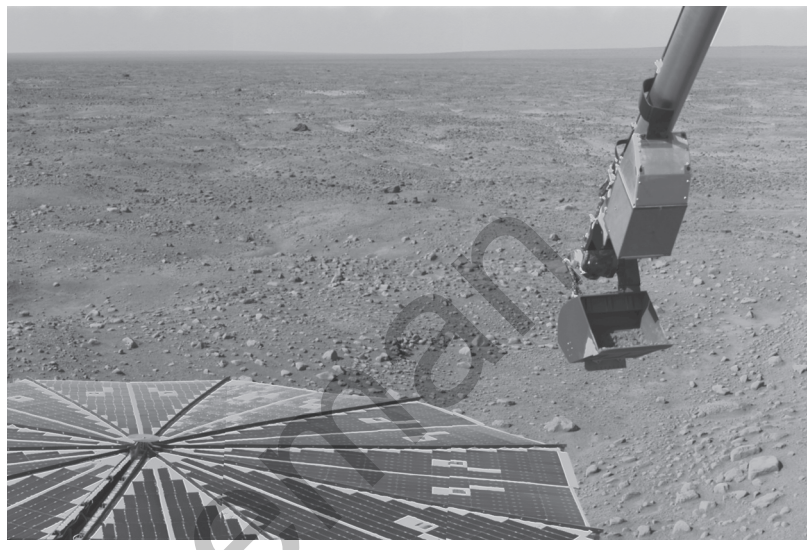
7 Let the Titrations Begin

TITRATION ON MARS



Robotic arm of *Phoenix Mars Lander* scoops up soil for chemical analysis on Mars. [NASA/JPL-Caltech/University of Arizona/Texas A&M University.]

In 2008, Professor Sam Kounaves and his students at Tufts University had the thrill of a lifetime as their Wet Chemistry Laboratory aboard the *Phoenix Mars Lander* returned a stream of information about the ionic composition of Martian soil scooped up by a robotic arm. The arm delivered ~1 gram of soil through a sieve into a "beaker" fitted with a suite of electrochemical sensors described in Chapter 15. Aqueous solution added to the beaker shown in Box 15-3 leached soluble salts from the soil, while sensors measured ions appearing in the liquid. Unlike other ions, sulfate was measured by a *precipitation titration* with Ba^{2+}:

$$BaCl_2(s) \rightarrow Ba^{2+} + 2Cl^-$$
$$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4(s)$$

As solid $BaCl_2$ from a reagent canister slowly dissolved in the aqueous liquid, $BaSO_4$ precipitated. In Problem 7-21, we see that one sensor showed a low level of Ba^{2+} until enough reagent had been added to react with all SO_4^{2-}. Another sensor found steadily increasing Cl^- as $BaCl_2$ dissolved. The end point of the titration is marked by a sudden increase of Ba^{2+} when the last SO_4^{2-} has precipitated and $BaCl_2$ continues to dissolve. The increase in Cl^- from the beginning of the titration up to the end point tells how much $BaCl_2$ was required to consume SO_4^{2-}. Titrations of two soil samples in two cells found ~1.3 (±0.5) wt% sulfate in the soil.[1] Other evidence suggests that the sulfate is mostly from $MgSO_4$.

Procedures in which we measure the volume of reagent needed to react with analyte are called **volumetric analysis.** In this chapter, we discuss principles that apply to all volumetric procedures and then focus on precipitation titrations. Acid-base, oxidation-reduction, complex formation, and spectrophotometric titrations are discussed later in the book in their respective chapters.

7-1 Titrations

In a **titration,** increments of reagent solution—the **titrant**—are added to analyte until their reaction is complete. From the quantity of titrant required, we can calculate the quantity of analyte that must have been present. Titrant is usually delivered from a buret (Figure 7-1).

The principal requirements for a titration reaction are that it have a large equilibrium constant and proceed rapidly. That is, each increment of titrant should be completely and quickly consumed by analyte until the analyte is used up. Common titrations rely on acid-base, oxidation-reduction, complex formation, or precipitation reactions.

The **equivalence point** occurs when the quantity of added titrant is the exact amount necessary for stoichiometric reaction with the analyte. For example, 5 mol of oxalic acid react with 2 mol of permanganate in hot acidic solution:

Reaction 7-1 is an oxidation-reduction reaction. Please study Appendix D if you need to relearn how to balance Reaction 7-1.

$$5HO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OH + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O \qquad \textbf{(7-1)}$$

Analyte	**Titrant**		
Oxalic acid	Permanganate		
colorless	purple	colorless	colorless

If the unknown contains 5.000 mmol of oxalic acid, the equivalence point is reached when 2.000 mmol of MnO_4^- have been added.

The equivalence point is the ideal (theoretical) result we seek in a titration. What we actually measure is the **end point,** which is marked by a sudden change in a physical property of the solution. In Reaction 7-1, a convenient end point is the abrupt appearance of the purple color of permanganate in the flask. Prior to the equivalence point, all permanganate is consumed by oxalic acid, and the titration solution remains colorless. After the equivalence point, unreacted MnO_4^- accumulates until there is enough to see. The *first trace* of purple color is the end point. The better your eyes, the closer will be your measured end point to the true equivalence point. Here, the end point cannot exactly equal the equivalence point, because extra MnO_4^-, beyond that needed to react with oxalic acid, is required to exhibit purple color.

Methods for determining when the analyte has been consumed include (1) detecting a sudden change in the voltage or current between a pair of electrodes (Figure 7-5), (2) observing an indicator color change (Color Plate 2), and (3) monitoring absorption of light (Figure 18-11). An **indicator** is a compound with a physical property (usually color) that changes abruptly near the equivalence point. The change is caused by the disappearance of analyte or the appearance of excess titrant.

The difference between the end point and the equivalence point is an inescapable **titration error.** By choosing a physical property whose change is easily observed (such as pH or the color of an indicator), the end point can be very close to the equivalence point. We estimate the titration error with a **blank titration,** in which we carry out the same procedure *without* analyte. For example, we can titrate a solution containing no oxalic acid to see how much MnO_4^- is needed to produce observable purple color. We then subtract this volume of MnO_4^- from the volume observed in the analytical titration.

The validity of an analytical result depends on knowing the amount of one of the reactants used. If a titrant is prepared by dissolving a weighed amount of pure reagent in a known volume of solution, its concentration can be calculated. We call such a reagent a **primary standard,** because it is pure enough to be weighed and used directly. A primary standard should be 99.9% pure, or better. It should not decompose under ordinary storage, and it should be stable when dried by heat or vacuum, because drying is required to remove traces of water adsorbed from the atmosphere. The highest quality, commercially available, primary standard pure materials, such as As_2O_3 (arsenic(III) oxide), $CaCO_3$, Hg metal, and Ni metal, have purities certified to within $\pm 0.05\%$. Primary standards for many elements are given in Appendix K. Box 7-1 discusses reagent purity. Box 3-2 describes certified reference materials that allow laboratories to test the accuracy of their procedures.

Many reagents used as titrants, such as HCl, are not available as primary standards. Instead, we prepare titrant with approximately the desired concentration and use it to titrate a primary standard. By this procedure, called **standardization,** we determine the concentration of titrant. We then say that the titrant is a **standard solution.** The validity of the analytical result ultimately depends on knowing the composition of a primary standard. Sodium oxalate ($Na_2C_2O_4$) is a commercially available primary standard for generating oxalic acid to standardize permanganate in Reaction 7-1.

In a **direct titration,** we add titrant to analyte until the reaction is complete. Occasionally, we perform a **back titration,** in which we add a known *excess* of one standard reagent to the analyte. Then we titrate the excess reagent with a second standard reagent. A back titration is useful when its end point is clearer than the end point of the direct titration, or

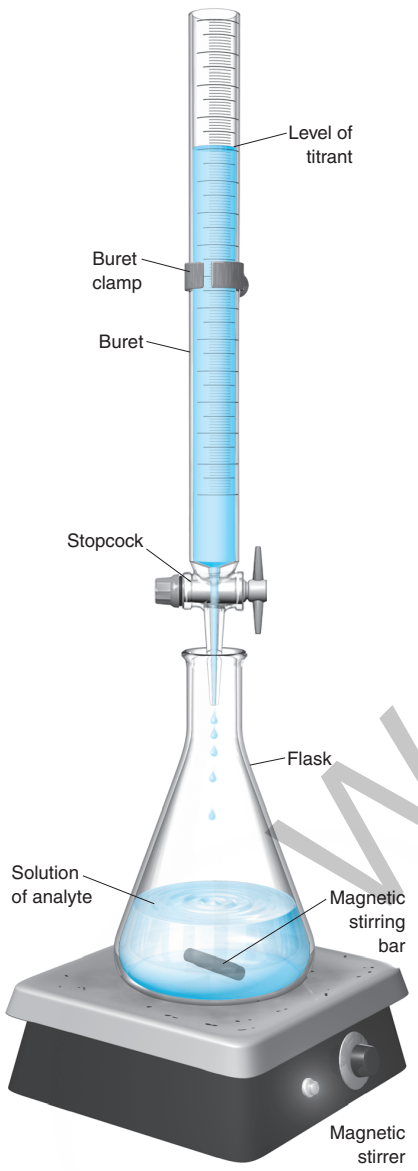


FIGURE 7-1 Typical setup for a titration. The analyte is contained in the flask, and the titrant is in the buret. The stirring bar is a magnet coated with Teflon, which is inert to most solutions. The bar is spun by a rotating magnet inside the stirring motor.

