comments by
Fatemeh Masdarolomoor
Shahrood University of Technology
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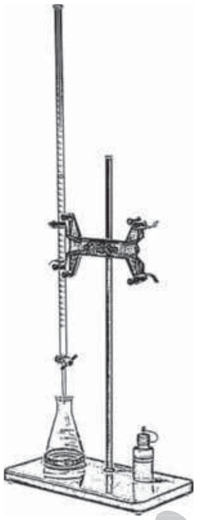
CHAPTER 13

Titrations in Analytical Chemistry

روشهای تیتراسیون برای اندازه گیری اسیدها،
بازها، اکسنده ها، کاهنده ها، یونهای فلزی،
پروتئین ها و بسیاری از مواد دیگر

Titrations are widely used in analytical chemistry to determine acids, bases, oxidants, reductants, metal ions, proteins, and many other species. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry. The volume, or the mass, of the titrant needed to react completely with the analyte is determined and used to calculate the quantity of analyte. A volume-based titration is shown in this figure in which the standard solution is added from a buret, and the reaction occurs in the Erlenmeyer flask. In some titrations, known as coulometric titrations, the quantity of charge required to completely consume the analyte is obtained. In any titration, the point of chemical equivalence, called the end point when determined experimentally, is signaled by an indicator color change or a change in an instrumental response. This chapter introduces the titration principle and the calculations that determine the amount of the unknown. Titration curves, which show the progress of the titration, are also introduced. Such curves will be used in several of the following chapters.



Charles D. Winters

اساس:
تعیین میزان واکنشگر با غلظت معلوم که برای واکنش کامل با آنالیت لازم است

Titration methods, often called titrimetric methods, include a large and powerful group of quantitative procedures based on measuring the amount of a reagent of known concentration that is consumed by an analyte in a chemical or electrochemical reaction. **Volumetric titrations** involve measuring the volume of a solution of known concentration that is needed to react completely with the analyte. In **Gravimetric titrations,** the mass of the reagent is measured instead of its volume. In **coulometric titrations,** the "reagent" is a constant direct electrical current of known magnitude that consumes the analyte. For this titration, the time required (and thus the total charge) to complete the electrochemical reaction is measured (see Section 22D-5).

This chapter provides introductory material that applies to all the different types of titrations. Chapters 14, 15, and 16 are devoted to the various types of neutralization titrations in which the analyte and titrants undergo acid/base reactions. Chapter 17 provides information about titrations in which the analytical reactions involve complex formation or formation of a precipitate. These methods are particularly important for determining a variety of cations. Finally, Chapters 18 and 19 are devoted to volumetric methods in which the analytical reactions involve electron transfer. These methods are often called **redox titrations.** Some additional titration methods are explored in later chapters. These methods include **amperometric titrations** in Section 23B-4 and **spectrophotometric titrations** in Section 26A-4.

Titration methods are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte. The reagent may be a standard solution of a chemical or an electric current of known magnitude.

In **volumetric titrations**, the volume of a standard reagent is the measured quantity.

In **coulometric titrations,** the quantity of charge required to complete a reaction with the analyte is the measured quantity.

13A SOME TERMS USED IN VOLUMETRIC TITRATIONS[1]

A **standard solution** (or a **standard titrant**) is a reagent of known concentration that is used to carry out a volumetric titration. The **titration** is performed by slowly adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete. The volume or mass of reagent needed to complete the titration is determined from the difference between the initial and final readings. A volumetric titration process is depicted in Figure 13-1.

A **standard solution** is a reagent of known concentration. Standard solutions are used in titrations and in many other chemical analyses.

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by **back-titration** with a second standard titrant. For example, the amount of phosphate in a sample can be determined by adding a measured excess of standard silver nitrate to a solution of the sample, which leads to the formation of insoluble silver phosphate:

محلول استاندارد نقره نیترات که به مقدار
معلوم اما "زیادی" به آنالیت اضافه می شود.

$$3Ag^+ + PO_4^{3-} \rightarrow Ag_3PO_4(s)$$

The excess silver nitrate is then back-titrated with a standard solution of potassium thiocyanate:

در تیتراسیون معکوس، زیادی نقره نیترات
با محلول استاندارد تیوسیانات تیتر می شود.

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

The amount of silver nitrate is chemically equivalent to the amount of phosphate ion plus the amount of thiocyanate used for the back-titration. The amount of phosphate is then the difference between the amount of silver nitrate and the amount of thiocyanate.

Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

13A-1 Equivalence Points and End Points

The **equivalence point** in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. For example, the equivalence point in the titration of sodium chloride with silver nitrate occurs after exactly one mole of silver ion has been added for each mole of chloride ion in the sample. The equivalence point in the titration of sulfuric acid with sodium hydroxide is reached after introducing 2 moles of base for each mole of acid.

The **equivalence point** is the point in a titration when the amount of added standard reagent is equivalent to the amount of analyte.

We cannot determine the equivalence point of a titration experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of chemical equivalence. The position of this change is called the **end point** for the titration. We try very hard to ensure that any volume or mass difference between the equivalence point and the end point is small. Such differences do exist, however, as a result of inadequacies in the physical changes and in our ability to observe them. The difference in volume or mass between the equivalence point and the end point is the **titration error**.

The **end point** is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

In volumetric methods, the **titration error**, E_t, is given by

$$E_t = V_{ep} - V_{eq}$$

where V_{ep} is the actual volume of reagent required to reach the end point and V_{eq} is the theoretical volume necessary to reach the equivalence point.

Indicators are often added to the analyte solution to produce an observable physical change (signaling the end point) at or near the equivalence point. Large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance. Typical

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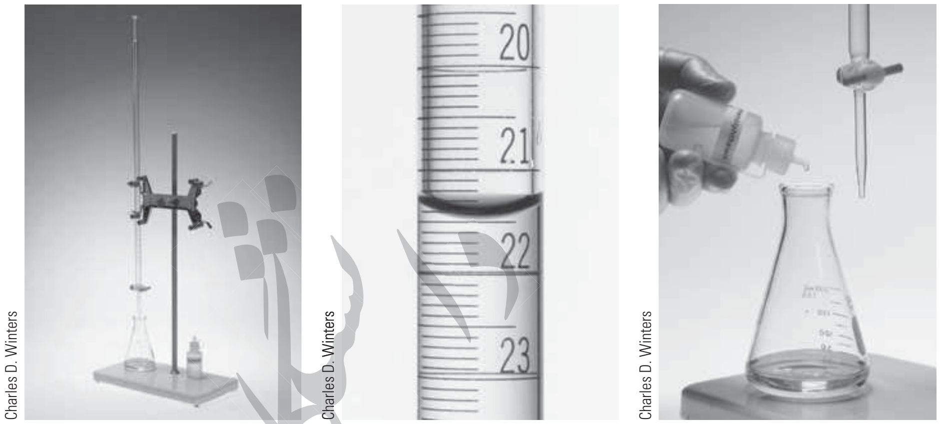
[1] For a detailed discussion of volumetric methods, see J. I. Watters, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 11, Chap. 114. New York: Wiley, 1975.



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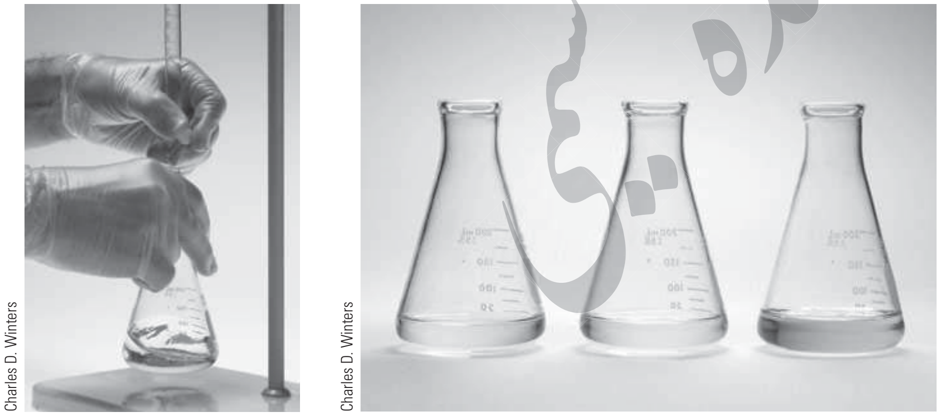
Typical setup for carrying out a titration. The apparatus consists of a buret, a buret stand and clamp with a white porcelain base to provide an appropriate background for viewing indicator changes, and a wide-mouth Erlenmeyer flask containing a precisely known volume of the solution to be titrated. The solution is normally delivered into the flask using a pipet, as shown in Figure 2-22.

Detail of the buret graduations. Normally, the buret is filled with titrant solution to within 1 or 2 mL of the zero position at the top. The initial volume of the buret is read to the nearest 0.01 mL. The reference point on the meniscus and the proper position of the eye for reading are depicted in Figure 2-21.

Before the titration begins. The solution to be titrated, an acid in this example, is placed in the flask, and the indicator is added as shown in the photo. The indicator in this case is phenolphthalein, which turns pink in basic solution.



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During titration. The titrant is added to the flask with swirling until the color of the indicator persists. In the initial region of the titration, titrant may be added rather rapidly, but as the end point is approached, increasingly smaller portions are added; at the end point, less than half a drop of titrant should cause the indicator to change color.

