representative Method 9.3

#### Determination of Total Chlorine Residual

##### DESCRIPTION OF THE METHOD

The chlorination of a public water supply produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine is present in a variety of chemical states, including the free residual chlorine, which consists of  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ , and the combined chlorine residual, which consists of  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$ . The total chlorine residual is determined by using the oxidizing power of chlorine to convert  $\text{I}^-$  to  $\text{I}_3^-$ . The amount of  $\text{I}_3^-$  formed is then determined by titrating with  $\text{Na}_2\text{S}_2\text{O}_3$  using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if  $\text{Cl}_2$  is the only source of chlorine, and is reported as mg Cl/L.

The best way to appreciate the theoretical and the 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.



**Figure 9.40** Titration curve for titration of 50.0 mL of 0.100 M  $\text{Fe}^{2+}$  with 0.100 M  $\text{Ce}^{4+}$ . 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.

**PROCEDURE**

Select a volume of sample that requires less than 20 mL of  $\text{Na}_2\text{S}_2\text{O}_3$  to reach the end point. Using glacial acetic acid, acidify the sample to a pH between 3 and 4, and add about 1 gram of KI. Titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  until the yellow color of  $\text{I}_3^-$  begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch- $\text{I}_3^-$  complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

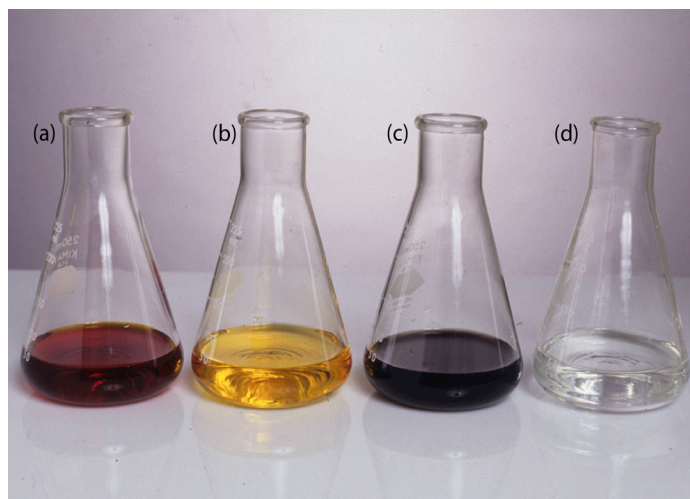
**QUESTIONS**

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  $\text{I}^-$  to  $\text{I}_3^-$ , and the amount of  $\text{I}_3^-$  is determined by titrating with  $\text{Na}_2\text{S}_2\text{O}_3$ .

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  $\text{I}^-$  does not have a single, well-defined equivalence point. By converting the chlorine residual to an equivalent amount of  $\text{I}_3^-$ , the indirect titration with  $\text{Na}_2\text{S}_2\text{O}_3$  has a single, useful equivalence point.



**Figure 9.41** Endpoint for the determination of the total chlorine residual. (a) Acidifying the sample and adding KI forms a brown solution of  $\text{I}_3^-$ . (b) Titrating with  $\text{Na}_2\text{S}_2\text{O}_3$  converts  $\text{I}_3^-$  to  $\text{I}^-$  with the solution fading to a pale yellow color as we approach the end point. (c) Adding starch forms the deep purple starch- $\text{I}_3^-$  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.

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 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 find relevance. 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 initially must be present in a single oxidation state. For example, iron is 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 initially may be present in both the +2 and +3 oxidation states. Before titrating, we must reduce any  $Fe^{3+}$  to  $Fe^{2+}$  if we want to determine the total concentration of iron in the sample. This type of pretreatment is 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 is removed before we begin the titration by removing the coiled wire or by filtering.

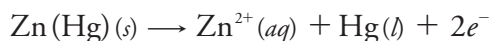
An alternative method for using an auxiliary reducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finely divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suc-

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

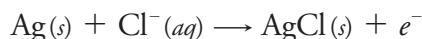
Oxidized Titrand	Walden Reductor	Jones Reductor
$\text{Cr}^{3+}$	—	$\text{Cr}^{3+}(\text{aq}) + e^{-} \rightarrow \text{Cr}^{2+}(\text{aq})$
$\text{Cu}^{2+}$	$\text{Cu}^{2+}(\text{aq}) + e^{-} \rightarrow \text{Cu}^{+}(\text{aq})$	$\text{Cu}^{2+}(\text{aq}) + 2e^{-} \rightarrow \text{Cu}(\text{s})$
$\text{Fe}^{3+}$	$\text{Fe}^{3+}(\text{aq}) + e^{-} \rightarrow \text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{3+}(\text{aq}) + e^{-} \rightarrow \text{Fe}^{2+}(\text{aq})$
$\text{TiO}^{2+}$	—	$\text{TiO}^{2+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + e^{-} \rightarrow \text{Ti}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
$\text{MoO}_2^{2+}$	$\text{MoO}_2^{2+}(\text{aq}) + e^{-} \rightarrow \text{MoO}_2^{+}(\text{aq})$	$\text{MoO}_2^{2+}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 3e^{-} \rightarrow \text{Mo}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
$\text{VO}_2^{2+}$	$\text{VO}_2^{+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + e^{-} \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\text{VO}_2^{+}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 3e^{-} \rightarrow \text{V}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

tion. 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,  $\text{Zn}(\text{Hg})$ , which is prepared by briefly placing Zn granules in a solution of  $\text{HgCl}_2$ . Oxidation of zinc

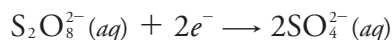


provides the electrons for reducing the titrand. In the **WALDEN REDUCTOR** the column is filled with granular Ag metal. The solution containing the titrand is acidified with HCl and passed through the column where the oxidation of silver

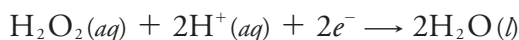


provides the necessary electrons for reducing the titrand. Table 9.17 provides a summary of several applications of reduction columns.

Several reagents are used as **AUXILIARY OXIDIZING AGENTS**, including ammonium peroxydisulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and hydrogen peroxide,  $\text{H}_2\text{O}_2$ . Peroxydisulfate is a powerful oxidizing agent



that is capable of oxidizing  $\text{Mn}^{2+}$  to  $\text{MnO}_4^{-}$ ,  $\text{Cr}^{3+}$  to  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ . Excess peroxydisulfate is destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in an acidic solution

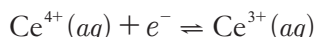


provides another method for oxidizing a titrand. Excess  $\text{H}_2\text{O}_2$  is destroyed by briefly boiling the solution.

### 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  $\text{MnO}_4^-$ ,  $\text{Ce}^{4+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{I}_3^-$ . Which titrant is used often depends on how easily it oxidizes 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  $\text{MnO}_4^-$  and  $\text{Ce}^{4+}$ , for which the reduction half-reactions are



A solution of  $\text{Ce}^{4+}$  in 1 M  $\text{H}_2\text{SO}_4$  usually is prepared from the primary standard cerium ammonium nitrate,  $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$ . When prepared using a reagent grade material, such as  $\text{Ce}(\text{OH})_4$ , the solution is standardized against a primary standard reducing agent such as  $\text{Na}_2\text{C}_2\text{O}_4$  or  $\text{Fe}^{2+}$  (prepared from iron wire) using ferroin as an indicator. Despite its availability as a primary standard and its ease of preparation,  $\text{Ce}^{4+}$  is not used as frequently as  $\text{MnO}_4^-$  because it is more expensive.

A solution of  $\text{MnO}_4^-$  is prepared from  $\text{KMnO}_4$ , which is not available as a primary standard. An aqueous solution of permanganate is thermodynamically unstable due to its ability to oxidize water.



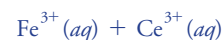
This reaction is catalyzed by the presence of  $\text{MnO}_2$ ,  $\text{Mn}^{2+}$ , heat, light, and the presence of acids and bases. A moderately stable solution of permanganate is prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid  $\text{MnO}_2$  that precipitates. Standardization is accomplished against a primary standard reducing agent such as  $\text{Na}_2\text{C}_2\text{O}_4$  or  $\text{Fe}^{2+}$  (prepared from iron wire), with the pink color of excess  $\text{MnO}_4^-$  signaling the end point. A solution of  $\text{MnO}_4^-$  prepared in this fashion is stable for 1–2 weeks, although you should recheck the standardization periodically.

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and its long term stability when in solution. It is not, however, as strong an oxidizing agent as  $\text{MnO}_4^-$  or  $\text{Ce}^{4+}$ , which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

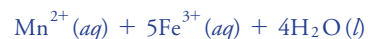
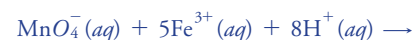


Although a solution of  $\text{Cr}_2\text{O}_7^{2-}$  is orange and a solution of  $\text{Cr}^{3+}$  is green, neither color is intense enough to serve as a useful indicator. Diphenyl-

The standardization reactions are

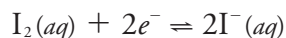


The standardization reactions are

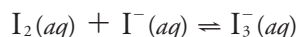


amine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with  $\text{Cr}_2\text{O}_7^{2-}$ .

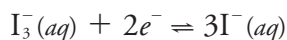
Iodine is another important oxidizing titrant. Because it is a weaker oxidizing agent than  $\text{MnO}_4^-$ ,  $\text{Ce}^{4+}$ , and  $\text{Cr}_2\text{O}_7^{2-}$ , it is useful only when the titrand is a stronger reducing agent. This apparent limitation, however, makes  $\text{I}_2$  a more selective titrant for the analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for  $\text{I}_2$  is



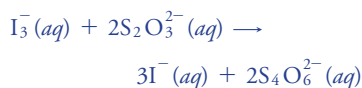
Because iodine is not very soluble in water, solutions are prepared by adding an excess of  $\text{I}^-$ . The complexation reaction



increases the solubility of  $\text{I}_2$  by forming the more soluble triiodide ion,  $\text{I}_3^-$ . Even though iodine is present as  $\text{I}_3^-$  instead of  $\text{I}_2$ , the number of electrons in the reduction half-reaction is unaffected.

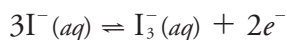


The standardization reaction is



Solutions of  $\text{I}_3^-$  normally are standardized against  $\text{Na}_2\text{S}_2\text{O}_3$  using starch as a specific indicator for  $\text{I}_3^-$ .

An oxidizing titrant such as  $\text{MnO}_4^-$ ,  $\text{Ce}^{4+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{I}_3^-$ , 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 its solutions are susceptible to the air-oxidation of  $\text{I}^-$  to  $\text{I}_3^-$ .



Instead, adding an excess of KI reduces the titrand and releases a stoichiometric amount of  $\text{I}_3^-$ . The amount of  $\text{I}_3^-$  produced is then determined by a back titration using thiosulfate,  $\text{S}_2\text{O}_3^{2-}$ , as a reducing titrant.



Solutions of  $\text{S}_2\text{O}_3^{2-}$  are prepared using  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and are standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard  $\text{KIO}_3$  in an acidic solution that contains an excess of KI. The reaction between  $\text{IO}_3^-$  and  $\text{I}^-$

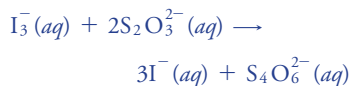


liberates a stoichiometric amount of  $\text{I}_3^-$ . By titrating this  $\text{I}_3^-$  with thiosulfate, using starch as a visual indicator, we can determine the concentration of  $\text{S}_2\text{O}_3^{2-}$  in the titrant.

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

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  $\text{I}_3^-$ .

The standardization titration is



which is the same reaction used to standardize solutions of  $\text{I}_3^-$ . This approach to standardizing solutions of  $\text{S}_2\text{O}_3^{2-}$  is similar to that used in the determination of the total chlorine residual outlined in [Representative Method 9.3](#).



bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate is restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which leads to a change in its concentration. This problem is minimized by adding a preservative such as  $\text{HgI}_2$  to the solution.

Another useful reducing titrant is ferrous ammonium sulfate,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in which iron is present in the +2 oxidation state. A solution of  $\text{Fe}^{2+}$  is susceptible to air-oxidation, but when prepared in 0.5 M  $\text{H}_2\text{SO}_4$  it remains stable for as long as a month. Periodic restandardization with  $\text{K}_2\text{Cr}_2\text{O}_7$  is advisable. Ferrous ammonium sulfate is used as the titrant in a direct analysis of the titrand, or, it is added to the titrand in excess and the amount of  $\text{Fe}^{3+}$  produced determined by back titrating with a standard solution of  $\text{Ce}^{4+}$  or  $\text{Cr}_2\text{O}_7^{2-}$ .

## 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 using the oxidizing power of chlorine to oxidize  $\text{I}^-$  to  $\text{I}_3^-$ . The amount of  $\text{I}_3^-$  is determined by back titrating with  $\text{S}_2\text{O}_3^{2-}$ .

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 that contribute to the free chlorine residual include  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ . The combined chlorine residual includes those species in which chlorine is in its reduced form and, therefore, no longer capable of providing disinfection. Species that contribute to the combined chlorine residual are  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$  and  $\text{NCl}_3$ .

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.