BOX 7-1 Reagent Chemicals and Primary Standards

Chemicals are sold in many grades of purity. For analytical chemistry, we usually use **reagent-grade chemicals** meeting purity requirements set by the American Chemical Society (ACS) Committee on Analytical Reagents.[2] Sometimes "reagent grade" simply meets purity standards set by the manufacturer. An actual lot analysis for specified impurities should appear on the reagent bottle. For example, here is a lot analysis of zinc sulfate:

$ZnSO_4$	ACS Reagent	Lot Analysis:
Assay: 100.6%	Fe: 0.000 5%	Ca: 0.001%
Insoluble matter: 0.002%	Pb: 0.002 8%	Mg: 0.000 3%
pH of 5% solution at 25°C: 5.6	Mn: 0.6 ppm	K: 0.002%
Ammonium: 0.000 8%	Nitrate: 0.000 4%	Na: 0.003%
Chloride: 1.5 ppm		

The assay value of 100.6% means that a specified analysis for one of the major components produced 100.6% of the theoretical value. For example, if $ZnSO_4$ is contaminated with the lower-molecular-mass $Zn(OH)_2$, the assay for Zn^{2+} will be higher than the value for pure $ZnSO_4$. Less pure chemicals, generally unsuitable for analytical chemistry, carry designations such as "chemically pure" (CP), "practical," "purified," or "technical."

A few chemicals are sold in high enough purity to be *primary standard grade*. Whereas reagent-grade potassium dichromate has a lot assay of ≥99.0%, primary standard grade $K_2Cr_2O_7$ must be in the range 99.95–100.05%. Besides high purity, a key quality of primary standards is that they are indefinitely stable.

For **trace analysis** (analysis of species at ppm and lower levels), impurities in reagent chemicals must be extremely low. For this purpose, we use very-high-purity, expensive grades of acids such as "trace metal grade" HNO_3 or HCl to dissolve samples. We must pay careful attention to reagents and vessels whose impurity levels could be greater than the quantity of analyte we seek to measure.

The following steps help you to protect the purity of chemical reagents:

- Avoid putting a spatula into a bottle. Instead, pour chemical out of the bottle into a clean container (or onto weighing paper) and dispense the chemical from the clean container.
- Never pour unused chemical back into the reagent bottle.
- Replace the cap on the bottle immediately to keep dust out.
- Never put a glass stopper from a liquid-reagent container down on the lab bench. Either hold the stopper or place it in a clean place (such as a clean beaker) while you dispense reagent.
- Store chemicals in a cool, dark place. Do not expose them unnecessarily to sunlight.

when an excess of the first reagent is required for complete reaction with analyte. To appreciate the difference between direct and back titrations, consider first the addition of permanganate titrant to oxalic acid analyte in Reaction 7-1; this reaction is a direct titration. Alternatively, to perform a back titration, we could add a known *excess* of permanganate to consume oxalic acid. Then we could back titrate the excess permanganate with standard Fe^{2+} to measure how much permanganate was left after reaction with the oxalic acid.

An alternative to measuring titrant by volume is to measure the *mass* of titrant solution delivered in each increment. We call this procedure a **gravimetric titration.** Titrant can be delivered from a pipet. Titrant concentration is expressed as moles of reagent per kilogram of solution. Precision is improved from 0.3% attainable with a buret to 0.1% with a balance (see the dilution example on page 55). Experiments by Guenther and by Butler and Swift provide examples.[3] "Gravimetric titrations should become the gold standard, and volumetric glassware should be seen in museums only."[4]

7-2 Titration Calculations

Here are some examples to illustrate stoichiometry calculations in volumetric analysis. The key step is to *relate moles of titrant to moles of analyte.*

EXAMPLE Standardization of Titrant Followed by Analysis of Unknown

The calcium content of urine can be determined by the following procedure:

Step 1 Precipitate Ca^{2+} with oxalate in basic solution:

$$\underset{}{Ca^{2+}} + \underset{\text{Oxalate}}{C_2O_4^{2-}} \rightarrow \underset{\text{Calcium oxalate}}{Ca(C_2O_4)\cdot H_2O(s)}$$

Step 2 Wash the precipitate with ice-cold water to remove free oxalate, and dissolve the solid in acid to obtain Ca^{2+} and $H_2C_2O_4$ in solution.

Step 3 Heat the solution to 60°C and titrate the oxalate with standardized potassium permanganate until the purple end point of Reaction 7-1 is observed.

Standardization Suppose that 0.356 2 g of $Na_2C_2O_4$ is dissolved in a 250.0-mL volumetric flask. If 10.00 mL of this solution require 48.36 mL of $KMnO_4$ solution for titration, what is the molarity of the permanganate solution?

Solution The concentration of the oxalate solution is

$$\frac{0.356\ 2\text{ g } Na_2C_2O_4/(134.00\text{ g } Na_2C_2O_4/\text{mol})}{0.250\ 0\text{ L}} = 0.010\ 63_3\text{ M}$$

The moles of $C_2O_4^{2-}$ in 10.00 mL are $(0.010\ 63_3\text{ mol/L})(0.010\ 00\text{ L}) = 1.063_3 \times 10^{-4}$ mol = 0.106 3_3 mmol. Reaction 7-1 requires 2 mol of permanganate for 5 mol of oxalate, so the MnO_4^- delivered must have been

$$\text{Moles of } MnO_4^- = \left(\frac{2\text{ mol } MnO_4^-}{5\text{ mol } C_2O_4^{2-}}\right)(\text{mol } C_2O_4^{2-}) = 0.042\ 53_1\text{ mmol}$$

The concentration of MnO_4^- in the titrant is therefore

$$\text{Molarity of } MnO_4^- = \frac{0.042\ 53_1\text{ mmol}}{48.36\text{ mL}} = 8.794_7 \times 10^{-4}\text{ M}$$

Analysis of Unknown Calcium in a 5.00-mL urine sample was precipitated with $C_2O_4^{2-}$ and redissolved; the sample then required 16.17 mL of standard MnO_4^- solution. Find the concentration of Ca^{2+} in the urine.

Solution In 16.17 mL of MnO_4^-, there are $(0.016\ 17\text{ L})(8.794_7 \times 10^{-4}\text{ mol/L}) = 1.422_1 \times 10^{-5}$ mol MnO_4^-. This quantity will react with

$$\text{Moles of } C_2O_4^{2-} = \left(\frac{5\text{ mol } C_2O_4^{2-}}{2\text{ mol } MnO_4^-}\right)(\text{mol } MnO_4^-) = 0.035\ 55_3\text{ mmol}$$

Because there is one oxalate ion for each calcium ion in $Ca(C_2O_4)\cdot H_2O$, there must have been 0.035 55_3 mmol of Ca^{2+} in 5.00 mL of urine:

$$[Ca^{2+}] = \frac{0.035\ 55_3\text{ mmol}}{5.00\text{ mL}} = 0.007\ 11_1\text{ M}$$

TEST YOURSELF In standardization, 10.00 mL of $Na_2C_2O_4$ solution required 39.17 mL of $KMnO_4$. Find the molarity of $KMnO_4$. The unknown required 14.44 mL of MnO_4^-. Find $[Ca^{2+}]$ in the urine. (***Answer:*** 1.086×10^{-3} M, 7.840×10^{-3} M)

We show an extra, subscripted digit for calculations. In general, retain all extra digits in your calculator. Do not round off until the end of a problem.

Reaction 7-1 requires 2 mol MnO_4^- for 5 mol $C_2O_4^{2-}$

Note that $\frac{\text{mmol}}{\text{mL}}$ is the same as $\frac{\text{mol}}{\text{L}}$.

Reaction 7-1 requires 5 mol $C_2O_4^{2-}$ for 2 mol MnO_4^-

EXAMPLE Titration of a Mixture

Solving for two unknowns requires two independent pieces of information. Here we have the mass of the mixture and the volume of titrant.

A solid mixture weighing 1.372 g containing only sodium carbonate and sodium bicarbonate required 29.11 mL of 0.734 4 M HCl for complete titration:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl(aq) + H_2O + CO_2$$
FM 105.99

$$NaHCO_3 + HCl \rightarrow NaCl(aq) + H_2O + CO_2$$
FM 84.01

Find the mass of each component of the mixture.

Solution Let's denote the grams of Na_2CO_3 by x and grams of $NaHCO_3$ by $1.372 - x$. The moles of each component must be

$$\text{Moles of } Na_2CO_3 = \frac{x\text{ g}}{105.99\text{ g/mol}} \qquad \text{Moles of } NaHCO_3 = \frac{(1.372 - x)\text{ g}}{84.01\text{ g/mol}}$$

We know that the total number of moles of HCl used was (0.029 11 L)(0.734 4 M) = 0.021 38 mol. From the stoichiometry of the two reactions, we can say that

$$2(\text{mol } Na_2CO_3) + \text{mol } NaHCO_3 = 0.021\ 38$$

$$2\left(\frac{x}{105.99}\right) + \frac{1.372 - x}{84.01} = 0.021\ 38 \quad \Rightarrow \quad x = 0.724\text{ g}$$

The mixture contains 0.724 g of Na_2CO_3 and 1.372 − 0.724 = 0.648 g of $NaHCO_3$.

TEST YOURSELF A 2.000-g mixture containing only K_2CO_3 (FM 138.21) and $KHCO_3$ (FM 100.12) required 15.00 mL of 1.000 M HCl for complete titration. Find the mass of each component of the mixture. (***Answer:*** K_2CO_3 = 1.811 g, $KHCO_3$ = 0.189 g)

7-3 Precipitation Titration Curves

Please review Section 6-3 on the solubility product prior to studying precipitation titration curves.

In gravimetric analysis, we could measure an unknown concentration of I^- by adding excess Ag^+ and weighing the AgI precipitate [$I^- + Ag^+ \rightarrow AgI(s)$]. In a *precipitation titration*, we monitor the course of the reaction between analyte (I^-) and titrant (Ag^+) to locate the *equivalence point* at which there is exactly enough titrant for stoichiometric reaction with the analyte. Knowing how much titrant was added tells us how much analyte was present. We seek the equivalence point in a titration, but we observe the *end point* at which there is an abrupt change in a physical property (such as an electrode potential) that is being measured. The physical property is chosen to make the end point as close as possible to the equivalence point.

Equivalence point: Point at which stoichiometric amounts of reactants have been mixed.

End point: Point near the equivalence point at which an abrupt change in a physical property is observed.