Titration end point. The end point is achieved when the barely perceptible pink color of phenolphthalein persists. The flask on the left shows the titration less than half a drop prior to the end point; the middle flask shows the end point. The final reading of the buret is made at this point, and the volume of base delivered in the titration is calculated from the difference between the initial and final buret readings. The flask on the right shows what happens when a slight excess of base is added to the titration mixture. The solution turns a deep pink color, and the end point has been exceeded. In color plate 9, the color change at the end point is much easier to see than in this black-and-white version.

Figure 13-1 The titration process.

indicator changes include the appearance or disappearance of a color, a change in color, or the appearance or disappearance of turbidity. As an example, the indicator used in the neutralization titration of hydrochloric acid with sodium hydroxide is phenolphthalein, which causes the solution to change from colorless to a pink color once excess sodium hydroxide has been added.

We often use instruments to detect end points. These instruments respond to properties of the solution that change in a characteristic way during the titration. Among such instruments are colorimeters, turbidimeters, spectrophotometers, temperature monitors, refractometers, voltmeters, current meters, and conductivity meters.

13A-2 Primary Standards

A **primary standard** is a highly purified compound that serves as a reference material in titrations and in other analytical methods. The accuracy of a method critically depends on the properties of the primary standard. Important requirements for a primary standard are the following:

خصوصیات استانداردهای اولیه

A **primary standard** is an ultrapure compound that serves as the reference material for a titration or for another type of quantitative analysis.

1. High purity. Established methods for confirming purity should be available.
2. Atmospheric stability.
3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
4. Modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

Very few compounds meet or even approach these criteria, and only a limited number of primary-standard substances are available commercially. As a consequence, less pure compounds must sometimes be used in place of a primary standard. The purity of such a **secondary standard** must be established by careful analysis.

A **secondary standard** is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

13B STANDARD SOLUTIONS

Standard solutions play a central role in all titrations. Therefore, we must consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed. The *ideal* standard solution for a titrimetric method will

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1. be sufficiently stable so that it is necessary to determine its concentration only once;
2. react rapidly with the analyte so that the time required between additions of reagent is minimized;
3. react more or less completely with the analyte so that satisfactory end points are realized;
4. undergo a selective reaction with the analyte that can be described by a balanced equation.

Few reagents completely meet these ideals.

The accuracy of a titration can be no better than the accuracy of the concentration of the standard solution used. Two basic methods are used to establish the concentration of such solutions. The first is the **direct method** in which a carefully determined mass of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask. The second is by **standardization** in which the titrant to be standardized is used to titrate (1) a known mass of a primary standard, (2) a known mass of a secondary standard, or (3) a measured volume of another standard solution. A titrant that is standardized is sometimes referred to as a **secondary-standard solution**. The concentration of a secondary-standard solution is subject to a larger uncertainty than is the concentration of a primary-standard solution. If there is a choice, then, solutions are best prepared by the direct method. Many reagents, however, lack the properties required for a primary standard and, therefore, require standardization.

In a **standardization,** the concentration of a volumetric solution is determined by titrating it against a carefully measured quantity of a primary or secondary standard or an exactly known volume of another standard solution.

13C VOLUMETRIC CALCULATIONS

As we indicated in Section 4B-1, we can express the concentration of solutions in several ways. For the standard solutions used in most titrations, either **molar concentration**, c, or **normal concentration**, c_N, is usually used. Molar concentration is the number of moles of reagent contained in one liter of solution, and normal concentration is the number of **equivalents** of reagent in the same volume.

Throughout this text, we base volumetric calculations exclusively on molar concentration and molar masses. We have also included in Appendix 7 a discussion of how volumetric calculations are performed based on normal concentration and equivalent masses because you may encounter these terms and their uses in the industrial and health science literature.

13C-1 Some Useful Relationships

Most volumetric calculations are based on two pairs of simple equations that are derived from definitions of the mole, the millimole, and the molar concentration. For the chemical species A, we can write

$$n_A = \frac{m_A}{\mathcal{M}_A}$$

where n_A is the amount of A, m_A is the mass of A, and $\mathcal{M}_A$ is the molar mass of A.

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} \qquad (13\text{-}1)$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}} \qquad (13\text{-}2)$$

$$c_A = \frac{n_A}{V} \quad \text{or} \quad n_A = V \times c_A$$

The second pair of equations is derived from the definition of molar concentration, that is,

$$\text{amount A (mol)} = V\,(\text{L}) \times c_A\left(\frac{\text{mol A}}{\text{L}}\right) \qquad (13\text{-}3)$$

$$\text{amount A (mmol)} = V\,(\text{mL}) \times c_A\left(\frac{\text{mmol A}}{\text{L}}\right) \qquad (13\text{-}4)$$

where V is the volume of the solution.

Any combination of grams, moles, and liters can be expressed in milligrams, millimoles, and milliliters. For example, a 0.1 M solution contains 0.1 mol of a species per liter or 0.1 mmol per milliliter. Similarly, the number of moles of a compound is equal to the mass in grams of that compound divided by its molar mass in grams or the mass in milligrams divided by its millimolar mass in milligrams.

Equations 13-1 and 13-3 are used when volumes are measured in liters, and Equations 13-2 and Equations 13-4 when the units are milliliters.

13C-2 Calculating the Molar Concentration of Standard Solutions

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The following three examples illustrate how the concentrations of volumetric reagents are calculated.

EXAMPLE 13-1

Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary-standard-grade solid.

Solution

$$\text{amount } AgNO_3 = V_{soln}(L) \times c_{AgNO_3}(mol/L)$$

$$= 2.00\ \cancel{L} \times \frac{0.0500\ mol\ AgNO_3}{\cancel{L}} = 0.100\ mol\ AgNO_3$$

To obtain the mass of $AgNO_3$, we rearrange Equation 13-2 to give

$$\text{mass } AgNO_3 = 0.1000\ \cancel{mol\ AgNO_3} \times \frac{169.87\ g\ AgNO_3}{\cancel{mol\ AgNO_3}}$$

$$= 16.987\ g\ AgNO_3$$

Therefore, the solution should be prepared by dissolving 16.987 g of $AgNO_3$ in water and diluting to the mark in a 2.000 L volumetric flask.

EXAMPLE 13-2

A standard 0.0100 M solution of Na^+ is required to calibrate an ion-selective electrode method to determine sodium. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mL).

Solution

We wish to compute the mass of reagent required to produce a species concentration of 0.0100 M. In this instance, we will use millimoles since the volume is in milliliters. Because Na_2CO_3 dissociates to give two Na^+ ions, we can write that the number of millimoles of Na_2CO_3 needed is

$$\text{amount } Na_2CO_3 = 500\ \cancel{mL} \times \frac{0.0100\ \cancel{mmol\ Na^+}}{\cancel{mL}} \times \frac{1\ mmol\ Na_2CO_3}{2\ \cancel{mmol\ Na^+}}$$

$$= 2.50\ mmol$$

From the definition of millimole, we write

$$\text{mass } Na_2CO_3 = 2.50\ \cancel{mmol\ Na_2CO_3} \times 105.99\ \frac{mg\ Na_2CO_3}{\cancel{mmol\ Na_2CO_3}}$$

$$= 264.975\ mg\ Na_2CO_3$$

Since there are 1000 mg/g, or 0.001 g/mg, the solution should be prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.

EXAMPLE 13-3

How would you prepare 50.0-mL portions of standard solutions that are 0.00500 M, 0.00200 M, and 0.00100 M in Na^+ from the solution in Example 13-2?

Solution

The number of millimoles of Na^+ taken from the concentrated solution must equal the number in the dilute solutions. Thus,

$$\text{amount } Na^+ \text{ from concd soln} = \text{amount } Na^+ \text{ in dil soln}$$

Recall that the number of millimoles is equal to the number of millimoles per milliliter times the number of milliliters, that is,

$$V_{\text{concd}} \times c_{\text{concd}} = V_{\text{dil}} \times c_{\text{dil}}$$

where V_{concd} and V_{dil} are the volumes in milliliters of the concentrated and diluted solutions, respectively, and c_{concd} and c_{dil} are their molar Na^+ concentrations. For the 0.00500-M solution, this equation can be rearranged to

$$V_{\text{concd}} = \frac{V_{\text{dil}} \times c_{\text{dil}}}{c_{\text{concd}}} = \frac{50.0 \text{ mL} \times 0.005 \cancel{\text{mmol Na}^+/\text{mL}}}{0.0100 \cancel{\text{mmol Na}^+/\text{mL}}} = 25.0 \text{ mL}$$

Therefore, to produce 50.0 mL of 0.00500 M Na^+, 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

Repeat the calculation for the other two molarities to confirm that diluting 10.0 and 5.00 mL of the concentrated solution to 50.0 mL produces the desired concentrations.

13C-3 Working with Titration Data

Two types of volumetric calculations are discussed here. In the first, we compute concentrations of solutions that have been standardized against either a primary-standard or another standard solution. In the second, we calculate the amount of analyte in a sample from titration data. Both types of calculation are based on three algebraic relationships. Two of these are Equations 13-2 and 13-4, which are based on millimoles and milliliters. The third relationship is the stoichiometric ratio of the number of millimoles of the analyte to the number of millimoles of titrant.

Calculating Molar Concentrations from Standardization Data

Examples 13-4 and 13-5 illustrate how standardization data are treated.

EXAMPLE 13-4

A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molar concentration of the HCl.

