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

Precipitation gravimetry developed as an analytical method without a general theory of precipitation. An empirical relationship between a precipitate’s mass and the mass of analyte—what analytical chemists call a gravimetric factor—was determined experimentally by taking a known mass of analyte through the procedure. Today, we recognize this as an early example of an external standardization. Gravimetric factors were not calculated using the stoichiometry of a precipitation reaction because chemical formulas and atomic weights were not yet available! Unlike gravimetry, the development and acceptance of titrimetry required a deeper understanding of stoichiometry, of thermodynamics, and of chemical equilibria. By the 1900s, the accuracy and precision of titrimetric methods were comparable to that of gravimetric methods, establishing titrimetry as an accepted analytical technique.
9A Overview of Titrimetry

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

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

9A.1 Equivalence Points and End Points

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

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

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

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

9A.2 Volume as a Signal

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

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

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

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

If the titration's reaction is too slow, if a suitable indicator is not available, or if there is no useful direct titration reaction, then an indirect analysis may be possible. Suppose you wish to determine the concentration of formaldehyde, H$_2$CO, in an aqueous solution. The oxidation of H$_2$CO by I$_3^-$

$$\text{H}_2\text{CO}(aq) + \text{I}_3^-(aq) + 3\text{OH}^-(aq) \rightleftharpoons \text{HCO}_2(aq) + 3\text{I}^-(aq) + 2\text{H}_2\text{O}(l)$$

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

$$\text{I}_3^-(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{S}_4\text{O}_6^{2-}(aq) + 3\text{I}^-(aq)$$

The difference between the initial amount of I$_3^-$ and the amount in excess gives us the amount of I$_3^-$ reacting with the formaldehyde. This is an example of a **back titration**.

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

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

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

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

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

\[
\text{Mg}^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons MgY^{2-}(aq)
\]

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

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

\[
S(s) + O_2(g) \rightarrow SO_2(g)
\]

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

\[
SO_2(g) + H_2O_2(aq) \rightarrow H_2SO_4(aq)
\]

Titrating H$_2$SO$_4$ with NaOH

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

provides an indirect determination of sulfur.

### 9A.3 Titration Curves

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

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

A **TITRATION CURVE** provides us with a visual picture of how a property of the titration reaction changes as we add the titrant to the titrand. The titration curve in Figure 9.1, for example, was obtained by suspending a pH electrode in a solution of 0.100 M HCl (the titrand) and monitoring the pH while adding 0.100 M NaOH (the titrant). A close examination of this titration curve should convince you that an end point pH of 6.8 produces a negligible titration error. Selecting a pH of 11.6 as the end point, however, produces an unacceptably large titration error.
Chapter 9 Titrimetric Method

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

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

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

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

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

Figure 9.2 Additional examples of titration curves. (a) Complexation titration of 25.0 mL of 1.0 mM Cd\(^{2+}\) with 1.0 mM EDTA at a pH of 10. The y-axis displays the titrand’s equilibrium concentration as pCd. (b) Redox titration of 25.0 mL of 0.050 M Fe\(^{2+}\) with 0.050 M Ce\(^{4+}\) in 1 M HClO\(_4\). The y-axis displays the titration mixture’s electrochemical potential, \(E\), which, through the Nernst equation is a logarithmic function of concentrations. (c) Precipitation titration of 25.0 mL of 0.10 M NaCl with 0.10 M AgNO\(_3\). The y-axis displays the titrant’s equilibrium concentration as pAg.
The only essential equipment for an acid–base titration is a means for delivering the titrant to the titrand's solution. The most common method for delivering titrant is a buret (Figure 9.4). A buret is a long, narrow tube with graduated markings, equipped with a stopcock for dispensing the titrant. The buret's small internal diameter provides a better defined meniscus, making it easier to read the titrant's volume precisely. Burets are available in a variety of sizes and tolerances (Table 9.1), with the choice of buret determined by the needs of the analysis. You can improve a buret's accuracy by calibrating it over several intermediate ranges of volumes using the method described in Chapter 5 for calibrating pipets. Calibrating a buret corrects for variations in the buret's internal diameter.

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

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>Class</th>
<th>Subdivision (mL)</th>
<th>Tolerance (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>A</td>
<td>0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td>10</td>
<td>A</td>
<td>0.02</td>
<td>±0.02</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.02</td>
<td>±0.04</td>
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<tr>
<td>25</td>
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<td>±0.05</td>
</tr>
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<td></td>
<td>B</td>
<td>0.1</td>
<td>±0.10</td>
</tr>
<tr>
<td>100</td>
<td>A</td>
<td>0.2</td>
<td>±0.10</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.2</td>
<td>±0.20</td>
</tr>
</tbody>
</table>
Before 1800, most acid–base titrations used H\textsubscript{2}SO\textsubscript{4}, HCl, or HNO\textsubscript{3} as acidic titrants, and K\textsubscript{2}CO\textsubscript{3} or Na\textsubscript{2}CO\textsubscript{3} as basic titrants. A titration's end point was determined using litmus as an indicator, which is red in acidic solutions and blue in basic solutions, or by the cessation of CO\textsubscript{2} effervescence when neutralizing CO\textsubscript{3}\textsuperscript{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 increasing availability of indicators, the absence of a theory of acid–base reactivity made it difficult to select an indicator. The development of equilibrium theory in the late 19th century led to significant improvements in the theoretical understanding of acid–base chemistry, and, in turn, of acid–base titrimetry. Sørenson’s establishment of the pH scale in 1909 provided a rigorous means for comparing indicators. The determination of acid–base dissociation constants made it possible to calculate a theoretical titration curve, as outlined by Bjerrum in 1914. For the first
time analytical chemists had a rational method for selecting an indicator, establishing acid–base titrimetry as a useful alternative to gravimetry.

9B.1 Acid–Base Titration Curves

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

Titrating Strong Acids and Strong Bases

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

$$\text{H}_2\text{O}^+ (aq) + \text{OH}^- (aq) \rightarrow 2\text{H}_2\text{O}(l)$$  \hspace{1cm} 9.1

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

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

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

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 that the pH is

$$\text{pH} = -\log[\text{H}_2\text{O}^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

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

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

$$= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0500 \text{ M}$$
and the pH increases to 1.30.

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

\[
K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = \left[H_3O^+\right]^2
\]

\[
[H_3O^+] = 1.00 \times 10^{-7} \text{ M}
\]

Thus, the pH at the equivalence point is 7.00.

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

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

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

To find the concentration of H\(_3\)O\(^+\) we use the \(K_w\) expression

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

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

**Practice Exercise 9.1**

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

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

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

<table>
<thead>
<tr>
<th>Volume of NaOH (mL)</th>
<th>pH</th>
<th>Volume of NaOH (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.00</td>
<td>26.0</td>
<td>11.42</td>
</tr>
<tr>
<td>5.00</td>
<td>1.14</td>
<td>28.0</td>
<td>11.89</td>
</tr>
<tr>
<td>10.0</td>
<td>1.30</td>
<td>30.0</td>
<td>12.10</td>
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<td>12.37</td>
</tr>
<tr>
<td>20.0</td>
<td>1.85</td>
<td>40.0</td>
<td>12.52</td>
</tr>
<tr>
<td>22.0</td>
<td>2.08</td>
<td>45.0</td>
<td>12.62</td>
</tr>
<tr>
<td>24.0</td>
<td>2.57</td>
<td>50.0</td>
<td>12.70</td>
</tr>
<tr>
<td>25.0</td>
<td>7.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Step 4: Calculate pH values after the equivalence point by determining the concentration of excess titrant.
Step 1: Calculate the volume of titrant needed to reach the equivalence point.

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

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.

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

**Titrating a Weak Acid with a Strong Base**

For this example, let’s consider the titration of 50.0 mL of 0.100 M acetic acid, CH₃COOH, with 0.200 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

\[
\text{moles CH}_3\text{COOH} = \text{moles NaOH} = M_a \times V_a = M_b \times V_b
\]

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

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

\[
\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}
\]

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

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

At the beginning of the titration the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base, CH₃COO⁻.

\[
\text{CH}_3\text{COOH}_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{CH}_3\text{COO}^-_{(aq)}
\]

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A⁻, is a buffer. As we learned in Chapter 6, we can calculate the pH of a buffer using the Henderson–Hasselbalch equation.
\[
pH = pK_a + \log \frac{[A^-]}{[HA]}
\]

Before the equivalence point the concentration of unreacted acetic acid is
\[
[CH_3COOH] = \frac{\text{initial moles CH}_3\text{COOH} - \text{moles NaOH added}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}
\]

and the concentration of acetate is
\[
[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}
\]

For example, after adding 10.0 mL of NaOH the concentrations of CH3COOH and CH3COO– are
\[
[CH_3COOH] = \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0500 \text{ M}
\]
\[
[CH_3COO^-] = \frac{(0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0333 \text{ M}
\]

which gives us a pH of
\[
pH = 4.76 + \log \frac{0.0333 \text{ M}}{0.0500 \text{ M}} = 4.58
\]

At the equivalence point the moles of acetic acid initially present and the moles of NaOH added are identical. Because their reaction effectively proceeds to completion, the predominate ion in solution is CH3COO–, which is a weak base. To calculate the pH we first determine the concentration of CH3COO–
\[
[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{(0.200 \text{ M})(25.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}
\]

Next, we calculate the pH of the weak base as shown earlier in Chapter 6.
\[
CH_3COO^- (aq) + H_2O(l) \rightleftharpoons OH^- (aq) + CH_3COOH(aq)
\]

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

Alternatively, we can calculate acetate’s concentration using the initial moles of acetic acid; thus
\[
[CH_3COO^-] = \frac{\text{initial moles CH}_3\text{COOH}}{\text{total volume}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}
\]
Construct a titration curve for the titration of 25.0 mL of 0.125 M NH₃ with 0.0625 M HCl.

Click here to review your answer to this exercise.

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

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

\[[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{6.17 \times 10^{-6}} = 1.62 \times 10^{-9} \text{ M}\]

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 OH⁻ is

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

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

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.

### Practice Exercise 9.2

Construct a titration curve for the titration of 25.0 mL of 0.125 M NH₃ with 0.0625 M HCl.

Click here to review your answer to this exercise.

| Table 9.3 Titration of 50.0 mL of 0.100 M Acetic Acid with 0.200 M NaOH |
|----------------------------------|------|----------------|------|------|
| Volume of NaOH (mL) | pH   | Volume of NaOH (mL) | pH   |
| 0.00              | 2.88 | 26.0            | 11.42 |
| 5.00              | 4.16 | 28.0            | 11.89 |
| 10.0              | 4.58 | 30.0            | 12.10 |
| 15.0              | 4.94 | 35.0            | 12.37 |
| 20.0              | 5.36 | 40.0            | 12.52 |
| 22.0              | 5.63 | 45.0            | 12.62 |
| 24.0              | 6.14 | 50.0            | 12.70 |
| 25.0              | 8.79 |                |      |
We can extend our approach for calculating a weak acid–strong base titration curve to reactions involving multiprotic acids or bases, and mixtures of acids or bases. As the complexity of the titration increases, however, the necessary calculations become more time consuming. Not surprisingly, a variety of algebraic\(^1\) and computer spreadsheet\(^2\) approaches have been described to aid in constructing titration curves.

**Sketching an Acid–Base Titration Curve**

To evaluate the relationship between a titration’s equivalence point and its end point, we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching an acid–base titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let’s use the titration of 50.0 mL of 0.100 M CH\(_3\)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 the y-axis and the titrant’s volume on the x-axis. To indicate the equivalence point volume, we draw a vertical line corresponding to 25.0 mL of NaOH. Figure 9.8 shows the result of the first step in our sketch.

Before the equivalence point the titration mixture’s pH is determined by a buffer of acetic acid, CH\(_3\)COOH, and acetate, CH\(_3\)COO\(^-\). Although we can easily calculate a buffer’s pH using the Henderson–Hasselbalch equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a buffer operates over a pH range extend-

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Figure 9.8 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M CH₃COOH 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.
Chapter 9 Titrimetric Methods

The pH is at the lower end of this range, pH = pK_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, pH = pK_a + 1, when the weak acid's concentration is 10 times smaller than that of its conjugate weak base. When titrating a weak acid or a weak base, the buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

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

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

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

Practice Exercise 9.3

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

Click here to review your answer to this exercise.

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

Example 9.1

Sketch titration curves for the following two systems: (a) the titration of 50.0 mL of 0.050 M H_2A, a diprotic weak acid with a pK_a1 of 3 and a pK_a2 of 7; and (b) the titration of a 50.0 mL mixture containing 0.075 M HA, a weak acid with a pK_a of 3, and 0.025 M HB, a weak acid with a pK_a of 7. For both titrations the titrant is 0.10 M NaOH.

Solution

Figure 9.9a shows the titration curve for H_2A, including the ladder diagram on the y-axis, the equivalence points at 25.0 mL and 50.0 mL, two points before each equivalence point, two points after the last equivalence point, and so on.
point, and the straight-lines that help in sketching the final curve. Before the first equivalence point the pH is controlled by a buffer consisting of $H_2A$ and $HA^-$. An $HA^-/A^{2-}$ buffer controls the pH between the two equivalence points. After the second equivalence point the pH reflects the concentration of excess NaOH.

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

**Practice Exercise 9.4**

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

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

### 9B.2 Selecting and Evaluating the End point

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

**Where is the Equivalence Point?**

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

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

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

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

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

Figure 9.11 shows titration curves for three diprotic weak acids. The titration curve for maleic acid, for which $K_{a1}$ is approximately 20,000 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 that for maleic acid. Finally, the titration curve for succinic acid, for which the two $K_a$ values differ by a factor of only 27, has only a single inflection point corresponding to the neutralization of $\text{HC}_4\text{H}_4\text{O}_4^-$ to $\text{C}_4\text{H}_4\text{O}_4^{2-}$. 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).

**Finding the End point with an Indicator**

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

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

$$\text{HIn}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{In}^-(aq)$$
has an equilibrium constant of

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

9.5

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

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

9.6

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

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

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

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

\[ pH = pK_a + \log\frac{10}{1} = pK_a + 1 \]

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

![Figure 9.12 Diagram showing the relationship between pH and an indicator's color. The ladder diagram defines pH values where HIn and In⁻ are the predominate species. The indicator changes color when the pH is between p\(K_a - 1\) and p\(K_a + 1\).](image)
For pHs between $pK_a - 1$ and $pK_a + 1$ the indicator's color passes through various shades of orange. The properties of several common acid–base indicators are shown in Table 9.4.

The relatively broad range of pHs over which an indicator changes color places additional limitations on its feasibility for signaling a titration's end point. To minimize a determinate titration error, an indicator's entire pH range must fall within the rapid change in pH at the equivalence point. For example, in Figure 9.12 we see that phenolphthalein is an appropriate indicator for the titration of 50.0 mL of 0.050 M acetic acid with 0.10 M NaOH. Bromothymol blue, on the other hand, is an inappropriate indicator because its change in color begins before the initial sharp rise in pH, and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining inaccurate results, while the range of possible end point volumes increases the probability of obtaining imprecise results.

### Practice Exercise 9.5

Suggest a suitable indicator for the titration of 25.0 mL of 0.125 M NH$_3$ with 0.0625 M NaOH. You constructed a titration curve for this titration in Practice Exercise 9.2 and Practice Exercise 9.3.

Click [here](#) to review your answer to this exercise.
Finding the End Point by Monitoring pH

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

The obvious sensor for monitoring an acid–base titration is a pH electrode and the result is a POTENTIOMETRIC TITRATION CURVE. For example, Figure 9.14a shows a small portion of the potentiometric titration curve for the titration of 50.0 mL of 0.050 M CH₃COOH with 0.10 M NaOH, focusing on the region containing the equivalence point. The simplest method for finding the end point is to locate the titration curve’s inflection point, as shown by the arrow. This is also the least accurate method, particularly if the titration curve has a shallow slope at the equivalence point.

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

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

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

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.65</td>
<td>6.00</td>
</tr>
<tr>
<td>23.91</td>
<td>6.10</td>
</tr>
<tr>
<td>24.13</td>
<td>6.20</td>
</tr>
</tbody>
</table>

Mathematically, we can approximate the first derivative as \( \frac{\Delta pH}{\Delta V} \), where \( \Delta pH \) is the change in pH between successive additions of titrant. Using the first two points, the first derivative is

\[
\frac{\Delta pH}{\Delta V} = \frac{6.10 - 6.00}{23.91 - 23.65} = 0.385
\]

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.

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>dP/dV</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.78</td>
<td>0.385</td>
</tr>
<tr>
<td>24.02</td>
<td>0.455</td>
</tr>
</tbody>
</table>

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

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

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

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

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

Consider again the titration of acetic acid, \( \text{CH}_3\text{COOH} \), with NaOH. At any point during the titration acetic acid is in equilibrium with \( \text{H}_3\text{O}^+ \) and \( \text{CH}_3\text{COO}^- \)

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

for which the equilibrium constant is

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

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 arrow shows the location of the titration’s end point.
Before the equivalence point the concentrations of CH$_3$COOH and CH$_3$COO$^-$ are

$$\text{[CH}_3\text{COOH]} = \frac{\text{initial moles CH}_3\text{COOH} - \text{moles NaOH added}}{\text{total volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$\text{[CH}_3\text{COO}^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_bV_b}{V_a + V_b}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+](M_bV_b)}{M_aV_a - M_bV_b}$$

$$K_aM_aV_a - K_aM_bV_b = [\text{H}_3\text{O}^+](M_bV_b)$$

$$\frac{K_aM_aV_a}{M_b} - K_aV_b = [\text{H}_3\text{O}^+] \times V_b$$

Finally, recognizing that the equivalence point volume is

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

leaves us with the following equation.

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

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, increasing its temperature. Monitoring the titrand’s temperature as we add the titrant provides us with another method for recording a titration curve and identifying the titration’s end point (Figure 9.15).

Before adding titrant, any change in the titrand’s temperature is the result of warming or cooling as it equilibrates with the surroundings. Adding titrant initiates the exothermic acid–base reaction, increasing the titrand’s temperature. This part of a thermometric titration curve is called the titra-
The temperature continues to rise with each addition of titrant until we reach the equivalence point. After the equivalence point, any change in temperature is due to the titrant’s enthalpy of dilution, and the difference between the temperatures of the titrant and titrand. Ideally, the equivalence point is a distinct intersection of the titration branch and the excess titrant branch. As shown in Figure 9.15, however, a thermometric titration curve usually shows curvature near the equivalence point due to an incomplete neutralization reaction, or to the excessive dilution of the titrand and the titrant during the titration. The latter problem is minimized by using a titrant that is 10–100 times more concentrated than the analyte, although this results in a very small end point volume and a larger relative error. If necessary, the end point is found by extrapolation.

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

### 9B.3 Titrations in Nonaqueous Solvents

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

For an amphoteric solvent, \(SH\), the autoprotolysis constant, \(K_s\), relates the concentration of its protonated form, \(SH_2^+\), to that of its deprotonated form, \(S^-\)
2SH ⇌ SH₂⁺ + S⁻

\[ K_s = [SH_2^+] [S^-] \]

and the solvent's pH and pOH are

\[ \text{pH} = -\log[SH_2^+] \]
\[ \text{pOH} = -\log[S^-] \]

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. 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 H₃O⁺ is

\[
[H_3O^+] = \frac{M_a V_a - M_b V_b}{V_a + V_b} = \frac{(1.0 \times 10^{-4} \text{ M})(50.0 \text{ mL}) - (1.0 \times 10^{-4} \text{ M})(45.0 \text{ mL})}{50.0 \text{ mL} + 45.0 \text{ mL}} = 5.3 \times 10^{-6} \text{ M}
\]

and the pH is 5.3. When the volume of NaOH is 110% of \( V_{eq} \), the concentration of OH⁻ is

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

Figure 9.16 Titration curves for the titration of 50.0 mL of 0.050 M H₃BO₃ with 0.50 M NaOH obtained by monitoring (a) pH, and (b) temperature. The red arrows show the end points for the titrations.

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.
and the pOH is 5.3. The titrand’s pH is
\[ \text{pH} = pK_w - \text{pOH} = 14 - 5.3 = 8.7 \]
and the change in the titrand’s pH as the titration goes from 90% to 110% of \( V_{eq} \) is
\[ \Delta \text{pH} = 8.7 - 5.3 = 3.4 \]
If we carry out the same titration in a nonaqueous solvent with a \( K_s \) of \( 1.0 \times 10^{-20} \), the pH after adding 45.0 mL of NaOH is still 5.3. However, the pH after adding 55.0 mL of NaOH is
\[ \text{pH} = pK_s - \text{pOH} = 20 - 5.3 = 14.7 \]
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 affecting the feasibility of an acid–base titration is the titrand’s dissociation constant. Here, too, the solvent plays an important role. The strength of an acid or a base is a relative measure of the ease transferring a proton from the acid to the solvent, or from the solvent to the base. For example, HF, with a \( K_a \) of \( 6.8 \times 10^{-4} \), is a better proton donor than CH\(_3\)COOH, for which \( K_a \) is \( 1.75 \times 10^{-5} \).

The strongest acid that can exist in water is the hydronium ion, H\(_3\)O\(^+\). HCl and HNO\(_3\) are strong acids because they are better proton donors than H\(_3\)O\(^+\) and essentially donate all their protons to H\(_2\)O, leveling their acid

![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 solvent, \( K_s = 1.0 \times 10^{-20} \).](image-url)
strength to that of H$_3$O$^+$. In a different solvent HCl and HNO$_3$ may not behave as strong acids.