The **titration curve** is a graph showing how the concentration of a reactant varies as titrant is added. We will derive equations that can be used to predict precipitation titration curves. One reason to calculate titration curves is to understand the chemistry that occurs during titrations. A second reason is to learn how experimental control can be exerted to influence the quality of an analytical titration. Concentrations of analyte and titrant and the size of the *solubility product* (K_{sp}) influence the sharpness of the end point.

Concentration varies over orders of magnitude, so it is useful to plot the p function:

p function: $$pX = -\log_{10}[X] \qquad (7\text{-}2)$$

In Chapter 8, we write the p function more correctly in terms of activity instead of concentration. For now, we use pX = −log[X].

where [X] is the concentration of X.

Consider the titration of 25.00 mL of 0.100 0 M I^- with 0.050 00 M Ag^+,

Titration reaction: $$I^- + Ag^+ \rightarrow AgI(s) \qquad (7\text{-}3)$$

and suppose that we are monitoring [Ag^+] with an electrode. Reaction 7-3 is the reverse of the dissolution of AgI(*s*), whose solubility product is rather small:

$$AgI(s) \rightleftharpoons Ag^+ + I^- \qquad K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17} \qquad (7\text{-}4)$$

The equilibrium constant for the *titration reaction* 7-3 is large ($K = 1/K_{sp} = 1.2 \times 10^{16}$), so the equilibrium lies far to the right. Each aliquot of Ag^+ reacts nearly completely with I^-, leaving only a tiny amount of Ag^+ in solution. At the equivalence point, there will be a sudden increase in [Ag^+] because there is no I^- left to consume the added Ag^+.

What volume of Ag^+ titrant is needed to reach the equivalence point? We calculate this volume, designated V_e, with the fact that 1 mol of Ag^+ reacts with 1 mol of I^-.

$$\underbrace{(0.025\ 00\ \text{L})(0.100\ 0\ \text{mol}\ I^-/\text{L})}_{\text{mol}\ I^-} = \underbrace{(V_e)(0.050\ 00\ \text{mol}\ Ag^+/\text{L})}_{\text{mol}\ Ag^+}$$

$$\Rightarrow V_e = 0.050\ 00\ \text{L} = 50.00\ \text{mL}$$

V_e = volume of titrant at equivalence point

The titration curve has three distinct regions, depending on whether we are before, at, or after the equivalence point. Let's consider each region separately.

Eventually, we will derive a single, unified equation for a spreadsheet that treats all regions of the titration curve. To understand the chemistry, we break the curve into three regions described by approximate equations that are easy to use.

Before the Equivalence Point

Suppose that 10.00 mL of Ag^+ have been added. There are more moles of I^- than Ag^+ at this point, so virtually all Ag^+ is "used up" to make AgI(*s*). We want to find the small concentration of Ag^+ remaining in solution after reaction with I^-. Imagine that Reaction 7-3 has gone to completion and that some AgI redissolves (Reaction 7-4). The solubility of Ag^+ is determined by the concentration of free I^- remaining in the solution:

$$[Ag^+] = \frac{K_{sp}}{[I^-]} \qquad (7\text{-}5)$$

When $V < V_e$, the concentration of unreacted I^- regulates the solubility of AgI.

Free I^- is overwhelmingly from the I^- that has not been precipitated by 10.00 mL of Ag^+. By comparison, I^- from dissolution of AgI(*s*) is negligible.

So let's find the concentration of unprecipitated I^-:

$$\begin{aligned}\text{Moles of } I^- &= \text{original moles of } I^- - \text{moles of } Ag^+ \text{ added}\\ &= (0.025\,00\text{ L})(0.100\text{ mol/L}) - (0.010\,00\text{ L})(0.050\,00\text{ mol/L})\\ &= 0.002\,000\text{ mol } I^-\end{aligned}$$

The volume is 0.035 00 L (25.00 mL + 10.00 mL), so the concentration is

$$[I^-] = \frac{0.002\,000\text{ mol } I^-}{0.035\,00\text{ L}} = 0.057\,14\text{ M} \qquad \textbf{(7-6)}$$

The concentration of Ag^+ in equilibrium with this much I^- is

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{0.057\,14} = 1.4_5 \times 10^{-15}\text{ M} \qquad \textbf{(7-7)}$$

Finally, the p function we seek is

$$pAg^+ = -\log[Ag^+] = -\log(1.4_5 \times 10^{-15}) = 14.84 \qquad \textbf{(7-8)}$$

$\log(1.4_5 \times 10^{-15}) = 14.84$
Two significant figures — Two digits in mantissa

Significant figures in logarithms were discussed in Section 3-2.

Two significant figures in K_{sp} provide two significant figures in $[Ag^+]$. The two figures in $[Ag^+]$ translate into two figures in the *mantissa* of the p function, which is written as 14.84.

The preceding step-by-step calculation is a tedious way to find the concentration of I^-. Here is a streamlined procedure that is well worth learning. Bear in mind that $V_e = 50.00$ mL. When 10.00 mL of Ag^+ have been added, the reaction is one-fifth complete because 10.00 mL out of the 50.00 mL of Ag^+ needed for complete reaction have been added. Therefore, four-fifths of the I^- is unreacted. If there were no dilution, $[I^-]$ would be four-fifths of its original value. However, the original volume of 25.00 mL has been increased to 35.00 mL. If no I^- had been consumed, the concentration would be the original value of $[I^-]$ times (25.00/35.00). Accounting for both the reaction and the dilution, we can write

Streamlined calculation *well worth using*.

$$[I^-] = \underbrace{\left(\frac{4.000}{5.000}\right)}_{\text{Fraction remaining}}\underbrace{(0.100\,0\text{ M})}_{\text{Original concentration}}\underbrace{\left(\frac{25.00}{35.00}\right)}_{\text{Dilution factor}} = 0.057\,14\text{ M}$$

(25.00: Original volume of I^-; 35.00: Total volume of solution)

This is the same result found in Equation 7-6.

EXAMPLE **Using the Streamlined Calculation**

Let's calculate pAg^+ when V_{Ag^+} (the volume added from the buret) is 49.00 mL.

Solution Because $V_e = 50.00$ mL, the fraction of I^- reacted is 49.00/50.00, and the fraction remaining is 1.00/50.00. The total volume is 25.00 + 49.00 = 74.00 mL.

$$[I^-] = \underbrace{\left(\frac{1.00}{50.00}\right)}_{\text{Fraction remaining}}\underbrace{(0.100\,0\text{ M})}_{\text{Original concentration}}\underbrace{\left(\frac{25.00}{74.00}\right)}_{\text{Dilution factor}} = 6.76 \times 10^{-4}\text{ M}$$

$$[Ag^+] = K_{sp}/[I^-] = (8.3 \times 10^{-17})/(6.76 \times 10^{-4}) = 1.2_3 \times 10^{-13}\text{ M}$$
$$pAg^+ = -\log[Ag^+] = 12.91$$

The concentration of Ag^+ is negligible compared with the concentration of unreacted I^-, even though the titration is 98% complete.

TEST YOURSELF Find pAg^+ at 49.1 mL. (***Answer:*** 12.86)

At the Equivalence Point

Now we have added exactly enough Ag^+ to react with all the I^-. Imagine that all AgI precipitates and some redissolves to give equal concentrations of Ag^+ and I^-. The value of pAg^+ is found by setting $[Ag^+] = [I^-] = x$ in the solubility product:

When $V = V_e$, $[Ag^+]$ is determined by the solubility of pure AgI. *This problem is the same as if we had just added AgI(s) to water.*

$$[Ag^+][I^-] = K_{sp}$$
$$(x)(x) = 8.3 \times 10^{-17} \Rightarrow x = 9.1 \times 10^{-9} \Rightarrow pAg^+ = -\log x = 8.04$$

This value of pAg^+ is independent of the original concentrations or volumes.

After the Equivalence Point

Virtually all Ag^+ added *before* the equivalence point has precipitated. The solution contains all of the Ag^+ added *after* the equivalence point. Suppose that $V_{Ag^+} = 52.00$ mL. The volume past the equivalence point is 2.00 mL. The calculation proceeds as follows:

When $V > V_e$, $[Ag^+]$ is determined by the excess Ag^+ added from the buret.

$$\text{Moles of } Ag^+ = (0.002\,00\text{ L})(0.050\,00\text{ mol } Ag^+/\text{L}) = 0.000\,100\text{ mol}$$

$$[Ag^+] = (0.000\,100\text{ mol})/(0.077\,00\text{ L}) = 1.30 \times 10^{-3}\text{ M} \Rightarrow pAg^+ = 2.89$$

Total volume = 77.00 mL

We could justify three significant figures for the mantissa of pAg^+ because there are three significant figures in $[Ag^+]$. For consistency with earlier results, we retain only two figures.