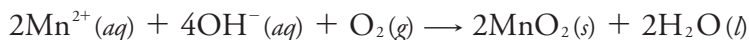
Having determined the free chlorine residual in the water sample, a small amount of KI is added, which catalyzes the reduction of monochloramine,  $\text{NH}_2\text{Cl}$ , and oxidizes a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of  $\text{NH}_2\text{Cl}$  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 react completely with any substance that can be oxidized by chlorine, while

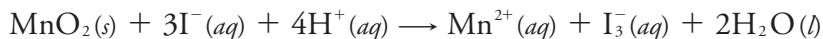
also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analysis, 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 dissolved  $O_2$  in 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 first is 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  $MnO_2$ .

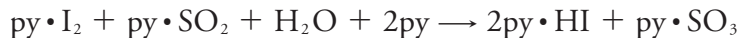


After the reaction is complete, the solution is acidified with  $H_2SO_4$ . Under the now acidic conditions,  $I^{-}$  is oxidized to  $I_3^{-}$  by  $MnO_2$ .



The amount of  $I_3^{-}$  that forms 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 reduces  $I_3^{-}$  to  $I^{-}$  under acidic conditions. This interference is eliminated by adding sodium azide,  $NaN_3$ , which reduces  $NO_2^{-}$  to  $N_2$ . Other reducing agents, such as  $Fe^{2+}$ , are eliminated by pretreating the sample with  $KMnO_4$  and destroying any 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  $py \cdot I_2$  and  $py \cdot SO_2$ . When added to a sample that contains water,  $I_2$  is reduced to  $I^{-}$  and  $SO_2$  is oxidized to  $SO_3$ .



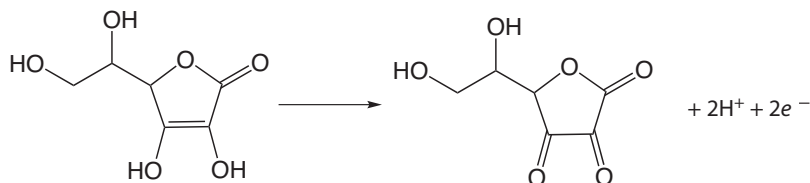
Methanol is included to prevent the further reaction of  $py \cdot SO_3$  with water. The titration's end point is signaled when the solution changes from the product's yellow color to the brown color of the Karl Fischer reagent.

## ORGANIC ANALYSIS

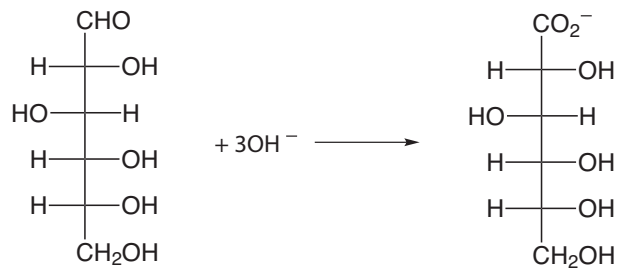
Redox titrimetry also is used for the analysis of organic analytes. One important example is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters. The COD is a measure of the quantity of oxygen necessary to oxidize completely all the organic matter in a sample to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Because no attempt is made to correct for organic matter that is 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 the management of industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or into the environment.

A sample's COD is determined by refluxing it in the presence of excess  $\text{K}_2\text{Cr}_2\text{O}_7$ , which serves as the oxidizing agent. The solution is acidified with  $\text{H}_2\text{SO}_4$ , using  $\text{Ag}_2\text{SO}_4$  to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate,  $\text{HgSO}_4$ , is added to complex any chloride that is present, which prevents the precipitation of the  $\text{Ag}^+$  catalyst as  $\text{AgCl}$ . 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  $\text{Cr}_2\text{O}_7^{2-}$  determined by a back titration using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to remove completely all traces of organic matter from the reagents, a blank titration is performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

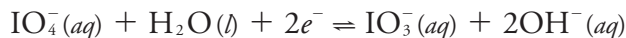
Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of  $\text{S}_2\text{O}_3^{2-}$  with  $\text{I}_3^-$  produces the tetrathionate ion,  $\text{S}_4\text{O}_6^{2-}$ . The tetrathionate ion is actually a dimer that consists of two thiosulfate ions connected through a disulfide ( $-\text{S}-\text{S}-$ ) linkage. In the same fashion,  $\text{I}_3^-$  is used to titrate mercaptans of the general formula  $\text{RSH}$ , forming the dimer  $\text{RSSR}$  as a product. The amino acid cysteine also can be titrated with  $\text{I}_3^-$ . The product of this titration is cystine, which is a dimer of cysteine. Triiodide also is used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone



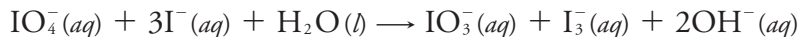
and for the analysis of reducing sugars, such as glucose, by oxidizing the aldehyde functional group to a carboxylate ion in a basic solution.



An organic compound that contains a hydroxyl, a carbonyl, or an amine functional group adjacent to an hydroxyl or a carbonyl group can be oxidized using metaperiodate,  $\text{IO}_4^-$ , as an oxidizing titrant.



A two-electron oxidation cleaves the C–C bond between the two functional groups with hydroxyl groups oxidized to aldehydes or ketones, carbonyl groups oxidized to carboxylic acids, and amines oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of  $\text{IO}_4^-$  to the solution that contains 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  $\text{IO}_4^-$  to  $\text{IO}_3^-$  and  $\text{I}_3^-$ .



The  $\text{I}_3^-$  is then determined by titrating with  $\text{S}_2\text{O}_3^{2-}$  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 its stoichiometry by remembering that the electrons in a redox reaction are conserved.

#### Example 9.11

The amount of Fe in a 0.4891-g sample of an ore is determined by titrating with  $\text{K}_2\text{Cr}_2\text{O}_7$ . After dissolving the sample in HCl, the iron is brought into a +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point requires 36.92 mL of 0.02153 M  $\text{K}_2\text{Cr}_2\text{O}_7$ . Report the ore's iron content as %w/w  $\text{Fe}_2\text{O}_3$ .

#### SOLUTION

Because we are not provided with the titration reaction, we will use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , and the titrant is reduced from  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ . Oxidizing  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  requires a single electron. Reducing  $\text{Cr}_2\text{O}_7^{2-}$ , in which each chromium is in the +6 oxidation state,

to  $\text{Cr}^{3+}$  requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with six moles of  $\text{Fe}^{2+}$ .

The moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  used to reach the end point is

$$(0.02153 \text{ M})(0.03692 \text{ L}) = 7.949 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

which means the sample contains

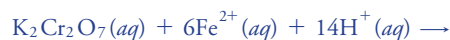
$$7.949 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 \times \frac{6 \text{ mol Fe}^{2+}}{\text{mol K}_2\text{Cr}_2\text{O}_7} = 4.769 \times 10^{-3} \text{ mol Fe}^{2+}$$

Thus, the %w/w  $\text{Fe}_2\text{O}_3$  in the sample of ore is

$$4.769 \times 10^{-3} \text{ mol Fe}^{2+} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}^{2+}} \times \frac{159.69 \text{ g Fe}_2\text{O}_3}{\text{mol Fe}_2\text{O}_3} = 0.3808 \text{ g Fe}_2\text{O}_3$$

$$\frac{0.3808 \text{ g Fe}_2\text{O}_3}{0.4891 \text{ g sample}} \times 100 = 77.86\% \text{ w/w Fe}_2\text{O}_3$$

Although we can deduce the stoichiometry between the titrant and the titrand without balancing the titration reaction, the balanced reaction



does provide useful information. For example, the presence of  $\text{H}^+$  reminds us that the reaction must take place in an acidic solution.

### Practice Exercise 9.20

The purity of a sample of sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , is determined by titrating with a standard solution of  $\text{KMnO}_4$ . If a 0.5116-g sample requires 35.62 mL of 0.0400 M  $\text{KMnO}_4$  to reach the titration's end point, what is the %w/w  $\text{Na}_2\text{C}_2\text{O}_4$  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 is diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample is transferred by pipet into an Erlenmeyer flask that contains an excess of KI, reducing the  $\text{OCl}^-$  to  $\text{Cl}^-$  and producing  $\text{I}_3^-$ . The liberated  $\text{I}_3^-$  is determined by titrating with 0.09892 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 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,  $\text{Na}_2\text{S}_2\text{O}_3$ , we need to consider both the reaction between  $\text{OCl}^-$  and  $\text{I}^-$ , and the titration of  $\text{I}_3^-$  with  $\text{Na}_2\text{S}_2\text{O}_3$ .

First, in reducing  $\text{OCl}^-$  to  $\text{Cl}^-$  the oxidation state of chlorine changes from +1 to -1, requiring two electrons. The oxidation of three  $\text{I}^-$  to form  $\text{I}_3^-$  releases two electrons as the oxidation state of each iodine changes from

$-1$  in  $\text{I}^-$  to  $-\frac{1}{3}$  in  $\text{I}_3^-$ . A conservation of electrons, therefore, requires that each mole of  $\text{OCl}^-$  produces one mole of  $\text{I}_3^-$ .

Second, in the titration reaction,  $\text{I}_3^-$  is reduced to  $\text{I}^-$  and  $\text{S}_2\text{O}_3^{2-}$  is oxidized to  $\text{S}_4\text{O}_6^{2-}$ . Reducing  $\text{I}_3^-$  to  $3\text{I}^-$  requires two electrons as each iodine changes from an oxidation state of  $-\frac{1}{3}$  to  $-1$ . In oxidizing  $\text{S}_2\text{O}_3^{2-}$  to  $\text{S}_4\text{O}_6^{2-}$ , each sulfur changes its oxidation state from  $+2$  to  $+2.5$ , releasing one electron for each  $\text{S}_2\text{O}_3^{2-}$ . A conservation of electrons, therefore, requires that each mole of  $\text{I}_3^-$  reacts with two moles of  $\text{S}_2\text{O}_3^{2-}$ .

Finally, because each mole of  $\text{OCl}^-$  produces one mole of  $\text{I}_3^-$ , and each mole of  $\text{I}_3^-$  reacts with two moles of  $\text{S}_2\text{O}_3^{2-}$ , we know that every mole of  $\text{NaOCl}$  in the sample ultimately results in the consumption of two moles of  $\text{Na}_2\text{S}_2\text{O}_3$ .

The moles of  $\text{Na}_2\text{S}_2\text{O}_3$  used to reach the titration's end point is

$$(0.09892 \text{ M})(0.00896 \text{ L}) = 8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3$$

which means the sample contains

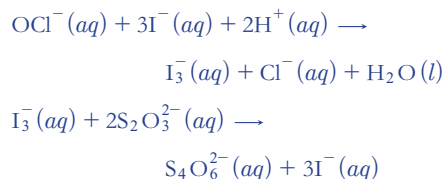
$$8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3 \times \frac{1 \text{ mol NaOCl}}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{74.44 \text{ g NaOCl}}{\text{mol NaOCl}} = 0.03299 \text{ g NaOCl}$$

Thus, the %w/v  $\text{NaOCl}$  in the diluted sample is

$$\frac{0.03299 \text{ g NaOCl}}{25.00 \text{ mL}} \times 100 = 0.132\% \text{ w/w NaOCl}$$

Because the bleach was diluted by a factor of 40 (25 mL to 1000 mL), the concentration of  $\text{NaOCl}$  in the bleach is 5.28% (w/v).

The balanced reactions for this analysis are:



### Example 9.13

The amount of ascorbic acid,  $\text{C}_6\text{H}_8\text{O}_6$ , in orange juice is determined by oxidizing ascorbic acid to dehydroascorbic acid,  $\text{C}_6\text{H}_6\text{O}_6$ , with a known amount of  $\text{I}_3^-$ , and back titrating the excess  $\text{I}_3^-$  with  $\text{Na}_2\text{S}_2\text{O}_3$ . A 5.00-mL sample of filtered orange juice is treated with 50.00 mL of 0.01023 M  $\text{I}_3^-$ . After the oxidation is complete, 13.82 mL of 0.07203 M  $\text{Na}_2\text{S}_2\text{O}_3$  is 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  $\text{I}_3^-$  and the analyte,  $\text{C}_6\text{H}_8\text{O}_6$ , and between  $\text{I}_3^-$  and the titrant,  $\text{Na}_2\text{S}_2\text{O}_3$ . The later is easy because we know from [Example 9.12](#) that each mole of  $\text{I}_3^-$  reacts with two moles of  $\text{Na}_2\text{S}_2\text{O}_3$ .

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from  $+\frac{2}{3}$  in  $\text{C}_6\text{H}_8\text{O}_6$  to  $+1$  in  $\text{C}_6\text{H}_6\text{O}_6$ . Each carbon

releases  $\frac{1}{3}$  of an electron, or a total of two electrons per ascorbic acid. As we learned in [Example 9.12](#), reducing  $\text{I}_3^-$  requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of  $\text{I}_3^-$ .

The total moles of  $\text{I}_3^-$  that react with  $\text{C}_6\text{H}_8\text{O}_6$  and with  $\text{Na}_2\text{S}_2\text{O}_3$  is

$$(0.01023 \text{ M})(0.05000 \text{ L}) = 5.115 \times 10^{-4} \text{ mol I}_3^-$$

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  $\text{I}_3^-$  that react with  $\text{Na}_2\text{S}_2\text{O}_3$  from the total moles of  $\text{I}_3^-$  gives the moles reacting with ascorbic acid.