If we place acetic acid in water the dissociation reaction

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

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

$$\text{CH}_3\text{COOH + NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{CH}_3\text{COO}^-$$

proceeds to a greater extent. In fact, both HCl and CH$_3$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 NH$_3$ is 4.75 in water and it is 6.40 in the more acidic glacial acetic acid. In contradiction to our expectations, NH$_3$ is a weaker base in the more acidic solvent. A full description of the solvent’s effect on the $pK_a$ of weak acid or the $pK_b$ of a weak base is beyond the scope of this text. You should be aware, however, that a titration that is not feasible in water may be feasible in a different solvent.

**Representative Method 9.1**

**Determination of Protein in Bread**

**Description of the Method**

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

**Procedure**

Transfer a 2.0-g sample of bread, which has previously been air-dried and ground into a powder, to a suitable digestion flask, along with 0.7 g of a HgO catalyst, 10 g of K$_2$SO$_4$, and 25 mL of concentrated H$_2$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

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical acid–base titrimetric method. Although each method is unique, the following description of the determination of protein in bread provides an instructive example of a typical procedure. The description here is based on Method 13.86 as published in *Official Methods of Analysis*, 8th Ed., Association of Official Agricultural Chemists: Washington, D. C., 1955.
below room temperature, remove the Hg\textsuperscript{2+} catalyst by adding 200 mL of H\textsubscript{2}O and 25 mL of 4\% w/v K\textsubscript{2}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 NH\textsubscript{3} into a collecting flask containing a known amount of standardized HCl. The tip of the condenser must be placed below the surface of the strong acid. After the distillation is complete, titrate the excess strong acid with a standard solution of NaOH using methyl red as an indicator (Figure 9.18).

**Questions**

1. Oxidizing the protein converts all of its nitrogen to NH\textsubscript{4}\textsuperscript{+}. Why is the amount of nitrogen not determined by titrating the NH\textsubscript{4}\textsuperscript{+} with a strong base?

   There are two reasons for not directly titrating the ammonium ion. First, because NH\textsubscript{4}\textsuperscript{+} is a very weak acid (its $K_a$ is $5.6 \times 10^{-10}$), its titration with NaOH yields a poorly defined end point. Second, even if the end point can be determined with acceptable accuracy and precision, the solution also contains a substantial larger concentration of unreacted H\textsubscript{2}SO\textsubscript{4}. The presence of two acids that differ greatly in concentration makes for a difficult analysis. If the titrant’s concentration is similar to that of H\textsubscript{2}SO\textsubscript{4}, then the equivalence point volume for the titration of NH\textsubscript{4}\textsuperscript{+} is too small to measure reliably. On the other hand, if the titrant’s concentration is similar to that of NH\textsubscript{4}\textsuperscript{+}, the volume needed to neutralize the H\textsubscript{2}SO\textsubscript{4} is unreasonably large.

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

   Any loss of NH\textsubscript{3} is loss of nitrogen and, therefore, a loss of protein. The result is a negative determinate error.

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

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

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**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.
9B.4 Quantitative Applications

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

Selecting and Standardizing a Titrant

The most common strong acid titrants are HCl, HClO₄, and H₂SO₄. Solutions of these titrants are usually prepared by diluting a commercially available concentrated stock solution. Because the concentrations of concentrated acids are known only approximately, the titrant’s concentration is determined by standardizing against one of the primary standard weak bases listed in Table 9.5.

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

Using NaOH as a titrant is complicated by potential contamination from the following reaction between CO₂ and OH⁻:

\[
\text{CO}_2(aq) + 2\text{OH}^- (aq) \rightarrow \text{CO}_3^{2-} (aq) + \text{H}_2\text{O}(l)
\]  

During the titration, NaOH reacts with both the titrand and CO₂, increasing the volume of NaOH needed to reach the titration’s end point. This is not a problem if end point pH is less than 6. Below this pH the CO₃²⁻ from reaction 9.7 reacts with H₃O⁺ to form carbonic acid.

\[
\text{CO}_3^{2-} (aq) + 2\text{H}_3\text{O}^+ (aq) \rightarrow \text{H}_2\text{CO}_3 (aq) + 2\text{H}_2\text{O}(l)
\]  

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

\[
\text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3 (aq)
\]
Under these conditions the presence of CO$_2$ does not affect the quantity of OH$^-$ used in the titration and is not a source of determinate error. If the end point pH is between 6 and 10, however, the neutralization of CO$_3^{2-}$ requires one proton

$$\text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l)$$

and the net reaction between CO$_2$ and OH$^-$ is

$$\text{CO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{HCO}_3^-(aq)$$

Under these conditions some OH$^-$ is consumed in neutralizing CO$_2$, resulting in a determinate error. We can avoid the determinate error if we use the same end point pH in both the standardization of NaOH and the analysis of our analyte, although this often is not practical.

Solid NaOH is always contaminated with carbonate due to its contact with the atmosphere, and can not be used to prepare a carbonate-free solution of NaOH. Solutions of carbonate-free NaOH can be prepared from 50% w/v NaOH because Na$_2$CO$_3$ is insoluble in concentrated NaOH.
When CO₂ is absorbed, Na₂CO₃ precipitates and settles to the bottom of the container, allowing access to the carbonate-free NaOH. When preparing a solution of NaOH, be sure to use water that is free from dissolved CO₂. Briefly boiling the water expels CO₂, and after cooling, it may be 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 should not be stored in glass bottles as NaOH reacts with glass to form silicate; instead, store such solutions in polyethylene bottles.

**Inorganic Analysis**

Acid–base titrimetry is a standard method for the quantitative analysis of many inorganic acids and bases. A standard solution of NaOH can be used to determine the concentration of inorganic acids, such as H₃PO₄ or H₃AsO₄, and inorganic bases, such as Na₂CO₃, can be analyzed using a standard solution of HCl.

An inorganic acid or base that is too weak to be analyzed by an aqueous acid–base titration can be analyzed by adjusting the solvent, or by an indirect analysis. For example, when analyzing boric acid, H₃BO₃, by titrating with NaOH, accuracy is limited by boric acid’s small acid dissociation constant of 5.8 × 10⁻¹⁰. Boric acid’s $K_a$ value increases to 1.5 × 10⁻⁴ in the presence of mannitol, because it forms a complex with the borate ion. The result is a sharper end point and a more accurate titration. Similarly, the analysis of ammonium salts is limited by the small acid dissociation constant of 5.7 × 10⁻¹⁰ for NH₄⁺. In this case, we can convert NH₄⁺ to NH₃ by neutralizing with strong base. The NH₃, for which $K_b$ is 1.58 × 10⁻⁵, is then removed by distillation and titrated with HCl.

We can analyze a neutral inorganic analyte if we can first convert it into an acid or base. For example, we can determine the concentration of NO₃⁻ by reducing it to NH₃ 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.

\[
3\text{NO}_3^-(aq) + 8\text{Al}(s) + 5\text{OH}^- (aq) + 2\text{H}_2\text{O}(l) \rightarrow 8\text{AlO}_2^-(aq) + 3\text{NH}_3(aq)
\]

The NH₃ is removed by distillation and titrated with HCl. Alternatively, we can titrate NO₃⁻ as a weak base by placing it in an acidic nonaqueous solvent such as anhydrous acetic acid and using HClO₄ as a titrant.

Acid–base titrimetry continues to be listed as a standard method for the determination of alkalinity, acidity, and free CO₂ in waters and wastewaters. **Alkalinity** is a measure of a sample’s capacity to neutralize acids. The most important sources of alkalinity are OH⁻, HCO₃⁻, and CO₃²⁻, although other weak bases, such as phosphate, may contribute to the overall alkalinity. Total alkalinity is determined by titrating to a fixed end point pH of 4.5 (or to the bromocresol green end point) using a standard solution of HCl or H₂SO₄. Results are reported as mg CaCO₃/L.

Figure 9.16a shows a typical result for the titration of H₃BO₃ with NaOH.

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 CaCO₃ is the only source provides a means for comparing the acid-neutralizing capacities of different samples.
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 containing only \( \text{OH}^- \) alkalinity, the volumes of strong acid needed to reach the two end points are identical (Figure 9.19a). When the only source of alkalinity is \( \text{CO}_3^{2-} \), 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 only \( \text{HCO}_3^- \) alkalinity, the volume of strong acid needed to reach the end point at a pH of 8.3 is zero, but that for the pH 4.5 end point is greater than zero (Figure 9.19c).

Mixtures of \( \text{OH}^- \) and \( \text{CO}_3^{2-} \), or of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) also are 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 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 titrating a mixture of these two ions, the volume of strong acid to reach a pH of 4.5 is less than twice that to reach a pH of 8.3. For a mixture of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) the volume of strong acid to reach a pH of 4.5 is more than twice that to reach a pH of 8.3. Table 9.6 summarizes the relationship between the sources of alkalinity and the volumes of titrant needed to reach the two end points.

**Acidity** is a measure of a water sample’s capacity for neutralizing base, and is conveniently divided into strong acid and weak acid acidity. Strong acid acidity, from inorganic acids such as HCl, HNO₃, and H₂SO₄, is common in industrial effluents and acid mine drainage. Weak acid acidity is usually dominated by the formation of H₂CO₃ from dissolved CO₂, but also includes contributions from hydrolyzable metal ions such as Fe³⁺, Al³⁺,

**Figure 9.19** Titration curves for 50.0 mL of (a) 0.10 M NaOH, (b) 0.050 M Na₂CO₃, and (c) 0.10 M NaHCO₃ using 0.10 M HCl. The dashed lines indicate the fixed pH end points of 8.3 and 4.5. The color gradients show the phenolphthalein (red → colorless) and bromocresol green (blue → green) endpoints. When titrating to the phenolphthalein endpoint, the titration continues until the last trace of red is lost.

Solutions containing \( \text{OH}^- \) and \( \text{HCO}_3^- \) alkalinities are unstable with respect to the formation of \( \text{CO}_3^{2-} \). Problem 9.15 in the end of chapter problems asks you to explain why this is true.
Table 9.6 Relationship Between End Point Volumes and Sources of Alkalinity

<table>
<thead>
<tr>
<th>Source of Alkalinity</th>
<th>Relationship Between End Point Volumes</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>( V_{\text{pH 4.5}} = V_{\text{pH 8.3}} )</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} )</td>
<td>( V_{\text{pH 4.5}} = 2 \times V_{\text{pH 8.3}} )</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>( V_{\text{pH 4.5}} &gt; 0; V_{\text{pH 8.3}} = 0 )</td>
</tr>
<tr>
<td>( \text{OH}^- ) and ( \text{CO}_3^{2-} )</td>
<td>( V_{\text{pH 4.5}} &lt; 2 \times V_{\text{pH 8.3}} )</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} ) and ( \text{HCO}_3^- )</td>
<td>( V_{\text{pH 4.5}} &gt; 2 \times V_{\text{pH 8.3}} )</td>
</tr>
</tbody>
</table>

Acidity is determined by titrating with a standard solution of NaOH to fixed pH of 3.7 (or the bromothymol blue end point) and a fixed pH 8.3 (or the phenolphthalein end point). Titrating to a pH of 3.7 provides a measure of strong acid acidity, and titrating to a pH of 8.3 provides a measure of total acidity. Weak acid acidity is the difference between the total and strong acid acidities. Results are expressed as the amount of CaCO₃ that can be neutralized by the sample’s acidity. An alternative approach for determining strong acid and weak acid acidity is to obtain a potentiometric titration curve and use a Gran plot to determine the two equivalence points. This approach has been used, for example, to determine the forms of acidity in atmospheric aerosols.⁴

Water in contact with either the atmosphere, or with carbonate-bearing sediments contains free CO₂ that exists in equilibrium with \( \text{CO}_2(g) \) and aqueous \( \text{H}_2\text{CO}_3, \text{HCO}_3^-, \) and \( \text{CO}_3^{2-} \). The concentration of free CO₂ 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 CO₂/L. This analysis is essentially the same as that for the determination of total acidity, and can only be applied to water samples that do not contain strong acid acidity.

**Organic Analysis**

Acid–base titrimetry continues to have a small, but important role for the analysis of organic compounds in pharmaceutical, biochemical, agricultural, and environmental laboratories. Perhaps the most widely employed acid–base titration is the Kjeldahl analysis for organic nitrogen. Examples of analytes determined by a Kjeldahl analysis include caffeine and saccharin in pharmaceutical products, proteins in foods, and the analysis of nitrogen in fertilizers, sludges, and sediments. Any nitrogen present in a –3 oxidation state is quantitatively oxidized to \( \text{NH}_4^+ \). Because some aromatic heterocyclic compounds, such as pyridine, are difficult to oxidize, a catalyst is used to ensure a quantitative oxidation. Nitrogen in other oxidation states, such as Mn⁴⁺. In addition, weak acid acidity may include a contribution from organic acids.

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

Several organic functional groups are weak acids or weak bases. Carboxylic (−COOH), sulfonic (−SO$_3$H) and phenolic (−C$_6$H$_5$OH) functional groups are weak acids that can be successfully titrated in either aqueous or nonaqueous solvents. Sodium hydroxide is the titrant of choice for aqueous solutions. Nonaqueous titrations are often carried out in a basic solvent, such as ethylenediamine, using tetrabutylammonium hydroxide, $(C_4H_9)_4NOH$, as the titrant. Aliphatic and aromatic amines are weak bases that can be titrated using HCl in aqueous solution, or HClO$_4$ in glacial acetic acid. Other functional groups can be analyzed indirectly following a reaction that produces or consumes an acid or base. Typical examples are shown in Table 9.8.

Many pharmaceutical compounds are weak acids or bases that can be analyzed by an aqueous or nonaqueous acid–base titration; examples include salicylic acid, phenobarbital, caffeine, and sulfanilamide. Amino acids and proteins can be analyzed in glacial acetic acid using HClO$_4$ as the titrant. For example, a procedure for determining the amount of nutritionally available protein uses an acid–base titration of lysine residues.

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

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

$^a$ The species that is titrated is shown in **bold**.

### Quantitative Calculations

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

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Example 9.2

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

**Solution**

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

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

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

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

$$7.3405 \times 10^{-5} \text{ mol NaOH} \times \frac{1 \text{ mol } C_6H_8O_7}{3 \text{ mol NaOH}} = 2.4468 \times 10^{-4} \text{ mol } C_6H_8O_7$$
Because this is the amount of citric acid in a 50.00 mL sample, the concentration of citric acid in the citrus drink is 0.09402 g/100 mL. The complete titration curve is shown in Figure 9.20b.

Practice Exercise 9.6

Your company recently received a shipment of salicylic acid, C₇H₆O₃, to be used in the production of acetylsalicylic acid (aspirin). The shipment can be accepted only if the salicylic acid is more than 99% pure. To evaluate the shipment’s purity, a 0.4208-g sample is dissolved in water and titrated to the phenolphthalein end point, requiring 21.92 mL of 0.1354 M NaOH. Report the shipment’s purity as %w/w C₇H₆O₃. Salicylic acid is a diprotic weak acid with $K_a$ values of 2.97 and 13.74.

Click here to review your answer to this exercise.

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

Example 9.3

The purity of a pharmaceutical preparation of sulfanilamide, C₆H₄N₂O₂S, is determined by oxidizing sulfur to SO₂ and bubbling it through H₂O₂ to produce H₂SO₄. The acid is titrated to the bromothymol blue end point with a standard solution of NaOH. Calculate the purity of the preparation given that a 0.5136-g sample requires 48.13 mL of 0.1251 M NaOH.

Solution

The bromothymol blue end point has a pH range of 6.0–7.6. Sulfuric acid is a diprotic acid, with a $K_{a2}$ of 1.99 (the first $K_a$ value is very large and the acid dissociation reaction goes to completion, which is why H₂SO₄ is a strong acid). The titration, therefore, proceeds to the second equivalence point and the titration reaction is

$$\text{H}_2\text{SO}_4(aq) + 2\text{OH}^- (aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{SO}_4^{2-} (aq)$$

Using the titration results, there are

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

$$6.021 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 3.010 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$
produced by bubbling SO₂ through H₂O₂. Because all the sulfur in H₂SO₄ comes from the sulfanilamide, we can use a conservation of mass to determine the amount of sulfanilamide in the sample.

\[ 3.010 \times 10^{-3} \text{ mol H}_2\text{SO}_4 \times \frac{1 \text{ mol S}}{\text{mol H}_2\text{SO}_4} \times \frac{1 \text{ mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol S}} \times \frac{168.18 \text{ g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}}{\text{mol C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}} = 0.5062 \text{ g C}_6\text{H}_4\text{N}_2\text{O}_2\text{S} \]

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

**Practice Exercise 9.7**

The concentration of NO₂ in air can be determined by passing the sample through a solution of H₂O₂, which oxidizes NO₂ to HNO₃, and titrating the HNO₃ with NaOH. What is the concentration of NO₂, in mg/L, if a 5.0 L sample of air requires 9.14 mL of 0.01012 M NaOH to reach the methyl red end point?

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

**Example 9.4**

The amount of protein in a sample of cheese is determined by a Kjeldahl analysis for nitrogen. After digesting a 0.9814-g sample of cheese, the nitrogen is oxidized to NH₄⁺, converted to NH₃ with NaOH, and distilled into a collection flask containing 50.00 mL of 0.1047 M HCl. The excess HCl is back titrated with 0.1183 M NaOH, requiring 22.84 mL to reach the bromothymol blue end point. Report the %w/w protein in the cheese assuming that there are 6.38 grams of protein for every gram of nitrogen in most dairy products.

**Solution**

The HCl in the collection flask reacts with two bases

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

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

The collection flask originally contains

\[ 0.1047 \text{ M HCl} \times 0.05000 \text{ L HCl} = 5.235 \times 10^{-3} \text{ mol HCl} \]

of which
0.1183 M NaOH × 0.02284 L NaOH × \[ \frac{1 \text{ mol HCl}}{\text{mol NaOH}} = 2.702 \times 10^{-3} \text{ mol HCl} \]

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

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

is the moles of HCl reacting with NH₃. Because all the nitrogen in NH₃ comes from the sample of cheese, we use a conservation of mass to determine the grams of nitrogen in the sample.

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

The mass of protein, therefore, is

\[ 0.03549 \text{ g N} × \frac{6.38 \text{ g protein}}{\text{g N}} = 0.2264 \text{ g protein} \]

and the % w/w protein is

\[ \frac{0.2264 \text{ g protein}}{0.9814 \text{ g sample}} × 100 = 23.1\% \text{ w/w protein} \]

Practice Exercise 9.8

Limestone consists mainly of CaCO₃, 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 CO₂, 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 CaCO₃.

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

Example 9.5

The alkalinity of natural waters is usually controlled by OH⁻, HCO₃⁻, and CO₃²⁻, which may be present singularly or in combination. Titrating a 100.0-mL sample to a pH of 8.3 requires 18.67 mL of a 0.02812 M HCl. A second 100.0-mL aliquot requires 48.12 mL of the same titrant to reach
a pH of 4.5. Identify the sources of alkalinity and their concentrations in milligrams per liter.

**Solution**

Because the volume of titrant to reach a pH of 4.5 is more than twice that needed to reach a pH of 8.3, we know, from Table 9.6, that the sample's alkalinity is controlled by \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \). Titrating to a pH of 8.3 neutralizes \( \text{CO}_3^{2-} \) to \( \text{HCO}_3^- \)

\[
\text{CO}_3^{2-}(aq) + \text{HCl}(aq) \rightarrow \text{HCO}_3^-(aq) + \text{Cl}^-(aq)
\]

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

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

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

Titrating to a pH of 4.5 neutralizes \( \text{CO}_3^{2-} \) to \( \text{H}_2\text{CO}_3 \), and \( \text{HCO}_3^- \) to \( \text{H}_2\text{CO}_3 \) (see Figures 9.19).

\[
\text{CO}_3^{2-}(aq) + 2\text{HCl}(aq) \rightarrow \text{H}_2\text{CO}_3(aq) + 2\text{Cl}^-(aq)
\]

\[
\text{HCO}_3^-(aq) + \text{HCl}(aq) \rightarrow \text{H}_2\text{CO}_3(aq) + 2\text{Cl}^-(aq)
\]

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

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

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

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

\[
\frac{3.031 \times 10^{-4} \text{ mol HCO}_3^-}{0.1000 \text{ L}} \times \frac{61.02 \text{ g HCO}_3^-}{\text{mol HCO}_3^-} \times \frac{1000 \text{ mg}}{\text{g}} = 185.0 \text{ mg/L}
\]
9B.5 Qualitative Applications

Example 9.5 shows how we can use an acid–base titration to assign the forms of alkalinity in waters. We can easily extend this approach to other systems. For example, by titrating with either a strong acid or a strong base to the methyl orange and phenolphthalein end points we can determine the composition of solutions containing one or two of the following species: $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, $\text{PO}_4^{3-}$, $\text{HCl}$, and $\text{NaOH}$. 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.

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

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>Relationship Between End Point Volumes with Strong Base Titrant$^a$</th>
<th>Relationship Between End Point Volumes With Strong Acid Titrant$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4$</td>
<td>$V_{PH} = 2 \times V_{MO}$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^-$</td>
<td>$V_{PH} &gt; 0$; $V_{MO} = 0$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-}$</td>
<td>$-^b$</td>
<td>$V_{MO} &gt; 0$; $V_{PH} = 0$</td>
</tr>
<tr>
<td>$\text{PO}_4^{3-}$</td>
<td>$-^b$</td>
<td>$V_{MO} = 2 \times V_{PH}$</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>$V_{PH} = V_{MO}$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>$\text{NaOH}$</td>
<td>$-^b$</td>
<td>$V_{MO} = V_{PH}$</td>
</tr>
<tr>
<td>$\text{HCl}$ and $\text{H}_3\text{PO}_4$</td>
<td>$V_{PH} &lt; 2 \times V_{MO}$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4$ and $\text{H}_2\text{PO}_4^-$</td>
<td>$V_{PH} &gt; 2 \times V_{MO}$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$</td>
<td>$V_{PH} &gt; 0$; $V_{MO} = 0$</td>
<td>$V_{MO} &gt; 0$; $V_{PH} = 0$</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$</td>
<td>$-^b$</td>
<td>$V_{MO} &gt; 2 \times V_{PH}$</td>
</tr>
<tr>
<td>$\text{PO}_4^{3-}$ and $\text{NaOH}$</td>
<td>$-^b$</td>
<td>$V_{MO} &lt; 2 \times V_{PH}$</td>
</tr>
</tbody>
</table>

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

$^b$ When no information is provided, the volume of titrant to each end point is zero.