For a streamlined calculation, the concentration of Ag^+ in the buret is 0.050 00 M, and 2.00 mL of titrant are being diluted to (25.00 + 52.00) = 77.00 mL. Hence, $[Ag^+]$ is

$$[Ag^+] = \underbrace{(0.050\,00\text{ M})}_{\text{Original concentration of } Ag^+}\underbrace{\left(\frac{2.00}{77.00}\right)}_{\text{Dilution factor}} = 1.30 \times 10^{-3}\text{ M}$$

Volume of excess Ag^+

Total volume of solution

The Shape of the Titration Curve

Titration curves in Figure 7-2 illustrate the effect of reactant concentration. The equivalence point is the steepest point of the curve. It is the point of maximum slope (a negative slope in this case) and is therefore an inflection point (at which the second derivative is 0):

Steepest slope: $\frac{dy}{dx}$ reaches its greatest value

Inflection point: $\frac{d^2y}{dx^2} = 0$

In titrations involving 1 : 1 stoichiometry of reactants, the equivalence point is the steepest point of the titration curve. For stoichiometries other than 1 : 1, such as $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4(s)$, the curve is not symmetric. The equivalence point is not at the center of the steepest section of the curve, and it is not an inflection point. In practice, conditions are chosen

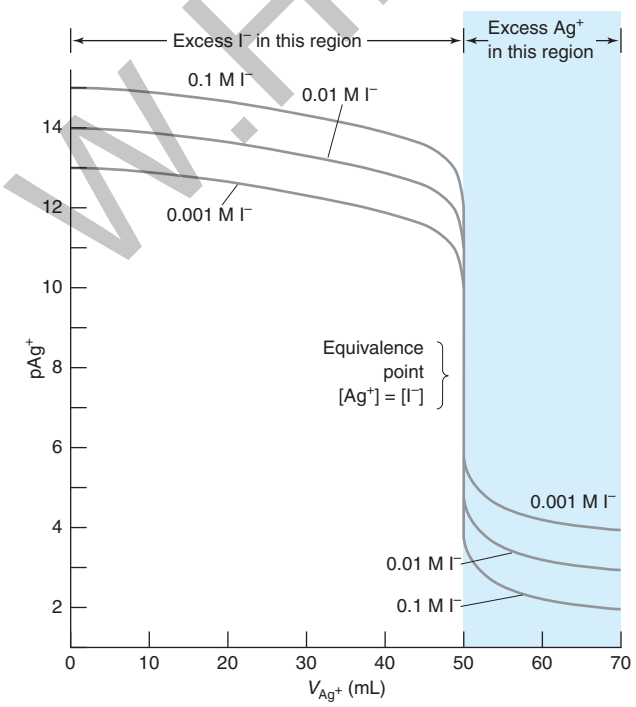


FIGURE 7-2 Titration curves showing the effect of diluting the reactants.

Outer curve: 25.00 mL of 0.100 0 M I^- titrated with 0.050 00 M Ag^+

Middle curve: 25.00 mL of 0.010 00 M I^- titrated with 0.005 000 M Ag^+

Inner curve: 25.00 mL of 0.001 000 M I^- titrated with 0.000 500 0 M Ag^+

such that titration curves are steep enough for the steepest point to be a good estimate of the equivalence point, regardless of the stoichiometry.

Figure 7-3 illustrates how K_{sp} affects the titration of halide ions. The least soluble product, AgI, gives the sharpest change at the equivalence point. However, even for AgCl, the curve is steep enough to locate the equivalence point accurately. The larger the equilibrium constant for a titration reaction, the more pronounced will be the change in concentration near the equivalence point.

At the equivalence point, the titration curve is steepest for the least soluble precipitate.

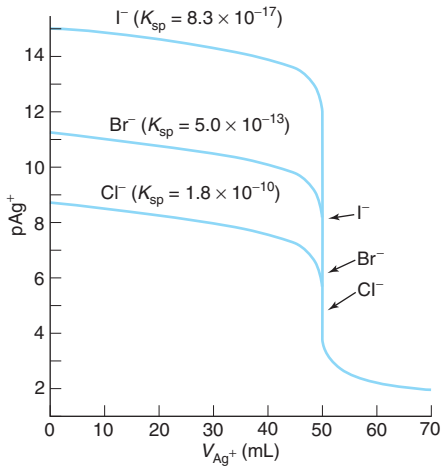


FIGURE 7-3 Titration curves showing the effect of K_{sp}. Each curve is calculated for 25.00 mL of 0.100 0 M halide titrated with 0.050 00 M Ag^+. Equivalence points are marked by arrows.

EXAMPLE **Calculating Concentrations During a Precipitation Titration**

25.00 mL of 0.041 32 M $Hg_2(NO_3)_2$ were titrated with 0.057 89 M KIO_3.

$$Hg_2^{2+} + 2IO_3^- \rightarrow \underset{\text{Iodate}}{Hg_2(IO_3)_2(s)}$$

For $Hg_2(IO_3)_2$, $K_{sp} = 1.3 \times 10^{-18}$. Find $[Hg_2^{2+}]$ in the solution after addition of **(a)** 34.00 mL of KIO_3; (**b**) 36.00 mL of KIO_3; and **(c)** at the equivalence point.

Solution The volume of iodate needed to reach the equivalence point is found as follows:

$$\text{Moles of } IO_3^- = \left(\frac{2 \text{ mol } IO_3^-}{1 \text{ mol } Hg_2^{2+}}\right)(\text{moles of } Hg_2^{2+})$$

$$\underbrace{(V_e)(0.057\ 89\ \text{M})}_{\text{Moles of } IO_3^-} = \underbrace{2(25.00\ \text{mL})(0.041\ 32\ \text{M})}_{\text{Moles of } Hg_2^{2+}} \Rightarrow V_e = 35.69\ \text{mL}$$

(a) When $V = 34.00$ mL, the precipitation of Hg_2^{2+} is not yet complete.

$$[Hg_2^{2+}] = \underbrace{\left(\frac{35.69 - 34.00}{35.69}\right)}_{\substack{\text{Fraction}\\ \text{remaining}}}\underbrace{(0.041\ 32\ \text{M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of } Hg_2^{2+}}}\underbrace{\left(\frac{25.00}{25.00 + 34.00}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 8.29 \times 10^{-4}\ \text{M}$$

(Original volume of Hg_2^{2+} over 25.00; Total volume of solution under 25.00 + 34.00)

(b) When $V = 36.00$ mL, the precipitation is complete. We have gone (36.00 − 35.69) = 0.31 mL *past* the equivalence point. The concentration of excess IO_3^- is

$$[IO_3^-] = \underbrace{(0.057\ 89\ \text{M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of } IO_3^-}}\underbrace{\left(\frac{0.31}{25.00 + 36.00}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 2.9_4 \times 10^{-4}\ \text{M}$$

(Volume of excess IO_3^- over 0.31; Total volume of solution under 25.00 + 36.00)

The concentration of Hg_2^{2+} in equilibrium with solid $Hg_2(IO_3)_2$ plus this much IO_3^- is

$$[Hg_2^{2+}] = \frac{K_{sp}}{[IO_3^-]^2} = \frac{1.3 \times 10^{-18}}{(2.9_4 \times 10^{-4})^2} = 1.5 \times 10^{-11}\ \text{M}$$

(c) At the equivalence point, there is exactly enough IO_3^- to react with all Hg_2^{2+}. We can imagine that all of the ions precipitate and then some $Hg_2(IO_3)_2(s)$ redissolves, giving two moles of iodate for each mole of mercurous ion:

$$Hg_2(IO_3)_2(s) \rightleftharpoons \underset{x}{Hg_2^{2+}} + \underset{2x}{2IO_3^-}$$

$$(x)(2x)^2 = K_{sp} \Rightarrow x = [Hg_2^{2+}] = 6.9 \times 10^{-7}\ \text{M}$$

TEST YOURSELF Find $[Hg_2^{2+}]$ at 34.50 and 36.5 mL. (***Answer:*** 5.79×10^{-4} M, 2.2×10^{-12} M)

Our calculations presume that the only chemistry that occurs is the reaction of anion with cation to precipitate solid salt. If other reactions occur, such as complex formation or ion-pair formation, we would have to modify the calculations.

7-4 Titration of a Mixture

If a mixture of two ions is titrated, the less soluble precipitate forms first. If the solubilities are sufficiently different, the first precipitation is nearly complete before the second commences.

Consider the addition of $AgNO_3$ to a solution containing KI and KCl. Because $K_{sp}(AgI) \ll K_{sp}(AgCl)$, AgI precipitates first. When precipitation of I^- is almost complete, the concentration of Ag^+ abruptly increases and AgCl begins to precipitate. When Cl^- is consumed, another abrupt increase in $[Ag^+]$ occurs. We expect two breaks in the titration curve, first at V_e for AgI and then at V_e for AgCl.

A liquid containing suspended particles is said to be **turbid** because the particles scatter light.

The product with the smaller K_{sp} precipitates first, if the stoichiometry of the precipitates is the same. Precipitation of I^- and Cl^- with Ag^+ produces two breaks in the titration curve, first for I^- and then for Cl^-.

Figure 7-4 shows an experimental curve for this titration. The apparatus used to measure the curve is shown in Figure 7-5, and the theory of how this system measures Ag^+ concentration is discussed in Section 15-2.

The I^- end point is taken as the intersection of the steep and nearly horizontal curves at 23.85 mL shown in the inset of Figure 7-4. Precipitation of I^- is not quite complete when Cl^- begins to precipitate. (The way we know that I^- precipitation is not complete is by a calculation. That's what these obnoxious calculations are for!) Therefore, the end of the steep portion (the intersection) is a better approximation of the equivalence point than is the middle of the steep section. The Cl^- end point is taken as the midpoint of the second steep section, at 47.41 mL. The moles of Cl^- in the sample equal the moles of Ag^+ delivered between the first and second end points. That is, it requires 23.85 mL of Ag^+ to precipitate I^-, and (47.41 − 23.85) = 23.56 mL of Ag^+ to precipitate Cl^-.

Comparison of the I^-/Cl^- and pure I^- titration curves in Figure 7-4 shows that the I^- end point is 0.38% too high in the I^-/Cl^- titration. We expect the first end point at 23.76 mL, but it is observed at 23.85 mL. Two factors contribute to this high value. One is experimental error, which is always present. This discrepancy is as likely to be positive as negative. However, the end point in some titrations, especially Br^-/Cl^- titrations, is systematically 0 to 3% high, depending on conditions. This error is attributed to *coprecipitation* of AgCl with AgBr. Even though the solubility of AgCl has not been exceeded, some Cl^- becomes attached to AgBr crystallites (small crystals) as they precipitate. Each Cl^- carries down an equivalent amount of Ag^+. A high concentration of nitrate reduces coprecipitation, perhaps because NO_3^- competes with Cl^- for binding sites on AgBr(*s*).