Solution

In the titration, 1 mmol of $Ba(OH)_2$ reacts with 2 mmol of HCl:

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

Thus, the stoichiometric ratio is

$$\text{stoichiometric ratio} = \frac{2\text{ mmol HCl}}{1\text{ mmol Ba(OH)}_2}$$

The number of millimoles of the standard is calculated by substituting into Equation 13-4:

$$\text{amount Ba(OH)}_2 = 29.71\ \cancel{\text{mL Ba(OH)}_2} \times 0.01963\ \frac{\text{mmol Ba(OH)}_2}{\cancel{\text{mL Ba(OH)}_2}}$$

To find the number of millimoles of HCl, we multiply this result by the stoichiometric ratio determined from the titration reaction:

$$\text{amount HCl} = (29.71 \times 0.01963)\ \cancel{\text{mmol Ba(OH)}_2} \times \frac{2\text{ mmol HCl}}{1\ \cancel{\text{mmol Ba(OH)}_2}}$$

To obtain the number of millimoles of HCl per mL, we divide by the volume of the acid. Therefore,

$$c_{\text{HCl}} = \frac{(29.71 \times 0.01963 \times 2)\text{ mmol HCl}}{50.0\text{ mL HCl}}$$

$$= 0.023328\ \frac{\text{mmol HCl}}{\text{mL HCl}} = 0.02333\text{ M}$$

In determining the number of significant figures to retain in volumetric calculations, the stoichiometric ratio is assumed to be known exactly without uncertainty.

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EXAMPLE 13-5

Titration of 0.2121 g of pure $Na_2C_2O_4$ (134.00 g/mol) required 43.31 mL of $KMnO_4$. What is the molar concentration of the $KMnO_4$ solution? The chemical reaction is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Solution

From this equation we see that

$$\text{stoichiometric ratio} = \frac{2\text{ mmol KMnO}_4}{5\text{ mmol Na}_2\text{C}_2\text{O}_4}$$

The amount of primary-standard $Na_2C_2O_4$ is given by Equation 13-2

$$\text{amount Na}_2\text{C}_2\text{O}_4 = 0.2121\ \cancel{\text{g Na}_2\text{C}_2\text{O}_4} \times \frac{1\text{ mmol Na}_2\text{C}_2\text{O}_4}{0.13400\ \cancel{\text{g Na}_2\text{C}_2\text{O}_4}}$$

(*continued*)

To obtain the number of millimoles of $KMnO_4$, we multiply this result by the stoichiometric ratio:

$$\text{amount } KMnO_4 = \frac{0.2121}{0.1340}\ \cancel{\text{mmol } Na_2C_2O_4} \times \frac{2 \text{ mmol } KMnO_4}{5\ \cancel{\text{mmol } Na_2C_2O_4}}$$

The concentration of $KMnO_4$ is then obtained by dividing by the volume consumed. Thus,

$$c_{KMnO_4} = \frac{\left(\dfrac{0.2121}{0.13400} \times \dfrac{2}{5}\right) \text{mmol } KMnO_4}{43.31 \text{ mL } KMnO_4} = 0.01462 \text{ M}$$

Note that units are carried through all calculations as a check on the correctness of the relationships used in Examples 13-4 and 13-5.

Calculating the Quantity of Analyte from Titration Data

As shown by the examples that follow, the systematic approach just described is also used to compute analyte concentrations from titration data.

EXAMPLE 13-6 تعیین آهن در سنگ معدن با استفاده از تیتراسیون اکسایش-کاهش

A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M $KMnO_4$ solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) % Fe_3O_4 (231.54 g/mol).

Solution

The reaction of the analyte with the reagent is described by the equation

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

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(a) $$\text{stoichiometric ratio} = \frac{5 \text{ mmol } Fe^{2+}}{1 \text{ mmol } KMnO_4}$$

$$\text{amount } KMnO_4 = 47.22\ \cancel{\text{mL } KMnO_4} \times \frac{0.02242 \text{ mmol } KMnO_4}{\cancel{\text{mL } KMnO_4}}$$

$$\text{amount } Fe^{2+} = (47.22 \times 0.02242)\ \cancel{\text{mmol } KMnO_4} \times \frac{5 \text{ mmol } Fe^{2+}}{1\ \cancel{\text{mmol } KMnO_4}}$$

The mass of Fe^{2+} is then given by

$$\text{mass } Fe^{2+} = (47.22 \times 0.02242 \times 5)\ \cancel{\text{mmol } Fe^{2+}} \times 0.055847 \frac{\text{g } Fe^{2+}}{\cancel{\text{mmol } Fe^{2+}}}$$

The percent Fe^{2+} is

$$\% \, Fe^{2+} = \frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g } Fe^{2+}}{0.8040 \text{ g sample}} \times 100\% = 36.77\%$$

(b) To determine the correct stoichiometric ratio, we note that

$$5 \, Fe^{2+} \equiv 1 \, MnO_4^-$$

Therefore,

$$5 \, Fe_3O_4 \equiv 15 \, Fe^{2+} \equiv 3 \, MnO_4^-$$

and

$$\text{stoichiometric ratio} = \frac{5 \text{ mmol } Fe_3O_4}{3 \text{ mmol } KMnO_4}$$

As in part (a),

$$\text{amount } KMnO_4 = \frac{47.22 \, \cancel{\text{mL } KMnO_4} \times 0.02242 \text{ mmol } KMnO_4}{\cancel{\text{mL } KMnO_4}}$$

$$\text{amount } Fe_3O_4 = (47.22 \times 0.02242) \, \cancel{\text{mmol } KMnO_4} \times \frac{5 \text{ mmol } Fe_3O_4}{3 \, \cancel{\text{mmol } KMnO_4}}$$

$$\text{mass } Fe_3O_4 = \left(47.22 \times 0.02242 \times \frac{5}{3}\right) \cancel{\text{mmol } Fe_3O_4} \times 0.23154 \frac{\text{g } Fe_3O_4}{\cancel{\text{mmol } Fe_3O_4}}$$

$$\% \, Fe_3O_4 = \frac{\left(47.22 \times 0.02242 \times \frac{5}{3}\right) \times 0.23154 \text{ g } Fe_3O_4}{0.8040 \text{ g sample}} \times 100\% = 50.81\%$$

FEATURE 13-1

Another Approach to Example 13-6(a)

Some people find it easier to write out the solution to a problem in such a way that the units in the denominator of each succeeding term eliminate the units in the numerator of the preceding one until the units of the answer are obtained.[2] For example, the solution to part (a) of Example 13-6 can be written

$$\boxed{\begin{gathered} 47.22 \, \cancel{\text{mL } KMnO_4} \times \frac{0.02242 \, \cancel{\text{mmol } KMnO_4}}{\cancel{\text{mL } KMnO_4}} \times \frac{5 \, \cancel{\text{mmol Fe}}}{1 \, \cancel{\text{mmol } KMnO_4}} \times \frac{0.055847 \text{ g Fe}}{\cancel{\text{mmol Fe}}} \\ \times \frac{1}{0.8040 \text{ g sample}} \times 100\% = 36.77\% \text{ Fe} \end{gathered}}$$

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[2] This process is often referred to as the factor-label method. It is sometimes erroneously called dimensional analysis. For an explanation of dimensional analysis, perform a search at the Wikipedia website. In earlier texts, the factor-label method was sometimes called the "picket fence" method.

EXAMPLE 13-7

A 100.0-mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M $AgNO_3$. The analytical reaction is

$$2Ag^{+} + S^{2-} \rightarrow Ag_2S(s)$$

Calculate the concentration of H_2S in the water in parts per million, c_{ppm}.

Solution

At the end point,

$$\text{stoichiometric ratio} = \frac{1 \text{ mmol } H_2S}{2 \text{ mmol } AgNO_3}$$

$$\text{amount } AgNO_3 = 16.47 \cancel{\text{mL } AgNO_3} \times 0.02310 \frac{\text{mmol } AgNO_3}{\cancel{\text{mL } AgNO_3}}$$

$$\text{amount } H_2S = (16.47 \times 0.02310) \cancel{\text{mmol } AgNO_3} \times \frac{1 \text{ mmol } H_2S}{2 \cancel{\text{mmol } AgNO_3}}$$

$$\text{mass } H_2S = \left(16.47 \times 0.02310 \times \frac{1}{2}\right) \cancel{\text{mmol } H_2S} \times 0.034081 \frac{\text{g } H_2S}{\cancel{\text{mmol } H_2S}}$$

$$= 6.483 \times 10^{-3} \text{ g } H_2S$$

$$c_{ppm} = \frac{6.483 \times 10^{-3} \text{ g } H_2S}{100.0 \cancel{\text{mL sample}} \times 1.00 \text{ g sample}/\cancel{\text{mL sample}}} \times 10^{6} \text{ ppm}$$

$$= 64.8 \text{ ppm}$$

به تعریف ppm توجه کنید.

FEATURE 13-2

Rounding the Answer to Example 13-7

Note that the input data for Example 13-7 all contained four or more significant figures, but the answer was rounded to three. Why?

We can make the rounding decision by doing a couple of rough calculations in our heads. Assume that the input data are uncertain to 1 part in the last significant figure. The largest *relative* error will then be associated with the sample size. In Example 13-7, the relative uncertainty is 0.1/100.0. Thus, the uncertainty is about 1 part in 1000 (compared with about 1 part in 1647 for the volume of $AgNO_3$ and 1 part in 2300 for the reagent concentration). We then assume that the calculated result is uncertain to about the same amount as the least precise measurement, or 1 part in 1000. The absolute uncertainty of the final result is then 64.8 ppm × 1/1000 = 0.065, or about 0.1 ppm, and we round to the first figure to the right of the decimal point. Thus, we report 64.8 ppm.