Practice Exercise 9.9

Samples containing the monoprotic weak acids 2–methylamaminium chloride ($\text{C}_7\text{H}_{10}\text{NCl}$, $pK_a = 4.447$) and 3–nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, $pK_a = 8.39$) 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.6 Characterization Applications

An acid–base titration can be used to characterize the chemical and physical properties of matter. Two useful characterization applications are the...
determination of a compound’s equivalent weight and its acid or its base dissociation constant.

**Equivalent Weights**

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

\[ \text{moles titrant} = \frac{n \text{ moles titrant}}{\text{moles analyte}} \times \text{moles analyte} \]

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

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

where \( \text{FW} \) is the analyte’s formula weight.

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

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

where

\[ \text{FW} = n \times \text{EW} \]

---

**Example 9.6**

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

- Ascorbic acid: \( \text{C}_8\text{H}_8\text{O}_6 \), \( \text{FW} = 176.1 \) monoprotic
- Malonic acid: \( \text{C}_3\text{H}_4\text{O}_4 \), \( \text{FW} = 104.1 \) diprotic
- Succinic acid: \( \text{C}_4\text{H}_6\text{O}_4 \), \( \text{FW} = 118.1 \) diprotic
- Citric acid: \( \text{C}_6\text{H}_8\text{O}_7 \), \( \text{FW} = 192.1 \) triprotic

**Solution**

The moles of NaOH needed to reach the end point is
0.1005 M NaOH × 0.04268 L NaOH = 4.289 × 10⁻³ mol NaOH

which gives the analyte’s equivalent weight as

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

The possible formula weights for the weak acid are

\[
\begin{align*}
n = 1: & \quad \text{FW} = \text{EW} = 58.78 \text{ g/equivalent} \\
n = 2: & \quad \text{FW} = 2 \times \text{EW} = 117.6 \text{ g/equivalent} \\
n = 3: & \quad \text{FW} = 3 \times \text{EW} = 176.3 \text{ g/equivalent}
\end{align*}
\]

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

**Practice Exercise 9.10**

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

Click [here](#) to review your answer to this exercise.
Another application of acid–base titrimetry is the determination of equilibrium constants. Consider, for example, a solution of acetic acid, CH₃COOH, for which the dissociation constant is

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

When the concentrations of CH₃COOH and CH₃COO⁻ are equal, the $K_a$ expression reduces to $K_a = [H_3O^+]$, or pH = p$K_a$. If we titrate a solution of acetic acid with NaOH, the pH equals the p$K_a$ when the volume of 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 p$K_a$.

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

**Practice Exercise 9.11**

Use the potentiometric titration curve in Figure 9.21 to estimate the 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.

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

A plot of $[\text{H}_3\text{O}^+] \times V_b$ versus $V_b$, for volumes less than the equivalence point, yields a straight line with a slope of $-K_a$. Other linearizations have been developed which use the entire titration curve, or that require no assumptions. This approach to determining acidity constants has been used to study the acid–base properties of humic acids, which are naturally occurring, large molecular weight organic acids with multiple acidic sites. In one study a humic acid was found to have six titratable sites, three of which were identified as carboxylic acids, two of which were believed to be secondary or tertiary amines, and one of which was identified as a phenolic group.

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

---

**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.

---


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

One goal of analytical chemistry is to extend analyses to smaller samples. Here we describe two interesting approaches to titrating μL and pL samples. In one experimental design (Figure 9.24), samples of 20–100 μL were held by capillary action between a flat-surface pH electrode and a stainless steel sample stage. The titrant was added by using the oscillations of a piezoelectric ceramic device to move an angled glass rod in and out of a tube connected to a reservoir containing the titrant. Each time the glass tube was withdrawn an approximately 2 nL microdroplet of titrant was released. The microdroplets were allowed to fall onto the sample, with mixing accomplished by spinning the sample stage at 120 rpm. A total of 450 microdroplets, with a combined volume of 0.81–0.84 μL, was dispensed between each pH measurement. In this fashion a titration curve was constructed. This method was used to titrate solutions of 0.1 M HCl and 0.1 M CH₃COOH with 0.1 M NaOH. Absolute errors ranged from a minimum of +0.1% to a maximum of –4.1%, with relative standard deviations from 0.15% to 4.7%. Sample as small as 20 μL were successfully titrated.

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

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

**Accuracy**

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.

---

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

---

**Precision**

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

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

**Sensitivity**

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

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

where \( k \), the sensitivity, is determined by the stoichiometry between the titrand and the titrant. Consider, for example, the determination of sulfuric acid, \( \text{H}_2\text{SO}_3 \), by titrating with \( \text{NaOH} \) to the first equivalence point

\[ \text{H}_2\text{SO}_3(\text{aq}) + \text{OH}^- \rightarrow \text{H}_2\text{O}(l) + \text{HSO}_3^- \]

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

\[ \text{mol } \text{NaOH} = \text{mol } \text{H}_2\text{SO}_3 \]

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

\[ M_{\text{NaOH}} \times V_{\text{NaOH}} = \text{mol } \text{H}_2\text{SO}_3 \]

\[ V_{\text{NaOH}} = \frac{1}{M_{\text{NaOH}}} \times \text{mol } \text{H}_2\text{SO}_3 \]

we find that \( k \) is

\[ k = \frac{1}{M_{\text{NaOH}}} \]
There are two ways in which we can improve a titration’s sensitivity. The first, and most obvious, is to decrease the titrant’s concentration because it is inversely proportional to the sensitivity, $k$.

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

$$\text{H}_2\text{SO}_3(\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{SO}_3^{2-} (\text{aq})$$

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

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

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 the larger volume of titrant requires us to refill the buret. Consequently, standard acid–base titrimetric procedures are written to ensure that titrations require 60–100% of the buret’s volume.

**Selectivity**

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

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

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

**Time, Cost, and Equipment**

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

**9C Complexation Titrations**

The earliest examples of metal–ligand complexation titrations are Liebig’s determinations, in the 1850s, of cyanide and chloride using, respectively, Ag⁺ and Hg²⁺ as the titrant. Practical analytical applications of complexation titrimetry were slow to develop because many metals and ligands form a series of metal–ligand complexes. Liebig’s titration of CN⁻ with Ag⁺ was successful because they form a single, stable complex of Ag(CN)₂⁻, giving a single, easily identified end point. Other metal–ligand complexes, such as CdI₄²⁻, are not analytically useful because they form a series of metal–ligand complexes (CdI⁺, CdI₂(aq), CdI₃⁻ and CdI₄²⁻) that produce a sequence of poorly defined end points.

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

**9C.1 Chemistry and Properties of EDTA**

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

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](image-url) Structures of (a) EDTA, in its fully deprotonated form, and (b) in a six-coordinate metal–EDTA complex with a divalent metal ion.
Metal–EDTA Formation Constants

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

$$\text{Cd}^{2+}(aq) + \text{Y}^{4−}(aq) \rightleftharpoons \text{CdY}^{2−}(aq)$$

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

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

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

EDTA is a Weak Acid

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

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

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

Conditional Metal–Ligand Formation Constants

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

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

$$C_{\text{EDTA}} = [H_6 Y^{2+}] + [H_5 Y^+] + [H_4 Y] +$$
$$[H_3 Y^-] + [H_2 Y^{2−}] + [HY^{3−}] + [Y^{4−}]$$

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

$$\alpha_{Y^{4−}} = \frac{[Y^{4−}]}{C_{\text{EDTA}}}$$
Chapter 9 Titrimetric Method

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

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

and rearranging gives

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

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

**EDTA Competes With Other Ligands**

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

<table>
<thead>
<tr>
<th>pH</th>
<th>$\alpha_{Y^{4-}}$</th>
<th>pH</th>
<th>$\alpha_{Y^{4-}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.9 \times 10^{-18}$</td>
<td>8</td>
<td>$5.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>$3.4 \times 10^{-14}$</td>
<td>9</td>
<td>$5.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>$2.6 \times 10^{-11}$</td>
<td>10</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>$3.8 \times 10^{-9}$</td>
<td>11</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>$3.7 \times 10^{-7}$</td>
<td>12</td>
<td>0.98</td>
</tr>
<tr>
<td>6</td>
<td>$2.4 \times 10^{-5}$</td>
<td>13</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>$5.0 \times 10^{-4}$</td>
<td>14</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>pH</th>
<th>$K_f'$</th>
<th>pH</th>
<th>$K_f'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$5.5 \times 10^{-2}$</td>
<td>8</td>
<td>$1.6 \times 10^{14}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.0 \times 10^{3}$</td>
<td>9</td>
<td>$1.6 \times 10^{15}$</td>
</tr>
<tr>
<td>3</td>
<td>$7.7 \times 10^{5}$</td>
<td>10</td>
<td>$1.1 \times 10^{16}$</td>
</tr>
<tr>
<td>4</td>
<td>$1.1 \times 10^{8}$</td>
<td>11</td>
<td>$2.5 \times 10^{16}$</td>
</tr>
<tr>
<td>5</td>
<td>$1.1 \times 10^{10}$</td>
<td>12</td>
<td>$2.9 \times 10^{16}$</td>
</tr>
<tr>
<td>6</td>
<td>$6.8 \times 10^{11}$</td>
<td>13</td>
<td>$2.9 \times 10^{16}$</td>
</tr>
<tr>
<td>7</td>
<td>$1.5 \times 10^{13}$</td>
<td>14</td>
<td>$2.9 \times 10^{16}$</td>
</tr>
</tbody>
</table>
NH₄⁺/NH₃ buffer includes NH₃, which forms several stable Cd²⁺–NH₃ complexes. Because EDTA forms a stronger complex with Cd²⁺ it will displace NH₃, but the stability of the Cd²⁺–EDTA complex decreases.

We can account for the effect of an **auxiliary complexing agent**, such as NH₃, in the same way we accounted for the effect of pH. Before adding EDTA, the mass balance on Cd²⁺, \( C_{\text{Cd}} \), 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 Cd²⁺, \( \alpha_{\text{Cd}^{2+}} \), is

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

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

\[
K'_{f} = K_{f} \times \frac{[\text{Cd}Y^{2-}]}{\alpha_{\text{Cd}^{2+}} C_{\text{Cd}} C_{\text{EDTA}}}
\]

Because the concentration of NH₃ in a buffer is essentially constant, we can rewrite this equation

\[
K''_{f} = K_{f} \times \alpha_{\text{Y}^{4-}} \times \alpha_{\text{Cd}^{2+}} = \frac{[\text{Cd}Y^{2-}]}{C_{\text{Cd}} C_{\text{EDTA}}}
\]

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 \( \alpha_{\text{M}^{2+}} \) for several metal ion when NH₃ is the complexing agent.

### 9C.2 Complexometric EDTA Titration Curves

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

| Table 9.12 | Values of \( \alpha_{\text{M}^{2+}} \) for Selected Concentrations of Ammonia |
|---|---|---|---|---|---|---|---|
| [NH₃] (M) | \( \alpha_{\text{Ca}^{2+}} \) | \( \alpha_{\text{Cd}^{2+}} \) | \( \alpha_{\text{Co}^{2+}} \) | \( \alpha_{\text{Cu}^{2+}} \) | \( \alpha_{\text{Mg}^{2+}} \) | \( \alpha_{\text{Ni}^{2+}} \) | \( \alpha_{\text{Zn}^{2+}} \) |
| 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 | \( 9.99 \times 10^{-1} \) | \( 6.09 \times 10^{-1} \) | \( 8.84 \times 10^{-1} \) | \( 4.15 \times 10^{-3} \) | \( 9.98 \times 10^{-1} \) | \( 5.76 \times 10^{-1} \) | \( 7.48 \times 10^{-1} \) |

The value of \( \alpha_{\text{Cd}^{2+}} \) depends on the concentration of NH₃. Contrast this with \( \alpha_{\text{Y}^{4-}} \), which depends on pH.
shape of a complexometric EDTA titration curve. In section 9B we learned that an acid–base titration curve shows how the titrand’s pH changes as we add titrant. The analogous result for a complexation titration shows the change in pM, where M is the metal ion, as a function of the volume of EDTA. In this section we will learn how to calculate a titration curve using the equilibrium calculations from Chapter 6. We also will learn how to quickly sketch a good approximation of any complexation titration curve using a limited number of simple calculations.

**Calculating the Titration Curve**

Let’s calculate the titration curve for 50.0 mL of $5.00 \times 10^{-3}$ M Cd$^{2+}$ using a titrant of 0.0100 M EDTA. Furthermore, let’s assume that the titrand is buffered to a pH of 10 with a buffer that is 0.0100 M in NH$_3$.

Because the pH is 10, some of the EDTA is present in forms other than Y$^{4-}$. In addition, EDTA must compete with NH$_3$ for the Cd$^{2+}$. To evaluate the titration curve, therefore, we first need to calculate the conditional formation constant for CdY$^{2-}$. From Table 9.10 and Table 9.11 we find that $a_{Y^{4-}}$ is 0.35 at a pH of 10, and that $a_{Cd^{2+}}$ is 0.0881 when the concentration of NH$_3$ is 0.0100 M. Using these values, the conditional formation constant is

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

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

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

as if it proceeds to completion.

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

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

$$M_{EDTA} \times V_{EDTA} = M_{Cd} \times V_{Cd}$$

Substituting in known values, we find that it requires

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

of EDTA to reach the equivalence point.

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

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

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

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

which gives a pCd of

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

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

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

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

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

\[
K'_{f}'' = \frac{[CdY^{2-}]}{C_{\text{Cd}} C_{\text{EDTA}}} = \frac{3.33 \times 10^{-3} - x}{x} = 9.5 \times 10^{14}
\]

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

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

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

and pCd is 9.77 at the equivalence point.

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

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

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


\[ C_{EDTA} = \frac{M_{EDTA} V_{EDTA} - M_{Cd} V_{Cd}}{V_{Cd} + V_{EDTA}} \]

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

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

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

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

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

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

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

<table>
<thead>
<tr>
<th>Volume of EDTA (mL)</th>
<th>pCd</th>
<th>Volume of EDTA (mL)</th>
<th>pCd</th>
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</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.36</td>
<td>27.0</td>
<td>14.95</td>
</tr>
<tr>
<td>5.00</td>
<td>3.49</td>
<td>30.0</td>
<td>15.33</td>
</tr>
<tr>
<td>10.0</td>
<td>3.66</td>
<td>35.0</td>
<td>15.61</td>
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<tr>
<td>15.0</td>
<td>3.87</td>
<td>40.0</td>
<td>15.76</td>
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<tr>
<td>20.0</td>
<td>4.20</td>
<td>45.0</td>
<td>15.86</td>
</tr>
<tr>
<td>23.0</td>
<td>4.62</td>
<td>50.0</td>
<td>15.94</td>
</tr>
<tr>
<td>25.0</td>
<td>9.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.28 Titration curve for the titration of 50.0 mL of 5.00 \times 10^{-3} \text{ M Cd}^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH\textsubscript{3}. The red points correspond to the data in Table 9.13. The blue line shows the complete titration curve.
Practice Exercise 9.12

Calculate titration curves for the titration of 50.0 mL of 5.00 \times 10^{-3} M \text{Cd}^{2+} with 0.0100 M \text{EDTA} (a) at a pH of 10 and (b) at a pH of 7. Neither titration includes an auxiliary complexing agent. Compare your results with Figure 9.28 and comment on the effect of pH and of \text{NH}_3 on the titration of \text{Cd}^{2+} with \text{EDTA}.

Click here to review your answer to this exercise.

Sketching an EDTA Titration Curve

To evaluate the relationship between a titration’s equivalence point and its end point, we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a complexation titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let’s use the titration of 50.0 mL of 5.00 \times 10^{-3} M \text{Cd}^{2+} with 0.0100 M \text{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 corresponding to 25.0 mL of \text{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 the unreacted \text{Cd}^{2+} is free—some is complexed with \text{NH}_3—we must account for 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 \text{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

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

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

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

\[ \text{pCd} = \log K_f' + \log \frac{C_{\text{EDTA}}}{[\text{CdY}^{2-}]} \]
Figure 9.29 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of $5.00 \times 10^{-3}$ M Cd$^{2+}$ with 0.0100 M EDTA in the presence of 0.0100 M NH$_3$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.
Note that after the equivalence point, the titrand’s solution is a metal–ligand complexation buffer, with pCd determined by $C_{\text{EDTA}}$ and $[\text{CdY}^{2-}]$. The buffer is at its lower limit of $pCD = \log K_f' - 1$ when

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

Making appropriate substitutions and solving, we find that

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

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

Figure 9.29c shows the third step in our sketch. First, we add a ladder diagram for the CdY$^{2-}$ complex, including its buffer range, using its $\log K_f'$ value of 16.04. Next, we add points representing pCd at 110% of $V_{\text{eq}}$ (a pCd of 15.04 at 27.5 mL) and 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 the line through the vertical line representing the equivalence point’s volume (Figure 9.29d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.29e). A comparison of our sketch to the exact titration curve (Figure 9.29f) shows that they are in close agreement.

### Practice Exercise 9.13

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

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

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

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

**Finding the End Point with an Indicator**

Most indicators for complexation titrations are organic dyes—known as *metallochromic indicators*—that form stable complexes with metal ions. The indicator, \( \text{In}^{m-} \), 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 \( \text{MIn}^{n-} \).

\[
\text{MIn}^{n-} + \text{Y}^{4-} \rightarrow \text{MY}^{2-} + \text{In}^{m-}
\]

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 that of the metal–EDTA complex. If the metal–indicator complex is too strong, the change in color occurs after the equivalence point. If the metal–indicator complex is too weak, however, the end point occurs before we reach the equivalence point.

Most metallochromic indicators also are weak acids. One consequence of this is that the conditional formation constant for the metal–indicator complex depends on the titrand's pH. This provides some control over an indicator's titration error because we can adjust the strength of a metal–indicator complex by adjusted the pH at which we carry out the titration. Unfortunately, because the indicator is a weak acid, the color of the uncomplexed indicator also changes with pH. Figure 9.30, for example, shows the color of the indicator calmagite as a function of pH and \( \text{pMg} \), 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, it 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 is often possible to complete an EDTA titration

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH Range</th>
<th>Metal Ions(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calmagite</td>
<td>8.5–11</td>
<td>Ba, ( \text{Ca} ), Mg, Zn</td>
</tr>
<tr>
<td>eryochrome Black T</td>
<td>7.5–10.5</td>
<td>Ba, ( \text{Ca} ), Mg, Zn</td>
</tr>
<tr>
<td>eryochrome Blue Black R</td>
<td>8–12</td>
<td>( \text{Ca} ), Mg, Zn, Cu</td>
</tr>
<tr>
<td>murexide</td>
<td>6–13</td>
<td>Ca, Ni, Cu</td>
</tr>
<tr>
<td>PAN</td>
<td>2–11</td>
<td>Cd, Cu, Zn</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>2–3</td>
<td>Fe</td>
</tr>
</tbody>
</table>

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

**Finding the End Point by Monitoring Absorbance**

An important limitation when using an indicator is that we must be able to see the indicator’s change in color at the end point. This may be difficult if the solution is already colored. For example, when titrating Cu$^{2+}$ with EDTA, ammonia is used to adjust the titrand’s pH. The intensely colored Cu(NH$_3$)$_4^{2+}$ complex obscures the indicator’s color, making an accurate determination of the end point difficult. Other absorbing species present within the sample matrix may also interfere. This is often a problem when analyzing clinical samples, such as blood, or environmental samples, such as natural waters.

---

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

See Chapter 11 for more details about ion selective electrodes.
If at least one species in a complexation titration absorbs electromagnetic radiation, we can identify the end point by monitoring the titrand’s absorbance at a carefully selected wavelength. For example, we can identify the end point for a titration of Cu\(^{2+}\) with EDTA, in the presence of NH\(_3\) by monitoring the titrand’s absorbance at a wavelength of 745 nm, where the Cu(NH\(_3\))\(_4^{2+}\) complex absorbs strongly. At the beginning of the titration the absorbance is at a maximum. As we add EDTA, however, the reaction

\[
\text{Cu(NH}_3\text{)}_4^{2+}(aq) + \text{Y}^4-(aq) \rightarrow \text{CuY}^2-(aq) + 4\text{NH}_3(aq)
\]

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

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

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

**Figure 9.31** Examples of spectrophotometric titration curves: (a) only the titrand absorbs; (b) only the titrant absorbs; (c) only the product of the titration reaction absorbs; (d) both the titrand and the titrant absorb; (e) both the titration reaction’s product and the titrant absorb; (f) only the indicator absorbs. The red arrows indicate the end points for each titration curve.
Representative Method 9.2

Determination of Hardness of Water and Wastewater

Description of the Method

The operational definition of water hardness is the total concentration of cations in a sample capable of forming insoluble complexes with soap. Although most divalent and trivalent metal ions contribute to hardness, the most important are Ca$^{2+}$ and Mg$^{2+}$. Hardness is determined by titrating with EDTA at a buffered pH of 10. Calmagite is used as an indicator. Hardness is reported as mg CaCO$_3$/L.

Procedure

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

Questions

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

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

Figure 9.32 End point for the titration of hardness with EDTA using calmagite as an indicator; the indicator is: (a) red prior to the end point due to the presence of the Mg$^{2+}$–indicator complex; (b) purple at the titration’s end point; and (c) blue after the end point due to the presence of uncomplexed indicator.
late end point and a positive determinate error are possible if we use a pH of 11.