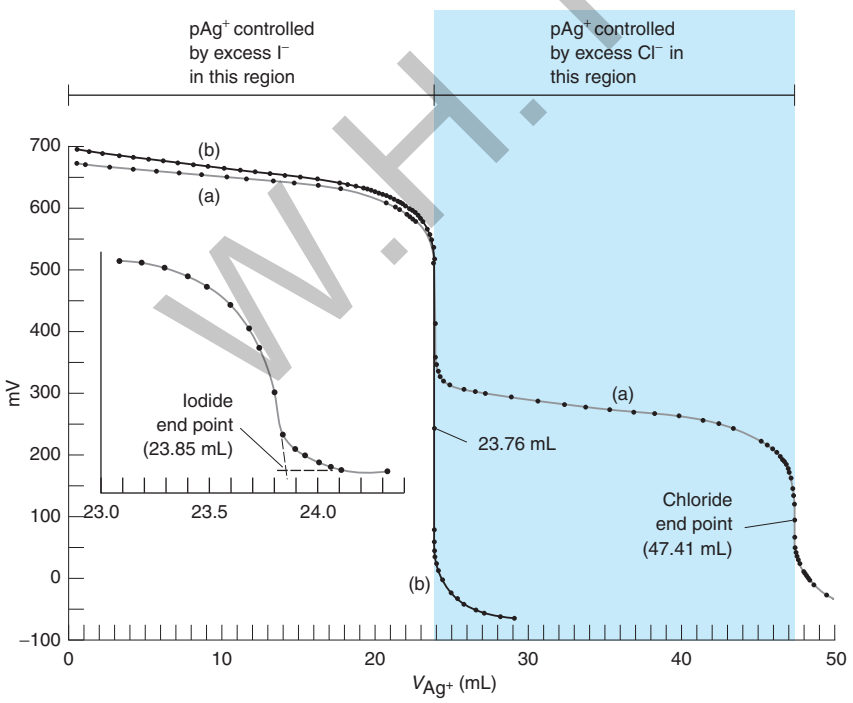


FIGURE 7-4 Experimental titration curves. (*a*) Titration curve for 40.00 mL of 0.050 2 M KI plus 0.050 0 M KCl titrated with 0.084 5 M $AgNO_3$. The inset is an expanded view of the region near the first equivalence point. (*b*) Titration curve for 20.00 mL of 0.100 4 M I^- titrated with 0.084 5 M Ag^+.

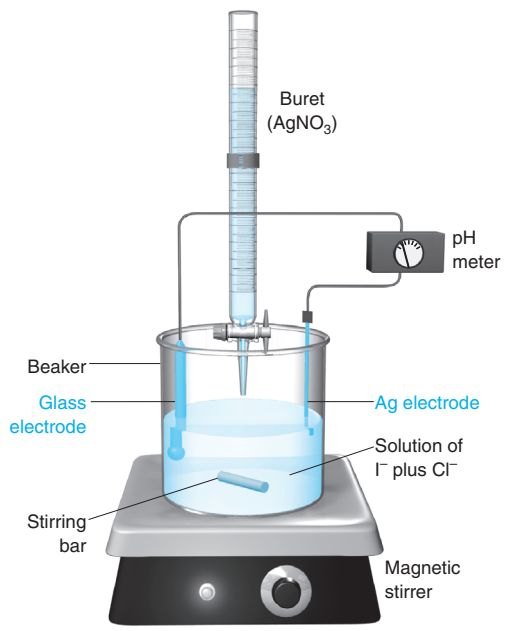


FIGURE 7-5 Apparatus for measuring the titration curves in Figure 7-4. The silver electrode responds to changes in Ag^+ concentration, and the glass electrode provides a constant reference potential in this experiment. The measured voltage changes by approximately 59 mV for each factor-of-10 change in $[Ag^+]$. All solutions, including $AgNO_3$, were maintained at pH 2.0 by using 0.010 M sulfate buffer prepared from H_2SO_4 and KOH.

The second end point in Figure 7-4 corresponds to complete precipitation of both halides. It is observed at the expected value of V_{Ag^+}. The concentration of Cl^-, found from the *difference* between the two end points, will be slightly low in Figure 7-4, because the first end point is slightly high.

7-5 Calculating Titration Curves with a Spreadsheet

Now you understand the chemistry that occurs at different stages of a precipitation titration, and you should know how to calculate the shape of a titration curve. We now introduce spreadsheet calculations that are more powerful than hand calculations and less prone to error. If you are not interested in spreadsheets at this time, you can skip this section.

Consider the addition of V_M liters of cation M^+ (whose initial concentration is C_M^0) to V_X^0 liters of solution containing anion X^- with a concentration C_X^0.

$$\underset{\substack{\text{Titrant}\\ C_M^0,\ V_M}}{M^+} + \underset{\substack{\text{Analyte}\\ C_X^0,\ V_X^0}}{X^-} \overset{K_{sp}}{\rightleftharpoons} MX(s) \qquad \textbf{(7-9)}$$

The total moles of added M ($= C_M^0 \cdot V_M$) must equal the moles of M^+ in solution ($= [M^+](V_M + V_X^0)$ plus the moles of precipitated MX(s). (This equality is called a *mass balance*, even though it is really a *mole balance*.) In a similar manner, we can write a mass balance for X.

The **mass balance** states that the moles of an element in all species in a mixture equal the total moles of that element delivered to the solution.

Mass balance for M:

$$\underset{\substack{\text{Total mol}\\ \text{of added M}}}{C_M^0 \cdot V_M} = \underbrace{[M^+](V_M + V_X^0)}_{\substack{\text{Moles of M}\\ \text{in solution}}} + \underset{\substack{\text{Moles of M in}\\ \text{precipitate}}}{\text{mol } MX(s)} \qquad \textbf{(7-10)}$$

Mass balance for X:

$$\underset{\substack{\text{Total mol}\\ \text{of added X}}}{C_X^0 \cdot V_X^0} = \underbrace{[X^-](V_M + V_X^0)}_{\substack{\text{Moles of X}\\ \text{in solution}}} + \underset{\substack{\text{Moles of X in}\\ \text{precipitate}}}{\text{mol } MX(s)} \qquad \textbf{(7-11)}$$

Now equate mol MX(s) from Equation 7-10 with mol MX(s) from Equation 7-11:

$$C_M^0 \cdot V_M - [M^+](V_M + V_X^0) = C_X^0 \cdot V_X^0 - [X^-](V_M + V_X^0)$$

which can be rearranged to

Precipitation of X^- with M^+:

$$V_M = V_X^0\left(\frac{C_X^0 + [M^+] - [X^-]}{C_M^0 - [M^+] + [X^-]}\right) \qquad \textbf{(7-12)}$$

A supplementary section at www.whfreeman.com/qca derives a spreadsheet equation for the titration of a mixture, such as that in Figure 7-4.

Equation 7-12 relates the volume of added M^+ to $[M^+]$, $[X^-]$, and the constants V_X^0, C_X^0, and C_M^0. To use Equation 7-12 in a spreadsheet, *enter values of pM and compute corresponding values of V_M*, as shown in Figure 7-6 for the iodide titration of Figure 7-3. This is the reverse of the way you normally calculate a titration curve in which V_M would be input and pM would be output. Column C of Figure 7-6 is calculated with the formula $[M^+] = 10^{-pM}$, and column D is given by $[X^-] = K_{sp}/[M^+]$. Column E is calculated from Equation 7-12. The

FIGURE 7-6 Spreadsheet for titration of 25 mL of 0.1 M I^- with 0.05 M Ag^+.

	A	B	C	D	E
1	Titration of I- with Ag+				
2					
3	Ksp(AgI) =	pAg	[Ag+]	[I-]	Vm
4	8.30E-17	15.08	8.32E-16	9.98E-02	0.035
5	Vo =	15	1.00E-15	8.30E-02	3.195
6	25	14	1.00E-14	8.30E-03	39.322
7	Co(I) =	12	1.00E-12	8.30E-05	49.876
8	0.1	10	1.00E-10	8.30E-07	49.999
9	Co(Ag) =	8	1.00E-08	8.30E-09	50.000
10	0.05	6	1.00E-06	8.30E-11	50.001
11		4	1.00E-04	8.30E-13	50.150
12		3	1.00E-03	8.30E-14	51.531
13		2	1.00E-02	8.30E-15	68.750
14	C4 = 10^-B4				
15	D4 = A4/C4				
16	E4 = A6*(A8+C4-D4)/(A10-C4+D4)				

first input value of pM (15.08) was selected by trial and error to produce a small V_M. You can start wherever you like. If your initial value of pM is before the true starting point, then V_M in column E will be negative. In practice, you will want more points than we have shown so that you can plot an accurate titration curve.

7-6 End-Point Detection

Precipitation titration end points are commonly found with electrodes (Figure 7-5) or indicators. We now describe two indicator methods for the titration of Cl^- with Ag^+:

Volhard titration: formation of a soluble, colored complex at the end point
Fajans titration: adsorption of a colored indicator on the precipitate at the end point

Volhard Titration

The Volhard method is a titration of Ag^+ in ~0.5 M HNO_3 with standard KSCN (potassium thiocyanate). To measure Cl^-, a back titration is necessary. First, Cl^- in ~0.5 M HNO_3 is precipitated in a vigorously stirred solution by a known, small excess of standard $AgNO_3$.

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

Vigorous stirring minimizes trapping of excess Ag^+ in the precipitate. $AgCl(s)$ is filtered and washed with dilute (~0.16 M) HNO_3 to collect excess Ag^+ from the precipitate. Then $Fe(NO_3)_3$ (ferric nitrate) or $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ (ferric ammonium sulfate also called ferric alum) solution is added to the combined filtrate to give ~0.02 M Fe^{3+}. Ag^+ is then titrated with standard KSCN:

$$Ag^+ + SCN^- \rightarrow AgSCN(s)$$

When Ag^+ has been consumed, the next drop of SCN^- reacts with Fe^{3+} to form a red complex.

$$Fe^{3+} + SCN^- \rightarrow \underset{\text{Red}}{FeSCN^{2+}}$$

The appearance of red color is the end point. Knowing how much SCN^- was required for the back titration tells us how much Ag^+ was left over from the reaction with Cl^-. The total amount of Ag^+ is known, so the amount consumed by Cl^- can be calculated.