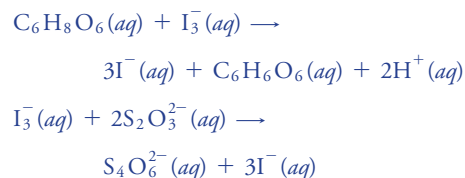
$$5.115 \times 10^{-4} \text{ mol I}_3^- - 4.977 \times 10^{-4} \text{ mol I}_3^- = 1.38 \times 10^{-5} \text{ mol I}_3^-$$

The grams of ascorbic acid in the 5.00-mL sample of orange juice is

$$1.38 \times 10^{-5} \text{ mol I}_3^- \times \frac{1 \text{ mol C}_6\text{H}_8\text{O}_6}{\text{mol I}_3^-} \times \frac{176.12 \text{ g C}_6\text{H}_8\text{O}_6}{\text{mol C}_6\text{H}_8\text{O}_6} = 2.43 \times 10^{-3} \text{ g C}_6\text{H}_8\text{O}_6$$

There are 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg per 100 mL of orange juice.

The balanced reactions for this analysis are:



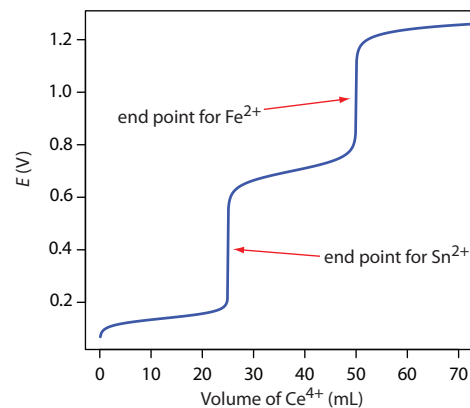
### Practice Exercise 9.21

A quantitative analysis for ethanol,  $\text{C}_2\text{H}_6\text{O}$ , is accomplished by a redox back titration. Ethanol is oxidized to acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , using excess dichromate,  $\text{Cr}_2\text{O}_7^{2-}$ , which is reduced to  $\text{Cr}^{3+}$ . The excess dichromate is titrated with  $\text{Fe}^{2+}$ , giving  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  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  $\text{K}_2\text{Cr}_2\text{O}_7$ . A back titration of the unreacted  $\text{Cr}_2\text{O}_7^{2-}$  requires 21.48 mL of 0.1014 M  $\text{Fe}^{2+}$ . 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 an acid–base or a complexation titration. As with an acid–base titration, 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  $\text{Fe}^{2+}$  and  $\text{Sn}^{2+}$



**Figure 9.42** Titration curve for the titration of 50.0 mL of 0.0125 M  $\text{Sn}^{2+}$  and 0.0250 M  $\text{Fe}^{2+}$  with 0.050 M  $\text{Ce}^{4+}$ . Both the titrand and the titrant are 1M in HCl.

using  $\text{Ce}^{4+}$  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.

## 9E Precipitation Titrations

Thus far we have examined titrimetric methods based on acid–base, complexation, and oxidation–reduction 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**.

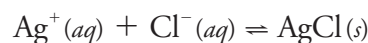
One of the earliest precipitation titrations—developed at the end of the eighteenth century—was the analysis of  $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{SO}_4$  in potash. Calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , was used as the titrant, which forms a precipitate of  $\text{CaCO}_3$  and  $\text{CaSO}_4$ . 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  $\text{Ag}^+$  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 did for other titrations, we first show how to calculate the titration curve and then demonstrate how we can 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  $\text{AgNO}_3$ . The reaction in this case is



Because the reaction's equilibrium constant is so large

$$K = (K_{\text{sp}})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

we may assume that  $\text{Ag}^+$  and  $\text{Cl}^-$  react completely.

By now you are familiar with our approach to calculating a titration curve. The first task is to calculate the volume of  $\text{Ag}^+$  needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{mol Ag}^+ = M_{\text{Ag}} V_{\text{Ag}} = M_{\text{Cl}} V_{\text{Cl}} = \text{mol Cl}^-$$

Solving for the volume of  $\text{Ag}^+$

$$V_{\text{eq}} = V_{\text{Ag}} = \frac{M_{\text{Cl}} V_{\text{Cl}}}{M_{\text{Ag}}} = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{0.100 \text{ M}} = 25.0 \text{ mL}$$

shows that we need 25.0 mL of  $\text{Ag}^+$  to reach the equivalence point.

Before the equivalence point the titrand,  $\text{Cl}^-$ , is in excess. The concentration of unreacted  $\text{Cl}^-$  after we add 10.0 mL of  $\text{Ag}^+$ , for example, is

Step 1: Calculate the volume of  $\text{AgNO}_3$  needed to reach the equivalence point.



Table 9.18 Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO<sub>3</sub>

Volume of AgNO <sub>3</sub> (mL)	pCl	Volume of AgNO <sub>3</sub> (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		

$$[\text{Cl}^-] = \frac{(\text{mol Cl}^-)_{\text{initial}} - (\text{mol Ag}^+)_{\text{added}}}{\text{total volume}} = \frac{M_{\text{Cl}} V_{\text{Cl}} - M_{\text{Ag}} V_{\text{Ag}}}{V_{\text{Cl}} + V_{\text{Ag}}}$$

$$\begin{aligned} [\text{Cl}^-] &= \frac{(0.0500 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} \\ &= 2.50 \times 10^{-2} \text{ M} \end{aligned}$$

which corresponds to a pCl of 1.60.

At the titration's equivalence point, we know that the concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> are equal. To calculate the concentration of Cl<sup>-</sup> we use the  $K_{\text{sp}}$  for AgCl; thus

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.8 \times 10^{-10}$$

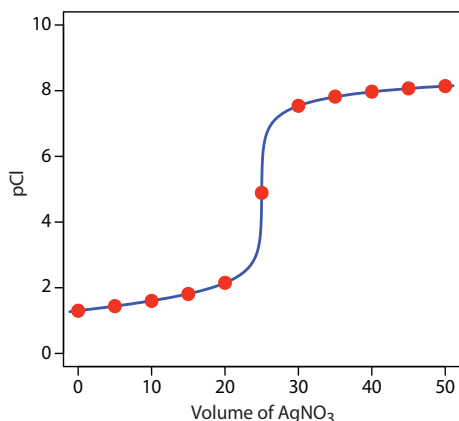
Solving for  $x$  gives [Cl<sup>-</sup>] as  $1.3 \times 10^{-5}$  M, or a pCl of 4.89.

After the equivalence point, the titrant is in excess. We first calculate the concentration of excess Ag<sup>+</sup> and then use the  $K_{\text{sp}}$  expression to calculate the concentration of Cl<sup>-</sup>. For example, after adding 35.0 mL of titrant

$$[\text{Ag}^+] = \frac{(\text{mol Ag}^+)_{\text{added}} - (\text{mol Cl}^-)_{\text{initial}}}{\text{total volume}} = \frac{M_{\text{Ag}} V_{\text{Ag}} - M_{\text{Cl}} V_{\text{Cl}}}{V_{\text{Ag}} + V_{\text{Cl}}}$$

$$\begin{aligned} [\text{Ag}^+] &= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{35.0 \text{ mL} + 50.0 \text{ mL}} \\ &= 1.18 \times 10^{-2} \text{ M} \end{aligned}$$

$$[\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$



**Figure 9.43** Titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO<sub>3</sub>. The **red** points corresponds to the data in Table 9.18. The **blue** line shows the complete titration curve.

Step 2: Calculate pCl before the equivalence point by determining the concentration of unreacted NaCl.

Step 3: Calculate pCl at the equivalence point using the  $K_{\text{sp}}$  for AgCl to calculate the concentration of Cl<sup>-</sup>.

Step 4: Calculate pCl after the equivalence point by first calculating the concentration of excess AgNO<sub>3</sub> and then calculating the concentration of Cl<sup>-</sup> using the  $K_{\text{sp}}$  for AgCl.

### 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<sub>3</sub> with 0.100 M NaCl as pAg versus  $V_{\text{NaCl}}$  and as pCl versus  $V_{\text{NaCl}}$ .

Click [here](#) to review your answer to this exercise.

or a pCl of 7.81. Additional results for the titration curve are shown in [Table 9.18](#) and [Figure 9.43](#).

### 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<sub>3</sub>.

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 that intersects the *x*-axis at 25.0 mL of AgNO<sub>3</sub>. [Figure 9.44a](#) shows the result of this first step in our sketch.

Before the equivalence point, Cl<sup>-</sup> is present in excess and pCl is determined by the concentration of unreacted Cl<sup>-</sup>. As we learned earlier, the calculations are straightforward. [Figure 9.44b](#) shows pCl after adding 10.0 mL and 20.0 mL of AgNO<sub>3</sub>.

After the equivalence point, Ag<sup>+</sup> is in excess and the concentration of Cl<sup>-</sup> is determined by the solubility of AgCl. Again, the calculations are straightforward. [Figure 9.44c](#) shows pCl after adding 30.0 mL and 40.0 mL of AgNO<sub>3</sub>.

Next, we draw a straight line through each pair of points, extending them through the vertical line that represents 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.

### FINDING THE END POINT WITH AN INDICATOR

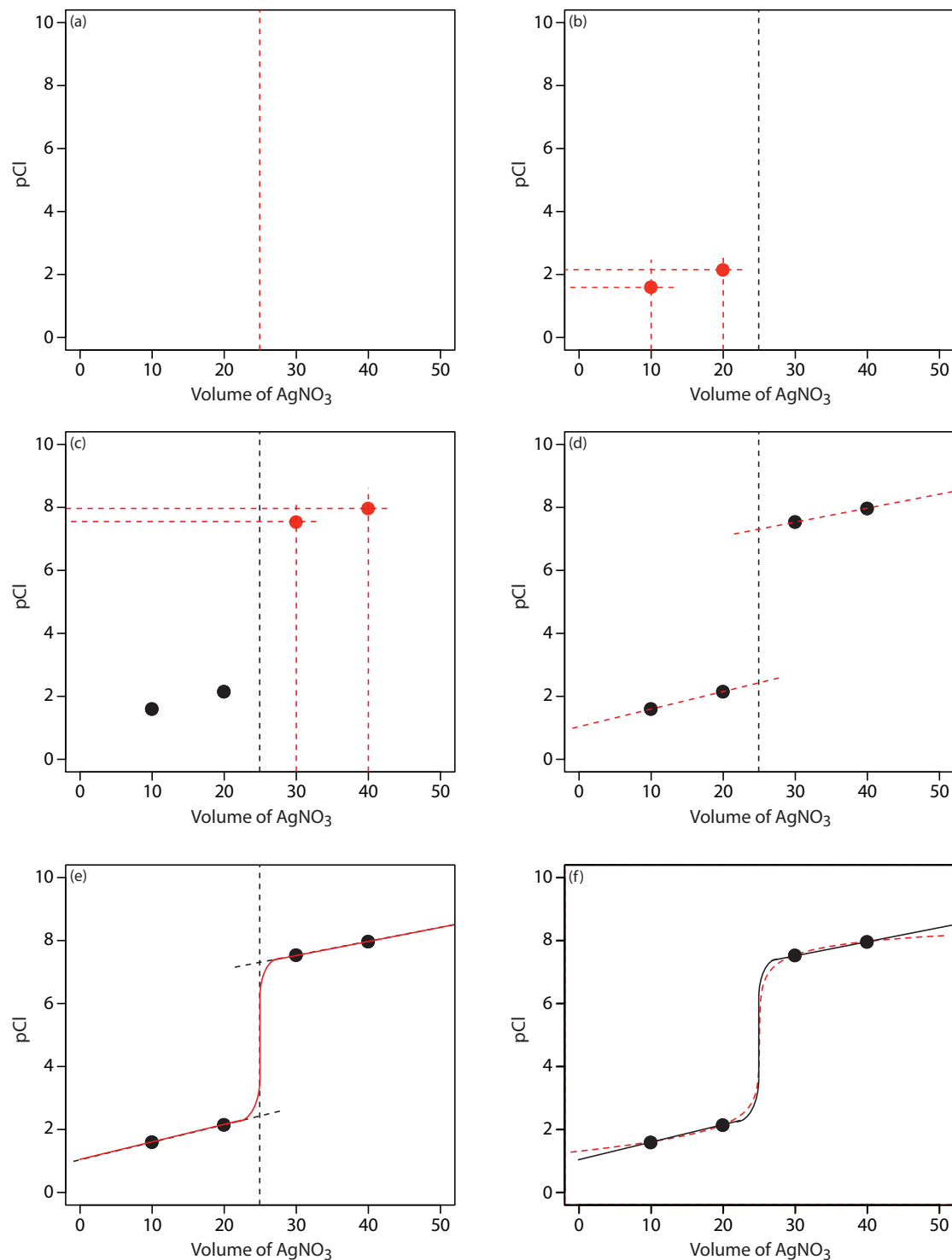
There are three general types of indicators for a precipitation titration, each of which changes color at or near the titration's equivalence point. The first type of indicator is a species that forms a precipitate with the titrant. In the **MOHR METHOD** for Cl<sup>-</sup> using Ag<sup>+</sup> as a titrant, for example, a small amount of K<sub>2</sub>CrO<sub>4</sub> is added to the titrand's solution. The titration's end point is the formation of a reddish-brown precipitate of Ag<sub>2</sub>CrO<sub>4</sub>.

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](#).

See [Table 9.18](#) for the values.

See [Table 9.18](#) for the values.

The Mohr method was first published in 1855 by Karl Friedrich Mohr.



**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<sub>3</sub>: (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.