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

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

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

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

A time limitation suggests that there is a kinetically controlled interference, possibly arising from a competing chemical reaction. In this case the interference is the possible precipitation of CaCO\(_3\) at a pH of 10.

**9C.4 Quantitative Applications**

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

**Selection and Standardization of Titrants**

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

Solutions of EDTA are prepared from its soluble disodium salt, Na\(_2\)H\(_2\)Y•2H\(_2\)O and standardized by titrating against a solution made from the primary standard CaCO\(_3\). Solutions of Ag\(^{+}\) and Hg\(^{2+}\) are prepared using AgNO\(_3\) and Hg(NO\(_3\))\(_2\), both of which are secondary standards. Standardization is accomplished by titrating against a solution prepared from primary standard grade NaCl.

---

**Figure 9.33** Titration curves for 50 mL of \(10^{-3}\) M Mg\(^{2+}\) with \(10^{-3}\) M EDTA at pHs 9, 10, and 11 using calmagite as an indicator. The range of pMg and volume of EDTA over which the indicator changes color is shown for each titration curve.
Complexation titrimetry continues to be listed as a standard method for the determination of hardness, Ca\(^{2+}\), CN\(^{-}\), and Cl\(^{-}\) in waters and wastewaters. The evaluation of hardness was described earlier in Representative Method 9.2. The determination of Ca\(^{2+}\) is complicated by the presence of Mg\(^{2+}\), which also reacts with EDTA. To prevent an interference the pH is adjusted to 12–13, precipitating Mg\(^{2+}\) as Mg(OH)\(_2\). Titrating with EDTA using murexide or Eriochrome Blue Black R as the indicator gives the concentration of Ca\(^{2+}\).

Cyanide is determined at concentrations greater than 1 mg/L by making the sample alkaline with NaOH and titrating with a standard solution of AgNO\(_3\), forming the soluble Ag(CN)\(_2^{-}\) complex. The end point is determined using \(p\)-dimethylaminobenzalrhodamine as an indicator, with the solution turning from a yellow to a salmon color in the presence of excess Ag\(^{+}\).

Chloride is determined by titrating with Hg(NO\(_3\))\(_2\), forming HgCl\(_2(aq)\). The sample is acidified to a pH of 2.3–3.8 and diphenylcarbazone, which forms a colored complex with excess Hg\(^{2+}\), serves as the indicator. A pH indicator—xylene cyanol FF—is added to ensure that the pH is within the desired range. The initial solution is a greenish blue, and the titration is carried out to a purple end point.

**Quantitative Calculations**

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

**Example 9.7**

The concentration of a solution of EDTA was determined by standardizing against a solution of Ca\(^{2+}\) prepared using a primary standard of CaCO\(_3\). A 0.4071-g sample of CaCO\(_3\) was transferred to a 500-mL volumetric flask, dissolved using a minimum of 6 M HCl, and diluted to volume. After transferring a 50.00-mL portion of this solution to a 250-mL Erlenmeyer flask, the pH was adjusted by adding 5 mL of a pH 10 NH\(_3\)–NH\(_4\)Cl buffer containing a small amount of Mg\(^{2+}\)–EDTA. After adding calmagite as an indicator, the solution was titrated with the EDTA, requiring 42.63 mL to reach the end point. Report the molar concentration of EDTA in the titrant.

**Solution**

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

\[
\frac{0.4071 \text{ g CaCO}_3}{0.5000 \text{ L}} \times \frac{1 \text{ mol Ca}^{2+}}{100.09 \text{ g CaCO}_3} = 8.135 \times 10^{-3} \text{ M Ca}^{2+}
\]
The moles of Ca\(^{2+}\) in the titrand is
\[
8.135 \times 10^{-3} \text{ M Ca}^{2+} \times 0.05000 \text{ L Ca}^{2+} = 4.068 \times 10^{-4} \text{ mol Ca}^{2+}
\]
which means that \(4.068 \times 10^{-4}\) moles of EDTA are used in the titration. The molarity of EDTA in the titrant is
\[
\frac{4.068 \times 10^{-4} \text{ mol EDTA}}{0.04263 \text{ L EDTA}} = 9.543 \times 10^{-3} \text{ M EDTA}
\]

**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 CaCO\(_3\)/L.

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

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

**Example 9.8**

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

**Solution**

The reaction between Cl\(^–\) and Hg\(^{2+}\) produces a metal–ligand complex of HgCl\(_2\)(aq). Each mole of Hg\(^{2+}\) reacts with 2 moles of Cl\(^–\); thus
\[
\frac{0.0516 \text{ mol Hg(NO}_3)_2}{\text{L}} \times \frac{0.00618 \text{ L Hg(NO}_3)_2}{\text{L}} \times \frac{2 \text{ mol Cl}^–}{\text{mol Hg(NO}_3)_2} \times \frac{35.453 \text{ g Cl}^–}{\text{mol Cl}^–} = 0.0226 \text{ g Cl}^–
\]

are in the sample. The concentration of Cl\(^–\) in the sample is
\[
\frac{0.0226 \text{ g Cl}^–}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 226 \text{ mg/L}
\]

**Practice Exercise 9.15**

A 0.4482-g sample of impure NaCN is titrated with 0.1018 M AgNO\(_3\), 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 containing Ni, Fe, and Cr was analyzed by a complexation titration using EDTA as the titrant. A 0.7176-g sample of the alloy was dissolved in HNO₃ and diluted to 250 mL in a volumetric flask. A 50.00-mL aliquot of the sample, treated with pyrophosphate to mask the Fe and Cr, required 26.14 mL of 0.05831 M EDTA to reach the murexide end point. A second 50.00-mL aliquot was treated with hexamethylenetetramine to mask the Cr. Titrating with 0.05831 M EDTA required 35.43 mL to reach the murexide end point. Finally, a third 50.00-mL aliquot was treated with 50.00 mL of 0.05831 M EDTA, and back titrated to the murexide end point with 6.21 mL of 0.06316 M Cu²⁺. Report the weight percents of Ni, Fe, and Cr in the alloy.

**Solution**

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

Titration 1: moles Ni = moles EDTA

Titration 2: moles Ni + moles Fe = moles EDTA

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

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

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

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

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

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

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

\[
\frac{0.05831 \text{ mol EDTA}}{L} \times 0.05000 \text{ L EDTA} = 2.916 \times 10^{-3} \text{ mol EDTA}
\]
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 reacting with Cu is

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

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.

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

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

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

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

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

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

**Practice Exercise 9.16**

A indirect complexation titration with EDTA can be used to determine the concentration of sulfate, $\text{SO}_4^{2-}$, in a sample. A 0.1557-g sample is dissolved in water, any sulfate present is precipitated as $\text{BaSO}_4$ by adding $\text{Ba(NO}_3)_2$. After filtering and rinsing the precipitate, it is dissolved in 25.00 mL of 0.02011 M EDTA. The excess EDTA is then titrated 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.
Evaluation of Complexation Titrimetry

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

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

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

Redox Titrations

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest REDOX TITRATION took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet...
introduced a method for the quantitative analysis of chlorine water (a mixture of Cl₂, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO₄⁻, Cr₂O₇²⁻, and I₂ as oxidizing titrants, and of Fe²⁺ and S₂O₃²⁻ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO₄⁻ ion serves as its own indicator since its reduced form, Mn²⁺, 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 H₃O⁺ (as pH) or Mⁿ⁺ (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction’s potential instead of the concentration of one species.

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

\[
A_{\text{red}} + B_{\text{ox}} \rightleftharpoons B_{\text{red}} + A_{\text{ox}}
\]

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

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

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.

\[
E_{B_{\text{ox}}/B_{\text{red}}} = E_{A_{\text{ox}}/A_{\text{red}}}
\]

This is an important observation because we can use either half-reaction to monitor the titration’s progress.
Before the equivalence point the titration mixture consists of appreciable quantities of the titrand’s oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand’s half-reaction

\[ E_{\text{ox}/\text{red}} = \frac{RT}{nF} \ln \left( \frac{[A_{\text{red}}]}{[A_{\text{ox}}]} \right) \]

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

\[ E_{\text{ox}/\text{red}} = \frac{RT}{nF} \ln \left( \frac{[B_{\text{red}}]}{[B_{\text{ox}}]} \right) \]

**Calculating the Titration Curve**

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

\[
\text{Fe}^{2+}(aq) + \text{Ce}^{4+}(aq) \rightleftharpoons \text{Ce}^{3+}(aq) + \text{Fe}^{3+}(aq) \quad (9.15)
\]

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 Ce\(^{4+}\) needed to reach the titration’s equivalence point. From the reaction’s stoichiometry we know that

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

\[
M_{\text{Fe}} \times V_{\text{Fe}} = M_{\text{Ce}} \times V_{\text{Ce}}
\]

Solving for the volume of 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 Fe\(^{2+}\) and the concentration of Fe\(^{3+}\) are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe\(^{3+}/\text{Fe}^{2+}\) half-reaction.

\[
E = E_{\text{ox}/\text{red}}^{\circ} - \frac{RT}{nF} \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) = +0.767 \text{V} - 0.05916 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right)
\]

For example, the concentrations of Fe\(^{2+}\) and Fe\(^{3+}\) after adding 10.0 mL of titrant are
Chapter 9 Titrimetric Methods

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

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

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

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

Substituting these concentrations into equation 9.16 gives a potential of

\[
E = +0.767 \text{ V} - 0.05916 \log \left( \frac{6.67 \times 10^{-2} \text{ M}}{1.67 \times 10^{-2} \text{ M}} \right) = +0.731 \text{ V}
\]

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

\[
E = E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{RT}{nF} \log \left( \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right) = +1.70 \text{ V} - 0.05916 \log \left( \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right)
\]

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

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

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

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

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

Substituting these concentrations into equation 9.17 gives a potential of

\[
E = +1.70 \text{ V} - 0.05916 \log \left( \frac{4.55 \times 10^{-2} \text{ M}}{9.09 \times 10^{-3} \text{ M}} \right) = +1.66 \text{ V}
\]

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

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.

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

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

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

### Practice Exercise 9.17

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

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

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

---

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

<table>
<thead>
<tr>
<th>Volume of Ce$^{4+}$ (mL)</th>
<th>E (V)</th>
<th>Volume Ce$^{4+}$ (mL)</th>
<th>E (V)</th>
</tr>
</thead>
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<td>0.731</td>
<td>60.0</td>
<td>1.66</td>
</tr>
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<td>20.0</td>
<td>0.757</td>
<td>70.0</td>
<td>1.68</td>
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<td>1.69</td>
</tr>
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<td>100.0</td>
<td>1.70</td>
</tr>
</tbody>
</table>

---

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

To evaluate the relationship between a titration’s equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let’s use the titration of 50.0 mL of 0.100 M Fe\(^{2+}\) with 0.100 M Ce\(^{4+}\) in a matrix of 1 M HClO\(_4\).

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

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

\[
E = E^o_{Fe^{3+}/Fe^{2+}} - 0.05916
\]

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

\[
E = E^o_{Fe^{3+}/Fe^{2+}} + 0.05916
\]

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

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

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

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

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

We 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 Mg\(^{2+}\) with EDTA.
Figure 9.37 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe$^{2+}$ with 0.100 M Ce$^{4+}$ in 1 M HClO$_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.
Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point’s volume (Figure 9.37d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.37e). A comparison of our sketch to the exact titration curve (Figure 9.37f) shows that they are in close agreement.

**Practice Exercise 9.18**

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

\[
\text{Sn}^{2+}(aq) + \text{Ti}^{3+}(aq) \rightarrow \text{Sn}^{4+}(aq) + \text{Ti}^+(aq)
\]

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

Click here to review your answer to this exercise.

### 9D.2 Selecting and Evaluating the End point

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

**Where is the Equivalence Point?**

For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at Figure 9.7 and Figure 9.28, you will see that the inflection point is in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves. We call this a **Symmetric Equivalence Point**.

If the stoichiometry of a redox titration is symmetric—one mole of titrant reacts with each mole of titrand—then the equivalence point is symmetric. If the titration reaction’s stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve’s sharp rise. In this case we have an **Asymmetric Equivalence Point**.

**Example 9.10**

Derive a general equation for the equivalence point’s potential when titrating Fe\(^{2+}\) with MnO\(_4^-\).

\[
5 \text{Fe}^{2+}(aq) + \text{MnO}_4^-(aq) + 8\text{H}^+(aq) \rightarrow 5 \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}
\]

We often use H\(^+\) instead of H\(_3\)O\(^+\) when writing a redox reaction.
**Solution**

The half-reactions for Fe$^{2+}$ and MnO$_4^-$ are

\[
\begin{align*}
\text{Fe}^{2+} (aq) & \rightarrow \text{Fe}^{3+} (aq) + e^- \\
\text{MnO}_4^- (aq) + 8\text{H}^+ (aq) + 5e^- & \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O}(l)
\end{align*}
\]

for which the Nernst equations are

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

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

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

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

At the equivalence point we know that

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

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

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

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

\[
E_{eq} = \frac{E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + 5E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}}{6} + \frac{0.05916 \times 8}{6} \log [\text{H}^+] \\
E_{eq} = \frac{E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + 5E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}}{6} - 0.07888 \text{pH}
\]

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

*Instead of standard state potentials, you can use formal potentials.*
Chapter 9 Titrimetric Methods

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

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

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.

**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

\[
\text{Ce}^{4+}(aq) + \text{U}^{4+}(aq) \rightarrow \text{UO}_2^{2+}(aq) + \text{Ce}^{3+}(aq)
\]

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

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

**Finding the End Point with an Indicator**

Three types of indicators are used to signal a redox titration's end point. The oxidized and reduced forms of some titrants, such as \( \text{MnO}_4^- \), 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 blue complex with \( I^-_3 \). We can use this distinct color to signal the presence of excess \( I^-_3 \) as a titrant—a change in color from colorless to blue—or the
completion of a reaction consuming $I_3^-$ as the titrand—a change in color from blue to colorless. Another example of a specific indicator is thiocyanate, $SCN^-$, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with $Fe^{3+}$.

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

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

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

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

$$E = E_{In_{ox}/In_{red}}^o - \frac{0.05916}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

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

$$E = E_{In_{ox}/In_{red}}^o \pm \frac{0.05916}{n}$$

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

$$E = E_{In_{ox}/In_{red}}^o \pm \frac{0.05916}{n}$$
Table 9.16  Selected Examples of Redox Indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Color of $\text{In}_{\text{ox}}$</th>
<th>Color of $\text{In}_{\text{red}}$</th>
<th>$E^\circ_{\text{In}<em>{\text{ox}}/\text{In}</em>{\text{red}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>indigo tetrasulfate</td>
<td>blue</td>
<td>colorless</td>
<td>0.36</td>
</tr>
<tr>
<td>methylene blue</td>
<td>blue</td>
<td>colorless</td>
<td>0.53</td>
</tr>
<tr>
<td>diphenylamine</td>
<td>violet</td>
<td>colorless</td>
<td>0.75</td>
</tr>
<tr>
<td>diphenylamine sulfonic acid</td>
<td>red-violet</td>
<td>colorless</td>
<td>0.85</td>
</tr>
<tr>
<td>tris(2,2´-bipyridine)iron</td>
<td>pale blue</td>
<td>red</td>
<td>1.120</td>
</tr>
<tr>
<td>ferroin</td>
<td>pale blue</td>
<td>red</td>
<td>1.147</td>
</tr>
<tr>
<td>tris(5-nitro-1,10-phenanthroline)iron</td>
<td>pale blue</td>
<td>red-violet</td>
<td>1.25</td>
</tr>
</tbody>
</table>

A partial list of redox indicators is shown in Table 9.16. Examples of appropriate and inappropriate indicators 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 adding the titrant to the titrand. The end point is found by visually examining the titration curve. The simplest experimental design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand’s or titrant’s redox half-reaction, and a reference electrode that has a fixed potential. A further discussion of potentiometry is found in Chapter 11. Other methods for locating the titration’s end point include thermometric titrations and spectrophotometric titrations.

![Figure 9.40](image-url) Titration curve for the 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.
Representative Method 9.3

**Determination of Total Chlorine Residual**

**Description of the Method**

The chlorination of public water supplies produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states, including the free residual chlorine, consisting of Cl₂, HOCl and OCl⁻, and the combined chlorine residual, consisting of NH₂Cl, NHOCl, and NCl₃. The total chlorine residual is determined by using the oxidizing power of chlorine to convert I⁻ to I₃⁻. The amount of I₃⁻ formed is then determined by titrating with Na₂S₂O₃ using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if Cl₂ is the only source of chlorine, and is reported as mg Cl/L.

**Procedure**

Select a volume of sample requiring less than 20 mL of Na₂S₂O₃ to reach the end point. Using glacial acetic acid, acidify the sample to a pH of 3–4, and add about 1 gram of KI. Titrate with Na₂S₂O₃ until the yellow color of I₃⁻ begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch–I₃⁻ complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

**Questions**

1. Is this an example of a direct or an indirect analysis?
   
   This is an indirect analysis because the chlorine-containing species do not react with the titrant. Instead, the total chlorine residual oxidizes I⁻ to I₃⁻, and the amount of I₃⁻ is determined by titrating with Na₂S₂O₃.

2. Why does the procedure rely on an indirect analysis instead of directly titrating the chlorine-containing species using KI as a titrant?
   
   Because the total chlorine residual consists of six different species, a titration with I⁻ does not have a single, well-defined equivalence.
point. By converting the chlorine residual to an equivalent amount of $I_3^-$, the indirect titration with $Na_2S_2O_3$ has a single, useful equivalence point.

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

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

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

**9D.3 Quantitative Applications**

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

**Adjusting the Titrant’s Oxidation State**

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

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

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

Two common reduction columns are used. In the **JONES REDUCTOR** the column is filled with amalgamated zinc, Zn(Hg), prepared by briefly placing Zn granules in a solution of HgCl₂. Oxidation of zinc

\[
\text{Zn(Hg)}(s) \rightarrow \text{Zn}^{2+}(aq) + \text{Hg}(l) + 2e^- 
\]

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

\[
\text{Ag}(s) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s) + e^- 
\]

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

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

\[
\text{S}_2\text{O}_8^{2-}(aq) + 2e^- \rightarrow 2\text{SO}_4^{2-}(aq) 
\]

<table>
<thead>
<tr>
<th>Oxidized Titrand</th>
<th>Walden Reductor</th>
<th>Jones Reductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(^{3+})</td>
<td>—</td>
<td>Cr(^{3+}(aq)) + e(^-) \rightarrow Cr(^{2+}(aq))</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>Cu(^{2+}(aq)) + e(^-) \rightarrow Cu(^{+}(aq))</td>
<td>Cu(^{2+}(aq)) + 2e(^-) \rightarrow Cr(s)</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>Fe(^{3+}(aq)) + e(^-) \rightarrow Fe(^{2+}(aq))</td>
<td>Fe(^{3+}(aq)) + e(^-) \rightarrow Fe(^{2+}(aq))</td>
</tr>
<tr>
<td>TiO(^{2+})</td>
<td>—</td>
<td>TiO(^{2+}(aq)) + 2H(^+)(aq) + e(^-) \rightarrow Ti(^{3+}(aq)) + H(_2)O(l)</td>
</tr>
<tr>
<td>MoO(_2^{2+})</td>
<td>MoO(_2^{2+}(aq)) + e(^-) \rightarrow MoO(_2^{+}(aq))</td>
<td>MoO(_2^{2+}(aq)) + 4H(^+)(aq) + 3e(^-) \rightarrow Mo(^{3+}(aq)) + 2H(_2)O(l)</td>
</tr>
<tr>
<td>VO(_2^{+})</td>
<td>VO(_2^{+}(aq)) + 2H(^+)(aq) + e(^-) \rightarrow VO(_2^{+}(aq)) + H(_2)O(l)</td>
<td>VO(_2^{+}(aq)) + 4H(^+)(aq) + 3e(^-) \rightarrow V(^{2+}(aq)) + 2H(_2)O(l)</td>
</tr>
</tbody>
</table>
capable of oxidizing Mn\(^{2+}\) to MnO\(_4^-\), Cr\(^{3+}\) to Cr\(_2\)O\(_7^{2-}\), and Ce\(^{3+}\) to Ce\(^{4+}\). Excess peroxydisulfate is easily destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in acidic solution

\[ \text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightarrow 2\text{H}_2\text{O}(l) \]

provides another method for oxidizing a titrand. Excess H\(_2\)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 MnO\(_4^-\), Ce\(^{4+}\), Cr\(_2\)O\(_7^{2-}\), and I\(_3^-\). Which titrant is used often depends on how easy it is to oxidize the titrand. A titrand that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point.

The two strongest oxidizing titrants are MnO\(_4^-\) and Ce\(^{4+}\), for which the reduction half-reactions are

\[ \text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightleftharpoons \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l) \]

\[ \text{Ce}^{4+}(aq) + e^- \rightleftharpoons \text{Ce}^{3+}(aq) \]

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

Solutions of MnO\(_4^-\) are prepared from KMnO\(_4\), which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water.

\[ 4\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) \rightleftharpoons 4\text{MnO}_2(s) + 3\text{O}_2(g) + 4\text{OH}^-(aq) \]

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

The standardization reactions are

\[ \text{Ce}^{4+}(aq) + \text{Fe}^{2+}(aq) \rightarrow \]

\[ \text{Ce}^{3+}(aq) + \text{Fe}^{3+}(aq) \]

\[ 2\text{Ce}^{4+}(aq) + \text{H}_2\text{C}_2\text{O}_4(aq) \rightarrow 2\text{Ce}^{3+}(aq) + 2\text{CO}_2(g) + 2\text{H}^+(aq) \]
Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO$_4^-$ or Ce$^{4+}$, which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

$$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$$

Although a solution of Cr$_2$O$_7^{2-}$ is orange and a solution of Cr$^{3+}$ is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with Cr$_2$O$_7^{2-}$.