The purpose of HNO_3 in the titration solution is to prevent hydrolysis of Fe^{3+} to form $Fe(OH)^{2+}$. Concentrated (~70 wt%) nitric acid is prepared for use by mixing with an equal volume of water and boiling for a few minutes (in a hood!) to remove NO_2, which has a red color that would make the color change at the end point harder to see. The Volhard analysis should not be conducted above room temperature to prevent oxidation of SCN^- by warm HNO_3. The ferric nitrate or ferric alum solutions used as indicators are stabilized by a few drops of concentrated HNO_3 to prevent precipitation of ferric hydroxide.

In the analysis of Cl^- by the Volhard method, the end point would slowly fade if AgCl were not filtered off, because AgCl is more soluble than AgSCN. AgCl slowly dissolves and is replaced by AgSCN. To eliminate this secondary reaction, we filter the AgCl, and titrate Ag^+ in the filtrate. An alternative to filtration is to add a few mL of nitrobenzene and stir vigorously to coat AgCl with nitrobenzene, which retards access to SCN^-. In the analysis of Br^- and I^-, whose silver salts are *less* soluble than AgSCN, it is not necessary to isolate the silver halide precipitate.

Fajans Titration

The Fajans titration uses an **adsorption indicator**. To see how this works, consider the electric charge at the surface of a precipitate. When Ag^+ is added to Cl^-, there is excess Cl^- in solution prior to the equivalence point. Some Cl^- is adsorbed onto the AgCl surface, imparting a negative charge to the crystal (Figure 7-7a). After the equivalence point, there is excess Ag^+ in solution. Adsorption of Ag^+ onto the AgCl surface places positive charge on the precipitate (Figure 7-7b). The abrupt change from negative to positive occurs at the equivalence point.

Common adsorption indicators are anionic dyes that are attracted to positively charged particles produced immediately after the equivalence point. Adsorption of the negatively charged dye onto the positively charged surface changes the color of the dye. The color change is the end point in the titration. Because the indicator reacts with the precipitate surface, we want as much surface area as possible. To attain maximum surface area, we use conditions that keep the particles as small as possible, because small particles have more

Titrations with Ag^+ are called **argentometric titrations.**

Because the Volhard method is a titration of Ag^+, it can be adapted for the determination of many anions that form insoluble silver salts.

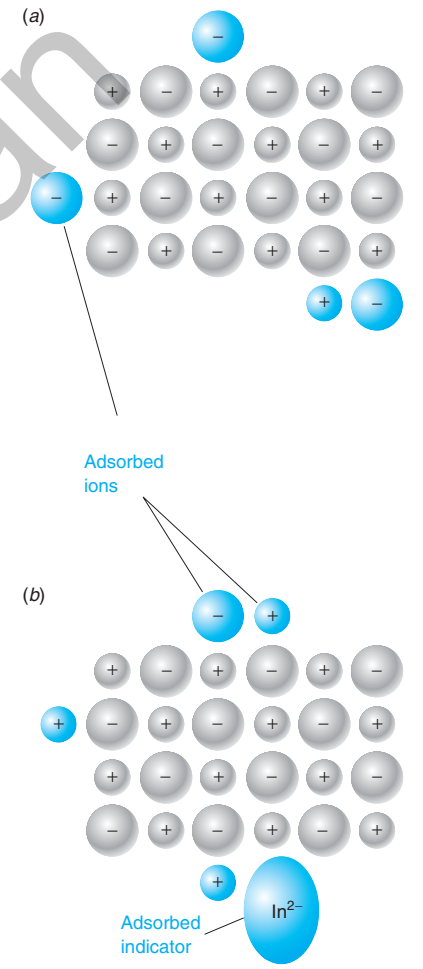
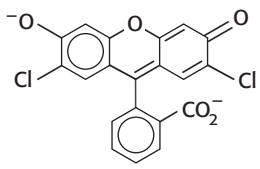


FIGURE 7-7 Ions from a solution are adsorbed on the surface of a growing crystallite. (*a*) A crystal growing in the presence of excess lattice anions (anions that belong in the crystal) will have a slight negative charge because anions are predominantly adsorbed. (*b*) A crystal growing in the presence of excess lattice cations will have a slight positive charge and can therefore adsorb a negative indicator ion. Anions and cations in the solution that do not belong in the crystal lattice are less likely to be adsorbed than are ions belonging to the lattice. These diagrams omit other ions in solution. Overall, each solution plus its growing crystallites must have zero total charge.

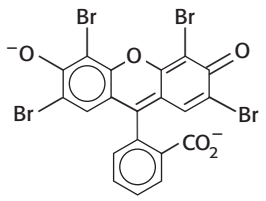
DEMONSTRATION 7-1 Fajans Titration

The Fajans titration of Cl^- with Ag^+ convincingly demonstrates indicator end points in precipitation titrations. Dissolve 0.5 g of NaCl plus 0.15 g of dextrin in 400 mL of water. The purpose of the dextrin is to retard coagulation of the AgCl precipitate. Add 1 mL of dichlorofluorescein indicator solution containing either 1 mg/mL of dichlorofluorescein in 95% aqueous ethanol or 1 mg/mL of the sodium salt in water. Titrate the NaCl solution with a solution containing 2 g of $AgNO_3$ in 30 mL H_2O. About 20 mL are required to reach the end point.

Color Plate 2a shows the yellow color of the indicator in the NaCl solution prior to the titration. Color Plate 2b shows the milky white appearance of the AgCl suspension during titration, before the end point is reached. The pink suspension in Color Plate 2c appears at the end point, when the anionic indicator becomes adsorbed on the cationic particles of precipitate.



Dichlorofluorescein



Tetrabromofluorescein (eosin)

surface area than an equal volume of large particles. Low electrolyte concentration helps prevent coagulation of the precipitate and maintains small particle size.

The most common indicator for AgCl is dichlorofluorescein. This dye is greenish yellow in solution but turns pink when adsorbed onto AgCl (Demonstration 7-1 and Color Plate 2). The pH of the reaction must be controlled because the indicator is a weak acid and must be present in its anionic form. The dye eosin is useful in the titration of Br^-, I^-, and SCN^-. It gives a sharper end point than dichlorofluorescein and is more sensitive (that is, less halide can be titrated). It cannot be used for AgCl, because eosin is more strongly bound than Cl^- to AgCl. Eosin binds to AgCl crystallites even before the particles become positively charged.

In all argentometric titrations, but especially with adsorption indicators, strong light (such as daylight through a window) should be avoided. Light decomposes silver salts, and adsorbed indicators are especially light sensitive.

Applications of precipitation titrations are listed in Table 7-1. Whereas the Volhard method is an argentometric titration, the Fajans method has wider applications. Because the Volhard titration is carried out in acidic solution (typically 0.2 M HNO_3), it avoids certain interferences that affect other titrations. Silver salts of CO_3^{2-}, $C_2O_4^{2-}$, and AsO_4^{3-} are soluble in acidic solution, so these anions do not interfere.

TABLE 7-1 Applications of precipitation titrations

Species analyzed	Notes
	Volhard Method
Br^-, I^-, SCN^-, CNO^-, AsO_4^{3-},	Precipitate removal is unnecessary.
Cl^-, PO_4^{3-}, CN^-, $C_2O_4^{2-}$, CO_3^{2-}, S^{2-}, CrO_4^{2-}	Precipitate removal required.
BH_4^-	Back titration of Ag^+ left after reaction with BH_4^-: $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$
	Fajans Method
Cl^-, Br^-, I^-, SCN^-, $Fe(CN)_6^{4-}$	Titration with Ag^+. Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.
Zn^{2+}	Titration with $K_4Fe(CN)_6$ to produce $K_2Zn_3[Fe(CN)_6]_2$. End-point detection with diphenylamine.
SO_4^{2-}	Titration with $Ba(OH)_2$ in 50 vol% aqueous methanol using alizarin red S as indicator.
Hg_2^{2+}	Titration with NaCl to produce Hg_2Cl_2. End point detected with bromophenol blue.
PO_4^{3-}, $C_2O_4^{2-}$	Titration with $Pb(CH_3CO_2)_2$ to give $Pb_3(PO_4)_2$ or PbC_2O_4. End point detected with dibromofluorescein (PO_4^{3-}) or fluorescein ($C_2O_4^{2-}$).

Terms to Understand

adsorption indicator
argentometric titration
back titration
blank titration
direct titration
end point
equivalence point
Fajans titration
gravimetric titration
indicator
primary standard
reagent-grade chemical
standardization
standard solution
titrant
titration
titration curve
titration error
trace analysis
Volhard titration
volumetric analysis

Summary

The volume of reagent (titrant) required for stoichiometric reaction of analyte is measured in volumetric analysis. The stoichiometric point of the reaction is called the equivalence point. What we measure by an abrupt change in a physical property (such as the color of an indicator or the potential of an electrode) is the end point. The difference between the end point and the equivalence point is a titration error. This error can be reduced by subtracting results of a blank titration, in which the same procedure is carried out in the absence of analyte, or by standardizing the titrant, using the same reaction and a similar volume as that used for analyte.

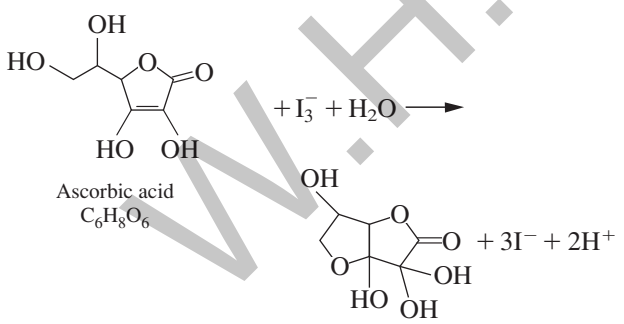
The validity of an analytical result depends on knowing the amount of a primary standard. A solution with an approximately desired concentration can be standardized by titrating a primary standard. In a direct titration, titrant is added to analyte until the reaction is complete. In a back titration, a known excess of reagent is added to analyte, and the excess is titrated with a second standard reagent. Calculations of volumetric analysis relate the known moles of titrant to the unknown moles of analyte.