Because  $\text{CrO}_4^{2-}$  imparts a yellow color to the solution, which might obscure the end point, only a small amount of  $\text{K}_2\text{CrO}_4$  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  $\text{CrO}_4^{2-}$  is a weak base, the titrand's solution is made slightly alkaline. If the pH is too acidic, chromate is present as  $\text{HCrO}_4^-$  instead of  $\text{CrO}_4^{2-}$ , and the  $\text{Ag}_2\text{CrO}_4$  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  $\text{Ag}^+$  using  $\text{KSCN}$  as the titrant, for example, a small amount of  $\text{Fe}^{3+}$  is added to the titrand's solution. The titration's end point is the formation of the reddish-colored  $\text{Fe}(\text{SCN})^{2+}$  complex. The titration is carried out in an acidic solution to prevent the precipitation of  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$ .

The third type of end point uses a species that changes color when it adsorbs to the precipitate. In the **FAJANS METHOD** for  $\text{Cl}^-$  using  $\text{Ag}^+$  as a titrant, for example, the anionic dye dichlorofluoroscein is added to the titrand's solution. Before the end point, the precipitate of  $\text{AgCl}$  has a negative surface charge due to the adsorption of excess  $\text{Cl}^-$ . 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  $\text{Ag}^+$ . Dichlorofluoroscein now adsorbs to the precipitate's surface where its color is pink. This change in the indicator's color signals the end point.

### 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.

### 9E.3 Quantitative Applications

Although precipitation titrimetry rarely is listed as a standard method of analysis, it is useful as a secondary analytical method to verify other analytical methods. Most precipitation titrations use  $\text{Ag}^+$  as either the titrand or the titrant. A titration in which  $\text{Ag}^+$  is the titrant is called an **ARGENTOMETRIC TITRATION**. [Table 9.19](#) provides a list of several typical precipitation titrations.

The Volhard method was first published in 1874 by Jacob Volhard.

The Fajans method was first published in the 1920s by Kasimir Fajans.

For a discussion of potentiometry and ion-selective electrodes, see Chapter 11.

**Table 9.19 Representative Examples of Precipitation Titrations**

Titrand	Titrant <sup>a</sup>	End Point <sup>b</sup>
AsO <sub>4</sub> <sup>3-</sup>	AgNO <sub>3</sub> , KSCN	Volhard
Br <sup>-</sup>	AgNO <sub>3</sub>	Mohr or Fajans
	AgNO <sub>3</sub> , KSCN	Volhard
Cl <sup>-</sup>	AgNO <sub>3</sub>	Mohr or Fajans
	AgNO <sub>3</sub> , KSCN	Volhard*
CO <sub>3</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
CrO <sub>4</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
I <sup>-</sup>	AgNO <sub>3</sub>	Fajans
	AgNO <sub>3</sub> , KSCN	Volhard
PO <sub>4</sub> <sup>3-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
S <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
SCN <sup>-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*

<sup>a</sup> 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.

<sup>b</sup> For those Volhard methods identified with an asterisk (\*) the precipitated silver salt is removed before carrying out the back titration.

### 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<sub>2</sub>CrO<sub>4</sub>, each mole of CrO<sub>4</sub><sup>2-</sup> reacts with two moles of Ag<sup>+</sup>.

#### 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<sub>2</sub>CrO<sub>4</sub> end point, requiring 36.85 mL of 0.1120 M AgNO<sub>3</sub>. 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

$$V_{\text{Ag}} = 36.85 \text{ mL} - 0.71 \text{ mL} = 36.14 \text{ mL}$$

$$(0.1120 \text{ M})(0.03614 \text{ L}) = 4.048 \times 10^{-3} \text{ mol AgNO}_3$$

Titration with  $\text{AgNO}_3$  produces a precipitate of  $\text{AgCl}$  and  $\text{AgBr}$ . In forming the precipitates, each mole of  $\text{KCl}$  consumes one mole of  $\text{AgNO}_3$  and each mole of  $\text{NaBr}$  consumes one mole of  $\text{AgNO}_3$ ; thus

$$\text{mol KCl} + \text{mol NaBr} = 4.048 \times 10^{-3}$$

We are interested in finding the mass of  $\text{KCl}$ , so let's rewrite this equation in terms of mass. We know that

$$\text{mol KCl} = \frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}}$$

$$\text{mol NaBr} = \frac{\text{g NaBr}}{102.89 \text{ g NaBr/mol NaBr}}$$

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— $\text{g KCl}$  and  $\text{g NaBr}$ —we need another equation that includes both unknowns. A simple equation takes advantage of the fact that the sample contains only  $\text{KCl}$  and  $\text{NaBr}$ ; 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  $\text{KCl}$  and the %w/w  $\text{KCl}$  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  $\text{I}^-$  using the Volhard method requires a back titration. A typical calculation is shown in the following example.

### Example 9.15

The %w/w  $\text{I}^-$  in a 0.6712-g sample is determined by a Volhard titration. After adding 50.00 mL of 0.05619 M  $\text{AgNO}_3$  and allowing the precipitate to form, the remaining silver is back titrated with 0.05322 M  $\text{KSCN}$ , requiring 35.14 mL to reach the end point. Report the %w/w  $\text{I}^-$  in the sample.

#### **SOLUTION**

There are two precipitates in this analysis:  $\text{AgNO}_3$  and  $\text{I}^-$  form a precipitate of  $\text{AgI}$ , and  $\text{AgNO}_3$  and  $\text{KSCN}$  form a precipitate of  $\text{AgSCN}$ . Each mole

of  $\text{I}^-$  consumes one mole of  $\text{AgNO}_3$  and each mole of  $\text{KSCN}$  consumes one mole of  $\text{AgNO}_3$ ; thus

$$\text{mol AgNO}_3 = \text{mol I}^- + \text{mol KSCN}$$

Solving for the moles of  $\text{I}^-$  we find

$$\text{mol I}^- = \text{mol AgNO}_3 - \text{mol KSCN} = M_{\text{Ag}} V_{\text{Ag}} - M_{\text{KSCN}} V_{\text{KSCN}}$$

$$\text{mol I}^- = (0.05619 \text{ M})(0.0500 \text{ L}) - (0.05322 \text{ M})(0.03514 \text{ L})$$

$$\text{mol I}^- = 9.393 \times 10^{-4}$$

The %w/w  $\text{I}^-$  in the sample is

$$\frac{(9.393 \times 10^{-4} \text{ mol I}^-) \times \frac{126.9 \text{ g I}^-}{\text{mol I}^-}}{0.6712 \text{ g sample}} \times 100 = 17.76\% \text{ w/w I}^-$$

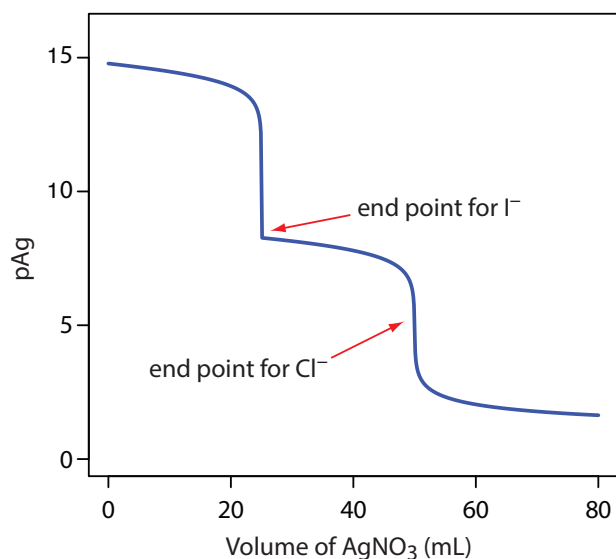
### Practice Exercise 9.23

A 1.963-g sample of an alloy is dissolved in  $\text{HNO}_3$  and diluted to volume in a 100-mL volumetric flask. Titrating a 25.00-mL portion with 0.1078 M  $\text{KSCN}$  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 there is a significant difference in the solubilities of the precipitates. Figure 9.45 shows an example of a titration curve for a mixture of  $\text{I}^-$  and  $\text{Cl}^-$  using  $\text{Ag}^+$  as a titrant.



**Figure 9.45** Titration curve for the titration of a 50.0 mL mixture of 0.0500 M  $\text{I}^-$  and 0.0500 M  $\text{Cl}^-$  using 0.100 M  $\text{Ag}^+$  as a titrant. The red arrows show the end points. Note that the end point for  $\text{I}^-$  is earlier than the end point for  $\text{Cl}^-$  because  $\text{AgI}$  is less soluble than  $\text{AgCl}$ .

## 9F Key Terms

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 that reacts stoichiometrically with a titrand provides quantitative information about the amount of analyte in a sample. The volume of titrant that corresponds 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 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 are possible 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 that contains 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, oxidation–reduction, 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



tions with reducing agents also are possible. Precipitation titrations often involve  $\text{Ag}^+$  as either the analyte or titrant.

## 9H Problems

- Calculate or sketch titration curves for the following acid–base titrations.
  - 25.0 mL of 0.100 M NaOH with 0.0500 M HCl
  - 50.0 mL of 0.0500 M HCOOH with 0.100 M NaOH
  - 50.0 mL of 0.100 M  $\text{NH}_3$  with 0.100 M HCl
  - 50.0 mL of 0.0500 M ethylenediamine with 0.100 M HCl
  - 50.0 mL of 0.0400 M citric acid with 0.120 M NaOH
  - 50.0 mL of 0.0400 M  $\text{H}_3\text{PO}_4$  with 0.120 M NaOH
- Locate the equivalence point(s) for each titration curve in problem 1 and, where feasible, calculate the pH at the equivalence point. What is the stoichiometric relationship between the moles of acid and the moles of base for each of these equivalence points?
- Suggest an appropriate visual indicator for each of the titrations in problem 1.
- To sketch the titration curve for a weak acid we approximate the pH at 10% of the equivalence point volume as  $\text{p}K_{\text{a}} - 1$ , and the pH at 90% of the equivalence point volume as  $\text{p}K_{\text{a}} + 1$ . Show that these assumptions are reasonable.
- Tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , is a diprotic weak acid with a  $\text{p}K_{\text{a}1}$  of 3.0 and a  $\text{p}K_{\text{a}2}$  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. Assume your buret has a maximum capacity of 50 mL.
- 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.

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](#)

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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
49.87	7.4	116.14	12.6
49.92	7.6		

7. Schwartz published the following simulated data for the titration of a  $1.02 \times 10^{-4}$  M solution of a monoprotic weak acid ( $pK_a = 8.16$ ) with  $1.004 \times 10^{-3}$  M NaOH.<sup>10</sup> 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

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[Appendix 10: Solubility Products](#)

[Appendix 11: Acid Dissociation Constants](#)

[Appendix 12: Metal-Ligand Formation Constants](#)

[Appendix 13: Standard State Reduction Potentials](#)

<sup>10</sup> Schwartz, L. M. *J. Chem. Educ.* **1992**, *69*, 879–883.

mL of NaOH	pH	mL of NaOH	pH
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
3.19	8.332	7.79	9.545
3.41	8.398	7.99	9.572
3.60	8.458	8.21	9.599
3.80	8.521	8.44	9.624
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

8. Calculate or sketch the titration curve for a 50.0 mL solution of a 0.100 M monoprotic weak acid ( $\text{p}K_{\text{a}} = 8.0$ ) with 0.1 M strong base in a nonaqueous solvent with  $K_{\text{s}} = 10^{-20}$ . You may assume that the change in solvent does not affect the weak acid's  $\text{p}K_{\text{a}}$ . Compare your titration curve to the titration curve when water is the solvent.
9. The titration of a mixture of *p*-nitrophenol ( $\text{p}K_{\text{a}} = 7.0$ ) and *m*-nitrophenol ( $\text{p}K_{\text{a}} = 8.3$ ) is followed spectrophotometrically. Neither acid absorbs at a wavelength of 545 nm, but their respective conjugate bases 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. A quantitative analysis for aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ,  $K_{\text{b}} = 3.94 \times 10^{-10}$ ) is carried out by an acid–base titration using glacial acetic acid as the solvent and  $\text{HClO}_4$  as the titrant. A known volume of sample that contains 3–4 mmol of aniline is transferred to a 250-mL Erlenmeyer flask

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](#)

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[Appendix 10: Solubility Products](#)

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[Appendix 13: Standard State Reduction Potentials](#)

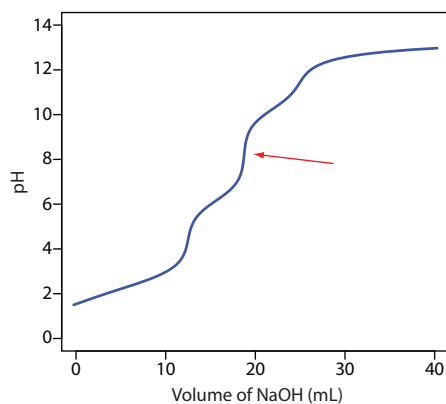
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**Figure 9.46** Titration curve for Problem 9.13.