Practice making this rough type of rounding decision whenever you make a computation.

EXAMPLE 13-8 اندازه گیری فسفر در یک غذای گیاهی با استفاده از تیتراسیون معکوس

The phosphorus in a 4.258-g sample of a plant food was converted to PO_4^{3-} and precipitated as Ag_3PO_4 by adding 50.00 mL of 0.0820 M $AgNO_3$. The excess $AgNO_3$ was back-titrated with 4.06 mL of 0.0625 M KSCN. Express the results of this analysis in terms of % P_2O_5.

Solution

The chemical reactions are

$$P_2O_5 + 9H_2O \rightarrow 2PO_4^{3-} + 6H_3O^+$$

$$2PO_4^{3-} + \underset{\text{excess}}{6\ Ag^+} \rightarrow 2Ag_3PO_4(s)$$

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

The stoichiometric ratios are

$$\boxed{\frac{1 \text{ mmol } P_2O_5}{6 \text{ mmol } AgNO_3}} \quad \text{and} \quad \frac{1 \text{ mmol KSCN}}{1 \text{ mmol } AgNO_3}$$

$$\text{total amount } AgNO_3 = 50.00 \cancel{\text{mL}} \times 0.0820 \frac{\text{mmol } AgNO_3}{\cancel{\text{mL}}} = 4.100 \text{ mmol}$$

$$\text{amount } AgNO_3 \text{ consumed by KSCN} = 4.06 \cancel{\text{mL}} \times 0.0625 \frac{\cancel{\text{mmol KSCN}}}{\cancel{\text{mL}}} \times \frac{1 \text{ mmol } AgNO_3}{\cancel{\text{mmol KSCN}}} = 0.2538 \text{ mmol}$$

$$\text{amount } P_2O_5 = (4.100 - 0.254) \cancel{\text{mmol } AgNO_3} \times \frac{1 \text{ mmol } P_2O_5}{6 \cancel{\text{ mmol } AgNO_3}} = 0.6410 \text{ mmol } P_2O_5$$

$$\% P_2O_5 = \frac{0.6410 \cancel{\text{mmol}} \times \frac{0.1419 \text{ g } P_2O_5}{\cancel{\text{mmol}}}}{4.258 \text{ g sample}} \times 100\% = 2.14\%$$

EXAMPLE 13-9 روش یدومتری

The CO in a 20.3-L sample of gas was converted to CO_2 by passing the sample over iodine pentoxide heated to 150°C:

$$I_2O_5(s) + 5CO(g) \rightarrow 5CO_2(g) + I_2(g)$$

The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M $Na_2S_2O_3$.

$$I_2(g) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

The excess $Na_2S_2O_3$ was back-titrated with 2.16 mL of 0.00947 M I_2 solution. Calculate the concentration of CO (28.01 g/mol) in mg per liter of sample.

(continued)

Solution

Based on the two reactions, the stoichiometric ratios are

$$\frac{5 \text{ mmol CO}}{1 \text{ mmol I}_2} \quad \text{and} \quad \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{1 \text{ mmol I}_2}$$

We divide the first ratio by the second to get a third useful ratio

$$\frac{5 \text{ mmol CO}}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}$$

This relationship reveals that 5 mmol of CO are responsible for the consumption of 2 mmol of $Na_2S_2O_3$. The total amount of $Na_2S_2O_3$ is

$$\text{amount Na}_2\text{S}_2\text{O}_3 = 8.25 \cancel{\text{mL Na}_2\text{S}_2\text{O}_3} \times 0.01101 \frac{\text{mmol Na}_2\text{S}_2\text{O}_3}{\cancel{\text{mL Na}_2\text{S}_2\text{O}_3}}$$

$$= 0.09083 \text{ mmol Na}_2\text{S}_2\text{O}_3$$

The amount of $Na_2S_2O_3$ consumed in the back-titration is

$$\text{amount Na}_2\text{S}_2\text{O}_3 = 2.16 \cancel{\text{mL I}_2} \times 0.00947 \frac{\cancel{\text{mmol I}_2}}{\cancel{\text{mL I}_2}} \times \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{\cancel{\text{mmol I}_2}}$$

$$= 0.04091 \text{ mmol Na}_2\text{S}_2\text{O}_3$$

The number of millimoles of CO can then be calculated by using the third stoichiometric ratio:

$$\text{amount CO} = (0.09083 - 0.04091) \cancel{\text{mmol Na}_2\text{S}_2\text{O}_3} \times \frac{5 \text{ mmol CO}}{2 \cancel{\text{mmol Na}_2\text{S}_2\text{O}_3}}$$

$$= 0.1248 \text{ mmol CO}$$

$$\text{mass CO} = 0.1248 \cancel{\text{mmol CO}} \times \frac{28.01 \text{ mg CO}}{\cancel{\text{mmol CO}}} = 3.4956 \text{ mg}$$

$$\frac{\text{mass CO}}{\text{vol sample}} = \frac{3.4956 \text{ mg CO}}{20.3 \text{ L sample}} = 0.172 \frac{\text{mg CO}}{\text{L sample}}$$

13D GRAVIMETRIC TITRATIONS

Mass (weight) or **gravimetric titrations** differ from their volumetric counterparts in that the mass of titrant is measured rather than the volume. Therefore, in a mass titration, a balance and a weighable solution dispenser are substituted for a buret and its markings. Gravimetric titrations actually predate volumetric titrations by more than 50 years. With the advent of reliable burets, however, mass titrations were largely supplanted by volumetric methods because the former required relatively elaborate equipment and were tedious and time consuming. The availability of sensitive, low-cost, top-loading digital analytical balances and convenient plastic solution dispensers has changed this situation completely, and mass titrations can now be performed as easily and rapidly as volumetric titrations.

Remember that for historical reasons we often refer to *weight* or *weighing*, but we really mean mass, although most of us cannot bring ourselves to say *massing*.

13D-1 Calculations Associated with Mass Titrations

The most common way to express concentration for mass titrations is the **weight concentration**, c_w, in weight molar concentration units, M_w, which is the number of moles of a reagent in one kilogram of solution or the number of millimoles in one gram of solution. Thus, aqueous 0.1 M_w NaCl contains 0.1 mol of the salt in 1 kg of solution or 0.1 mmol in 1 g of the solution.

The weight molar concentration $c_w(A)$ of a solution of a solute A is computed using either one of two equations that are analogous to Equation 4-2:

$$\text{weight molar concentration} = \frac{\text{no. mol A}}{\text{no. kg solution}} = \frac{\text{no. mmol A}}{\text{no. g solution}} \tag{13-5}$$

$$c_w(A) = \frac{n_A}{m_{soln}}$$

where n_A is the number of moles of species A and m_{soln} is the mass of the solution. Gravimetric titration data can then be treated by using the methods illustrated in Sections 13C-2 and 13C-3 after substitution of weight concentration for molar concentration and grams and kilograms for milliliters and liters.

13D-2 Advantages of Gravimetric Titrations

In addition to greater speed and convenience, mass titrations offer certain other advantages over their volumetric counterparts:

1. Calibration of glassware and tedious cleaning to ensure proper drainage are completely eliminated.
2. Temperature corrections are unnecessary because the mass (weight) molar concentration does not change with temperature, in contrast to the volume molar concentration. This advantage is particularly important in nonaqueous titrations because of the high coefficients of expansion of most organic liquids (about 10 times that of water).
3. Mass measurements can be made with considerably greater precision and accuracy than can volume measurements. For example, 50 g or 100 g of an aqueous solution can be readily measured to ±1 mg, which corresponds to ±0.001 mL. This greater sensitivity makes it possible to choose sample sizes that lead to significantly smaller consumption of standard reagents.
4. Gravimetric titrations are more easily automated than are volumetric titrations.

13E TITRATION CURVES

As noted in Section 13A-1, an end point is signaled by an observable physical change near the equivalence point of a titration. The two most widely used signals involve (1) changes in color due to the reagent (titrant), the analyte, or an indicator and (2) a change in potential of an electrode that responds to the titrant concentration or the analyte concentration.

To understand the theoretical basis of end point determinations and the sources of titration errors, we calculate the data points necessary to construct **titration curves** for the systems under consideration. A titration curve is a plot of some function of the analyte or titrant concentration on the y axis versus titrant volume on the x axis.

Titration curves are plots of a concentration-related variable versus titrant volume.

13E-1 Types of Titration Curves

The vertical axis in a sigmoidal titration curve is either the p-function of the analyte or titrant or the potential of an analyte- or titrant-sensitive electrode.

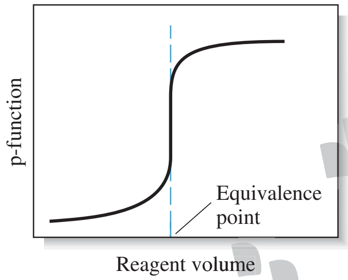
The vertical axis of a linear-segment titration curve is an instrument signal that is proportional to the concentration of the analyte or titrant.