Concentrations of reactants and products during a precipitation titration are calculated in three regions. Before the equivalence point, there is excess analyte. Its concentration is the product (fraction remaining) × (original concentration) × (dilution factor). The concentration of titrant can be found from the solubility product of the precipitate and the known concentration of excess analyte. At the equivalence point, concentrations of both reactants are governed by the solubility product. After the equivalence point, the concentration of analyte can be determined from the known concentration of excess titrant and the solubility product.

The end points of two common argentometric titrations of anions that precipitate with with Ag^+ are marked by color changes. In the Volhard titration, excess standard $AgNO_3$ is added to the anion and the resulting precipitate is filtered off. Excess Ag^+ in the filtrate is back titrated with standard KSCN in the presence of Fe^{3+}. When Ag^+ has been consumed, SCN^- reacts with Fe^{3+} to form a red complex. The Fajans titration uses an adsorption indicator to find the end point of a direct titration of anion with standard $AgNO_3$. The indicator color changes right after the equivalence point when the charged indicator is adsorbed onto the oppositely charged surface of the precipitate.

Exercises

7-A. Ascorbic acid (vitamin C) reacts with I_3^- according to the equation



Ascorbic acid
$C_6H_8O_6$

Dehydroascorbic acid
$C_6H_8O_7$

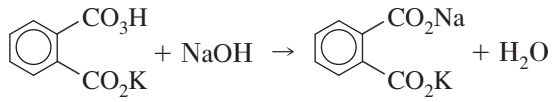
Starch is used as an indicator in the reaction. The end point is marked by the appearance of a deep blue starch-iodine complex when the first fraction of a drop of unreacted I_3^- remains in the solution.

(a) Verify that the structures above have the chemical formulas written beneath them. You must be able to locate every atom in the formula. Use atomic masses from the periodic table on the inside cover of this book to find the formula mass of ascorbic acid.

(b) If 29.41 mL of I_3^- solution are required to react with 0.197 0 g of pure ascorbic acid, what is the molarity of the I_3^- solution?

(c) A vitamin C tablet containing ascorbic acid plus inert binder was ground to a powder, and 0.424 2 g was titrated by 31.63 mL of I_3^-. Find the weight percent of ascorbic acid in the tablet.

7-B. A solution of NaOH was standardized by gravimetric titration of a known quantity of the primary standard, potassium hydrogen phthalate:



Potassium hydrogen phthalate
$C_8H_5O_4K$, FM 204.22

The NaOH was then used to find the concentration of an unknown solution of H_2SO_4:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

(a) Verify from the structure of potassium hydrogen phthalate that its formula is $C_8H_5O_4K$.

(b) Titration of 0.824 g of potassium hydrogen phthalate required 38.314 g of NaOH solution to reach the end point detected by phenolphthalein indicator. Find the concentration of NaOH (mol NaOH/kg solution).

(c) A 10.00-mL aliquot of H_2SO_4 solution required 57.911 g of NaOH solution to reach the phenolphthalein end point. Find the molarity of H_2SO_4.

7-C. A solid sample weighing 0.237 6 g contained only malonic acid and aniline hydrochloride. It required 34.02 mL of 0.087 71 M NaOH to neutralize the sample. Find the weight percent of each component in the solid mixture. The reactions are

$$CH_2(CO_2H)_2 + 2OH^- \rightarrow CH_2(CO_2^-)_2 + 2H_2O$$

Malonic acid FM 104.06 — Malonate

Aniline hydrochloride FM 129.59 — Aniline

7-D. A 50.0-mL sample of 0.080 0 M KSCN is titrated with 0.040 0 M Cu^+. The solubility product of CuSCN is 4.8×10^{-15}. At each of the following volumes of titrant, calculate pCu^+, and construct a graph of pCu^+ versus milliliters of Cu^+ added: 0.10, 10.0, 25.0, 50.0, 75.0, 95.0, 99.0, 100.0, 100.1, 101.0, 110.0 mL.

7-E. Construct a graph of pAg^+ versus milliliters of Ag^+ for the titration of 40.00 mL of solution containing 0.050 00 M Br^- and 0.050 00 M Cl^-. The titrant is 0.084 54 M $AgNO_3$. Calculate pAg^+ at the following volumes: 2.00, 10.00, 22.00, 23.00, 24.00, 30.00, 40.00 mL, second equivalence point, 50.00 mL.

7-F. Consider the titration of 50.00 (±0.05) mL of a mixture of I^- and SCN^- with 0.068 3 (±0.000 1) M Ag^+. The first equivalence point is observed at 12.6 (±0.4) mL, and the second occurs at 27.7 (±0.3) mL.

(a) Find the molarity and the uncertainty in molarity of thiocyanate in the original mixture.

(b) Suppose that the uncertainties are all the same, except that the uncertainty of the first equivalence point (12.6 ± ? mL) is variable. What is the maximum uncertainty (milliliters) of the first equivalence point if the uncertainty in SCN^- molarity is to be ≤4.0%?

Problems

Volumetric Procedures and Calculations

7-1. Explain the following statement: "The validity of an analytical result ultimately depends on knowing the composition of some primary standard."

7-2. Distinguish between the terms *equivalence point* and *end point*.

7-3. How does a blank titration reduce titration error?

7-4. What is the difference between a direct titration and a back titration?

7-5. What is the difference between a reagent-grade chemical and a primary standard?

7-6. Why are ultrapure acid solvents required to dissolve samples for trace analysis?

7-7. How many milliliters of 0.100 M KI are needed to react with 40.0 mL of 0.040 0 M $Hg_2(NO_3)_2$ if the reaction is $Hg_2^{2+} + 2I^- \rightarrow Hg_2I_2(s)$?

7-8. For Reaction 7-1, how many milliliters of 0.165 0 M $KMnO_4$ are needed to react with 108.0 mL of 0.165 0 M oxalic acid? How many milliliters of 0.165 0 M oxalic acid are required to react with 108.0 mL of 0.165 0 M $KMnO_4$?

7-9. Ammonia reacts with hypobromite, OBr^-, by the reaction $2NH_3 + 3OBr^- \rightarrow N_2 + 3Br^- + 3H_2O$. What is the molarity of a hypobromite solution if 1.00 mL of the OBr^- solution reacts with 1.69 mg of NH_3?

7-10. Sulfamic acid is a primary standard that can be used to standardize NaOH.

$$^+H_3NSO_3^- + OH^- \longrightarrow H_2NSO_3^- + H_2O$$

Sulfamic acid FM 97.094

What is the molarity of a sodium hydroxide solution if 34.26 mL react with 0.333 7 g of sulfamic acid?

7-11. Limestone consists mainly of the mineral calcite, $CaCO_3$. The carbonate content of 0.541 3 g of powdered limestone was measured by suspending the powder in water, adding 10.00 mL of 1.396 M HCl, and heating to dissolve the solid and expel CO_2:

$$CaCO_3(s) + 2H^+ \longrightarrow Ca^{2+} + CO_2\uparrow + H_2O$$

Calcium carbonate FM 100.087

The excess acid required 39.96 mL of 0.100 4 M NaOH for complete titration to a phenolphthalein end point. Find the weight percent of calcite in the limestone.

7-12. Arsenic(III) oxide (As_2O_3) is available in pure form and is a useful (but carcinogenic) primary standard for oxidizing agents such as MnO_4^-. The As_2O_3 is dissolved in base and then titrated with MnO_4^- in acidic solution. A small amount of iodide (I^-) or iodate (IO_3^-) is used to catalyze the reaction between H_3AsO_3 and MnO_4^-.

$$As_2O_3 + 4OH^- \rightleftharpoons 2HAsO_3^{2-} + H_2O$$
$$HAsO_3^{2-} + 2H^+ \rightleftharpoons H_3AsO_3$$
$$5H_3AsO_3 + 2MnO_4^- + 6H^+ \rightarrow 5H_3AsO_4 + 2Mn^{2+} + 3H_2O$$

(a) A 3.214-g aliquot of $KMnO_4$ (FM 158.034) was dissolved in 1.000 L of water, heated to cause any reactions with impurities to occur, cooled, and filtered. What is the theoretical molarity of this solution if no MnO_4^- was consumed by impurities?

(b) What mass of As_2O_3 (FM 197.84) would be just sufficient to react with 25.00 mL of the $KMnO_4$ solution in part **(a)**?

(c) It was found that 0.146 8 g of As_2O_3 required 29.98 mL of $KMnO_4$ solution for the faint color of unreacted MnO_4^- to appear. In a blank titration, 0.03 mL of MnO_4^- was required to produce enough color to be seen. Calculate the molarity of the permanganate solution.

7-13. A 0.238 6-g sample contained only NaCl and KBr. It was dissolved in water and required 48.40 mL of 0.048 37 M $AgNO_3$ for complete titration of both halides [giving AgCl(*s*) and AgBr(*s*)]. Calculate the weight percent of Br in the solid sample.

7-14. A solid mixture weighing 0.054 85 g contained only ferrous ammonium sulfate and ferrous chloride. The sample was dissolved in 1 M H_2SO_4, and the Fe^{2+} required 13.39 mL of 0.012 34 M Ce^{4+} for complete oxidation to Fe^{3+} ($Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$). Calculate the weight percent of Cl in the original sample.

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ — Ferrous ammonium sulfate FM 392.13

$FeCl_2 \cdot 6H_2O$ — Ferrous chloride FM 234.84

7-15. A cyanide solution with a volume of 12.73 mL was treated with 25.00 mL of Ni^{2+} solution (containing excess Ni^{2+}) to convert the cyanide into tetracyanonickelate(II):

$$4CN^- + Ni^{2+} \rightarrow Ni(CN)_4^{2-}$$

The excess Ni^{2+} was then titrated with 10.15 mL of 0.013 07 M ethylenediaminetetraacetic acid (EDTA):

$$Ni^{2+} + EDTA^{4-} \rightarrow Ni(EDTA)^{2-}$$

$Ni(CN)_4^{2-}$ does not react with EDTA. If 39.35 mL of EDTA were required to react with 30.10 mL of the original Ni^{2+} solution, calculate the molarity of CN^- in the 12.73-mL cyanide sample.