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](#)

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[Appendix 13: Standard State Reduction Potentials](#)

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  $\text{HClO}_4$  (prepared in glacial acetic acid using anhydrous  $\text{HClO}_4$ ) 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 using water.
  - (b) One problem with using glacial acetic acid as solvent is its relatively high coefficient of thermal expansion of  $0.11\%/^{\circ}\text{C}$ . For example, 100.00 mL of glacial acetic acid at  $25^{\circ}\text{C}$  occupies 100.22 mL at  $27^{\circ}\text{C}$ . What is the effect on the reported concentration of aniline if the standardization of  $\text{HClO}_4$  is conducted at a temperature that is lower than that for the analysis of the unknown?
  - (c) The procedure calls for a sample that contains 3–4 mmoles of aniline. Why is this requirement necessary?
11. Using a ladder diagram, explain why the presence of dissolved  $\text{CO}_2$  leads to a determinate error for the standardization of  $\text{NaOH}$  if the end point's pH is 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  $\text{HCl}$  and 0.10 M  $\text{H}_2\text{CO}_3$  with 0.20 M strong base, and use it to justify the choice of these end points.
  13. Ethylenediaminetetraacetic acid,  $\text{H}_4\text{Y}$ , is a weak acid with successive acid dissociation constants of 0.010,  $2.19 \times 10^{-3}$ ,  $6.92 \times 10^{-7}$ , and  $5.75 \times 10^{-11}$ . Figure 9.46 shows a titration curve for  $\text{H}_4\text{Y}$  with  $\text{NaOH}$ . What is the stoichiometric relationship between  $\text{H}_4\text{Y}$  and  $\text{NaOH}$  at the equivalence point marked with the red arrow?
  14. A Gran plot method has been described for the quantitative analysis of a mixture that consists of a strong acid and a monoprotic weak acid.<sup>11</sup> A 50.00-mL mixture of  $\text{HCl}$  and  $\text{CH}_3\text{COOH}$  is transferred to an Erlenmeyer flask and titrated by using a digital pipet to add successive 1.00-mL aliquots of 0.09186 M  $\text{NaOH}$ . 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  $\text{HCl}$  and  $\text{CH}_3\text{COOH}$ .

<sup>11</sup> (a) Boiani, J. A. *J. Chem. Educ.* **1986**, *63*, 724–726; (b) Castillo, C. A.; Jaramillo, A. *J. Chem. Educ.* **1989**, *66*, 341.

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

15. Explain why it is not possible for a sample of water to simultaneously have  $\text{OH}^-$  and  $\text{HCO}_3^-$  as sources of alkalinity.

16. For each of the samples a–e, determine the sources of alkalinity ( $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) and their respective concentrations in parts per million. 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

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17. A sample may contain any of the following: HCl, NaOH,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , or  $\text{PO}_4^{3-}$ . 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 to the methyl orange end points. For each of the following samples, determine which species are present 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

18. The protein in a 1.2846-g sample of an oat cereal is determined by a Kjeldahl analysis. The sample is digested with  $\text{H}_2\text{SO}_4$ , the resulting solution made basic with NaOH, and the  $\text{NH}_3$  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  $\text{SO}_2$  in air is determined by bubbling a sample of air through a trap that contains  $\text{H}_2\text{O}_2$ . Oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$  results in the formation of  $\text{H}_2\text{SO}_4$ , which is then determined by titrating with NaOH. In a typical analysis, a sample of air is 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  $\mu\text{L/L}$   $\text{SO}_2$  in the sample of air. The density of  $\text{SO}_2$  at the temperature of the air sample is 2.86 mg/mL.
20. The concentration of  $\text{CO}_2$  in air is determined by an indirect acid–base titration. A sample of air is bubbled through a solution that contains an excess of  $\text{Ba}(\text{OH})_2$ , precipitating  $\text{BaCO}_3$ . The excess  $\text{Ba}(\text{OH})_2$  is back titrated with HCl. In a typical analysis a 3.5-L sample of air is bubbled through 50.00 mL of 0.0200 M  $\text{Ba}(\text{OH})_2$ . Back titrating with 0.0316 M HCl requires 38.58 mL to reach the end point. Determine the ppm  $\text{CO}_2$  in the sample of air given that the density of  $\text{CO}_2$  at the temperature of the sample is 1.98 g/L.

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21. The purity of a synthetic preparation of methylethyl ketone,  $\text{C}_4\text{H}_8\text{O}$ , 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 is diluted to 50.00 mL and treated with an excess of hydroxylamine hydrochloride. The liberated HCl is 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?
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	$1.36 \times 10^{-10}$
glycine	75.1	$1.67 \times 10^{-10}$
methionine	149.2	$8.9 \times 10^{-10}$
taurine	125.2	$1.8 \times 10^{-9}$
asparagine	150	$1.9 \times 10^{-9}$
leucine	131.2	$1.79 \times 10^{-10}$
phenylalanine	166.2	$4.9 \times 10^{-10}$
valine	117.2	$1.91 \times 10^{-10}$

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 can be used to determine an analyte's equivalent weight, but it can not be used to determine its formula weight. Explain why.

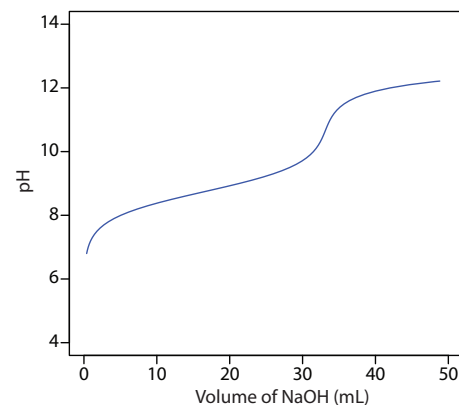
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**Figure 9.47** Titration curve for Problem 9.24.

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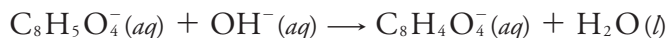
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28. Commercial washing soda is approximately 30–40% w/w  $\text{Na}_2\text{CO}_3$ . One procedure for the quantitative analysis of washing soda contains the following instructions:

Transfer an approximately 4-g sample of the washing soda to a 250-mL volumetric flask. Dissolve the sample in about 100 mL of  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  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  $\text{Na}_2\text{CO}_3$  that is >98% pure?

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 sources of systematic error or random error, or if they have no effect on the error. If the error is systematic, then indicate whether the experimentally determined molarity for NaOH is too high or too low. The standardization reaction is



- The balance used to weigh KHP is not properly calibrated and always reads 0.15 g too low.
- The indicator for the titration changes color between a pH of 3–4.
- An air bubble, which is lodged in the buret's tip at the beginning of the analysis, dislodges during the titration.
- Samples of KHP are weighed into separate Erlenmeyer flasks, but the balance is tarred only for the first flask.
- The KHP is not dried before it is used.
- The NaOH is not dried before it is used.
- 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.

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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 extracts into the aqueous solution where it reacts with the titrant. The titrant is added slowly to allow sufficient time for the extraction to take place.
- 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 50.0 mL of 0.100 Mg<sup>2+</sup> with 0.100 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<sup>2+</sup> with 0.025 M EDTA at a pH of 10 and in the presence of 10<sup>-3</sup> M and 10<sup>-1</sup> M NH<sub>3</sub>. Locate the equivalence point for each titration curve.
33. Sketch the spectrophotometric titration curve for the titration of a mixture of 5.00 × 10<sup>-3</sup> M Bi<sup>3+</sup> and 5.00 × 10<sup>-3</sup> M Cu<sup>2+</sup> with 0.0100 M EDTA. Assume that only the Cu<sup>2+</sup>–EDTA complex absorbs at the selected wavelength.
34. The EDTA titration of mixtures of Ca<sup>2+</sup> and Mg<sup>2+</sup> can be followed thermometrically because the formation of the Ca<sup>2+</sup>–EDTA complex is exothermic and the formation of the Mg<sup>2+</sup>–EDTA complex is endothermic. Sketch the thermometric titration curve for a mixture of 5.00 × 10<sup>-3</sup> M Ca<sup>2+</sup> and 5.00 × 10<sup>-3</sup> M Mg<sup>2+</sup> using 0.0100 M EDTA as the titrant. The heats of formation for CaY<sup>2-</sup> and MgY<sup>2-</sup> 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*<sub>f</sub> values for the complexes of six such ligands with Ca<sup>2+</sup> and Mg<sup>2+</sup>. Which ligand is the best choice for a direct titration of Ca<sup>2+</sup> in the presence of Mg<sup>2+</sup>?

	ligand	Mg <sup>2+</sup>	Ca <sup>2+</sup>
EDTA	ethylenediaminetetraacetic acid	8.7	10.7
HEDTA	N-hydroxyethylenediaminetriacetic acid	7.0	8.0
EEDTA	ethyletherdiaminetetraacetic acid	8.3	10.0
EGTA	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 is determined by a complexometric titration with EDTA. In one such analysis a 0.100-mL sample of a blood serum is 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.

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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 that contains 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  $\text{CaCO}_3$ .
38. The concentration of cyanide,  $\text{CN}^-$ , in a copper electroplating bath is determined by a complexometric titration using  $\text{Ag}^+$  as the titrant, forming the soluble  $\text{Ag}(\text{CN})_2^-$  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  $\text{H}_2\text{O}$ , 5 mL of 20% w/v NaOH and 5 mL of 10% w/v KI. The sample is titrated with 0.1012 M  $\text{AgNO}_3$ , 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  $\text{Ag}^+$  or  $\text{CN}^-$  as the titrant. The analysis for  $\text{Cd}^{2+}$ , for example, was accomplished indirectly by adding an excess of KCN to form  $\text{Cd}(\text{CN})_4^{2-}$ , and back titrating the excess  $\text{CN}^-$  with  $\text{Ag}^+$ , forming  $\text{Ag}(\text{CN})_2^-$ . In one such analysis a 0.3000-g sample of an ore is dissolved and treated with 20.00 mL of 0.5000 M KCN. The excess  $\text{CN}^-$  requires 13.98 mL of 0.1518 M  $\text{AgNO}_3$  to reach the end point. Determine the %w/w Cd in the ore.
40. Solutions that contain both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are selectively analyzed for  $\text{Fe}^{3+}$  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 the formation of the  $\text{Al}^{3+}$ -EDTA complex. The excess EDTA is back-titrated using a standard solution of  $\text{Fe}^{3+}$ , providing an indirect analysis for  $\text{Al}^{3+}$ .
- (a) At a pH of 2, verify that the formation of the  $\text{Fe}^{3+}$ -EDTA complex is favorable, and that the formation of the  $\text{Al}^{3+}$ -EDTA complex is not favorable.
- (b) A 50.00-mL aliquot of a sample that contains  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  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  $\text{Fe}^{3+}$ -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  $\text{Fe}^{3+}$ -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

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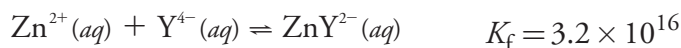
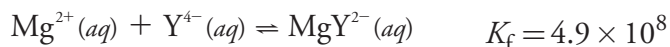
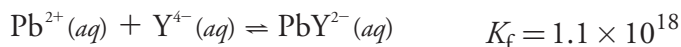
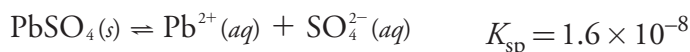
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the  $\text{Al}^{3+}$ -EDTA complex is complete, the excess EDTA is back titrated with 0.04109 M  $\text{Fe}^{3+}$ , requiring 17.84 mL to reach the end point as signaled by the reappearance of the red-colored  $\text{Fe}^{3+}$ -salicylic acid complex. Report the molar concentrations of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in the sample.

41. Prada and colleagues described an indirect method for determining sulfate in natural samples, such as seawater and industrial effluents.<sup>12</sup> The method consists of three steps: precipitating the sulfate as  $\text{PbSO}_4$ ; dissolving the  $\text{PbSO}_4$  in an ammonical solution of excess EDTA to form the soluble  $\text{PbY}^{2-}$  complex; and titrating the excess EDTA with a standard solution of  $\text{Mg}^{2+}$ . The following reactions and equilibrium constants are known



- (a) Verify that a precipitate of  $\text{PbSO}_4$  will dissolve in a solution of  $\text{Y}^{4-}$ .
- (b) Sporek proposed a similar method using  $\text{Zn}^{2+}$  as a titrant and found that the accuracy frequently was poor.<sup>13</sup> One explanation is that  $\text{Zn}^{2+}$  might react with the  $\text{PbY}^{2-}$  complex, forming  $\text{ZnY}^{2-}$ . Show that this might be a problem when using  $\text{Zn}^{2+}$  as a titrant, but that it is not a problem when using  $\text{Mg}^{2+}$  as a titrant. Would such a displacement of  $\text{Pb}^{2+}$  by  $\text{Zn}^{2+}$  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 is carried through the procedure using 50.00 mL of 0.05000 M EDTA. Titrating the excess EDTA requires 12.42 mL of 0.1000 M  $\text{Mg}^{2+}$ . Report the molar concentration of  $\text{SO}_4^{2-}$  in the sample of effluent.
42. [Table 9.10](#) provides values for the fraction of EDTA present as  $\text{Y}^{4-}$ ,  $\alpha_{\text{Y}^{4-}}$ . Values of  $\alpha_{\text{Y}^{4-}}$  are calculated using the equation

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

where  $[\text{Y}^{4-}]$  is the concentration of the fully deprotonated EDTA and  $C_{\text{EDTA}}$  is the total concentration of EDTA in all of its forms

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<sup>12</sup> Prada, S.; Guekezian, M.; Suarez-Iba, M. E. V. *Anal. Chim. Acta* **1996**, *329*, 197–202.

<sup>13</sup> Sporek, K. F. *Anal. Chem.* **1958**, *30*, 1030–1032.