Two general types of titration curves (and thus two general types of end points) occur in titrimetric methods. In the first type, called a sigmoidal curve, important observations are confined to a small region (typically ±0.1 to ±0.5 mL) surrounding the equivalence point. A **sigmoidal curve** in which the p-function of analyte (or sometimes the titrant) is plotted as a function of titrant volume is shown in **Figure 13-2a**.

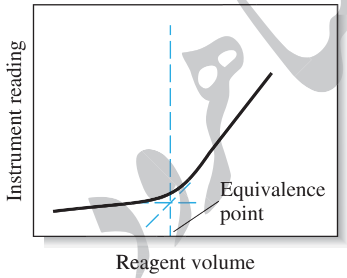
In the second type of curve, called a **linear segment curve**, measurements are made on both sides of, but well away from, the equivalence point. Measurements near equivalence are avoided. In this type of curve, the vertical axis represents an instrument reading that is directly proportional to the concentration of the analyte or the titrant. A typical linear segment curve is found in **Figure 13-2b**.

The sigmoidal type offers the advantages of speed and convenience. The linear segment type is advantageous for reactions that are complete only in the presence of a considerable excess of the reagent or analyte.

In this chapter and several that follow, we deal exclusively with sigmoidal titration curves. We explore linear segment curves in Chapters 23 and 26.



(a) Sigmoidal curve



(b) Linear segment curve

Figure 13-2 Two types of titration curves.

13E-2 Concentration Changes During Titrations

The equivalence point in a titration is characterized by major changes in the *relative* concentrations of reagent and analyte. **Table 13-1** illustrates this phenomenon. The data in the second column of the table show the changes in the hydronium ion concentration as a 50.00-mL aliquot of a 0.1000 M solution of hydrochloric acid is titrated with 0.1000 M sodium hydroxide. The neutralization reaction is described by the equation

$$H_3O^+ + OH^- \rightarrow 2H_2O \tag{13-6}$$

To emphasize the changes in *relative* concentration that occur in the equivalence point region, the volume increments computed are those required to cause tenfold decreases in the concentration of H_3O^+ (or tenfold increases in hydroxide ion concentration). Thus, we see in the third column that an addition of 40.91 mL of base is needed to decrease the concentration of H_3O^+ by one order of magnitude from 0.100 M to 0.0100 M. An addition of only 8.11 mL is required to lower the concentration by another factor of 10 to 0.00100 M; 0.89 mL causes yet another tenfold decrease. Corresponding increases in OH^- concentration occur at the same time. End-point detection then depends on this large change in the *relative* concentration of the analyte (or titrant) that occurs at the equivalence point for every type of titration. Feature 13-3 describes how the volumes in the first column of Table 13-1 are calculated.

The large changes in relative concentration that occur in the region of chemical equivalence are shown by plotting the negative logarithm of the analyte or the titrant concentration (the p-function) against reagent volume, as seen in **Figure 13-3**. The data for these plots are found in the fourth and fifth columns of Table 13-1. Titration curves for reactions involving complex formation, precipitation, and oxidation/reduction all exhibit the same sharp increase or decrease in p-function in the equivalence-point region as those shown in Figure 13-3. Titration curves define the properties required of an indicator or instrument and allow us to estimate the error associated with titration methods.

TABLE 13-1

Concentration Changes During a Titration of 50.00 mL of 0.1000 M HCl

Volume of 0.1000 M NaOH, mL	$[H_3O^+]$, mol/L	Volume of 0.1000 M NaOH to Cause a Tenfold Decrease in $[H_3O^+]$, mL	pH	pOH
0.00	0.1000		1.00	13.00
40.91	0.0100	40.91	2.00	12.00
49.01	1.000×10^{-3}	8.11	3.00	11.00
49.90	1.000×10^{-4}	0.89	4.00	10.00
49.99	1.000×10^{-5}	0.09	5.00	9.00
49.999	1.000×10^{-6}	0.009	6.00	8.00
50.00	1.000×10^{-7}	0.001	7.00	7.00
50.001	1.000×10^{-8}	0.001	8.00	6.00
50.01	1.000×10^{-9}	0.009	9.00	5.00
50.10	1.000×10^{-10}	0.09	10.00	4.00
51.10	1.000×10^{-11}	0.91	11.00	3.00
61.11	1.000×10^{-12}	10.10	12.00	2.00

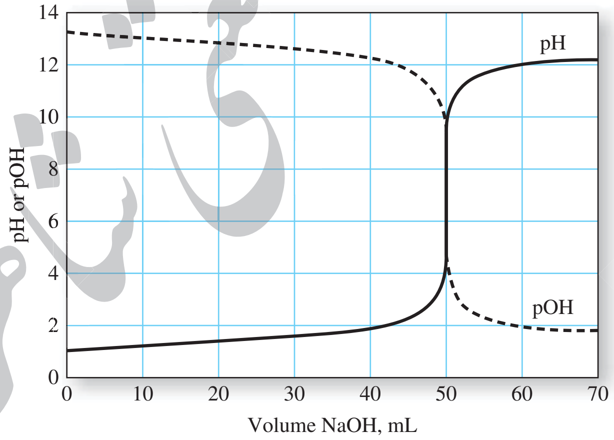


Figure 13-3 Titration curves of pH and pOH versus volume of base for the titration of 0.1000 M HCl with 0.1000 M NaOH.

FEATURE 13-3

Calculating the NaOH Volumes Shown in the First Column of Table 13-1

Prior to the equivalence point, $[H_3O^+]$ equals the concentration of unreacted HCl (c_{HCl}). The concentration of HCl is equal to the original number of millimoles of HCl (50.00 mL × 0.1000 M) minus the number of millimoles of NaOH added (V_{NaOH} × 0.1000 M) divided by the total volume of the solution:

$$c_{HCl} = [H_3O^+] = \frac{50.00 \times 0.1000 - V_{NaOH} \times 0.1000}{50.00 + V_{NaOH}}$$

where V_{NaOH} is the volume of 0.1000 M NaOH added. This equation reduces to

$$50.00[H_3O^+] + V_{NaOH}[H_3O^+] = 5.000 - 0.1000V_{NaOH}$$

Collecting the terms containing V_{NaOH} gives

$$V_{NaOH}(0.1000 + [H_3O^+]) = 5.000 - 50.00[H_3O^+]$$

(continued)

or

$$V_{\text{NaOH}} = \frac{5.000 - 50.00[\text{H}_3\text{O}^+]}{0.1000 + [\text{H}_3\text{O}^+]}$$

Thus to obtain $[\text{H}_3\text{O}^+] = 0.0100$ M, we find

$$V_{\text{NaOH}} = \frac{5.000 - 50.00 \times 0.0100}{0.1000 + 0.0100} = 40.91 \text{ mL}$$

Challenge: Use the same reasoning to show that beyond the equivalence point,

$$V_{\text{NaOH}} = \frac{50.000[\text{OH}^-] + 5.000}{0.1000 - [\text{OH}^-]}$$

Spreadsheet Summary Chapter 7 of *Applications of Microsoft® Excel in Analytical Chemistry,* 2nd ed., deals with plotting titration curves. Several types of titrations are presented and ordinary titration curves are plotted along with derivative plots and Gran plots. The stoichiometric approach developed in this chapter is used and a master equation approach is explored.

WEB WORKS

Look up *titration* in Wikipedia, the online encyclopedia. Give the definition of titration found there. Is a chemical reaction necessary for a quantitative procedure to be called a titration? From what Latin word does titration derive? Who developed the first buret and in what year? List five different methods to determine the end point of a titration. Define the term *acid number*, also called the *acid value*. How are titrations applied to biodiesel fuels?

QUESTIONS AND PROBLEMS

13-1. Define
- *(a) millimole.
- (b) titration.
- *(c) stoichiometric ratio.
- (d) titration error.

13-2. Write two equations that—along with the stoichiometric factor—form the basis for the calculations of volumetric titrations.

13-3. Distinguish between
- *(a) the equivalence point and the end point of a titration.
- (b) a primary standard and a secondary standard.

13-4. Briefly explain why the concentration units of milligrams of solute per liter and parts per million can be used interchangeably for a dilute aqueous solution.

13-5. Calculations of volumetric analysis ordinarily consist of transforming the quantity of titrant used (in chemical units) to a chemically equivalent quantity of analyte (also in chemical units) through use of a stoichiometric factor. Use chemical formulas (NO CALCULATIONS REQUIRED) to express this ratio for calculation of the percentage of
- *(a) hydrazine in rocket fuel by titration with standard iodine. Reaction:

$$\text{H}_2\text{NNH}_2 + 2\text{I}_2 \rightarrow \text{N}_2(g) + 4\text{I}^- + 4\text{H}^+$$

- (b) hydrogen peroxide in a cosmetic preparation by titration with standard permanganate. Reaction:

$$5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2(g) + 8\text{H}_2\text{O}$$

- *(c) boron in a sample of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, by titration with standard acid. Reaction:

$$\text{B}_4\text{O}_7^{2-} + 2\text{H}^+ + 5\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{BO}_3$$

(d) sulfur in an agricultural spray that was converted to thiocyanate with an unmeasured excess of cyanide. Reaction:

$$S(s) + CN^- \rightarrow SCN^-$$

After removal of the excess cyanide, the thiocyanate was titrated with a standard potassium iodate solution in strong HCl. Reaction:

$$2SCN^- + 3IO_3^- + 2H^+ + 6Cl^- \rightarrow$$
$$2SO_4^{2-} + 2CN^- + 3ICl_2^- + H_2O$$

13-6. How many millimoles of solute are contained in
(a) 2.00 L of 2.76×10^{-3} M $KMnO_4$?
(b) 250.0 mL of 0.0423 M KSCN?
(c) 500.0 mL of a solution containing 2.97 ppm $CuSO_4$?
(d) 2.50 L of 0.352 M KCl?