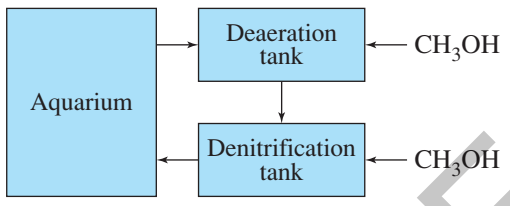
7-16. *Managing a salt-water aquarium.* A tank at the New Jersey State Aquarium has a volume of 2.9 million liters.[5] Bacteria are used to remove nitrate that would otherwise build up to toxic levels. Aquarium water is first pumped into a 2 700-L deaeration tank containing bacteria that consume O_2 in the presence of added methanol:

$$\underset{\text{Methanol}}{2CH_3OH} + 3O_2 \xrightarrow{\text{Bacteria}} 2CO_2 + 4H_2O \qquad (1)$$

Anoxic (deoxygenated) water from the deaeration tank flows into a 1 500-L denitrification reactor containing colonies of *Pseudomonas* bacteria in a porous medium. Methanol is injected continuously and nitrate is converted into nitrite and then into nitrogen:

$$\underset{\text{Nitrate}}{3NO_3^-} + CH_3OH \xrightarrow{\text{Bacteria}} \underset{\text{nitrite}}{3NO_2^-} + CO_2 + 2H_2O \qquad (2)$$

$$2NO_2^- + CH_3OH \xrightarrow{\text{Bacteria}} N_2 + CO_2 + H_2O + 2OH^- \qquad (3)$$



(a) Deaeration can be thought of as a slow, bacteria-mediated titration of O_2 by CH_3OH. The concentration of O_2 in seawater at 24°C is 220 μM. How many liters of CH_3OH (FM 32.04, density = 0.791 g/mL) are required by Reaction 1 for 2.9 million liters of aquarium water?

(b) Write the net reaction showing nitrate plus methanol going to nitrogen. How many liters of CH_3OH are required by the net reaction for 2.9 million liters of aquarium water with a nitrate concentration of 8 100 μM?

(c) In addition to consuming methanol for Reactions 1 through 3, the bacteria require 30% more methanol for their own growth. What is the total volume of methanol required to denitrify 2.9 million liters of aquarium water?

Shape of a Precipitation Curve

7-17. Describe the chemistry that occurs in each of the following regions in Figure 7-2: (i) before the equivalence point; (ii) at the equivalence point; and (iii) past the equivalence point. Write the equation to find $[Ag^+]$ in each region.

7-18. Consider the titration of 25.00 mL of 0.082 30 M KI with 0.051 10 M $AgNO_3$. Calculate pAg^+ at the following volumes of added $AgNO_3$: **(a)** 39.00 mL; **(b)** V_e; **(c)** 44.30 mL.

7-19. A 25.00-mL solution containing 0.031 10 M $Na_2C_2O_4$ was titrated with 0.025 70 M $Ca(NO_3)_2$ to precipitate calcium oxalate: $Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4(s)$. Find pCa^{2+} at the following volumes of $Ca(NO_3)_2$: **(a)** 10.00, **(b)** V_e, **(c)** 35.00 mL.

7-20. In precipitation titrations of halides by Ag^+, the ion pair $AgX(aq)$ (X = Cl, Br, I) is in equilibrium with the precipitate. Use Appendix J to find the concentrations of $AgCl(aq)$, $AgBr(aq)$, and $AgI(aq)$ during the precipitations.

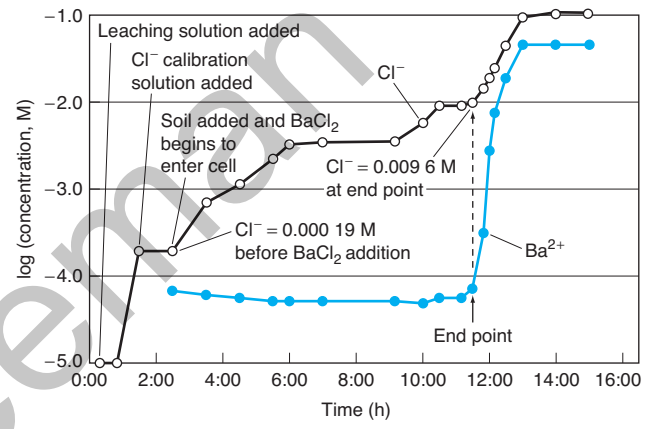
7-21. *Sulfate in soil on Mars.* A barium sulfate precipitation titration described at the opening of this chapter is shown in the figure. The initial concentration of Cl^- before adding $BaCl_2$ was 0.000 19 M in 25 mL of aqueous extract of Martian soil. At the end point, when there is a sudden rise in Ba^{2+}, $[Cl^-] = 0.009\ 6$ M.

(a) Write the titration reaction.

(b) How many mmol of $BaCl_2$ were required to reach the end point?

(c) How many mmol of SO_4^{2-} were contained in the 25 mL?

(d) If SO_4^{2-} is derived from 1.0 g of soil, what is the wt% of SO_4^{2-} in the soil?



Barium sulfate precipitation titration from *Phoenix Mars Lander*. [Data from Reference 1. Courtesy S. Kounaves, Tufts University.]

Titration of a Mixture

7-22. Describe the chemistry that occurs in each of the following regions in curve (a) in Figure 7-4: (i) before the first equivalence point; (ii) at the first equivalence point; (iii) between the first and second equivalence points; (iv) at the second equivalence point; and (v) past the second equivalence point. For each region except (ii), write the equation that you would use to calculate $[Ag^+]$.

7-23. The text claims that precipitation of I^- is not complete before Cl^- begins to precipitate in the titration in Figure 7-4. Calculate the concentration of Ag^+ at the equivalence point in the titration of I^- alone. Show that this concentration of Ag^+ will precipitate Cl^-.

7-24. A procedure[6] for determining halogens in organic compounds uses an argentometric titration. To 50 mL of anhydrous ether is added a carefully weighed sample (10–100 mg) of unknown, plus 2 mL of sodium dispersion and 1 mL of methanol. (Sodium dispersion is finely divided solid sodium suspended in oil. With methanol, it makes sodium methoxide, $CH_3O^-Na^+$, which attacks the organic compound, liberating halides.) Excess sodium is destroyed by slow addition of 2-propanol, after which 100 mL of water are added. (Sodium should not be treated directly with water, because the H_2 produced can explode in the presence of O_2: $2Na + 2H_2O \rightarrow 2NaOH + H_2$.) This procedure gives a two-phase mixture, with an ether layer floating on top of the aqueous layer that contains the halide salts. The aqueous layer is adjusted to pH 4 and titrated with Ag^+, using the electrodes in Figure 7-5. How much 0.025 70 M $AgNO_3$ solution will be required to reach each equivalence point when 82.67 mg of 1-bromo-4-chlorobutane ($BrCH_2CH_2CH_2CH_2Cl$; FM 171.46) are analyzed?

7-25. Calculate pAg^+ at the following points in titration (a) in Figure 7-4: **(a)** 10.00 mL; **(b)** 20.00 mL; **(c)** 30.00 mL; **(d)** second equivalence point; **(e)** 50.00 mL.

7-26. A mixture having a volume of 10.00 mL and containing 0.100 0 M Ag^+ and 0.100 0 M Hg_2^{2+} was titrated with 0.100 0 M KCN to precipitate $Hg_2(CN)_2$ and AgCN.

(a) Calculate pCN^- at each of the following volumes of added KCN: 5.00, 10.00, 15.00, 19.90, 20.10, 25.00, 30.00, 35.00 mL.

(b) Should any AgCN be precipitated at 19.90 mL?

Using Spreadsheets

7-27. Derive an expression analogous to Equation 7-12 for the titration of M^+ (concentration = C_M^0, volume = V_M^0) with X^- (titrant concentration = C_X^0). Your equation should allow you to compute the volume of titrant (V_X) as a function of $[X^-]$.

7-28. Use Equation 7-12 to reproduce the curves in Figure 7-3. Plot your results on a single graph.

7-29. Consider precipitation of X^{x-} with M^{m+}:

$$xM^{m+} + mX^{x-} \rightleftharpoons M_xX_m(s) \qquad K_{sp} = [M^{m+}]^x[X^{x-}]^m$$

Write mass balance equations for M and X and derive the equation

$$V_M = V_X^0\left(\frac{xC_X^0 + m[M^{m+}] - x[X^{x-}]}{mC_M^0 - m[M^{m+}] + x[X^{x-}]}\right)$$

where $[X^{x-}] = (K_{sp}/[M^{m+}]^x)^{1/m}$.

7-30. Use the equation in Problem 7-29 to calculate the titration curve for 10.0 mL of 0.100 M CrO_4^{2-} titrated with 0.100 M Ag^+ to produce $Ag_2CrO_4(s)$.

End-Point Detection

7-31. Why does the surface charge of a precipitate change sign at the equivalence point?

7-32. Examine the procedure in Table 7-1 for the Fajans titration of Zn^{2+}. Do you expect the charge on the precipitate to be positive or negative after the equivalence point?

7-33. Describe how to analyze a solution of NaI by using the Volhard titration.

7-34. A 30.00-mL solution of HBr was treated with 5 mL of freshly boiled and cooled 8 M HNO_3, and then with 50.00 mL of 0.365 0 M $AgNO_3$ with vigorous stirring. Then 1 mL of saturated ferric alum was added and the solution was titrated with 0.287 0 M KSCN. When 3.60 mL had been added, the solution turned red. What was the concentration of HBr in the original solution? How many milligrams of Br^- were in the original solution?

7-35. *What is wrong with this procedure?* According to Table 7-1, carbonate can be measured by a Volhard titration. Removal of the precipitate is required. To analyze an unknown solution of Na_2CO_3, I acidified the solution with freshly boiled and cooled HNO_3 to give ~0.5 M HNO_3. Then I added excess standard $AgNO_3$, but no Ag_2CO_3 precipitate formed. What happened?