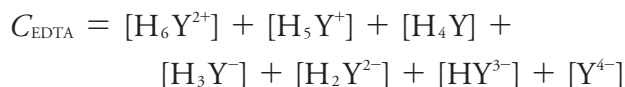
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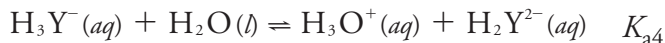
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Use the following equilibrium reactions and equilibrium constants



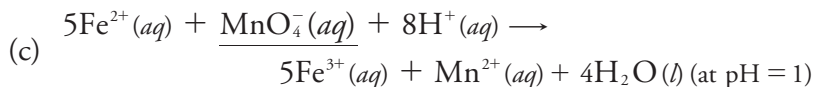
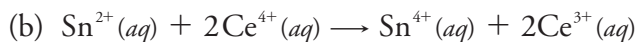
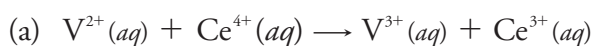
to show that

$$\alpha_{\text{Y}^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}{d}$$

where

$$d = [\text{H}_3\text{O}^+]^6 + [\text{H}_3\text{O}^+]^5 K_{a1} + [\text{H}_3\text{O}^+]^4 K_{a1}K_{a2} + \\ [\text{H}_3\text{O}^+]^3 K_{a1}K_{a2}K_{a3} + [\text{H}_3\text{O}^+]^2 K_{a1}K_{a2}K_{a3}K_{a4} + \\ [\text{H}_3\text{O}^+] K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$$

43. Calculate or sketch titration curves for the following redox titration reactions at 25 °C. Assume the analyte initially is 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, has a concentration of 0.0100 M.



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 is determined by a redox titration that uses  $\text{K}_2\text{Cr}_2\text{O}_7$  as the titrant. A sample of the ore is dissolved in concentrated HCl using  $\text{Sn}^{2+}$  to speed its dissolution by reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . After the sample is dissolved,  $\text{Fe}^{2+}$  and any excess  $\text{Sn}^{2+}$  are oxidized to  $\text{Fe}^{3+}$  and  $\text{Sn}^{4+}$  using  $\text{MnO}_4^-$ . The iron is then carefully reduced to  $\text{Fe}^{2+}$  by adding a 2–3 drop excess of  $\text{Sn}^{2+}$ . A solution of  $\text{HgCl}_2$  is added and, if a white precipitate of  $\text{Hg}_2\text{Cl}_2$  forms, the analysis is continued by titrating with  $\text{K}_2\text{Cr}_2\text{O}_7$ . The sample is discarded without completing the

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analysis if a precipitate of  $\text{Hg}_2\text{Cl}_2$  does not form or if a gray precipitate (due to Hg) forms.

- Explain why the sample is discarded if a white precipitate of  $\text{Hg}_2\text{Cl}_2$  does not form or if a gray precipitate forms.
- Is a determinate error introduced if the analyst forgets to add  $\text{Sn}^{2+}$  in the step where the iron ore is dissolved?
- Is a determinate error introduced if the iron is not quantitatively oxidized back to  $\text{Fe}^{3+}$  by the  $\text{MnO}_4^-$ ?

47. The amount of  $\text{Cr}^{3+}$  in an inorganic salt is determined by a redox titration. A portion of sample that contains approximately 0.25 g of  $\text{Cr}^{3+}$  is accurately weighed and dissolved in 50 mL of  $\text{H}_2\text{O}$ . The  $\text{Cr}^{3+}$  is oxidized to  $\text{Cr}_2\text{O}_7^{2-}$  by adding 20 mL of 0.1 M  $\text{AgNO}_3$ , which serves as a catalyst, and 50 mL of 10% w/v  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which serves as the oxidizing agent. After the reaction is complete, the resulting solution is boiled for 20 minutes to destroy the excess  $\text{S}_2\text{O}_8^{2-}$ , cooled to room temperature, and diluted to 250 mL in a volumetric flask. A 50-mL portion of the resulting solution is transferred to an Erlenmeyer flask, treated with 50 mL of a standard solution of  $\text{Fe}^{2+}$ , and acidified with 200 mL of 1 M  $\text{H}_2\text{SO}_4$ , reducing the  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ . The excess  $\text{Fe}^{2+}$  is then determined by a back titration with a standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  using an appropriate indicator. The results are reported as %w/w  $\text{Cr}^{3+}$ .

- There are several places in the procedure where a reagent's volume is specified (see *italicized text*). Which of these measurements must be made using a volumetric pipet.
- Excess peroxydisulfate,  $\text{S}_2\text{O}_8^{2-}$  is destroyed by boiling the solution. What is the effect on the reported %w/w  $\text{Cr}^{3+}$  if some of the  $\text{S}_2\text{O}_8^{2-}$  is not destroyed during this step?
- Solutions of  $\text{Fe}^{2+}$  undergo slow air oxidation to  $\text{Fe}^{3+}$ . What is the effect on the reported %w/w  $\text{Cr}^{3+}$  if the standard solution of  $\text{Fe}^{2+}$  is inadvertently allowed to be partially oxidized?

48. The exact concentration of  $\text{H}_2\text{O}_2$  in a solution that is nominally 6% w/v  $\text{H}_2\text{O}_2$  is determined by a redox titration using  $\text{MnO}_4^-$  as the titrant. 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  $\text{H}_2\text{SO}_4$ . The resulting solution is titrated with a standard solution of  $\text{KMnO}_4$  until a faint pink color persists for 30 s. The results are reported as %w/v  $\text{H}_2\text{O}_2$ .

- Many commercially available solutions of  $\text{H}_2\text{O}_2$  contain an inorganic or an organic stabilizer to prevent the autodecomposition of

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the peroxide to  $\text{H}_2\text{O}$  and  $\text{O}_2$ . What effect does the presence of this stabilizer have on the reported %w/v  $\text{H}_2\text{O}_2$  if it also reacts with  $\text{MnO}_4^-$ ?

- (b) Laboratory distilled water often contains traces of dissolved organic material that may react with  $\text{MnO}_4^-$ . Describe a simple method to correct for this potential interference.
- (c) What modifications to the procedure, if any, are needed if the sample has a nominal concentration of 30% w/v  $\text{H}_2\text{O}_2$ .
49. The amount of iron in a meteorite is determined by a redox titration using  $\text{KMnO}_4$  as the titrant. A 0.4185-g sample is dissolved in acid and the liberated  $\text{Fe}^{3+}$  quantitatively reduced to  $\text{Fe}^{2+}$  using a Walden reductor. Titrating with 0.02500 M  $\text{KMnO}_4$  requires 41.27 mL to reach the end point. Determine the %w/w  $\text{Fe}_2\text{O}_3$  in the sample of meteorite.
50. Under basic conditions,  $\text{MnO}_4^-$  is used as a titrant for the analysis of  $\text{Mn}^{2+}$ , with both the analyte and the titrant forming  $\text{MnO}_2$ . In the analysis of a mineral sample for manganese, a 0.5165-g sample is dissolved and the manganese reduced to  $\text{Mn}^{2+}$ . The solution is made basic and titrated with 0.03358 M  $\text{KMnO}_4$ , 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 is determined by an indirect redox titration. The analysis is accomplished by dissolving the ore in sulfuric acid and reducing  $\text{UO}_2^{2+}$  to  $\text{U}^{4+}$  with a Walden reductor. The solution is treated with an excess of  $\text{Fe}^{3+}$ , forming  $\text{Fe}^{2+}$  and  $\text{U}^{6+}$ . The  $\text{Fe}^{2+}$  is titrated with a standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ . 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  $\text{Fe}^{3+}$ . Back titrating with 0.00987 M  $\text{K}_2\text{Cr}_2\text{O}_7$  requires 10.52 mL. What is the %w/w U in the sample?
52. The thickness of the chromium plate on an auto fender is determined by dissolving a 30.0-cm<sup>2</sup> section in acid and oxidizing  $\text{Cr}^{3+}$  to  $\text{Cr}_2\text{O}_7^{2-}$  with peroxydisulfate. After removing excess peroxydisulfate by boiling, 500.0 mg of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is added, reducing the  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ . The excess  $\text{Fe}^{2+}$  is back titrated, requiring 18.29 mL of 0.00389 M  $\text{K}_2\text{Cr}_2\text{O}_7$  to reach the end point. Determine the average thickness of the chromium plate given that the density of Cr is 7.20 g/cm<sup>3</sup>.
53. The concentration of CO in air is determined by passing a known volume of air through a tube that contains  $\text{I}_2\text{O}_5$ , forming  $\text{CO}_2$  and  $\text{I}_2$ . The  $\text{I}_2$  is removed from the tube by distilling it into a solution that contains an excess of KI, producing  $\text{I}_3^-$ . The  $\text{I}_3^-$  is titrated with a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . In a typical analysis a 4.79-L sample of air is sampled as described here, requiring 7.17 mL of 0.00329 M  $\text{Na}_2\text{S}_2\text{O}_3$  to reach

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the end point. If the air has a density of  $1.23 \times 10^{-3}$  g/mL, determine the parts per million CO in the air.

54. The level of dissolved oxygen in a water sample is determined by the Winkler method. In a typical analysis a 100.0-mL sample is made basic and treated with a solution of  $\text{MnSO}_4$ , resulting in the formation of  $\text{MnO}_2$ . An excess of KI is added and the solution is acidified, resulting in the formation of  $\text{Mn}^{2+}$  and  $\text{I}_2$ . The liberated  $\text{I}_2$  is titrated with a solution of 0.00870 M  $\text{Na}_2\text{S}_2\text{O}_3$ , requiring 8.90 mL to reach the starch indicator end point. Calculate the concentration of dissolved oxygen as parts per million  $\text{O}_2$ .
55. Calculate or sketch the titration curve for the titration of 50.0 mL of 0.0250 M KI with 0.0500 M  $\text{AgNO}_3$ . Prepare separate titration curves using pAg and pI on the  $y$ -axis.
56. Calculate or sketch the titration curve for the titration of a 25.0 mL mixture of 0.0500 M KI and 0.0500 M KSCN using 0.0500 M  $\text{AgNO}_3$  as the titrant.
57. The analysis for  $\text{Cl}^-$  using the Volhard method requires a back titration. A known amount of  $\text{AgNO}_3$  is added, precipitating  $\text{AgCl}$ . The unreacted  $\text{Ag}^+$  is determined by back titrating with KSCN. There is a complication, however, because  $\text{AgCl}$  is more soluble than  $\text{AgSCN}$ .
- Why do the relative solubilities of  $\text{AgCl}$  and  $\text{AgSCN}$  lead to a titration error?
  - Is the resulting titration error a positive or a negative determinate error?
  - How might you modify the procedure to eliminate this source of determinate error?
  - Is this source of determinate error of concern when using the Volhard method to determine  $\text{Br}^-$ ?
58. 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.<sup>14</sup> For example, when titrating  $\text{Pb}^{2+}$  with  $\text{K}_2\text{CrO}_4$  the solution that contains the analyte initially is acidified to a pH of 3.50 using  $\text{HNO}_3$ . Before the equivalence point the concentration of  $\text{CrO}_4^{2-}$  is controlled by the solubility product of  $\text{PbCrO}_4$ . After the equivalence point the concentration of  $\text{CrO}_4^{2-}$  is determined by the amount of excess titrant. Considering the reactions that control the concentration of  $\text{CrO}_4^{2-}$ , sketch the expected titration curve of pH versus volume of titrant.

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59. A 0.5131-g sample that contains KBr is dissolved in 50 mL of distilled water. Titrating with 0.04614 M  $\text{AgNO}_3$  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  $\text{Na}_2\text{CO}_3$  is analyzed by the Volhard method. After adding 50.00 mL of 0.06911 M  $\text{AgNO}_3$ , the sample is back titrated with 0.05781 M KSCN, requiring 27.36 mL to reach the end point. Report the purity of the  $\text{Na}_2\text{CO}_3$  sample.
61. A 0.1036-g sample that contains only  $\text{BaCl}_2$  and NaCl is dissolved in 50 mL of distilled water. Titrating with 0.07916 M  $\text{AgNO}_3$  requires 19.46 mL to reach the Fajans end point. Report the %w/w  $\text{BaCl}_2$  in the sample.

## 9I Solutions to Practice Exercises

### Practice Exercise 9.1

The volume of HCl needed to reach the equivalence point is

$$V_{eq} = V_a = \frac{M_a V_a}{M_b} = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{(0.0625 \text{ M})} = 50.0 \text{ mL}$$

Before the equivalence point, NaOH is present in excess and the pH is determined by the concentration of unreacted  $\text{OH}^-$ . For example, after adding 10.0 mL of HCl

$$[\text{OH}^-] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0714 \text{ M}} = 1.40 \times 10^{-13} \text{ M}$$

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

$$[\text{HCl}] = \frac{(0.0625 \text{ M})(70.0 \text{ mL}) - (0.125 \text{ M})(25.0 \text{ mL})}{70.0 \text{ mL} + 25.0 \text{ mL}} = 0.0132 \text{ M}$$

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



Volume of HCl (mL)	pH	Volume of HCl (mL)	pH
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

$$V_{eq} = V_a = \frac{M_a V_a}{M_b} = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{(0.0625 \text{ M})} = 50.0 \text{ mL}$$

Before adding HCl the pH is that for a solution of 0.100 M  $\text{NH}_3$ .

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{(x)(x)}{0.125 - x} = 1.75 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.48 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{1.48 \times 10^{-3} \text{ M}} = 6.76 \times 10^{-12} \text{ M}$$

The pH at the beginning of the titration, therefore, is 11.17.