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

$$\text{I}_2(aq) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(aq)$$

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

$$\text{I}_2(aq) + \text{I}^-(aq) \rightleftharpoons \text{I}_3^-(aq)$$

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

$$\text{I}_3^-(aq) + 2\text{e}^- \rightleftharpoons 3\text{I}^-(aq)$$

Solutions of I$_3^-$ are normally standardized against Na$_2$S$_2$O$_3$ using starch as a specific indicator for I$_3^-$. An oxidizing titrant such as MnO$_4^-$, Ce$^{4+}$, Cr$_2$O$_7^{2-}$, and I$_3^-$, is used when the titrand is in a reduced state. If the titrand is in an oxidized state, we can first reduce it with an auxiliary reducing agent and then complete the titration using an oxidizing titrant. Alternatively, we can titrate it using a reducing titrant. Iodide is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I$^-$ is susceptible to the air-oxidation of I$^-$ to I$_3^-$. Instead, adding an excess of KI reduces the titrand, releasing a stoichiometric amount of I$_3^-$. The amount of I$_3^-$ produced is then determined by a back titration using thiosulfate, S$_2$O$_3^{2-}$, as a reducing titrant.

The standardization reaction is

$$\text{I}_3^-(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightarrow 3\text{I}^-(aq) + 2\text{S}_4\text{O}_6^{2-}(aq)$$

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of I$_3^-$. 

$$3\text{I}^-(aq) \rightleftharpoons \text{I}_3^-(aq) + 2\text{e}^-$$
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 must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard $\text{KIO}_3$ in an acidic solution containing 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 bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as $\text{HgI}_2$ to the solution.

Another useful reducing titrant is ferrous ammonium sulfate, $\text{Fe(NH}_4\text{)}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 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. The titrant can be used to directly titrate the titrand by oxidizing $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$. Alternatively, ferrous ammonium sulfate is added to the titrand in excess and the quantity 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 by 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 contributing 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 contributing 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

$$2\text{S}_2\text{O}_3^{2-}(aq) \xrightleftharpoons{} 2\text{S}_4\text{O}_6^{2-}(aq) + 2\text{e}^-$$
oxidizes a stoichiometric portion of DPD to its red-colored form. The oxidized DPD is then back titrated to its colorless form using ferrous ammonium sulfate as the titrant. The volume of titrant is proportional to the free residual chlorine.

Having determined the free chlorine residual in the water sample, a small amount of KI is added, catalyzing the reduction monochloramine, NH₂Cl, and oxidizing a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of NH₂Cl in the sample. The amount of dichloramine and trichloramine are determined in a similar fashion.

The methods described above for determining the total, free, or combined chlorine residual also are used to establish a water supply’s chlorine demand. Chlorine demand is defined as the quantity of chlorine needed to completely react with any substance that can be oxidized by chlorine, while also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, such as lakes and rivers, the level of dissolved O₂ 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 O₂ is essential for the aerobic oxidation of waste materials. If the concentration of dissolved O₂ falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases, such as CH₄ and H₂S.

One standard method for determining the dissolved O₂ content of natural waters and wastewaters is the Winkler method. A sample of water is collected without exposing it to the atmosphere, which might change the concentration of dissolved O₂. The sample is first treated with a solution of MnSO₄, and then with a solution of NaOH and KI. Under these alkaline conditions the dissolved oxygen oxidizes Mn²⁺ to MnO₂.

\[
2\text{Mn}^{2+}(aq) + 4\text{OH}^{-}(aq) + \text{O}_2(g) \rightarrow 2\text{MnO}_2(s) + 2\text{H}_2\text{O}(l)
\]

After the reaction is complete, the solution is acidified with H₂SO₄. Under the now acidic conditions I⁻ is oxidized to I₃⁻ by MnO₂.

\[
\text{MnO}_2(s) + 3\text{I}^-(aq) + 4\text{H}^+(aq) \rightarrow \text{Mn}^{2+} + \text{I}_3^-(aq) + 2\text{H}_2\text{O}(l)
\]

The amount of I₃⁻ formed is determined by titrating with S₂O₃²⁻ 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, NO₂⁻ interferes because it can reduce I₃⁻ to I⁻ un-
der acidic conditions. This interference is eliminated by adding sodium azide, NaN$_3$, reducing NO$_2^-$ to N$_2$. Other reducing agents, such as Fe$^{2+}$, are eliminated by pretreating the sample with KMnO$_4$, and destroying the excess permanganate with K$_2$C$_2$O$_4$.

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 containing water, I$_2$ is reduced to I$^-^-$ and SO$_2$ is oxidized to SO$_3$.

$$\text{py} \cdot \text{I}_2 + \text{py} \cdot \text{SO}_2 + \text{py} + \text{H}_2\text{O} \rightarrow 2\text{py} \cdot \text{HI} + \text{py} \cdot \text{SO}_3$$

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 provides a measure of the quantity of oxygen necessary to completely oxidize all the organic matter in a sample to CO$_2$ and H$_2$O. Because no attempt is made to correct for organic matter that can not be decomposed biologically, or for slow decomposition kinetics, the COD always overestimates a sample's true oxygen demand. The determination of COD is particularly important in managing industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or the environment.

A sample's COD is determined by refluxing it in the presence of excess K$_2$Cr$_2$O$_7$, which serves as the oxidizing agent. The solution is acidified with H$_2$SO$_4$ using Ag$_2$SO$_4$ to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate, HgSO$_4$, is added to complex any chloride that is present, preventing the precipitation of the Ag$^+$ catalyst as AgCl. Under these conditions, the efficiency for oxidizing organic matter is 95–100%. After refluxing for two hours, the solution is cooled to room temperature and the excess Cr$_2$O$_7^{2-}$ is determined by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to completely remove all traces of organic matter from the reagents, a blank titration must be performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of S$_2$O$_3^{2-}$
with $I_3^-$ produces the tetrathionate ion, $S_4O_6^{2-}$. The tetrathionate ion is actually a dimer consisting of two thiosulfate ions connected through a disulfide ($-S-S-$) linkage. In the same fashion, $I_3^-$ can be used to titrate mercaptans of the general formula RSH, forming the dimer RSSR as a product. The amino acid cysteine also can be titrated with $I_3^-$. The product of this titration is cystine, which is a dimer of cysteine. Triiodide also can be used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone

$$
\text{CHO} \quad \text{OH} \quad \text{OH} \\
\text{HO} \quad \text{H} \quad \text{H}
\rightarrow
\text{CO}_2^- \\
\text{OH} \quad \text{H} \quad \text{H}
\quad \text{OH}
\quad \text{CH}_2\text{OH}
$$

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

$$
\text{CHO} \quad \text{OH} \quad \text{OH} \\
\text{HO} \quad \text{H} \quad \text{H}
\rightarrow
\text{CO}_2^- \\
\text{OH} \quad \text{H} \quad \text{H}
\quad \text{OH}
\quad \text{CH}_2\text{OH}
$$

An organic compound containing 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.

$$\text{IO}_4^-(aq) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{IO}_3^-(aq) + 2\text{OH}^- (aq)$$

A two-electron oxidation cleaves the C–C bond between the two functional groups, with hydroxyl groups being oxidized to aldehydes or ketones, carbonyl functional groups being oxidized to carboxylic acids, and amines being oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of $\text{IO}_4^-$ to the solution containing the analyte, and allowing the oxidation to take place for approximately one hour at room temperature. When the oxidation is complete, an excess of KI is added, which converts any unreacted $\text{IO}_4^-$ to $\text{IO}_3^-$ and $I_3^-$. 

$$\text{IO}_4^-(aq) + 3\text{I}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq) + I_3^-(aq) + 2\text{OH}^- (aq)$$

The $I_3^-$ is then determined by titrating with $S_2\text{O}_3^{2-}$ using starch as an indicator.
Chapter 9 Titrimetric Methods

**Quantitative Calculations**

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry by remembering that the electrons in a redox reaction must be conserved.

**Example 9.11**

The amount of Fe in a 0.4891-g sample of an ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore’s iron content as %w/w $Fe_2O_3$.

**Solution**

Because we have not been provided with the titration reaction, let’s use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from $Fe^{2+}$ to $Fe^{3+}$, and the titrant is reduced from $Cr_2O_7^{2–}$ to $Cr^{3+}$. Oxidizing $Fe^{2+}$ to $Fe^{3+}$ requires only a single electron. Reducing $Cr_2O_7^{2–}$, in which each chromium is in the +6 oxidation state, to $Cr^{3+}$ requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of $K_2Cr_2O_7$ reacts with six moles of $Fe^{2+}$.

The moles of $K_2Cr_2O_7$ used in reaching the end point is

$$\left(0.02153\text{ M }K_2Cr_2O_7\right) \times \left(0.03692\text{ L }K_2Cr_2O_7\right) = 7.949 \times 10^{-4}\text{ mol }K_2Cr_2O_7$$

which means that the sample contains

$$7.949 \times 10^{-4}\text{ mol }K_2Cr_2O_7 \times \frac{6\text{ mol }Fe^{2+}}{\text{ mol }K_2Cr_2O_7} = 4.769 \times 10^{-3}\text{ mol }Fe^{2+}$$

Thus, the %w/w $Fe_2O_3$ in the sample of ore is

$$4.769 \times 10^{-3}\text{ mol }Fe^{2+} \times \frac{1\text{ mol }Fe_2O_3}{2\text{ mol }Fe^{2+}} \times \frac{159.69\text{ g }Fe_2O_3}{\text{ mol }Fe_2O_3} = 0.3808\text{ g }Fe_2O_3$$

$$\frac{0.3808\text{ g }Fe_2O_3 \times 100}{0.4891\text{ g sample}} = 77.86\%\text{ w/w }Fe_2O_3$$

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

$$K_2Cr_2O_7(\text{aq}) + 6Fe^{2+}(\text{aq}) + 14H^+(\text{aq}) \rightarrow 2Cr^{3+}(\text{aq}) + 2K^+(\text{aq}) + 6Fe^{3+}(\text{aq}) + 7H_2O(l)$$

does provide useful information. For example, the presence of $H^+$ reminds us that the reaction’s feasibility is pH-dependent.
As shown in the following two examples, we can easily extend this approach to an analysis that requires an indirect analysis or a back titration.

**Example 9.12**

A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl$^-$ to Cl$^-$, and producing I$_3^-$.

The liberated I$_3^-$ was determined by titrating with 0.09892 M Na$_2$S$_2$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, Na$_2$S$_2$O$_3$, we need to consider both the reaction between OCl$^-$ and I$^-$, and the titration of I$_3^-$ with Na$_2$S$_2$O$_3$.

First, in reducing OCl$^-$ to Cl$^-$, the oxidation state of chlorine changes from +1 to –1, requiring two electrons. The oxidation of three I$^-$ to form I$_3^-$ releases two electrons as the oxidation state of each iodine changes from –1 in I$^-$ to –⅓ in I$_3^-$. A conservation of electrons, therefore, requires that each mole of OCl$^-$ produces one mole of I$_3^-$.  

Second, in the titration reaction, I$_3^-$ is reduced to I$^-$ and S$_2$O$_3^{2-}$ is oxidized to S$_4$O$_6^{2-}$. Reducing I$_3^-$ to 3I$^-$ requires two elections as each iodine changes from an oxidation state of –⅓ to –1. In oxidizing S$_2$O$_3^{2-}$ to S$_4$O$_6^{2-}$, each sulfur changes its oxidation state from +2 to +2.5, releasing one electron for each S$_2$O$_3^{2-}$. A conservation of electrons, therefore, requires that each mole of I$_3^-$ reacts with two moles of S$_2$O$_3^{2-}$.

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

The moles of Na$_2$S$_2$O$_3$ used in reaching the titration’s end point is

\[
(0.09892 \text{ M } \text{Na}_2\text{S}_2\text{O}_3) \times (0.00896 \text{ L } \text{Na}_2\text{S}_2\text{O}_3)
\]

\[
= 8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3
\]

which means the sample contains

The balanced reactions for this analysis are:

\[
\text{OCl}^- (aq) + 3\text{I}^- (aq) + 2\text{H}^+ (aq) \rightarrow \\
\text{I}_3^- (aq) + \text{Cl}^- (aq) + \text{H}_2\text{O} (l)
\]

\[
\text{I}_3^- (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) \rightarrow \text{S}_4\text{O}_6^{2-} (aq) + 3\text{I}^- (aq)
\]
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\[ 8.86 \times 10^{-4} \text{ mol Na}_2S_2O_3 \times \frac{1 \text{ mol NaOCl}}{2 \text{ mol Na}_2S_2O_3} \times \frac{74.44 \text{ g NaOCl}}{\text{ mol NaOCl}} = 0.03299 \text{ g NaOCl} \]

Thus, the %w/v NaOCl in the diluted sample is

\[ \frac{0.03299 \text{ g NaOCl}}{25.00 \text{ mL}} \times 100 = 1.32\% \text{ w/v NaOCl} \]

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

**Example 9.13**

The amount of ascorbic acid, \( C_6H_8O_6 \), in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, \( C_6H_6O_6 \), with a known amount of I\(_3^-\), and back titrating the excess I\(_3^-\) with Na\(_2S_2O_3\). A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of 0.01023 M I\(_3^-\). After the oxidation was complete, 13.82 mL of 0.07203 M Na\(_2S_2O_3\) was needed to reach the starch indicator end point. Report the concentration ascorbic acid in mg/100 mL.

**Solution**

For a back titration we need to determine the stoichiometry between I\(_3^-\) and the analyte, \( C_6H_8O_6 \), and between I\(_3^-\) and the titrant, Na\(_2S_2O_3\). The later is easy because we know from Example 9.12 that each mole of I\(_3^-\) reacts with two moles of Na\(_2S_2O_3\).

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from +\( \frac{2}{3} \) in \( C_6H_8O_6 \) to +1 in \( C_6H_6O_6 \). 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 I\(_3^-\) requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of I\(_3^-\).

The total moles of I\(_3^-\) reacting with \( C_6H_8O_6 \) and with Na\(_2S_2O_3\) is

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

The back titration consumes

\[ 0.01382 \text{ L Na}_2S_2O_3 \times \frac{0.07203 \text{ mol Na}_2S_2O_3}{\text{ L Na}_2S_2O_3} \times \frac{1 \text{ mol I}_3^-}{2 \text{ mol Na}_2S_2O_3} = 4.977 \times 10^{-4} \text{ mol I}_3^- \]
Subtracting the moles of $I_3^-$ reacting with $Na_2S_2O_3$ from the total moles of $I_3^-$ gives the moles reacting with ascorbic acid.

$$5.115 \times 10^{-4} \text{ mol } I_3^- - 4.977 \times 10^{-4} \text{ mol } I_3^- = 1.38 \times 10^{-5} \text{ mol } I_3^-$$

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

$$1.38 \times 10^{-5} \text{ mol } I_3^- \times \frac{1 \text{ mol } C_6H_8O_6}{\text{mol } I_3^-} \times \frac{176.13 \text{ g } C_6H_8O_6}{\text{mol } C_6H_8O_6} = 2.43 \times 10^{-3} \text{ g } C_6H_8O_6$$

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

**Practice Exercise 9.21**

A quantitative analysis for ethanol, $C_2H_6O$, can be accomplished by a redox back titration. Ethanol is oxidized to acetic acid, $C_2H_4O_2$, using excess dichromate, $Cr_2O_7^{2-}$, which is reduced to $Cr^{3+}$. The excess dichromate is titrated with $Fe^{2+}$, giving $Cr^{3+}$ and $Fe^{3+}$ as products. In a typical analysis, a 5.00-mL sample of a brandy is diluted to 500 mL in a volumetric flask. A 10.00-mL sample is taken and the ethanol is removed by distillation and collected in 50.00 mL of an acidified solution of 0.0200 M $K_2Cr_2O_7$. A back titration of the unreacted $Cr_2O_7^{2-}$ requires 21.48 mL of 0.1014 M $Fe^{2+}$. Calculate the %w/v ethanol in the brandy.

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

### 9D.4 Evaluation of Redox Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a redox titration are similar to those described earlier in this chapter for acid–base or a complexation titration. As with acid–base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials. Figure 9.42 shows an example of the titration curve for a mixture of $Fe^{2+}$ and $Sn^{2+}$ using $Ce^{4+}$ as the titrant. A titration of a mixture of analytes is possible if their standard state potentials or formal potentials differ by at least 200 mV.

### 9E Precipitation Titrations

Thus far we have examined titrimetric methods based on acid–base, complexation, and redox reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can serve as the basis for a titration. We call this type of titration a **precipitation titration**.

One of the earliest precipitation titrations—developed at the end of the eighteenth century—was the analysis of $K_2CO_3$ and $K_2SO_4$ in potash.
Calcium nitrate, Ca(NO₃)₂, was used as the titrant, forming a precipitate of CaCO₃ and CaSO₄. The titration's end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag⁺ and halide ions.

### 9E.1 Titration Curves

A precipitation titration curve follows the change in either the titrand’s or the titrant’s concentration as a function of the titrant’s volume. As we have done with other titrations, we first show how to calculate the titration curve and then demonstrate how we can quickly sketch a reasonable approximation of the titration curve.

#### Calculating the Titration Curve

Let’s calculate the titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO₃. The reaction in this case is

\[
\text{Ag}^+ (aq) + \text{Cl}^- (aq) \rightleftharpoons \text{AgCl}(s)
\]

Because the reaction’s equilibrium constant is so large

\[
K = (K_w)^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9
\]

we may assume that Ag⁺ and Cl⁻ react completely.

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

\[
\text{moles Ag}^+ = \text{moles Cl}^-
\]

\[
M_{\text{Ag}} \times V_{\text{Ag}} = M_{\text{Cl}} \times V_{\text{Cl}}
\]

Solving for the volume of 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 Ag⁺ to reach the equivalence point.

Before the equivalence point the titrand, Cl⁻, is in excess. The concentration of unreacted Cl⁻ after adding 10.0 mL of Ag⁺, for example, is

\[
[\text{Cl}^-] = \frac{\text{initial moles Cl}^- - \text{moles Ag}^+ \text{ added}}{\text{total volume}} = \frac{M_{\text{Cl}}V_{\text{Cl}} - M_{\text{Ag}}V_{\text{Ag}}}{V_{\text{Cl}} + V_{\text{Ag}}}
\]

\[
= \frac{(0.0500 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 2.50 \times 10^{-2} \text{ M}
\]
which corresponds to a pCl of 1.60.

At the titration’s equivalence point, we know that the concentrations of Ag\(^+\) and Cl\(^-\) are equal. To calculate the concentration of Cl\(^-\) we use the $K_{sp}$ expression for AgCl; thus

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

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

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

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

$$= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} = 1.18 \times 10^{-2} \text{ M}$$

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

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

### Table 9.18 Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO\(_3\)

<table>
<thead>
<tr>
<th>Volume of AgNO(_3) (mL)</th>
<th>pCl</th>
<th>Volume of AgNO(_3) (mL)</th>
<th>pCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.30</td>
<td>30.0</td>
<td>7.54</td>
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<td>5.00</td>
<td>1.44</td>
<td>35.0</td>
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<td>10.0</td>
<td>1.60</td>
<td>40.0</td>
<td>7.97</td>
</tr>
<tr>
<td>15.0</td>
<td>1.81</td>
<td>45.0</td>
<td>8.07</td>
</tr>
<tr>
<td>20.0</td>
<td>2.15</td>
<td>50.0</td>
<td>8.14</td>
</tr>
<tr>
<td>25.0</td>
<td>4.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 9.43](image-url)  
**Figure 9.43** Titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO\(_3\). The red points corresponds to the data in Table 9.18. The blue line shows the complete titration curve.
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 AgNO₃.

We begin by calculating the titration’s equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pCl on the y-axis and the titrant’s volume on the x-axis. To indicate the equivalence point’s volume, we draw a vertical line corresponding to 25.0 mL of AgNO₃. Figure 9.44a shows the result of this first step in our sketch.

Before the equivalence point, Cl⁻ is present in excess and pCl is determined by the concentration of unreacted Cl⁻. As we learned earlier, the calculations are straightforward. Figure 9.44b shows pCl after adding 10.0 mL and 20.0 mL of AgNO₃.

After the equivalence point, Ag⁺ is in excess and the concentration of Cl⁻ is determined by the solubility of AgCl. Again, the calculations are straightforward. Figure 4.43c shows pCl after adding 30.0 mL and 40.0 mL of AgNO₃.

Next, we draw a straight line through each pair of points, extending them through the vertical line representing the equivalence point’s volume (Figure 9.44d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.44e). A comparison of our sketch to the exact titration curve (Figure 9.44f) shows that they are in close agreement.

9E.2 Selecting and Evaluating the End point

At the beginning of this section we noted that the first precipitation titration used the cessation of precipitation to signal the end point. At best, this is a cumbersome method for detecting a titration’s end point. Before precipitation titrimetry became practical, better methods for identifying the end point were necessary.
Figure 9.44 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M AgNO₃: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details. A better fit is possible if the two points before the equivalence point are further apart—for example, 0 mL and 20 mL—and the two points after the equivalence point are further apart.
FINDING THE END POINT WITH AN INDICATOR

There are three general types of indicators for precipitation titrations, each of which changes color at or near the titration’s equivalence point. The first type of indicator is a species that forms a precipitate with the titrant. In the Mohr method for \( \text{Cl}^- \) using \( \text{Ag}^+ \) as a titrant, for example, a small amount of \( \text{K}_2\text{CrO}_4 \) is added to the titrand’s solution. The titration’s end point is the formation of a reddish-brown precipitate of \( \text{Ag}_2\text{CrO}_4 \).