***13-7.** How many millimoles of solute are contained in
(a) 2.95 mL of 0.0789 M KH_2PO_4?
(b) 0.2011 L of 0.0564 M $HgCl_2$?
(c) 2.56 L of a 47.5 ppm solution of $Mg(NO_3)_2$?
(d) 79.8 mL of 0.1379 M NH_4VO_3 (116.98 g/mol)?

13-8. What mass of solute in milligrams is contained in
(a) 26.0 mL of 0.250 M sucrose (342 g/mol)?
(b) 2.92 L of 5.23×10^{-4} M H_2O_2?
(c) 673 mL of a solution that contains 5.76 ppm $Pb(NO_3)_2$ (331.20 g/mol)?
(d) 6.75 mL of 0.0426 M KNO_3?

***13-9.** What mass of solute in grams is contained in
(a) 450.0 mL of 0.0986 M H_2O_2?
(b) 26.4 mL of 9.36×10^{-4} M benzoic acid (122.1 g/mol)?
(c) 2.50 L of a solution that contains 23.4 ppm $SnCl_2$?
(d) 21.7 mL of 0.0214 M $KBrO_3$?

13-10. Calculate the molar concentration of a solution that is 50.0% NaOH (w/w) and has a specific gravity of 1.52.

***13-11.** Calculate the molar concentration of a 20.0% solution (w/w) of KCl that has a specific gravity of 1.13.

13-12. Describe the preparation of
(a) 500 mL of 0.0750 M $AgNO_3$ from the solid reagent.
(b) 2.00 L of 0.325 M HCl, starting with a 6.00 M solution of the reagent.
(c) 750 mL of a solution that is 0.0900 M in K^+, starting with solid $K_4Fe(CN)_6$.
(d) 600 mL of 2.00% (w/v) aqueous $BaCl_2$ from a 0.500 M $BaCl_2$ solution.
(e) 2.00 L of 0.120 M $HClO_4$ from the commercial reagent [60% $HClO_4$ (w/w), sp gr 1.60].
(f) 9.00 L of a solution that is 60.0 ppm in Na^+, starting with solid Na_2SO_4.

***13-13.** Describe the preparation of
(a) 1.00 L of 0.150 M $KMnO_4$ from the solid reagent.
(b) 2.50 L of 0.500 M $HClO_4$, starting with a 9.00 M solution of the reagent.
(c) 400 mL of a solution that is 0.0500 M in I^-, starting with MgI_2.
(d) 200 mL of 1.00% (w/v) aqueous $CuSO_4$ from a 0.218 M $CuSO_4$ solution.
(e) 1.50 L of 0.215 M NaOH from the concentrated commercial reagent [50% NaOH (w/w), sp gr 1.525].
(f) 1.50 L of a solution that is 12.0 ppm in K^+, starting with solid $K_4Fe(CN)_6$.

13-14. A solution of $HClO_4$ was standardized by dissolving 0.4008 g of primary-standard-grade HgO in a solution of KBr:

$$HgO(s) + 4Br^- + H_2O \rightarrow HgBr_4^{2-} + 2OH^-$$

The liberated OH^- consumed 43.75 mL of the acid. Calculate the molar concentration of the $HClO_4$.

***13-15.** A 0.4723-g sample of primary-standard-grade Na_2CO_3 required 34.78 mL of an H_2SO_4 solution to reach the end point in the reaction

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2(g)$$

What is the molar concentration of the H_2SO_4?

13-16. A 0.5002-g sample that assayed 96.4% Na_2SO_4 required 48.63 mL of a barium chloride solution. Reaction:

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

Calculate the analytical molar concentration of $BaCl_2$ in the solution.

***13-17.** A 0.4126-g sample of primary-standard Na_2CO_3 was treated with 40.00 mL of dilute perchloric acid. The solution was boiled to remove CO_2, following which the excess $HClO_4$ was back-titrated with 9.20 mL of dilute NaOH. In a separate experiment, it was established that 26.93 mL of the $HClO_4$ neutralized the NaOH in a 25.00-mL portion. Calculate the molarities of the $HClO_4$ and NaOH.

مسئله
13-13
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13-18. Titration of 50.00 mL of 0.04715 M $Na_2C_2O_4$ required 39.25 mL of a potassium permanganate solution.

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

Calculate the molar concentration of the $KMnO_4$ solution.

***13-19.** Titration of the I_2 produced from 0.1142 g of primary-standard KIO_3 required 27.95 mL of sodium thiosulfate.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate the concentration of the $Na_2S_2O_3$.

13-20. A 4.912-g sample of a petroleum product was burned in a tube furnace, and the SO_2 produced was collected in 3% H_2O_2. Reaction:

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

A 25.00-mL portion of 0.00873 M NaOH was introduced into the solution of H_2SO_4, following which the excess base was back-titrated with 15.17 mL of 0.01102 M HCl. Calculate the sulfur concentration in the sample in parts per million.

***13-21.** A 100.0-mL sample of spring water was treated to convert any iron present to Fe^{2+}. Addition of 25.00-mL of 0.002517 M $K_2Cr_2O_7$ resulted in the reaction

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow$$
$$6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The excess $K_2Cr_2O_7$ was back-titrated with 8.53 mL of 0.00949 M Fe^{2+} solution. Calculate the concentration of iron in the sample in parts per million.

13-22. The arsenic in a 1.203-g sample of a pesticide was converted to H_3AsO_4 by suitable treatment. The acid was then neutralized, and 40.00 mL of 0.05871 M $AgNO_3$ was added to precipitate the arsenic quantitatively as Ag_3AsO_4. The excess Ag^+ in the filtrate and in the washings from the precipitate was titrated with 9.63 mL of 0.1000 M KSCN, and the reaction was

13-18

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

Find the percentage of As_2O_3 in the sample.

***13-23.** The thiourea in a 1.455-g sample of organic material was extracted into a dilute H_2SO_4 solution and titrated with 37.31 mL of 0.009372 M Hg^{2+} via the reaction

$$4(NH_2)_2CS + Hg^{2+} \rightarrow [(NH_2)_2CS]_4Hg^{2+}$$

Find the percentage of $(NH_2)_2CS$ (76.12 g/mol) in the sample.

13-24. A solution of $Ba(OH)_2$ was standardized against 0.1215 g of primary-standard-grade benzoic acid, C_6H_5COOH (122.12 g/mol). An end point was observed after addition of 43.25 mL of base.

13-21

(a) Calculate the molar concentration of the base.
(b) Calculate the standard deviation of the molar concentration if the standard deviation for the mass measurement was ±0.3 mg and that for the volume measurement was ±0.02 mL.
(c) Assuming an error of −0.3 mg in the mass measurement, calculate the absolute and relative systematic error in the molar concentration.

***13-25.** The ethyl acetate concentration in an alcoholic solution was determined by diluting a 10.00-mL sample to 100.00 mL. A 20.00-mL portion of the diluted solution was refluxed with 40.00 mL of 0.04672 M KOH:

$$CH_3COOC_2H_5 + OH^- \rightarrow$$
$$CH_3COO^- + C_2H_5OH$$

After cooling, the excess OH^- was back-titrated with 3.41 mL of 0.05042 M H_2SO_4. Calculate the amount of ethyl acetate (88.11 g/mol) in the original sample in grams.

13-26. A 0.1475-M solution of $Ba(OH)_2$ was used to titrate the acetic acid (60.05 g/mol) in a dilute aqueous solution. The following results were obtained.

Sample	Sample Volume, mL	$Ba(OH)_2$ Volume, mL
1	50.00	43.17
2	49.50	42.68
3	25.00	21.47
4	50.00	43.33

(a) Calculate the mean w/v percentage of acetic acid in the sample.
(b) Calculate the standard deviation for the results.
(c) Calculate the 90% confidence interval for the mean.
(d) At the 90% confidence level, could any of the results be discarded?

***13-27.** (a) A 0.3147-g sample of primary-standard-grade $Na_2C_2O_4$ was dissolved in H_2SO_4 and titrated with 31.67 mL of dilute $KMnO_4$:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$$
$$2Mn^{2+} + 10CO_2(g) + 8H_2O$$

Calculate the molar concentration of the $KMnO_4$ solution.

(b) The iron in a 0.6656-g ore sample was reduced quantitatively to the +2 state and then titrated with 26.75 mL of the $KMnO_4$ solution from part (a). Calculate the percent Fe_2O_3 in the sample.

13-28. (a) A 0.1527-g sample of primary-standard $AgNO_3$ was dissolved in 502.3 g of distilled water.

Calculate the weight molar concentration of Ag^+ in this solution.

(b) The standard solution described in part (a) was used to titrate a 25.171-g sample of a KSCN solution. An end point was obtained after adding 24.615 g of the $AgNO_3$ solution. Calculate the weight molar concentration of the KSCN solution.

(c) The solutions described in parts (a) and (b) were used to determine the $BaCl_2 \cdot 2H_2O$ in a 0.7120-g sample. A 20.102-g sample of the $AgNO_3$ was added to a solution of the sample, and the excess $AgNO_3$ was back-titrated with 7.543 g of the KSCN solution. Calculate the percent $BaCl_2 \cdot 2H_2O$ in the sample.