Before the equivalence point the pH is determined by an  $\text{NH}_3/\text{NH}_4^+$  buffer. For example, after adding 10.0 mL of HCl

$$[\text{NH}_3] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$[\text{NH}_4^+] = \frac{(0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0179 \text{ M}$$

$$\text{pH} = 9.244 + \log \frac{0.0714 \text{ M}}{0.0179 \text{ M}} = 9.84$$

At the equivalence point the predominate ion in solution is  $\text{NH}_4^+$ . To calculate the pH we first determine the concentration of  $\text{NH}_4^+$

$$[\text{NH}_4^+] = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 50.0 \text{ mL}} = 0.0417 \text{ M}$$

and then calculate the pH

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.0417 - x} = 5.70 \times 10^{-10}$$

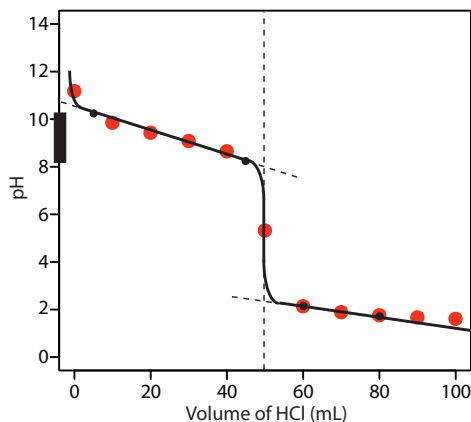
$$x = [\text{H}_3\text{O}^+] = 4.88 \times 10^{-6} \text{ M}$$

obtaining a value of 5.31.

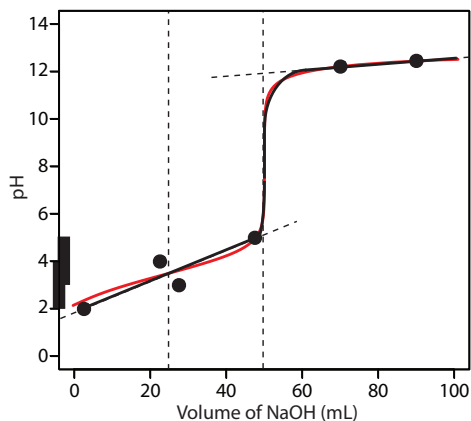
After the equivalence point, the pH is determined by the excess HCl. For example, after adding 70.0 mL of HCl

$$[\text{HCl}] = \frac{(0.0625 \text{ M})(70.0 \text{ mL}) - (0.125 \text{ M})(25.0 \text{ mL})}{70.0 \text{ mL} + 25.0 \text{ mL}} = 0.0132 \text{ M}$$

and the pH is 1.88. Some additional results are shown here.



**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.

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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### Practice Exercise 9.3

Figure 9.48 shows a sketch of the titration curve. The two points before the equivalence point ( $V_{\text{HCl}} = 5 \text{ mL}$ ,  $\text{pH} = 10.24$  and  $V_{\text{HCl}} = 45 \text{ mL}$ ,  $\text{pH} = 8.24$ ) are plotted using the  $\text{p}K_a$  of 9.244 for  $\text{NH}_4^+$ . The two points after the equivalence point ( $V_{\text{HCl}} = 60 \text{ mL}$ ,  $\text{pH} = 2.13$  and  $V_{\text{HCl}} = 80 \text{ mL}$ ,  $\text{pH} = 1.75$ ) 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 ( $\text{H}_2\text{A} \rightarrow \text{HA}^-$ ) and one at 50.0 mL ( $\text{HA}^- \rightarrow \text{A}^{2-}$ ). In sketching the curve, we plot two points before the first equivalence point using the  $\text{p}K_a$  of 3 for  $\text{H}_2\text{A}$

$$V_{\text{HCl}} = 2.5 \text{ mL}, \text{pH} = 2 \text{ and } V_{\text{HCl}} = 22.5 \text{ mL}, \text{pH} = 4$$

two points between the equivalence points using the  $\text{p}K_a$  of 5 for  $\text{HA}^-$

$$V_{\text{HCl}} = 27.5 \text{ mL}, \text{pH} = 3, \text{ and } V_{\text{HCl}} = 47.5 \text{ mL}, \text{pH} = 5$$

and two points after the second equivalence point

$$V_{\text{HCl}} = 70 \text{ mL}, \text{pH} = 12.22 \text{ and } V_{\text{HCl}} = 90 \text{ mL}, \text{pH} = 12.46$$

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 ( $V_{\text{HCl}} = 2.5 \text{ mL}$ ,  $\text{pH} = 2$ ) to the fourth point ( $V_{\text{HCl}} = 47.5 \text{ mL}$ ,  $\text{pH} = 5$ ), ignoring the second and third points. The result 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 its  $pK_a$  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 2.97 and 13.74, and the second equivalence point is at a pH greater than 13.74. From [Table 9.4](#), phenolphthalein's end point is 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

$$\begin{aligned} (0.1354 \text{ M})(0.02192 \text{ L}) &= 2.968 \times 10^{-3} \text{ mol NaOH} \\ 2.968 \times 10^{-3} \text{ mol NaOH} &\times \frac{1 \text{ mol C}_7\text{H}_6\text{O}_3}{\text{mol NaOH}} \times \\ &\frac{138.12 \text{ g C}_7\text{H}_6\text{O}_3}{\text{mol C}_7\text{H}_6\text{O}_3} = 0.4099 \text{ g C}_7\text{H}_6\text{O}_3 \\ \frac{0.4099 \text{ g C}_7\text{H}_6\text{O}_3}{0.4208 \text{ g sample}} \times 100 &= 97.41\% \text{ w/w C}_7\text{H}_6\text{O}_3 \end{aligned}$$

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  $\text{HNO}_3$  produced by pulling the sample through  $\text{H}_2\text{O}_2$  is

$$(0.01012 \text{ M})(0.00914 \text{ L}) \times \frac{1 \text{ mol HNO}_3}{\text{mol NaOH}} = 9.25 \times 10^{-5} \text{ mol HNO}_3$$

A conservation of mass on nitrogen requires that each mole of  $\text{NO}_2$  produces one mole of  $\text{HNO}_3$ ; thus, the mass of  $\text{NO}_2$  in the sample is

$$\begin{aligned} 9.25 \times 10^{-5} \text{ mol HNO}_3 &\times \frac{1 \text{ mol NO}_2}{\text{mol HNO}_3} \times \\ &\frac{46.01 \text{ g NO}_2}{\text{mol NO}_2} = 4.26 \times 10^{-3} \text{ g NO}_2 \end{aligned}$$

and the concentration of  $\text{NO}_2$  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

$$(1.396 \text{ M})(0.01000 \text{ L}) = 1.396 \times 10^{-2} \text{ mol HCl}$$

Of the total moles of HCl

$$(0.1004 \text{ M NaOH})(0.03996 \text{ L}) \times \frac{1 \text{ mol HCl}}{\text{mol NaOH}} \\ = 4.012 \times 10^{-3} \text{ mol HCl}$$

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  $\text{CaCO}_3$ . Because  $\text{CO}_3^{2-}$  is dibasic, each mole of  $\text{CaCO}_3$  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.

$$(0.200 \text{ M NaOH})(0.01965 \text{ L}) \times \frac{1 \text{ mol C}_7\text{H}_{10}\text{NCl}}{\text{mol NaOH}} \\ \times \frac{143.61 \text{ g C}_7\text{H}_{10}\text{NCl}}{\text{mol C}_7\text{H}_{10}\text{NCl}} = 0.564 \text{ g C}_7\text{H}_{10}\text{NCl}$$

$$\frac{0.564 \text{ g C}_7\text{H}_{10}\text{NCl}}{2.006 \text{ g sample}} \times 100 = 28.1\% \text{ w/w C}_7\text{H}_{10}\text{NCl}$$

Titrating from the bromocresol purple end point to the phenolphthalein end point, a total of  $48.41 \text{ mL} - 19.65 \text{ mL} = 28.76 \text{ mL}$ , gives the amount of NaOH that reacts with 3-nitrophenol. The amount of 3-nitrophenol in the sample, therefore, is

$$(0.200 \text{ M NaOH})(0.02876 \text{ L}) \times \frac{1 \text{ mol C}_6\text{H}_5\text{NO}_3}{\text{mol NaOH}} \\ \times \frac{139.11 \text{ g C}_6\text{H}_5\text{NO}_3}{\text{mol C}_6\text{H}_5\text{NO}_3} = 0.800 \text{ g C}_6\text{H}_5\text{NO}_3$$

$$\frac{0.800 \text{ g C}_6\text{H}_5\text{NO}_3}{2.006 \text{ g sample}} \times 100 = 39.8\% \text{ w/w C}_6\text{H}_5\text{NO}_3$$

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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

$$(0.1032 \text{ M NaOH})(0.037 \text{ L}) \times \frac{1 \text{ equivalent}}{\text{mol NaOH}} = 3.8 \times 10^{-3} \text{ equivalents}$$

$$EW = \frac{0.5000 \text{ g}}{3.8 \times 10^{-3} \text{ equivalents}} = 1.3 \times 10^2 \text{ g/equivalent}$$

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### Practice Exercise 9.11

At  $\frac{1}{2}V_{eq}$  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 where 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

$$[Cd^{2+}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL}) - (0.0100 \text{ M})(5.00 \text{ mL})}{50.0 \text{ mL} + 5.00 \text{ mL}}$$

which gives  $[Cd^{2+}]$  as  $3.64 \times 10^{-3}$  and pCd as 2.43.

At the equivalence point all  $Cd^{2+}$  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  $CdY^{2-}$ .

$$[CdY^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.00 \text{ mL}} = 3.33 \times 10^{-3} \text{ M}$$

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

$$K_f' = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}] C_{\text{EDTA}}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 1.1 \times 10^{16}$$

Solving gives  $[\text{Cd}^{2+}]$  as  $5.50 \times 10^{-10}$  M or a pCd of 9.26 at the equivalence point.

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

$$[\text{CdY}^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.00 \text{ mL}} = 3.12 \times 10^{-3} \text{ M}$$

$$C_{\text{EDTA}} = \frac{(0.0100 \text{ M})(30.00 \text{ mL}) - (5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.00 \text{ mL}}$$

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

Substituting into the equation for the conditional formation constant

$$K_f' = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}] C_{\text{EDTA}}} = \frac{3.12 \times 10^{-3} \text{ M}}{(x)(6.25 \times 10^{-4} \text{ M})} = 1.1 \times 10^{16}$$

and solving for  $[\text{Cd}^{2+}]$  gives  $4.54 \times 10^{-16}$  M or a pCd of 15.34.

The calculations at a pH of 7 are identical, except the conditional formation constant for  $\text{CdY}^{2-}$  is  $1.5 \times 10^{13}$  instead of  $1.1 \times 10^{16}$ . The following table summarizes results for these two titrations as well as the results from [Table 9.13](#) for the titration of  $\text{Cd}^{2+}$  at a pH of 10 in the presence of 0.0100 M  $\text{NH}_3$  as an auxiliary complexing agent.

Volume of EDTA (mL)	pCd at pH 10	pCd	
		at pH 10 w/ 0.0100 M $\text{NH}_3$	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 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 in the presence of 0.0100 M  $\text{NH}_3$ , 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 ( $V_{\text{EDTA}} = 5 \text{ mL}$ ,  $\text{pCd} = 2.43$  and  $V_{\text{EDTA}} = 15 \text{ mL}$ ,  $\text{pCd} = 2.81$ ) are the same for both pHs and taken from the results of [Practice Exercise 9.12](#). The two points after the equivalence point for a pH of 7 ( $V_{\text{EDTA}} = 27.5 \text{ mL}$ ,  $\text{pCd} = 12.2$  and  $V_{\text{EDTA}} = 50 \text{ mL}$ ,  $\text{pCd} = 13.2$ ) are plotted using the  $\log K_f'$  of 13.2 for  $\text{CdY}^{2-}$ . The two points after the equivalence point for a pH of 10 ( $V_{\text{EDTA}} = 27.5 \text{ mL}$ ,  $\text{pCd} = 15.0$  and  $V_{\text{EDTA}} = 50 \text{ mL}$ ,  $\text{pCd} = 16.0$ ) are plotted using the  $\log K_f'$  of 16.0 for  $\text{CdY}^{2-}$ .

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### Practice Exercise 9.14

In an analysis for hardness we treat the sample as if  $\text{Ca}^{2+}$  is the only metal ion that reacts with EDTA. The grams of  $\text{Ca}^{2+}$  in the sample, therefore, are

$$(0.0109 \text{ M EDTA})(0.02363 \text{ L}) \times \frac{1 \text{ mol Ca}^{2+}}{\text{mol EDTA}} = 2.58 \times 10^{-4} \text{ mol Ca}^{2+}$$

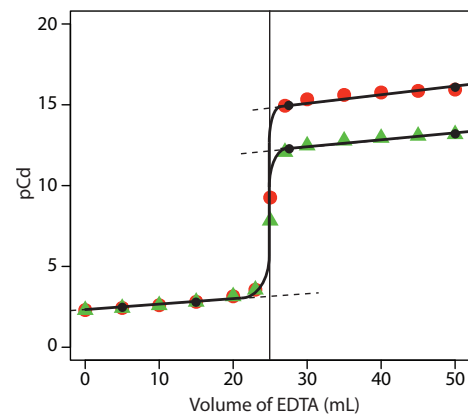
$$2.58 \times 10^{-4} \text{ mol Ca}^{2+} \times \frac{1 \text{ mol CaCO}_3}{\text{mol Ca}^{2+}} \times \frac{100.09 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.0258 \text{ g CaCO}_3$$

and the sample's hardness is

$$\frac{0.0258 \text{ g CaCO}_3}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 258 \text{ g CaCO}_3/\text{L}$$

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### Practice Exercise 9.15



**Figure 9.50** Titration curve for Practice Exercise 9.13. The **black** dots and curves are 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.