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 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 \( \text{Fe(SCN)}^2+ \) complex. The titration must be carried out in an acidic solution to prevent the precipitation of \( \text{Fe}^{3+} \) as \( \text{Fe(OH)}_3 \).

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. A further discussion of potentiometry is found in Chapter 11.
9E.3 Quantitative Applications

Although precipitation titrimetry is rarely listed as a standard method of analysis, it may still be useful as a secondary analytical method for verifying other analytical methods. Most precipitation titrations use Ag\(^+\) as either the titrand or the titration. A titration in which Ag\(^+\) is the titrant is called an argentometric titration. Table 9.19 provides a list of several typical precipitation titrations.

### Table 9.19 Representative Examples of Precipitation Titrations

<table>
<thead>
<tr>
<th>Titrand</th>
<th>Titrant(^a)</th>
<th>End Point(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsO(_4^{3-})</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>AgNO(_3)</td>
<td>Mohr or Fajans</td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
<tr>
<td>C(_2)O(_4^{2-})</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
<tr>
<td>CrO(_4^{2-})</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
<tr>
<td>I(^-)</td>
<td>AgNO(_3)</td>
<td>Fajans</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
<tr>
<td>S(^2-)</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>AgNO(_3), KSCN</td>
<td>Volhard*</td>
</tr>
</tbody>
</table>

\(^a\) When two reagents are listed, the analysis is by a back titration. The first reagent is added in excess and the second reagent used to back titrate the excess.

\(^b\) For those Volhard methods identified with an asterisk (\*) the precipitated silver salt must be removed before carrying out the back titration.

### 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\(_2\)CrO\(_4\), each mole of CrO\(_4^{2-}\) reacts with two moles of Ag\(^+\).

#### Example 9.14

A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172-g sample is dissolved in 50 mL of water and titrated to the Ag\(_2\)CrO\(_4\) end point, requiring 36.85 mL of 0.1120 M AgNO\(_3\). A blank titration requires 0.71 mL of titrant to reach the same end point. Report the %w/w KCl in the sample.
**Solution**

To find the moles of titrant reacting with the sample, we first need to correct for the reagent blank; thus

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

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

Titration with AgNO₃ produces a precipitate of AgCl and AgBr. In forming the precipitates, each mole of KCl consumes one mole of AgNO₃ and each mole of NaBr consumes one mole of AgNO₃; thus

\[ \text{moles KCl} + \text{moles NaBr} = 4.048 \times 10^{-3} \]

We are interested in finding the mass of KCl, so let’s rewrite this equation in terms of mass. We know that

\[ \text{moles KCl} = \left( \frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}} \right) \]

\[ \text{moles NaBr} = \left( \frac{\text{g NaBr}}{102.89 \text{ g NaBr/mol NaBr}} \right) \]

which we substitute back into the previous equation

\[ \left( \frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}} \right) + \left( \frac{\text{g NaBr}}{102.89 \text{ g NaBr/mol NaBr}} \right) = 4.048 \times 10^{-3} \]

Because this equation has two unknowns—g KCl and g NaBr—we need another equation that includes both unknowns. A simple equation takes advantage of the fact that the sample contains only KCl and NaBr; thus,

\[ \text{g NaBr} = 0.3172 \text{ g} - \text{g KCl} \]

\[ \left( \frac{\text{g KCl}}{74.551 \text{ g KCl/mol KCl}} \right) + \left( \frac{0.3172 \text{ g} - \text{g KCl}}{102.89 \text{ g NaBr/mol NaBr}} \right) = 4.048 \times 10^{-3} \]

\[ 1.341 \times 10^{-2} (\text{g KCl}) + 3.083 \times 10^{-3} - 9.719 \times 10^{-3} (\text{g KCl}) = 4.048 \times 10^{-3} \]

\[ 3.69 \times 10^{-3} (\text{g KCl}) = 9.65 \times 10^{-4} \]

The sample contains 0.262 g of KCl and the %w/w KCl in the sample is

\[ \frac{0.262 \text{ g KCl}}{0.3172 \text{ g sample}} \times 100 = 82.6\% \text{ w/w KCl}\]

The analysis for I⁻ using the Volhard method requires a back titration. A typical calculation is shown in the following example.
Example 9.15

The %w/w I− in a 0.6712-g sample was determined by a Volhard titration. After adding 50.00 mL of 0.05619 M AgNO3 and allowing the precipitate to form, the remaining silver was back titrated with 0.05322 M KSCN, requiring 35.14 mL to reach the end point. Report the %w/w I− in the sample.

**Solution**

There are two precipitates in this analysis: AgNO3 and I− form a precipitate of AgI, and AgNO3 and KSCN form a precipitate of AgSCN. Each mole of I− consumes one mole of AgNO3, and each mole of KSCN consumes one mole of AgNO3; thus

\[
\text{moles AgNO}_3 = \text{moles I}^- + \text{moles KSCN}
\]

Solving for the moles of I− we find

\[
\text{moles I}^- = \text{moles AgNO}_3 - \text{moles KSCN}
\]

\[
\text{moles I}^- = M_{Ag} \times V_{Ag} - M_{KSCN} \times V_{KSCN}
\]

\[
\text{moles I}^- = (0.05619 \text{ M AgNO}_3) \times (0.05000 \text{ L AgNO}_3) - (0.05322 \text{ M KSCN}) \times (0.03514 \text{ L KSCN})
\]

that there are \(9.393 \times 10^{-4}\) moles of I− in the sample. The %w/w I− in the sample is

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

Practice Exercise 9.23

A 1.963-g sample of an alloy is dissolved in HNO3 and diluted to volume in a 100-mL volumetric flask. Titrating a 25.00-mL portion with 0.1078 M KSCN requires 27.19 mL to reach the end point. Calculate the %w/w Ag in the alloy.

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

9E.4 Evaluation of Precipitation Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a precipitation titration is similar to those described elsewhere in this chapter for acid–base, complexation, and redox titrations. Precipitation titrations also can be extended to the analysis of mixtures provided that there is a sig-
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
- argentometric titration
- auxiliary oxidizing agent
- buret
- direct titration
- equivalence point
- Gran plot
- Kjeldahl analysis
- Mohr method
- redox indicator
- symmetric equivalence point
- titrant
- titrimetry
- acidity
- asymmetric equivalence point
- auxiliary complexing agent
- back titration
- complexation titration
- conditional formation constant
- displacement titration
- end point
- Fajans method
- indicator
- leveling
- potentiometric titration
- precipitation titration
- redox titration
- spectrophotometric titration
- thermometric titration
- titrand
- titration curve
- titration error
- Volhard method
- Walden reductor

**9G Chapter Summary**

In a titrimetric method of analysis, the volume of titrant reacting stoichiometrically with a titrand provides quantitative information about the amount of analyte in a sample. The volume of titrant corresponding to this stoichiometric reaction is called the equivalence point. Experimentally we determine the titration’s end point using an indicator that changes color near the equivalence point. Alternatively, we can locate the end point by...
continuously monitoring a property of the titrand’s solution—absorbance, potential, and temperature are typical examples—that changes as the titration progresses. In either case, an accurate result requires that the end point closely match the equivalence point. Knowing the shape of a titration curve is critical to evaluating the feasibility of a titrimetric method.

Many titrations are direct, in which the analyte participates in the titration as the titrand or the titrant. Other titration strategies may be used when a direct reaction between the analyte and titrant is not feasible. In a back titration a reagent is added in excess to a solution containing the analyte. When the reaction between the reagent and the analyte is complete, the amount of excess reagent is determined by a titration. In a displacement titration the analyte displaces a reagent, usually from a complex, and the amount of displaced reagent is determined by an appropriate titration.

Titrimetric methods have been developed using acid–base, complexation, redox, and precipitation reactions. Acid–base titrations use a strong acid or a strong base as a titrant. The most common titrant for a complexation titration is EDTA. Because of their stability against air oxidation, most redox titrations use an oxidizing agent as a titrant. Titrations with reducing agents also are possible. Precipitation titrations often involve Ag⁺ as either the analyte or titrant.

9H Problems

1. Calculate or sketch titration curves for the following acid–base titrations.
   a. 25.0 mL of 0.100 M NaOH with 0.0500 M HCl
   b. 50.0 mL of 0.0500 M HCOOH with 0.100 M NaOH
   c. 50.0 mL of 0.100 M NH₃ with 0.100 M HCl
   d. 50.0 mL of 0.0500 M ethylenediamine with 0.100 M HCl
   e. 50.0 mL of 0.0400 M citric acid with 0.120 M NaOH
   f. 50.0 mL of 0.0400 M H₃PO₄ with 0.120 M NaOH

2. Locate the equivalence point for each titration curve in problem 1. What is the stoichiometric relationship between the moles of acid and the moles of base at each of these equivalence points?

3. Suggest an appropriate visual indicator for each of the titrations in problem 1.

4. In sketching the titration curve for a weak acid we approximate the pH at 10% of the equivalence point volume as \(pK_a - 1\), and the pH at 90% of the equivalence point volume as \(pK_a + 1\). Show that these assumptions are reasonable.
5. Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a diprotic weak acid with a $pK_{a1}$ of 3.0 and a $pK_{a2}$ of 4.4. Suppose you have a sample of impure tartaric acid (purity $> 80\%$), and that you plan to determine its purity by titrating with a solution of 0.1 M NaOH using an indicator to signal the end point. Describe how you will carry out the analysis, paying particular attention to how much sample to use, the desired pH range for the indicator, and how you will calculate the %w/w tartaric acid.

6. The following data for the titration of a monoprotic weak acid with a strong base were collected using an automatic titrator. Prepare normal, first derivative, second derivative, and Gran plot titration curves for this data, and locate the equivalence point for each.

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<thead>
<tr>
<th>Volume of NaOH (ml)</th>
<th>pH</th>
<th>Volume of NaOH (mL)</th>
<th>pH</th>
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<tbody>
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</table>

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
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.

<table>
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<th>pH</th>
<th>mL of NaOH</th>
<th>pH</th>
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<td>9.374</td>
</tr>
<tr>
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<td>8.077</td>
<td>6.92</td>
<td>9.414</td>
</tr>
<tr>
<td>2.60</td>
<td>8.146</td>
<td>7.15</td>
<td>9.451</td>
</tr>
<tr>
<td>2.79</td>
<td>8.208</td>
<td>7.36</td>
<td>9.484</td>
</tr>
<tr>
<td>3.01</td>
<td>8.273</td>
<td>7.56</td>
<td>9.514</td>
</tr>
<tr>
<td>3.41</td>
<td>8.332</td>
<td>7.79</td>
<td>9.545</td>
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<tr>
<td>3.60</td>
<td>8.458</td>
<td>8.21</td>
<td>9.572</td>
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<td>3.80</td>
<td>8.521</td>
<td>8.44</td>
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<tr>
<td>3.99</td>
<td>8.584</td>
<td>8.64</td>
<td>9.645</td>
</tr>
<tr>
<td>4.18</td>
<td>8.650</td>
<td>8.84</td>
<td>9.666</td>
</tr>
<tr>
<td>4.40</td>
<td>8.720</td>
<td>9.07</td>
<td>9.688</td>
</tr>
<tr>
<td>4.57</td>
<td>8.784</td>
<td>9.27</td>
<td>9.706</td>
</tr>
</tbody>
</table>

8. Calculate or sketch the titration curve for a 50.0 mL solution of a 0.100 M monoprotic weak acid ($\text{pK}_a = 8$) with 0.1 M strong base in a nonaqueous solvent with $K_s = 10^{-20}$. You may assume that the change in solvent does not affect the weak acid’s $\text{pK}_a$. Compare your titration curve to the titration curve when water is the solvent.

9. The titration of a mixture of $p$-nitrophenol ($\text{pK}_a = 7.0$) and $m$-nitrophenol ($\text{pK}_a = 8.3$) can be 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. The quantitative analysis for aniline (\(C_6H_5NH_2, K_b = 3.94 \times 10^{-10}\)) can be carried out by an acid–base titration using glacial acetic acid as the solvent and \(\text{HClO}_4\) as the titrant. A known volume of sample containing 3–4 mmol of aniline is transferred to a 250-mL Erlenmeyer flask and diluted to approximately 75 mL with glacial acetic acid. Two drops of a methyl violet indicator are added, and the solution is titrated with previously standardized 0.1000 M \(\text{HClO}_4\) (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 water.

(b) One problem with using glacial acetic acid as solvent is its relatively high coefficient of thermal expansion of 0.11%/°C. For example, 100.00 mL of glacial acetic acid at 25°C occupies 100.22 mL at 27°C. What is the effect on the reported concentration of aniline if the standardization of \(\text{HClO}_4\) is conducted at a temperature that is lower than that for the analysis of the unknown?

(c) The procedure calls for a sample containing 3–4 mmol 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 falls between 6–10, but no determinate error if the end point’s pH is less than 6.

12. A water sample’s acidity is determined by titrating to fixed end point pHs of 3.7 and 8.3, with the former providing a measure of the concentration of strong acid, and the latter 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?

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
14. A Gran plot method has been described for the quantitative analysis of a mixture consisting of a strong acid and a monoprotic weak acid. A 50.00-mL mixture of HCl and CH$_3$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 NaOH. The progress of the titration is monitored by recording the pH after each addition of titrant. Using the two papers listed in the footnote as a reference, prepare a Gran plot for the following data, and determine the concentrations of HCl and CH$_3$COOH.

<table>
<thead>
<tr>
<th>Volume of NaOH (ml)</th>
<th>pH</th>
<th>Volume of NaOH (mL)</th>
<th>pH</th>
<th>Volume of NaOH (ml)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.83</td>
<td>24.00</td>
<td>4.45</td>
<td>47.00</td>
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<td>4.53</td>
<td>48.00</td>
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</tr>
<tr>
<td>3.00</td>
<td>1.89</td>
<td>26.00</td>
<td>4.61</td>
<td>49.00</td>
<td>12.20</td>
</tr>
<tr>
<td>4.00</td>
<td>1.92</td>
<td>27.00</td>
<td>4.69</td>
<td>50.00</td>
<td>12.23</td>
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<td>28.00</td>
<td>4.76</td>
<td>51.00</td>
<td>12.26</td>
</tr>
<tr>
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<td>1.99</td>
<td>29.00</td>
<td>4.84</td>
<td>52.00</td>
<td>12.28</td>
</tr>
<tr>
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<td>2.03</td>
<td>30.00</td>
<td>4.93</td>
<td>53.00</td>
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</tr>
<tr>
<td>8.00</td>
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<td>31.00</td>
<td>5.02</td>
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</tr>
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<td>55.00</td>
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<td>5.23</td>
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</tr>
<tr>
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<td>2.51</td>
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<td>5.37</td>
<td>57.00</td>
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<td>35.00</td>
<td>5.52</td>
<td>58.00</td>
<td>12.39</td>
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<tr>
<td>13.00</td>
<td>3.16</td>
<td>36.00</td>
<td>5.75</td>
<td>59.00</td>
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<tr>
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<td>37.00</td>
<td>6.14</td>
<td>60.00</td>
<td>12.42</td>
</tr>
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<td>15.00</td>
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<td>10.30</td>
<td>61.00</td>
<td>12.43</td>
</tr>
<tr>
<td>16.00</td>
<td>3.69</td>
<td>39.00</td>
<td>11.31</td>
<td>62.00</td>
<td>12.44</td>
</tr>
<tr>
<td>17.00</td>
<td>3.81</td>
<td>40.00</td>
<td>11.58</td>
<td>63.00</td>
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<td>18.00</td>
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</tr>
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<td>11.93</td>
<td>66.00</td>
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<td>12.00</td>
<td>67.00</td>
<td>12.50</td>
</tr>
<tr>
<td>22.00</td>
<td>4.30</td>
<td>45.00</td>
<td>12.05</td>
<td>68.00</td>
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</tr>
<tr>
<td>23.00</td>
<td>4.38</td>
<td>46.00</td>
<td>12.10</td>
<td>69.00</td>
<td>12.52</td>
</tr>
</tbody>
</table>

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

16. For each of the following, determine the sources of alkalinity (OH$^-$, HCO$_3^-$, CO$_3^{2-}$) and their respective concentrations in parts per mil-

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In each case a 25.00-mL sample is titrated with 0.1198 M HCl to the bromocresol green and the phenolphthalein end points.

<table>
<thead>
<tr>
<th>Volume of HCl (mL) to the phenolphthalein end point</th>
<th>Volume of HCl (mL) to the bromocresol green end point</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 21.36</td>
<td>21.38</td>
</tr>
<tr>
<td>b 5.67</td>
<td>21.13</td>
</tr>
<tr>
<td>c 0.00</td>
<td>14.28</td>
</tr>
<tr>
<td>d 17.12</td>
<td>34.26</td>
</tr>
<tr>
<td>e 21.36</td>
<td>25.69</td>
</tr>
</tbody>
</table>

17. A sample may contain any of the following: HCl, NaOH, H₃PO₄, H₂PO₄⁻, HPO₄²⁻, or PO₄³⁻. The composition of a sample is determined by titrating a 25.00-mL portion with 0.1198 M HCl or 0.1198 M NaOH to the phenolphthalein and the methyl orange end points. For each of the following, determine which species are present in the sample, and their respective molar concentrations.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Phenolphthalein end point volume (mL)</th>
<th>methyl orange end point volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a HCl</td>
<td>11.54</td>
<td>35.29</td>
</tr>
<tr>
<td>b NaOH</td>
<td>19.79</td>
<td>9.89</td>
</tr>
<tr>
<td>c HCl</td>
<td>22.76</td>
<td>22.78</td>
</tr>
<tr>
<td>d NaOH</td>
<td>39.42</td>
<td>17.48</td>
</tr>
</tbody>
</table>

18. The protein in a 1.2846-g sample of an oat cereal is determined by a Kjeldahl analysis. The sample is digested with H₂SO₄, the resulting solution made basic with NaOH, and the NH₃ 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 SO₂ in air is determined by bubbling a sample of air through a trap containing H₂O₂. Oxidation of SO₂ by H₂O₂ results in the formation of H₂SO₄, which is then determined by titrating with NaOH. In a typical analysis, a sample of air was passed through the peroxide trap at a rate of 12.5 L/min for 60 min and required 10.08 mL of 0.0244 M NaOH to reach the phenolphthalein end point. Calculate the µL/L SO₂ in the sample of air. The density of SO₂ at the temperature of the air sample is 2.86 mg/mL.

20. The concentration of CO₂ in air is determined by an indirect acid–base titration. A sample of air is bubbled through a solution containing an excess of Ba(OH)₂, precipitating BaCO₃. The excess Ba(OH)₂ is back titrated with HCl. In a typical analysis a 3.5-L sample of air was bubbled through 50.00 mL of 0.0200 M Ba(OH)₂. Back titrating with
0.0316 M HCl required 38.58 mL to reach the end point. Determine the ppm CO₂ in the sample of air given that the density of CO₂ at the temperature of the sample is 1.98 g/L.

21. The purity of a synthetic preparation of methyl ethyl ketone, C₃H₈O, is determined by reacting it with hydroxylamine hydrochloride, liberating HCl (see reaction in Table 9.8). In a typical analysis a 3.00-mL sample was diluted to 50.00 mL and treated with an excess of hydroxylamine hydrochloride. The liberated HCl was titrated with 0.9989 M NaOH, requiring 32.68 mL to reach the end point. Report the percent purity of the sample given that the density of methyl ethyl 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.

<table>
<thead>
<tr>
<th>amino acid</th>
<th>formula weight (g/mol)</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alanine</td>
<td>89.1</td>
<td>$1.36 \times 10^{-10}$</td>
</tr>
<tr>
<td>glycine</td>
<td>75.1</td>
<td>$1.67 \times 10^{-10}$</td>
</tr>
<tr>
<td>methionine</td>
<td>149.2</td>
<td>$8.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>taurine</td>
<td>125.2</td>
<td>$1.8 \times 10^{-9}$</td>
</tr>
<tr>
<td>asparagine</td>
<td>150</td>
<td>$1.9 \times 10^{-9}$</td>
</tr>
<tr>
<td>leucine</td>
<td>131.2</td>
<td>$1.79 \times 10^{-10}$</td>
</tr>
<tr>
<td>phenylalanine</td>
<td>166.2</td>
<td>$4.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>valine</td>
<td>117.2</td>
<td>$1.91 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

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

Figure 9.47 Titration curve for Problem 9.24.
25. Using its titration curve, determine the acid dissociation constant for the weak acid in problem 9.6.

26. Where in the scale of operations do the microtitration techniques discussed in section 9B.7 belong?

27. An acid–base titration may be used to determine an analyte’s gram equivalent weight, but it cannot be used to determine its gram formula weight. Explain why.

28. Commercial washing soda is approximately 30–40% w/w Na₂CO₃. 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 H₂O 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 H₂O 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 Na₂CO₃ 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 systematic or random sources of error, or if they have no effect. If the error is systematic, then indicate whether the experimentally determined molarity for NaOH is too high or too low. The standardization reaction is

\[
C_8H_4O_4^{-}(aq) + OH^- (aq) \rightarrow C_8H_4O_4^{2-}(aq) + H_2O(l)
\]

(a) The balance used to weigh KHP is not properly calibrated and always reads 0.15 g too low.
(b) The indicator for the titration changes color between a pH of 3–4.
(c) An air bubble, which is lodged in the buret’s tip at the beginning of the analysis, dislodges during the titration.
(d) Samples of KHP are weighed into separate Erlenmeyer flasks, but the balance is only tarred with the first flask.
(e) The KHP is not dried before it was used.
(f) The NaOH is not dried before it was used.
(g) The procedure states that the sample of KHP should be dissolved in 25 mL of water, but it is accidentally dissolved in 35 mL of water.