***13-29.** A solution was prepared by dissolving 7.48 g of $KCl \cdot MgCl_2 \cdot 6H_2O$ (277.85 g/mol) in sufficient water to give 2.000 L. Calculate

(a) the molar analytical concentration of $KCl \cdot MgCl_2$ in this solution.

(b) the molar concentration of Mg^{2+}.

(c) the molar concentration of Cl^-.

(d) the weight/volume percentage of $KCl \cdot MgCl_2 \cdot 6H_2O$.

(e) the number of millimoles of Cl^- in 25.0 mL of this solution.

(f) the concentration of K^+ in ppm.

13-30. A solution was prepared by dissolving 367 mg of $K_3Fe(CN)_6$ (329.2 g/mol) in sufficient water to give 750.0 mL. Calculate

(a) the molar analytical concentration of $K_3Fe(CN)_6$.

(b) the molar concentration of K^+.

(c) the molar concentration of $Fe(CN)_6^{3-}$.

(d) the weight/volume percentage of $K_3Fe(CN)_6$.

(e) the number of millimoles of K^+ in 50.0 mL of this solution.

(f) the concentration of $Fe(CN)_6^{3-}$ in ppm.

13-31. **Challenge Problem:** For each of the following acid/base titrations, calculate the H_3O^+ and OH^- concentrations at equivalence and at titrant volumes corresponding to ±20.00 mL, ±10.00 mL, and ±1.00 mL of equivalence. Construct a titration curve from the data, plotting the p-function versus titrant volume.

(a) 25.00 mL of 0.05000 M HCl with 0.02500 M NaOH.

(b) 20.00 mL of 0.06000 M HCl with 0.03000 M NaOH.

(c) 30.00 mL of 0.07500 M H_2SO_4 with 0.1000 M NaOH.

(d) 40.00 mL of 0.02500 M NaOH with 0.05000 M HCl.

(e) 35.00 mL of 0.2000 M Na_2CO_3 with 0.2000 M HCl.

FEATURE 17-2

Determination of Hydrogen Cyanide in Acrylonitrile Plant Streams

Acrylonitrile, $CH_2{=}CH{-}C{\equiv}N$, is an important chemical in the production of polyacrylonitrile. This thermoplastic was drawn into fine threads and woven into synthetic fabrics such as Orlon, Acrilan, and Creslan. Although acrylic fibers are no longer produced in the US, they are still made in many countries. Hydrogen cyanide is an impurity in the plant streams that carry aqueous acrylonitrile. The cyanide is commonly determined by titration with $AgNO_3$. The titration reaction is

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

In order to determine the end point of the titration, the aqueous sample is mixed with a basic solution of potassium iodide before the titration. Before the equivalence point, cyanide is in excess, and all the Ag^+ is complexed. As soon as all the cyanide has been reacted, the first excess of Ag^+ causes a permanent turbidity to appear in the solution because of the formation of the AgI precipitate according to

$$Ag^+ + I^- \rightarrow AgI(s)$$

10^8. Curve *C* involves a unidentate ligand, A, that forms MA_4 in four steps with successive formation constants of 10^8, 10^6, 10^4, and 10^2. These curves demonstrate that a much sharper end point is obtained with a reaction that takes place in a single step. For this reason, multidentate ligands are usually preferred for complexometric titrations.

The most widely used complexometric titration with a unidentate ligand is the titration of cyanide with silver nitrate, a method introduced by Liebig in the 1850s. This method involves the formation of soluble $Ag(CN)_2^-$, as discussed in Feature 17-2. Other common inorganic complexing agents and their applications are listed in Table 17-1.

Spreadsheet Summary The complexometric titration of Cd(II) with Cl^- is considered in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. A master equation approach is used.

17B-2 Precipitation Titrations

Precipitation titrations are based on reactions that yield ionic compounds of limited solubility. Precipitation titrimetry is one of the oldest analytical techniques, dating back to the mid-1800s. The slow rate at which most precipitates form, however, limits the number of precipitating agents that can be used in titrations to a handful. We limit our discussion here to the most widely used and important precipitating reagent, silver nitrate, which is used for the determination of the halogens, the

مهمترین واکنشگر رسوب دهنده

TABLE 17-1

Typical Inorganic Complex-Forming Titrations

Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is AgI; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions. Titrations with silver nitrate are sometimes called **argentometric titrations**.

The Shapes of Titration Curves

شکل منحنی مشابه منحنی تیتراسیون اسید قوی/باز قوی

Titration curves for precipitation reactions are calculated in a completely analogous way to the methods described in Section 14B for titrations involving strong acids and strong bases. The only difference is that the solubility product of the precipitate is substituted for the ion-product constant for water. Most indicators for argentometric titrations respond to changes in the concentrations of silver ions. Because of this response, titration curves for precipitation reactions usually consist of a plot of pAg versus volume of the silver reagent (usually $AgNO_3$). Example 17-1 illustrates how p-functions are obtained for the preequivalence-point region, the postequivalence-point region, and the equivalence point for a typical precipitation titration.

محاسبه $[Ag^+]$ طی تیتراسیون سدیم کلرید با نقره نیترات

EXAMPLE 17-1

ابتدا بایستی حجم نقطه هم ارزی محاسبه شود. $N_1V_1=N_2V_2$

Calculate the silver ion concentration in terms of pAg during the titration of 50.00 mL of 0.05000 M NaCl with 0.1000 M $AgNO_3$ after the addition of the following volumes of reagent: (a) in the preequivalence point region at 10.00 mL, (b) at the equivalence point (25.00 mL), (c) after the equivalence point at 26.00 mL. For AgCl, $K_{sp} = 1.82 \times 10^{-10}$.

Solution

نقاط پیش هم ارزی:
رسوب AgCl و Cl^- اضافی

(a) Preequivalence-Point Data

At 10.00 mL, $[Ag^+]$ is very small and cannot be computed from stoichiometric considerations, but the molar concentration of chloride, c_{NaCl} can be obtained readily. The equilibrium concentration of chloride is essentially equal to c_{NaCl}.

$$[Cl^-] \approx c_{NaCl} = \frac{\text{original no. mmol } Cl^- - \text{no. mol } AgNO_3 \text{ added}}{\text{total volume of solution}}$$

$$= \frac{(50.00 \times 0.05000 - 10.00 \times 0.1000)}{50.00 + 10.00} = 0.02500\ M$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}\ M$$

$$pAg = -\log(7.28 \times 10^{-9}) = 8.14$$

Additional points in the preequivalence-point region can be obtained in the same way. Results of calculations of this kind are shown in the second column of Table 17-2.

TABLE 17-2

Changes in pAg in Titration of Cl^- with Standard $AgNO_3$

Volume of $AgNO_3$	pAg 50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$	pAg 50.00 mL of 0.005 M NaCl with 0.0100 M $AgNO_3$
10.00	8.14	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

نقطه هم ارزی:
محلول از رسوب سیرشده است و حاوی یون مشترک (اضافی) نیست.

(b) Equivalence Point pAg
At the equivalence point, $[Ag^+] = [Cl^-]$, and $[Ag^+][Cl^-] = K_{sp} = 1.82 \times 10^{-10} = [Ag^+]^2$

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}$$

$$pAg = -\log(1.35 \times 10^{-5}) = 4.87$$

(c) Postequivalence-Point Region
At 26.00 mL of $AgNO_3$, Ag^+ is in excess so

نقاط پس هم ارزی:
محلول حاوی رسوب و Ag^+ زیادی است

$$[Ag^+] = c_{AgNO_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.05000)}{76.00} = 1.32 \times 10^{-3}\ M$$

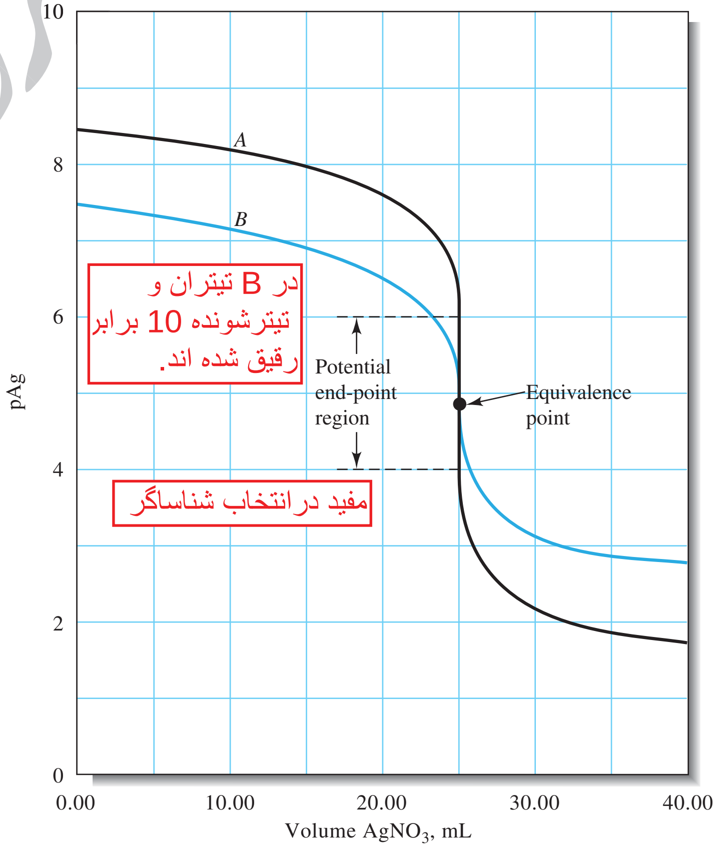
$$pAg = -\log(1.32 \times 10^{-3}) = 2.88$$

به نظر شما آیا از تقریب استفاده شده است؟

Additional results in the postequivalence-point region are obtained in the same way and are shown in Table 17-2. The titration curve can also be derived from the charge-balance equation as shown for an acid/base titration in Feature 14-1.