The titration of  $\text{CN}^-$  with  $\text{Ag}^+$  produces the metal-ligand complex  $\text{Ag}(\text{CN})_2^-$ ; thus, each mole of  $\text{AgNO}_3$  reacts with two moles of  $\text{NaCN}$ . The grams of  $\text{NaCN}$  in the sample is

$$(0.1018 \text{ M AgNO}_3)(0.03968 \text{ L}) \times \frac{2 \text{ mol NaCN}}{\text{mol AgNO}_3} \times \frac{49.01 \text{ g NaCN}}{\text{mol NaCN}} = 0.3959 \text{ g NaCN}$$

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

$$(0.02011 \text{ M EDTA})(0.02500 \text{ L}) = 5.028 \times 10^{-4} \text{ mol EDTA}$$

Of this,

$$(0.01113 \text{ M Mg}^{2+})(0.00423 \text{ L}) \times \frac{1 \text{ mol EDTA}}{\text{mol Mg}^{2+}} = 4.708 \times 10^{-5} \text{ mol EDTA}$$

are consumed in the back titration with  $\text{Mg}^{2+}$ , which means that

$$\begin{aligned} 5.028 \times 10^{-4} \text{ mol EDTA} - \\ 4.708 \times 10^{-5} \text{ mol EDTA} = \\ 4.557 \times 10^{-4} \text{ mol EDTA} \end{aligned}$$

react with the  $\text{BaSO}_4$ . Each mole of  $\text{BaSO}_4$  reacts with one mole of EDTA; thus

$$\begin{aligned} 4.557 \times 10^{-4} \text{ mol EDTA} \times \frac{1 \text{ mol BaSO}_4}{\text{mol EDTA}} \times \\ \frac{1 \text{ mol Na}_2\text{SO}_4}{\text{mol BaSO}_4} \times \frac{142.04 \text{ g Na}_2\text{SO}_4}{\text{mol Na}_2\text{SO}_4} = 0.06473 \text{ g Na}_2\text{SO}_4 \\ \frac{0.06473 \text{ g Na}_2\text{SO}_4}{0.1557 \text{ g sample}} \times 100 = 41.57\% \text{ w/w Na}_2\text{SO}_4 \end{aligned}$$

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### Practice Exercise 9.17

The volume of  $\text{Tl}^{3+}$  needed to reach the equivalence point is

$$V_{eq} = V_{\text{Tl}} = \frac{M_{\text{Sn}} V_{\text{Sn}}}{M_{\text{Tl}}} = \frac{(0.050 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, the concentration of unreacted  $\text{Sn}^{2+}$  and the concentration of  $\text{Sn}^{4+}$  are easy to calculate. For this reason we find the potential using the Nernst equation for the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  half-reaction.



For example, the concentrations of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  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  $\text{Tl}^+$  and the concentration of excess  $\text{Tl}^{3+}$  are easy to calculate. For this reason we find the potential using the Nernst equation for the  $\text{Tl}^{3+}/\text{Tl}^+$  half-reaction. For example, after adding 40.0 mL of titrant, the concentrations of  $\text{Tl}^+$  and  $\text{Tl}^{3+}$  are

$$[\text{Tl}^+] = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 40.0 \text{ mL}} = 0.0278 \text{ M}$$

$$[\text{Tl}^{3+}] = \frac{(0.100 \text{ M})(40.0 \text{ mL}) - (0.050 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 40.0 \text{ mL}} = 0.0167 \text{ M}$$

and the potential is

$$E = +0.77 \text{ V} - \frac{0.05916}{2} \log \frac{0.0278 \text{ M}}{0.0167 \text{ M}} = +0.76 \text{ V}$$

At the titration's equivalence point, the potential,  $E_{\text{eq}}$ , potential is

$$E_{\text{eq}} = \frac{0.139 \text{ V} + 0.77 \text{ V}}{2} = +0.45 \text{ V}$$

Some additional results are shown here.

Volume of $\text{Tl}^{3+}$ (mL)	$E$ (V)	Volume of $\text{Tl}^{3+}$ (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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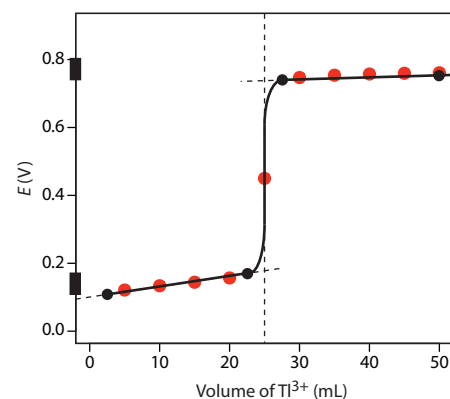
### Practice Exercise 9.18

Figure 9.51 shows a sketch of the titration curve. The two points before the equivalence point

$$V_{\text{Tl}} = 2.5 \text{ mL}, E = +0.109 \text{ V} \text{ and } V_{\text{Tl}} = 22.5 \text{ mL}, E = +0.169 \text{ V}$$

are plotted using the redox buffer for  $\text{Sn}^{4+}/\text{Sn}^{2+}$ , which spans a potential range of  $+0.139 \pm 0.5916/2$ . The two points after the equivalence point

$$V_{\text{Tl}} = 27.5 \text{ mL}, E = +0.74 \text{ V} \text{ and } V_{\text{EDTA}} = 50 \text{ mL}, E = +0.77 \text{ V}$$



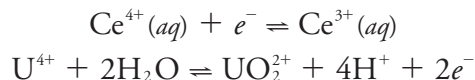
**Figure 9.51** Titration curve for Practice Exercise 9.18. The **black** dots and curve are the approximate sketch of the titration curve. The points in **red** are the calculations from [Practice Exercise 9.17](#).

are plotted using the redox buffer for  $\text{Tl}^{3+}/\text{Tl}^+$ , 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



for which the Nernst equations are

$$\begin{aligned} E &= E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ - \frac{0.05916}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \\ E &= E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ - \frac{0.05916}{2} \log \frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}][\text{H}^+]^4} \end{aligned}$$

Before adding these two equations together we must multiply the second equation by 2 so that we can combine the log terms; thus

$$3E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ + 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ - 0.05916 \log \frac{[\text{Ce}^{3+}][\text{U}^{4+}]}{[\text{Ce}^{4+}][\text{UO}_2^{2+}][\text{H}^+]^4}$$

At the equivalence point we know that

$$[\text{Ce}^{3+}] = 2 \times [\text{UO}_2^{2+}] \quad \text{and} \quad [\text{Ce}^{4+}] = 2 \times [\text{U}^{4+}]$$

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

$$\begin{aligned} 3E &= E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ + 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ - 0.05916 \log \frac{2[\text{UO}_2^{2+}][\text{U}^{4+}]}{2[\text{U}^{4+}][\text{UO}_2^{2+}][\text{H}^+]^4} \\ E &= \frac{E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ + 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ}{3} - \frac{0.05916}{3} \log \frac{1}{[\text{H}^+]^4} \\ E &= \frac{E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ + 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ}{3} + \frac{0.05916 \times 4}{3} \log [\text{H}^+] \\ E &= \frac{E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ + 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^\circ}{3} - 0.07888 \text{pH} \end{aligned}$$

At a pH of 1 the equivalence point has a potential of

$$E = \frac{1.72 + 2 \times 0.327}{3} - 0.07888 \times 1 = +0.712 \text{ V}$$

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### Practice Exercise 9.20

Because we are not provided with a balanced reaction, let's use a conservation of electrons to deduce the stoichiometry. Oxidizing  $\text{C}_2\text{O}_4^{2-}$ , in which each carbon has a +3 oxidation state, to  $\text{CO}_2$ , in which carbon has an oxidation state of +4, requires one electron per carbon or a total of two electrons for each mole of  $\text{C}_2\text{O}_4^{2-}$ . Reducing  $\text{MnO}_4^-$ , in which each manganese is in the +7 oxidation state, to  $\text{Mn}^{2+}$  requires five electrons. A conservation of electrons for the titration, therefore, requires that two

moles of  $\text{KMnO}_4$  (10 moles of  $e^-$ ) react with five moles of  $\text{Na}_2\text{C}_2\text{O}_4$  (10 moles of  $e^-$ ).

The moles of  $\text{KMnO}_4$  used to reach the end point is

$$(0.0400 \text{ M KMnO}_4)(0.03562 \text{ L}) = 1.42 \times 10^{-3} \text{ mol KMnO}_4$$

which means 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  $\text{Na}_2\text{C}_2\text{O}_4$  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  $\text{Cr}_2\text{O}_7^{2-}$  and the analyte,  $\text{C}_2\text{H}_6\text{O}$ , and between  $\text{Cr}_2\text{O}_7^{2-}$  and the titrant,  $\text{Fe}^{2+}$ . In oxidizing ethanol to acetic acid, the oxidation state of carbon changes from  $-2$  in  $\text{C}_2\text{H}_6\text{O}$  to  $0$  in  $\text{C}_2\text{H}_4\text{O}_2$ . Each carbon releases two electrons, or a total of four electrons per  $\text{C}_2\text{H}_6\text{O}$ . In reducing  $\text{Cr}_2\text{O}_7^{2-}$ , in which each chromium has an oxidation state of  $+6$ , to  $\text{Cr}^{3+}$ , each chromium loses three electrons, for a total of six electrons per  $\text{Cr}_2\text{O}_7^{2-}$ . Oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  requires one electron. A conservation of electrons requires that each mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  (6 moles of  $e^-$ ) reacts with six moles of  $\text{Fe}^{2+}$  (6 moles of  $e^-$ ), and that four moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  (24 moles of  $e^-$ ) react with six moles of  $\text{C}_2\text{H}_6\text{O}$  (24 moles of  $e^-$ ).

The total moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  that react with  $\text{C}_2\text{H}_6\text{O}$  and with  $\text{Fe}^{2+}$  is

$$(0.0200 \text{ M K}_2\text{Cr}_2\text{O}_7)(0.05000 \text{ L}) = 1.00 \times 10^{-3} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

The back titration with  $\text{Fe}^{2+}$  consumes

$$(0.1014 \text{ M Fe}^{2+})(0.02148 \text{ L}) \times \frac{1 \text{ mol K}_2\text{Cr}_2\text{O}_7}{6 \text{ mol Fe}^{2+}} = 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

Subtracting the moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  that react with  $\text{Fe}^{2+}$  from the total moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  gives the moles that react with the analyte.

$$\begin{aligned} 1.00 \times 10^{-3} \text{ mol K}_2\text{Cr}_2\text{O}_7 - \\ 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 = \\ 6.37 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

The grams of ethanol in the 10.00-mL sample of diluted brandy is

$$6.37 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 \times \frac{6 \text{ mol C}_2\text{H}_6\text{O}}{4 \text{ mol K}_2\text{Cr}_2\text{O}_7} \times \frac{46.07 \text{ g C}_2\text{H}_6\text{O}}{\text{mol C}_2\text{H}_6\text{O}} = 0.0440 \text{ g C}_2\text{H}_6\text{O}$$

The %w/v C<sub>2</sub>H<sub>6</sub>O in the brandy is

$$\frac{0.0440 \text{ g C}_2\text{H}_6\text{O}}{10.0 \text{ mL diluted brandy}} \times \frac{500.0 \text{ mL diluted brandy}}{5.00 \text{ mL brandy}} \times 100 = 44.0\% \text{ w/v C}_2\text{H}_6\text{O}$$

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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

$$V_{eq} = V_{\text{NaCl}} = \frac{M_{\text{Ag}} V_{\text{Ag}}}{M_{\text{NaCl}}} = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point the titrand, Ag<sup>+</sup>, is in excess. The concentration of unreacted Ag<sup>+</sup> after adding 10.0 mL of NaCl, for example, is

$$[\text{Ag}^+] = \frac{(0.0500 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} \\ = 2.50 \times 10^{-2} \text{ M}$$

which corresponds to a pAg of 1.60. To find the concentration of Cl<sup>-</sup> we use the *K*<sub>sp</sub> for AgCl; thus

$$[\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9} \text{ M}$$

or a pCl of 8.14.

At the titration's equivalence point, we know that the concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> are equal. To calculate their concentrations we use the *K*<sub>sp</sub> expression for AgCl; thus

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.8 \times 10^{-10}$$

Solving for *x* gives the concentration of Ag<sup>+</sup> and the concentration of Cl<sup>-</sup> as 1.3 × 10<sup>-5</sup> 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

$$[\text{Cl}^-] = \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} \\ = 1.18 \times 10^{-2} \text{ M}$$

or a pCl of 1.93. To find the concentration of Ag<sup>+</sup> we use the *K*<sub>sp</sub> for AgCl; thus

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$

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

$$(0.1078 \text{ M KSCN})(0.02719 \text{ L}) = 2.931 \times 10^{-3} \text{ mol KSCN}$$

The stoichiometry between  $\text{SCN}^-$  and  $\text{Ag}^+$  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  $\frac{1}{4}$  of the total solution, there are  $0.3162 \times 4$  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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