30. The concentration of o-phthalic acid in an organic solvent, such as n-butanol, is determined by an acid–base titration using aqueous NaOH as the titrant. As the titrant is added, the o-phthalic acid is extracted into the aqueous solution where it reacts with the titrant. The titrant must be added slowly to allow sufficient time for the extraction to take place.

(a) What type of error do you expect if the titration is carried out too quickly?

(b) Propose an alternative acid–base titrimetric method that allows for a more rapid determination of the concentration of o-phthalic acid in n-butanol.

31. Calculate or sketch titration curves for 50.00 mL of 0.0500 M Mg$^{2+}$ with 0.0500 M EDTA at a pH of 7 and 10. Locate the equivalence point for each titration curve.

32. Calculate or sketch titration curves for 25.0 mL of 0.0500 M Cu$^{2+}$ with 0.025 M EDTA at a pH of 10, and in the presence of 10$^{-3}$ M and 10$^{-1}$ M NH$_3$. Locate the equivalence point for each titration curve.

33. Sketch the spectrophotometric titration curve for the titration of a mixture of 5.00 $\times$ 10$^{-3}$ M Bi$^{3+}$ and 5.00 $\times$ 10$^{-3}$ M Cu$^{2+}$ with 0.0100 M EDTA. Assume that only the Cu$^{2+}$–EDTA complex absorbs at the selected wavelength.

34. The EDTA titration of mixtures of Ca$^{2+}$ and Mg$^{2+}$ can be followed thermometrically because the formation of the Ca$^{2+}$–EDTA complex is exothermic and the formation of the Mg$^{2+}$–EDTA complex is endothermic. Sketch the thermometric titration curve for a mixture of 5.00 $\times$ 10$^{-3}$ M Ca$^{2+}$ and 5.00 $\times$ 10$^{-3}$ M Mg$^{2+}$ with 0.0100 M EDTA. The heats of formation for CaY$^{2-}$ and MgY$^{2-}$ are, respectively, –23.9 kJ/mole and 23.0 kJ/mole.

35. EDTA is one member of a class of aminocarboxylate ligands that form very stable 1:1 complexes with metal ions. The following table provides log$K_f$ values for the complexes of six such ligands with Ca$^{2+}$ and Mg$^{2+}$. Which ligand is the best choice for the direct titration of Ca$^{2+}$ in the presence of Mg$^{2+}$?

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$K_f$ (Ca$^{2+}$)</th>
<th>$K_f$ (Mg$^{2+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA ethylenediaminetetraacetic acid</td>
<td>8.7</td>
<td>10.7</td>
</tr>
<tr>
<td>HEDTA N-hydroxyethylenediaminetriacetic acid</td>
<td>7.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>
36. The amount of calcium in physiological fluids can be determined by a complexometric titration with EDTA. In one such analysis a 0.100-mL sample of a blood serum was made basic by adding 2 drops of NaOH and titrated with 0.00119 M EDTA, requiring 0.268 mL to reach the end point. Report the concentration of calcium in the sample as milligrams Ca per 100 mL.

37. After removing the membranes from an eggshell, the shell is dried and its mass recorded as 5.613 g. The eggshell is transferred to a 250-mL beaker and dissolved in 25 mL of 6 M HCl. After filtering, the solution containing the dissolved eggshell is diluted to 250 mL in a volumetric flask. A 10.00-mL aliquot is placed in a 125-mL Erlenmeyer flask and buffered to a pH of 10. Titrating with 0.04988 M EDTA requires 44.11 mL to reach the end point. Determine the amount of calcium in the eggshell as %w/w CaCO₃.

38. The concentration of cyanide, CN⁻, in a copper electroplating bath can be determined by a complexometric titration with Ag⁺, forming the soluble Ag(CN)₂⁻ complex. In a typical analysis a 5.00-mL sample from an electroplating bath is transferred to a 250-mL Erlenmeyer flask, and treated with 100 mL of H₂O, 5 mL of 20% w/v NaOH and 5 mL of 10% w/v KI. The sample is titrated with 0.1012 M AgNO₃, requiring 27.36 mL to reach the end point as signaled by the formation of a yellow precipitate of AgI. Report the concentration of cyanide as parts per million of NaCN.

39. Before the introduction of EDTA most complexation titrations used Ag⁺ or CN⁻ as the titrant. The analysis for Cd²⁺, for example, was accomplished indirectly by adding an excess of KCN to form Cd(CN)₄²⁻, and back titrating the excess CN⁻ with Ag⁺, forming Ag(CN)₂⁻. In one such analysis a 0.3000-g sample of an ore was dissolved and treated with 20.00 mL of 0.5000 M KCN. The excess CN⁻ required 13.98 mL of 0.1518 M AgNO₃ to reach the end point. Determine the %w/w Cd in the ore.

40. Solutions containing both Fe³⁺ and Al³⁺ can be selectively analyzed for Fe³⁺ 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 Al\(^{3+}\)–EDTA complex. The excess EDTA is back-
titrated using a standard solution of Fe\(^{3+}\), providing an indirect analysis
for Al\(^{3+}\).

(a) At a pH of 2, verify that the formation of the Fe\(^{3+}\)–EDTA complex
is favorable, and that the formation of the Al\(^{3+}\)–EDTA complex is
not favorable.

(b) A 50.00-mL aliquot of a sample containing Fe\(^{3+}\) and Al\(^{3+}\) is trans-
ferred to a 250-mL Erlenmeyer flask and buffered to a pH of 2. A
small amount of salicylic acid is added, forming the soluble red-
colored Fe\(^{3+}\)–salicylic acid complex. The solution is titrated with
0.05002 M EDTA, requiring 24.82 mL to reach the end point as
signaled by the disappearance of the Fe\(^{3+}\)–salicylic acid complex's
red color. The solution is buffered to a pH of 5 and 50.00 mL of
0.05002 M EDTA is added. After ensuring that the formation of
the Al\(^{3+}\)–EDTA complex is complete, the excess EDTA was back
titrated with 0.04109 M Fe\(^{3+}\), requiring 17.84 mL to reach the
end point as signaled by the reappearance of the red-colored Fe\(^{3+}\)–
salicylic acid complex. Report the molar concentrations of Fe\(^{3+}\) and
Al\(^{3+}\) in the sample.

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

\[
\begin{align*}
\text{PbSO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) & \quad K_{sp} = 1.6 \times 10^{-8} \\
\text{Pb}^{2+}(aq) + \text{Y}^{4-}(aq) \rightleftharpoons \text{PbY}^{2-}(aq) & \quad K_f = 1.1 \times 10^{18} \\
\text{Mg}^{2+}(aq) + \text{Y}^{4-}(aq) \rightleftharpoons \text{MgY}^{2-}(aq) & \quad K_f = 4.9 \times 10^{8} \\
\text{Zn}^{2+}(aq) + \text{Y}^{4-}(aq) \rightleftharpoons \text{ZnY}^{2-}(aq) & \quad K_f = 3.2 \times 10^{16}
\end{align*}
\]

(a) Verify that a precipitate of PbSO\(_4\) dissolves in a solution of Y\(^{4-}\).

(b) Sporek proposed a similar method using Zn\(^{2+}\) as a titrant and found
that the accuracy was frequently poor.\(^{13}\) One explanation is that
Zn\(^{2+}\) might react with the PbY\(^{2-}\) complex, forming ZnY\(^{2-}\). Show
that this might be a problem when using Zn\(^{2+}\) as a titrant, but that
it is not a problem when using Mg\(^{2+}\) as a titrant. Would such a

displacement of Pb$^{2+}$ by Zn$^{2+}$ lead to the reporting of too much or too little sulfate?

(c) In a typical analysis, a 25.00-mL sample of an industrial effluent was carried through the procedure using 50.00 mL of 0.05000 M EDTA. Titrating the excess EDTA required 12.42 mL of 0.1000 M Mg$^{2+}$. Report the molar concentration of SO$_4^{2-}$ in the sample of effluent.

42. Table 9.10 provides values for the fraction of EDTA present as $Y^{4-}$, $\alpha_{Y^{4-}}$. Values of $\alpha_{Y^{4-}}$ are calculated using the equation

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

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

$$C_{\text{EDTA}} = [H_6Y^{2+}] + [H_5Y^+] + [H_4Y] +$$

$$[H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

Using the following equilibria

$$H_6Y^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_5Y^+(aq) \quad K_{a1}$$

$$H_5Y^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_4Y(aq) \quad K_{a2}$$

$$H_4Y(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_3Y^-(aq) \quad K_{a3}$$

$$H_3Y^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2Y^{2-}(aq) \quad K_{a4}$$

$$H_2Y^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HY^{3-}(aq) \quad K_{a5}$$

$$HY^{3-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Y^{4-}(aq) \quad K_{a6}$$

show that

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

where

$$d = [H^+]^6 + [H^+]^5K_{a1} + [H^+]^4K_{a1}K_{a2} +$$

$$[H^+]^3K_{a1}K_{a2}K_{a3} + [H^+]^2K_{a1}K_{a2}K_{a3}K_{a4} +$$

$$[H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$$
43. Calculate or sketch titration curves for the following (unbalanced) redox titration reactions at 25°C. Assume the analyte is initially present at a concentration of 0.0100 M and that a 25.0-mL sample is taken for analysis. The titrant, which is the underlined species in each reaction, is 0.0100 M.

(a) \( \text{V}^{2+} (aq) + \text{Ce}^{4+} (aq) \rightarrow \text{V}^{3+} (aq) + \text{Ce}^{3+} (aq) \)

(b) \( \text{Ti}^{2+} (aq) + \text{Fe}^{3+} (aq) \rightarrow \text{Ti}^{3+} (aq) + \text{Fe}^{2+} (aq) \)

(c) \( \text{Fe}^{2+} (aq) + \text{MnO}_4^{-} (aq) \rightarrow \text{Fe}^{3+} (aq) + \text{Mn}^{2+} (aq) \) (at pH = 1)

44. What is the equivalence point for each titration in problem 43?

45. Suggest an appropriate indicator for each titration in problem 43.

46. The iron content of an ore can be determined by a redox titration using \( \text{K}_2\text{Cr}_2\text{O}_7 \) 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 analysis if a precipitate of \( \text{Hg}_2\text{Cl}_2 \) does not form, or if a gray precipitate (due to \( \text{Hg} \)) forms.

(a) Explain why the analysis is not completed if a white precipitate of \( \text{Hg}_2\text{Cl}_2 \) forms, or if a gray precipitate forms.

(b) Is a determinate error introduced if the analyst forgets to add \( \text{Sn}^{2+} \) in the step where the iron ore is dissolved?

(c) Is a determinate error introduced if the iron is not quantitatively oxidized back to \( \text{Fe}^{3+} \) by the \( \text{MnO}_4^- \)?

47. The amount of \( \text{Cr}^{3+} \) in an inorganic salt can be determined by a redox titration. A portion of sample containing 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 \( \text{(NH}_4\text{)}_2\text{S}_2\text{O}_8 \), 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 K$_2$Cr$_2$O$_7$ using an appropriate indicator. The results are reported as %w/w Cr$^{3+}$.

(a) There are several places in the procedure where a reagent’s volume is specified (see underlined text). Which of these measurements must be made using a volumetric pipet.

(b) Excess peroxydisulfate, S$_2$O$_8^{2-}$ is destroyed by boiling the solution. What is the effect on the reported %w/w Cr$^{3+}$ if some of the S$_2$O$_8^{2-}$ is not destroyed during this step?

(c) Solutions of Fe$^{2+}$ undergo slow air oxidation to Fe$^{3+}$. What is the effect on the reported %w/w Cr$^{3+}$ if the standard solution of Fe$^{2+}$ is inadvertently allowed to be partially oxidized?

48. The exact concentration of H$_2$O$_2$ in a solution that is nominally 6% w/v H$_2$O$_2$ can be determined by a redox titration with MnO$_4^-$.

(a) Many commercially available solutions of H$_2$O$_2$ contain an inorganic or organic stabilizer to prevent the autodecomposition of the peroxide to H$_2$O and O$_2$. What effect does the presence of this stabilizer have on the reported %w/v H$_2$O$_2$ if it also reacts with MnO$_4^-$?

(b) Laboratory distilled water often contains traces of dissolved organic material that may react with MnO$_4^-$. Describe a simple method to correct for this potential interference.

(c) What modifications to the procedure, if any, are need if the sample has a nominal concentration of 30% w/v H$_2$O$_2$.

49. The amount of iron in a meteorite was determined by a redox titration using KMnO$_4$ as the titrant. A 0.4185-g sample was dissolved in acid and the liberated Fe$^{3+}$ quantitatively reduced to Fe$^{2+}$ using a Walden reductor. Titrating with 0.02500 M KMnO$_4$ requires 41.27 mL to reach the end point. Determine the %w/w Fe$_2$O$_3$ in the sample of meteorite.

50. Under basic conditions, MnO$_4^-$ can be used as a titrant for the analysis of Mn$^{2+}$, with both the analyte and the titrant forming MnO$_2$. In the analysis of a mineral sample for manganese, a 0.5165-g sample is dissolved and the manganese reduced to Mn$^{2+}$. The solution is made basic...
51. The amount of uranium in an ore can be determined by a redox back titration. The analysis is accomplished by dissolving the ore in sulfuric acid and reducing the resulting $\text{UO}_2^{2+}$ to $\text{U}^{4+}$ with a Walden reductor. The resulting 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 was determined by dissolving a 30.0-cm$^2$ section in acid, and oxidizing the liberated $\text{Cr}^{3+}$ to $\text{Cr}_2\text{O}_7^{2–}$ with peroxydisulfate. After removing the excess peroxydisulfate by boiling, 500.0 mg of $\text{Fe(NH}_4\text{)}_2(\text{SO}_4)_2\cdot6\text{H}_2\text{O}$ was added, reducing the $\text{Cr}_2\text{O}_7^{2–}$ to $\text{Cr}^{3+}$. The excess $\text{Fe}^{2+}$ was 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$^3$.

53. The concentration of CO in air can be determined by passing a known volume of air through a tube containing $\text{I}_2\text{O}_5$, forming $\text{CO}_2$ and $\text{I}_2$. The $\text{I}_2$ is removed from the tube by distilling it into a solution containing 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 was sampled as described here, requiring 7.17 mL of 0.00329 M $\text{Na}_2\text{S}_2\text{O}_3$ to reach 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 can be determined by the Winkler method. In a typical analysis a 100.0-mL sample is made basic and treated with a solution of $\text{MnSO}_4$, 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. 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 $\text{AgSCN}$. 

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.
(a) Why do the relative solubilities of AgCl and AgSCN lead to a titration error?

(b) Is the resulting titration error a positive or a negative determinate error?

(c) How might you modify the procedure to prevent this or eliminate this source of determinate error?

(d) Will this source of determinate error be of concern when using the Volhard method to determine Br\(^{-}\)?

56. Voncina and co-workers suggest that a precipitation titration can be monitored by measuring pH as a function of the volume of titrant if the titrant is a weak base\(^{14}\). For example, when titrating Pb\(^{2+}\) with CrO\(_4^{2-}\) the solution containing the analyte is initially acidified to a pH of 3.50 using HNO\(_3\). Before the equivalence point the concentration of CrO\(_4^{2-}\) is controlled by the solubility product of PbCrO\(_4\). After the equivalence point the concentration of CrO\(_4^{2-}\) is determined by the amount of excess titrant. Considering the reactions controlling the concentration of CrO\(_4^{2-}\), sketch the expected titration curve of pH versus volume of titrant.

57. Calculate or sketch the titration curve for the titration of 50.0 mL of 0.0250 M KI with 0.0500 M AgNO\(_3\). Prepare separate titration curve using pAg and pI on the y-axis.

58. Calculate or sketch the titration curve for the titration of 25.0 mL mixture of 0.0500 M KI and 0.0500 M KSCN with 0.0500 M AgNO\(_3\).

59. A 0.5131-g sample containing KBr is dissolved in 50 mL of distilled water. Titrating with 0.04614 M AgNO\(_3\) requires 25.13 mL to reach the Mohr end point. A blank titration requires 0.65 mL to reach the same end point. Report the %w/w KBr in the sample.

60. A 0.1093-g sample of impure Na\(_2\)CO\(_3\) was analyzed by the Volhard method. After adding 50.00 mL of 0.06911 M AgNO\(_3\), the sample was back titrated with 0.05781 M KSCN, requiring 27.36 mL to reach the end point. Report the purity of the Na\(_2\)CO\(_3\) sample.

61. A 0.1036-g sample containing only BaCl\(_2\) and NaCl is dissolved in 50 mL of distilled water. Titrating with 0.07916 M AgNO\(_3\) requires 19.46 mL to reach the Fajans end point. Report the %w/w BaCl\(_2\) in the sample.

---

9I Solutions to Practice Exercises

Practice Exercise 9.1

The volume of HCl needed to reach the equivalence point is

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

Before the equivalence point, NaOH is present in excess and the pH is determined by the concentration of unreacted \( \text{OH}^- \). 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.

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<th>pH</th>
<th>Volume of HCl (mL)</th>
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Practice Exercise 9.2

The volume of HCl needed to reach the equivalence point is

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

Before adding HCl the pH is that for a solution of 0.100 M \( \text{NH}_3 \).
Chapter 9 Titrimetric Methods

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

\[ x = [\text{OH}^-] = 1.47 \times 10^{-3} \text{ M} \]

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

Before the equivalence point the pH is determined by an NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} 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 NH\textsubscript{4}\textsuperscript{+}. To calculate the pH we first determine the concentration of NH\textsubscript{4}\textsuperscript{+}

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

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

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

and the pH is 1.88. Some additional results are shown here.

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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 \((V_{\text{HCl}} = 5 \text{ mL}, \text{pH} = 10.24 \text{ and } V_{\text{HCl}} = 45 \text{ mL}, \text{pH} = 8.24)\) are plotted using the \(pK_a\) of 9.244 for \(\text{NH}_4^+\). The two points after the equivalence point \((V_{\text{HCl}} = 60 \text{ mL}, \text{pH} = 2.13 \text{ and } V_{\text{HCl}} = 80 \text{ mL}, \text{pH} = 1.75)\) 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 \(pK_a\) of 3 for \(\text{H}_2\text{A}\)

\[
V_{\text{HCl}} = 2.5 \text{ mL, pH = 2 and } V_{\text{HCl}} = 22.5 \text{ mL, pH = 4}
\]

two points between the equivalence points using the \(pK_a\) of 5 for \(\text{HA}^-\)

\[
V_{\text{HCl}} = 27.5 \text{ mL, pH = 3, and } V_{\text{HCl}} = 47.5 \text{ mL, pH = 5}
\]

and two points after the second equivalence point

\[
V_{\text{HCl}} = 70 \text{ mL, pH = 12.22 and } V_{\text{HCl}} = 90 \text{ mL, pH = 12.46}
\]

Drawing a smooth curve through these points presents us with the following dilemma—the pH appears to increase as the titrant’s volume approaches the first equivalence point and then appears to decrease as it passes through the first equivalence point. This is, of course, absurd; as we add \(\text{NaOH}\) the pH cannot decrease. Instead, we model the titration curve before the second equivalence point by drawing a straight line from the first point \((V_{\text{HCl}} = 2.5 \text{ mL, pH = 2})\) to the fourth \((V_{\text{HCl}} = 47.5 \text{ mL, pH = 5})\), ignoring the second and third points. The results is a reasonable approximation of the exact titration curve.

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Practice Exercise 9.5

The pH at the equivalence point is 5.31 (see Practice Exercise 9.2) and the sharp part of the titration curve extends from a pH of approximately 7 to a pH of approximately 4. Of the indicators in Table 9.4, methyl red is the best choice because it \(pK_a\) value of 5.0 is closest to the equivalence point’s pH and because the pH range of 4.2–6.3 for its change in color will not produce a significant titration error.

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Practice Exercise 9.6

Because salicylic acid is a diprotic weak acid, we must first determine to which equivalence point it is being titrated. Using salicylic acid’s \(pK_a\)
values as a guide, the pH at the first equivalence point is between a pH of 2.97 and 13.74, and the second equivalence points is at a pH greater than 13.74. From Table 9.4, phenolphthalein’s end point falls in the pH range 8.3–10.0. The titration, therefore, is to the first equivalence point for which the moles of NaOH equal the moles of salicylic acid; thus

\[
\frac{0.1354 \text{ mol NaOH}}{L} \times 0.02192 \text{ L} = 2.968 \times 10^{-5} \text{ mol NaOH}
\]

\[
2.968 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol } C_7H_6O_3}{\text{mol NaOH}} \times \frac{138.12 \text{ g } C_7H_6O_3}{\text{mol } C_7H_6O_3} = 0.4099 \text{ g } C_7H_6O_3
\]

\[
\frac{0.4099 \text{ g } C_7H_6O_3}{0.4208 \text{ g sample}} \times 100 = 97.41% \text{ w/w } C_7H_6O_3
\]

Because the purity of the sample is less than 99%, we reject the shipment.

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**Practice Exercise 9.7**

The moles of HNO₃ produced by pulling the air sample through the solution of H₂O₂ is

\[
\frac{0.01012 \text{ mol NaOH}}{L} \times 0.00914 \text{ L} \times \frac{1 \text{ mol HNO}_3}{\text{mol NaOH}} = 9.25 \times 10^{-5} \text{ mol HNO}_3
\]

A conservation of mass on nitrogen requires that each mole of NO₂ in the sample of air produces one mole of HNO₃; thus, the mass of NO₂ in the sample is

\[
9.25 \times 10^{-5} \text{ mol HNO}_3 \times \frac{1 \text{ mol NO}_2}{\text{mol HNO}_3} \times \frac{46.01 \text{ g NO}_2}{\text{mol NO}_2} = 4.26 \times 10^{-3} \text{ g NO}_2
\]

and the concentration of NO₂ is

\[
\frac{4.26 \times 10^{-3} \text{ g NO}_2}{5 \text{ L air}} \times \frac{1000 \text{ mg}}{\text{g}} = 0.852 \text{ mg NO}_2/L \text{ air}
\]

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**Practice Exercise 9.8**

The total moles of HCl used in this analysis is

\[
\frac{1.396\text{ mol NaOH}}{L} \times 0.01000\text{ L} = 1.396 \times 10^{-2} \text{ mol HCl}
\]

Of this,

\[
\frac{0.1004\text{ mol NaOH}}{L} \times 0.03996\text{ L} \times \frac{1 \text{ mol HCl}}{\text{mol NaOH}} = 4.012 \times 10^{-3} \text{ mol HCl}
\]

are consumed in the back titration with NaOH, which means that

\[
1.396 \times 10^{-2} \text{ mol HCl} - 4.012 \times 10^{-3} \text{ mol HCl} = 9.95 \times 10^{-3} \text{ mol HCl}
\]

react with the CaCO\(_3\). Because CO\(_3^{2-}\) is dibasic, each mole of CaCO\(_3\) consumes two moles of HCl; thus

\[
9.95 \times 10^{-3} \text{ mol HCl} \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol HCl}} \times \frac{100.09 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.498 \text{ g CaCO}_3
\]

\[
\frac{0.498 \text{ g CaCO}_3}{0.5143 \text{ g sample}} \times 100 = 96.8\% \text{ w/w CaCO}_3
\]

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**Practice Exercise 9.9**

Of the two analytes, 2-methylanilinium is the stronger acid and is the first to react with the titrant. Titrating to the bromocresol purple end point, therefore, provides information about the amount of 2-methylanilinium in the sample.

\[
\frac{0.200\text{ mol NaOH}}{L} \times 0.01965\text{ L} \times \frac{1 \text{ mol } C_7H_{10}NCl}{\text{mol NaOH}} \times \frac{143.61 \text{ g } C_7H_{10}NCl}{\text{mol } C_7H_{10}NCl} = 0.564 \text{ g } C_7H_{10}NCl
\]

\[
\frac{0.564 \text{ g } C_7H_{10}NCl}{2.006 \text{ g sample}} \times 100 = 28.1\% \text{ w/w } C_7H_{10}NCl
\]

Titrating from the bromocresol purple end point to the phenolphthalein end point, a total of 48.41 mL – 19.65 mL, or 28.76 mL, gives the amount of NaOH reacting with 3-nitrophenol. The amount of 3-nitrophenol in the sample, therefore, is
0.200 mol NaOH
L × 0.02876 L × \frac{1 \text{ mol } C_6H_5NO_3}{\text{mol NaOH}}
× \frac{139.11 \text{ g } C_6H_5NO_3}{\text{mol } C_6H_5NO_3} = 0.800 \text{ g } C_6H_5NO_3

\frac{0.800 \text{ g } C_6H_5NO_3}{2.006 \text{ g sample}} \times 100 = 38.8\% \text{ w/w } C_6H_5NO_3

Practice Exercise 9.10

The first of the two visible end points is approximately 37 mL of NaOH. The analyte’s equivalent weight, therefore, is

\frac{0.1032 \text{ mol NaOH}}{L} \times 0.037 \text{ L} \times \frac{1 \text{ equivalent}}{\text{mol NaOH}} = 3.8 \times 10^{-3} \text{ equivalents}

EW = \frac{0.5000 \text{ g}}{3.8 \times 10^{-3} \text{ equivalents}} = 1.3 \times 10^2 \text{ g/equivalent}

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.

Practice Exercise 9.12

Let’s begin with the calculations at a pH of 10. At a pH of 10 some of the EDTA is present in forms other than Y^{4-}. To evaluate the titration curve, therefore, we need the conditional formation constant for CdY^{2-}, which, from Table 9.1 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

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

of EDTA.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}. For example, after adding 5.00 mL of EDTA, the total concentration of Cd^{2+} is
\[
[Cd^{2+}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL}) - (0.0100 \text{ M})(5.00 \text{ mL})}{50.0 \text{ mL} + 5.00 \text{ mL}} = 3.64 \times 10^{-3} \text{ M}
\]

which gives a pCd of 2.43.

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

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

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

\[
K'_f = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{\text{EDTA}}} = \frac{3.33 \times 10^{-3} - x}{x(x)} = 1.1 \times 10^{16}
\]

Solving gives [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 Cd\(^{2+}\) is determined by the dissociation of the CdY\(^{2-}\) complex. First, we calculate the concentrations of CdY\(^{2-}\) and of unreacted EDTA. For example, after adding 30.0 mL of EDTA

\[
[CdY^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 3.13 \times 10^{-3} \text{ M}
\]

\[
C_{\text{EDTA}} = \frac{(0.0100 \text{ M})(30.0 \text{ mL}) - (5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 6.25 \times 10^{-4} \text{ M}
\]

Substituting into the equation for the conditional formation constant and solving for [Cd\(^{2+}\)] gives

\[
\frac{3.13 \times 10^{-3} \text{ M}}{[Cd^{2+]}(6.25 \times 10^{-4} \text{ M})} = 1.1 \times 10^{16}
\]

[Cd\(^{2+}\)] as 4.55 \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 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 Cd\(^{2+}\) at a pH of 10 in the presence of 0.0100 M NH\(_3\) as an auxiliary complexing agent.
Examining these results allows us to draw several conclusions. First, in the absence of an auxiliary complexing agent the titration curve before the equivalence point is independent of pH (compare columns 2 and 4). Second, for any pH, the titration curve after the equivalence point is the same regardless of whether or not an auxiliary complexing agent is present (compare columns 2 and 3). Third, the largest change in pH through the equivalence point occurs at higher pHs and in the absence of an auxiliary complexing agent. For example, from 23.0 mL to 27.0 mL of EDTA the change in pCd is 11.38 at a pH of 10, 10.33 at a pH of 10 and in the presence of 0.0100 M NH$_3$, and 8.52 at a pH of 7.

**Practice Exercise 9.13**

Figure 9.50 shows a sketch of the titration curves. The two points before the equivalence point ($V_{\text{EDTA}} = 5$ mL, pCd = 2.43 and $V_{\text{EDTA}} = 15$ mL, pCd = 2.81) are the same for both pHs and are taken from the results of Practice Exercise 9.12. The two points after the equivalence point for a pH of 7 ($V_{\text{EDTA}} = 27.5$ mL, pCd = 12.2 and $V_{\text{EDTA}} = 50$ mL, pCd = 13.2) are plotted using the log$K_f'$ of 13.2 for CdY$^{2-}$. The two points after the equivalence point for a pH of 10 ($V_{\text{EDTA}} = 27.5$ mL, pCd = 15.0 and $V_{\text{EDTA}} = 50$ mL, pCd = 16.0) are plotted using the log$K_f'$ of 16.0 for CdY$^{2-}$.

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Practice Exercise 9.14

In an analysis for hardness we treat the sample as if Ca$^{2+}$ is the only metal ion reacting with EDTA. The grams of Ca$^{2+}$ in the sample, therefore, is

$$\frac{0.0109 \text{ mol EDTA}}{L} \times 0.02363 \text{ L} \times \frac{1 \text{ mol Ca}^{2+}}{\text{mol EDTA}} = 2.58 \times 10^{-4} \text{ mol Ca}^{2+}$$

$$2.58 \times 10^{-4} \text{ mol Ca}^{2+} \times \frac{1 \text{ mol CaCO}_3}{\text{mol Ca}^{2+}} \times \frac{100.09 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.0258 \text{ g CaCO}_3$$

and the sample’s hardness is

$$\frac{0.0258 \text{ g CaCO}_3}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 258 \text{ mg CaCO}_3/L$$

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Practice Exercise 9.15

The titration of CN$^-$ with Ag$^+$ produces a metal-ligand complex of Ag(CN)$_2$$^{2-}$; thus, each mole of AgNO$_3$ reacts with two moles of NaCN. The grams of NaCN in the sample is

$$\frac{0.1018 \text{ mol AgNO}_3}{L} \times 0.03968 \text{ L} \times \frac{2 \text{ mol NaCN}}{\text{mol AgNO}_3} \times \frac{49.01 \text{ g NaCN}}{\text{mol NaCN}} = 0.3959 \text{ g NaCN}$$

and the purity of the sample is

$$\frac{0.3959 \text{ g NaCN}}{0.4482 \text{ g sample}} \times 100 = 88.33\% \text{ w/w NaCN}$$

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Practice Exercise 9.16

The total moles of EDTA used in this analysis is

$$\frac{0.02011 \text{ mol EDTA}}{L} \times 0.02500 \text{ L} = 5.028 \times 10^{-4} \text{ mol EDTA}$$

Of this,

$$\frac{0.01113 \text{ mol Mg}^{2+}}{L} \times 0.00423 \text{ L} \times \frac{1 \text{ mol EDTA}}{\text{mol Mg}^{2+}} = 4.708 \times 10^{-5} \text{ mol EDTA}$$
are consumed in the back titration with Mg\(^{2+}\), which means that
\[
5.028 \times 10^{-4} \text{ mol EDTA} - 4.708 \times 10^{-5} \text{ mol EDTA} = 4.557 \times 10^{-4} \text{ mol EDTA}
\]
react with the BaSO\(_4\). Each mole of BaSO\(_4\) reacts with one mole of EDTA; thus
\[
4.557 \times 10^{-4} \text{ mol EDTA} \times \frac{1 \text{ mol BaSO}_4}{\text{mol EDTA}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{\text{mol BaSO}_4} \times \frac{142.04 \text{ g Na}_2\text{SO}_4}{\text{mol Na}_2\text{SO}_4} = 0.06473 \text{ g Na}_2\text{SO}_4
\]
\[
\frac{0.06473 \text{ g Na}_2\text{SO}_4}{0.1557 \text{ g sample}} \times 100 = 41.23\% \text{ w/w Na}_2\text{SO}_4
\]

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**Practice Exercise 9.17**

The volume of Tl\(^{3+}\) needed to reach the equivalence point is
\[
V\_eq = V\_Tl = \frac{M\_Sn \times V\_Sn}{M\_Tl} = \frac{(0.050 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL}
\]

Before the equivalence point, the concentration of unreacted Sn\(^{2+}\) and the concentration of Sn\(^{4+}\) are easy to calculate. For this reason we find the potential using the Nernst equation for the Sn\(^{4+}/\text{Sn}^{2+}\) half-reaction. For example, the concentrations of Sn\(^{2+}\) and Sn\(^{4+}\) after adding 10.0 mL of titrant are
\[
[\text{Sn}^{2+}] = \frac{(0.050 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0250 \text{ M}
\]
\[
[\text{Sn}^{4+}] = \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0167 \text{ M}
\]
and the potential is
\[
E = +0.139 \text{ V} - \frac{0.05916}{2} \log \frac{0.0250 \text{ M}}{0.0167 \text{ M}} = +0.134 \text{ V}
\]

After the equivalence point, the concentration of Tl\(^+\) and the concentration of excess Tl\(^{3+}\) are easy to calculate. For this reason we find the potential using the Nernst equation for the Tl\(^{3+}/\text{Tl}^{+}\) half-reaction. For example, after adding 40.0 mL of titrant, the concentrations of Tl\(^+\) and Tl\(^{3+}\) are
\[
[\text{Tl}^+] = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 40.0 \text{ mL}} = 0.0278 \text{ M}
\]
\[ [\text{Tl}^{3+}] = \frac{(0.100 \ \text{M})(40.0 \ \text{mL}) - (0.0500 \ \text{M})(50.0 \ \text{mL})}{50.0 \ \text{mL} + 40.0 \ \text{mL}} = 0.0167 \ \text{M} \]

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.

<table>
<thead>
<tr>
<th>Volume of \text{Tl}^{3+} (mL)</th>
<th>( E ) (V)</th>
<th>Volume of \text{Tl}^{3+} (mL)</th>
<th>( E ) (V)</th>
</tr>
</thead>
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</tr>
<tr>
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<td>40</td>
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</tr>
<tr>
<td>25</td>
<td>0.45</td>
<td>50</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Figure 9.51 Titration curve for Practice Exercise 9.18. The black dots and curve are the approximate sketch of the titration curve. The points in red are the calculations from Practice Exercise 9.17.

**Practice Exercise 9.18**

Figure 9.51 shows a sketch of the titration curve. The two points before the equivalence point

\[ V_{\text{Tl}} = 2.5 \ \text{mL}, \ E = +0.109 \ \text{V} \text{ and } V_{\text{Tl}} = 22.5 \ \text{mL}, \ E = +0.169 \ \text{V} \]

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

\[ V_{\text{Tl}} = 27.5 \ \text{mL}, \ E = +0.74 \ \text{V} \text{ and } V_{\text{EDTA}} = 50 \ \text{mL}, \ E = +0.77 \ \text{V} \]

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

\[ \text{Ce}^{4+}(aq) + e^- \rightarrow \text{Ce}^{3+}(aq) \]
\[ \text{U}^{4+}(aq) + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+}(aq) + 4\text{H}^+(aq) + 2e^- \]

for which the Nernst equations are

\[ E = E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{0.05916}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \]
Before adding these two equations together we must multiply the second equation by 2 so that we can combine the log terms; thus

\[
3E = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} + 2E^\circ_{\text{UO}_2^{2+}/\text{U}^{4+}} - 0.05916\log \frac{[\text{Ce}^{3+}][U^{4+}]}{[\text{Ce}^{4+}][\text{UO}_2^{2+}][H^+]^4}
\]

At the equivalence point we know that

\[
[\text{Ce}^{3+}] = 2\times[UO_2^{2+}]
\]
\[
[\text{Ce}^{4+}] = 2\times[U^{4+}]
\]

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

\[
3E = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} + 2E^\circ_{\text{UO}_2^{2+}/\text{U}^{4+}} - 0.05916\log \frac{2[UO_2^{2+}][U^{4+}]}{2[U^{4+}][\text{UO}_2^{2+}][H^+]^4}
\]

\[
E = \frac{E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} + 2E^\circ_{\text{UO}_2^{2+}/\text{U}^{4+}}}{3} - \frac{0.05916}{3}\log \frac{1}{[H^+]^4}
\]

\[
E = \frac{E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} + 2E^\circ_{\text{UO}_2^{2+}/\text{U}^{4+}}}{3} + \frac{0.05916\times4}{3}\log[H^+]\]

\[
E = \frac{E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} + 2E^\circ_{\text{UO}_2^{2+}/\text{U}^{4+}}}{3} - 0.07888\text{pH}
\]

At a pH of 1 the equivalence point has a potential of

\[
E_{\text{eq}} = \frac{1.72 + 2\times0.327}{3} - 0.07888\times1 = 0.712 \text{ V}
\]

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**Practice Exercise 9.20**

Because we have not been provided with a balanced reaction, let’s use a conservation of electrons to deduce the stoichiometry. Oxidizing C\(_2\)O\(_4\)^{2−}\), in which each carbon has a +3 oxidation state, to CO\(_2\), in which carbon has an oxidation state of +4, requires one electron per carbon, or a total of two electrons for each mole of C\(_2\)O\(_4\)^{2−}. Reducing MnO\(_4\)^{−}\), in which each manganese is in the +7 oxidation state, to Mn\(^{2+}\) requires five electrons. A conservation of electrons for the titration, therefore, requires that two moles of KMnO\(_4\) (10 moles of \(e^−\)) reacts with five moles of Na\(_2\)C\(_2\)O\(_4\) (10 moles of \(e^−\)).

The moles of KMnO\(_4\) used in reaching the end point is
(0.0400 M KMnO₄) × (0.03562 L KMnO₄) = 1.42 × 10⁻³ mol KMnO₄

which means that the sample contains

1.42 × 10⁻³ mol KMnO₄ × \( \frac{5 \text{ mol Na}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \) = 3.55 × 10⁻³ mol Na₂C₂O₄

Thus, the \% w/w Na₂C₂O₄ in the sample of ore is

\[
\frac{3.55 \times 10^{-3} \text{ mol Na}_2\text{C}_2\text{O}_4 \times \frac{134.00 \text{ g Na}_2\text{C}_2\text{O}_4}{\text{mol Na}_2\text{C}_2\text{O}_4}}{0.5116 \text{ g sample}} = 0.476 \text{ g Na}_2\text{C}_2\text{O}_4
\]

\[
\frac{0.476 \text{ g Na}_2\text{C}_2\text{O}_4 \times 100}{\text{mol Na}_2\text{C}_2\text{O}_4} = 93.0\% \text{ w/w Na}_2\text{C}_2\text{O}_4
\]

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**Practice Exercise 9.21**

For a back titration we need to determine the stoichiometry between Cr₂O₇²⁻ and the analyte, C₂H₆O, and between Cr₂O₇²⁻ and the titrant, Fe²⁺. In oxidizing ethanol to acetic acid, the oxidation state of carbon changes from -2 in C₂H₆O to 0 in C₂H₄O₂. Each carbon releases two electrons, or a total of four electrons per C₂H₆O. In reducing Cr₂O₇²⁻, in which each chromium has an oxidation state of +6, to Cr³⁺, each chromium loses three electrons, for a total of six electrons per Cr₂O₇²⁻. Oxidation of Fe²⁺ to Fe³⁺ requires one electron. A conservation of electrons requires that each mole of K₂Cr₂O₇ (6 moles of e⁻) reacts with six moles of Fe²⁺ (6 moles of e⁻), and that four moles of K₂Cr₂O₇ (24 moles of e⁻) react with six moles of C₂H₆O (24 moles of e⁻).

The total moles of K₂Cr₂O₇ reacting with C₂H₆O and with Fe²⁺ is

\[
(0.0200 \text{ M K}_2\text{Cr}_2\text{O}_7) \times (0.05000 \text{ L I}_3) = 1.00 \times 10^{-3} \text{ mol K}_2\text{Cr}_2\text{O}_7
\]

The back titration with Fe²⁺ consumes

\[
0.02148 \text{ L Fe}^{2+} \times \frac{0.1014 \text{ mol Fe}^{2+}}{\text{L Fe}^{2+}} \times \frac{1 \text{ mol K}_2\text{Cr}_2\text{O}_7}{6 \text{ mol Fe}^{2+}} = 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7
\]

Subtracting the moles of K₂Cr₂O₇ reacting with Fe²⁺ from the total moles of K₂Cr₂O₇ gives the moles reacting with the analyte.

\[
1.00 \times 10^{-3} \text{ K}_2\text{Cr}_2\text{O}_7 - 3.63 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7 = 6.37 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7
\]

The grams of ethanol in the 10.00-mL sample of diluted brandy is
6.37 × 10^{-4} \text{ mol } K_2Cr_2O_7 \times \frac{6 \text{ mol } C_2H_6O}{4 \text{ mol } K_2Cr_2O_7} \times \frac{46.50 \text{ g } C_2H_6O}{\text{ mol } C_2H_6O} = 0.0444 \text{ g } C_2H_6O

The %w/v C_2H_6O in the brandy is

\[
\frac{0.0444 \text{ g } C_2H_6O}{10.00 \text{ mL dilute brandy}} \times \frac{500.0 \text{ mL dilute brandy}}{5.00 \text{ mL brandy}} \times 100 = 44.4\% \text{ w/v } C_2H_6O
\]

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**Practice Exercise 9.22**

The first task is to calculate the volume of NaCl needed to reach the equivalence point; thus

\[ V_{eq} = V_{NaCl} = \frac{M_{NaCl} \cdot V_{Ag}}{M_{Ag}} = \frac{(0.0500 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL} \]

Before the equivalence point the titrand, Ag^+, is in excess. The concentration of unreacted Ag^+ after adding 10.0 mL of NaCl, for example, is

\[
[Ag^+] = \frac{(0.0500 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 2.50 \times 10^{-2} \text{ M}
\]

which corresponds to a pAg of 1.60. To find the concentration of Cl^- we use the \( K_{sp} \) for AgCl; thus

\[
[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9} \text{ M}
\]

or a pCl of 8.14.

At the titration’s equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. To calculate their concentrations we use the \( K_{sp} \) expression for AgCl; thus

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

Solving for \( x \) gives a concentration of Ag^+ and the concentration of Cl^- as 1.3 \times 10^{-5} \text{ M}, or a pAg and a pCl of 4.89.

After the equivalence point, the titrant is in excess. For example, after adding 35.0 mL of titrant

\[
[Cl^-] = \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} = 1.18 \times 10^{-2} \text{ M}
\]
or a pCl of 1.93. To find the concentration of Ag$^+$ we use the $K_{sp}$ for AgCl; thus

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

or a pAg of 7.82. The following table summarizes additional results for this titration.

<table>
<thead>
<tr>
<th>Volume of NaCl (mL)</th>
<th>pAg</th>
<th>pCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.30</td>
<td>–</td>
</tr>
<tr>
<td>5.00</td>
<td>1.44</td>
<td>8.31</td>
</tr>
<tr>
<td>10.0</td>
<td>1.60</td>
<td>8.14</td>
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Click [here](#) to return to the chapter.

**Practice Exercise 9.23**

The titration uses

$$\frac{0.1078 \text{ M KSCN}}{L} \times 0.02719 \text{ L} = 2.931 \times 10^{-3} \text{ mol KSCN}$$

The stoichiometry between SCN$^-$ and Ag$^+$ is 1:1; thus, there are

$$2.931 \times 10^{-3} \text{ mol Ag}^+ \times \frac{107.87 \text{ g Ag}}{\text{mol Ag}} = 0.3162 \text{ g Ag}$$

in the 25.00 mL sample. Because this represents $\frac{1}{4}$ 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

$$\frac{1.265 \text{ g Ag}}{1.963 \text{ g sample}} \times 100 = 64.44\% \text{ w/w Ag}$$

Click [here](#) to return to the chapter.