The Effect of Concentration on Titration Curves

The effect of reagent and analyte concentration on titration curves can be seen in the data in Table 17-2 and the two curves shown in **Figure 17-2**. With 0.1000 M $AgNO_3$ (Curve *A*), the change in pAg in the equivalence-point region is large, about 2 pAg units. With the 0.01000 M reagent, the change is about 1 pAg unit, but still pronounced. An indicator that produces a signal in the 4.0 to 6.0 pAg region should give a minimal error for the stronger solution. For the more dilute chloride solution (Curve *B*), the change in pAg in the equivalence-point region would be drawn out over a fairly large volume of reagent (~3 mL as shown by the dashed lines in the



در B تیتران و تیترشونده 10 برابر رقیق شده اند.

مفید در انتخاب شناساگر

Figure 17-2 Titration curve for (*A*), 50.00 mL of 0.05000 M NaCl titrated with 0.1000 M $AgNO_3$, and (*B*), 50.00 mL of 0.00500 M NaCl titrated with 0.01000 M $AgNO_3$. Note the increased sharpness of the break at the end point with the more concentrated solution.

figure) so that to determine the end point accurately would be impossible. The effect here is analogous to that illustrated for acid/base titrations in Figure 14-4.

The Effect of Reaction Completeness on Titration Curves

اثر کامل بودن واکنش

Figure 17-3 illustrates the effect of solubility product on the sharpness of the end point for titrations with 0.1 M silver nitrate. Note that the change in pAg at the equivalence point becomes greater as the solubility products become smaller, that is, as the reaction between the analyte and silver nitrate becomes more complete. By choosing an indicator that changes color in the pAg region of 4 to 6, titration of chloride ions should be possible with a minimal titration error. Note that ions forming precipitates with solubility products much larger than about 10^{-10} do not yield satisfactory end points.

A useful relationship can be derived by taking the negative logarithm of both sides of a solubility-product expression. Thus, for silver chloride,

$$-\log K_{sp} = -\log([Ag^+][Cl^-])$$
$$= -\log[Ag^+] - \log[Cl^-]$$

$$pK_{sp} = pAg + pCl$$

This expression is similar to the acid-base expression for pK_w

$$pK_w = pH + pOH$$

Titration Curves for Mixtures of Anions

تکلیف گروهی:
منحنی کالیبراسیون مخلوط آنیون ها

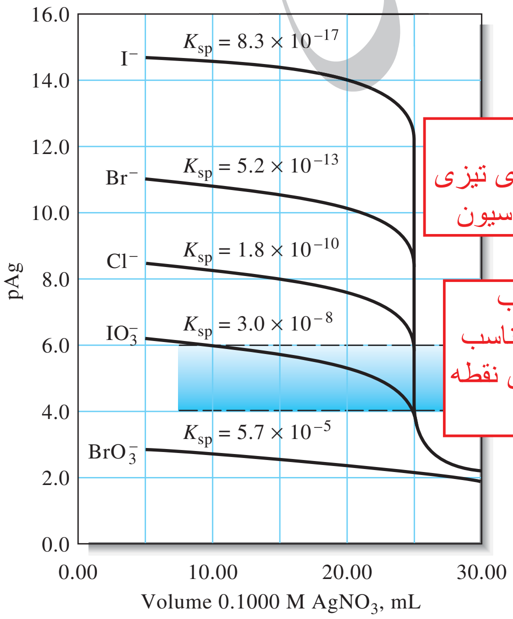
The methods developed in Example 17-1 for constructing precipitation titration curves can be extended to mixtures that form precipitates of different solubilities. To illustrate, consider 50.00 mL of a solution that is 0.0500 M in iodide ion and 0.0800 M in chloride ion titrated with 0.1000 M silver nitrate. The curve for the initial stages of this titration is identical to the curve shown for iodide in Figure 17-3 because silver chloride, with its much larger solubility product, does not begin to precipitate until well into the titration.

It is interesting to determine how much iodide is precipitated before appreciable amounts of silver chloride form. With the appearance of the smallest amount of solid silver chloride, the solubility-product expressions for both precipitates apply, and division of one by the other provides the useful relationship

$$\frac{K_{sp}(\text{AgI})}{K_{sp}(\text{AgCl})} = \frac{\cancel{[Ag^+]}[I^-]}{\cancel{[Ag^+]}[Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7}$$

$$[I^-] = (4.56 \times 10^{-7})[Cl^-]$$

From this relationship, we see that the iodide concentration decreases to a tiny fraction of the chloride ion concentration before silver chloride begins to precipitate.



شکل 17-3:
اثر Ksp روی تیزی منحنی کالیبراسیون

لزوم انتخاب شناساگر مناسب برای تعیین نقطه اکی والان

Figure 17-3 Effect of reaction completeness on precipitation titration curves. For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M $AgNO_3$. Note that smaller values of K_{sp} give much sharper breaks at the end point.

So, for all practical purposes, silver chloride forms only after 25.00 mL of titrant have been added in this titration. At this point, the chloride ion concentration is approximately

$$c_{\mathrm{Cl}^-} \approx [\mathrm{Cl}^-] = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533\ \mathrm{M}$$

Substituting into the previous equation yields

$$[\mathrm{I}^-] = 4.56 \times 10^{-7}[\mathrm{Cl}^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8}\ \mathrm{M}$$

The percentage of iodide unprecipitated at this point can be calculated as follows:

$$\text{amount I}^-\text{unprecipitated} = (75.00\,\cancel{\mathrm{mL}})(2.43 \times 10^{-8}\,\mathrm{mmol\,I}^-/\cancel{\mathrm{mL}}) = 1.82 \times 10^{-6}\,\mathrm{mmol}$$

$$\text{original amount I}^- = (50.00\ \cancel{\mathrm{mL}})(0.0500\ \mathrm{mmol}/\cancel{\mathrm{mL}}) = 2.50\ \mathrm{mmol}$$

$$\text{percentage I}^-\text{ unprecipitated} = \frac{1.82 \times 10^{-6}}{2.50} \times 100\% = 7.3 \times 10^{-5}\%$$

Thus, to within about 7.3×10^{-5} percent of the equivalence point for iodide, no silver chloride forms. Up to this point, the titration curve is indistinguishable from that for iodide alone, as shown in **Figure 17-4**. The data points for the first part of the titration curve, shown by the solid line, were computed on this basis.

As chloride ion begins to precipitate, however, the rapid decrease in pAg ends abruptly at a level that can be calculated from the solubility product for silver chloride and the computed chloride concentration (0.0533 M):

$$[\mathrm{Ag}^+] = \frac{K_{\mathrm{sp}}(\mathrm{AgCl})}{[\mathrm{Cl}^-]} = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9}\ \mathrm{M}$$

$$\mathrm{pAg} = -\log(3.41 \times 10^{-9}) = \boxed{8.47}$$

The sudden end to the sharp decrease in $[\mathrm{Ag}^+]$ can be clearly seen in Figure 17-4 at pAg = 8.47. Further additions of silver nitrate decrease the chloride ion concentration, and the curve then becomes that for the titration of chloride by itself.

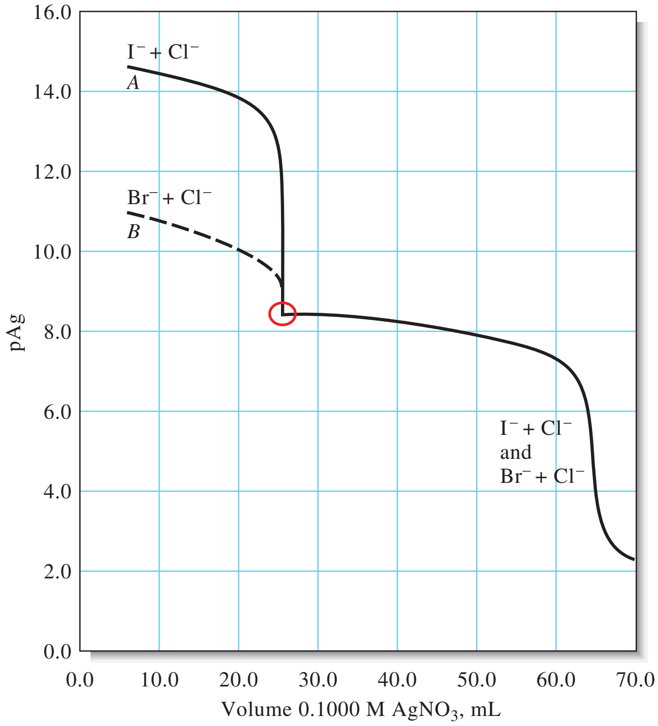


Figure 17-4 Titration curves for 50.00 mL of a solution 0.0800 M in Cl^- and 0.0500 M in I^- or Br^-.

For example, after 30.00 mL of titrant have been added,

$$c_{\text{Cl}^-} = [\text{Cl}^-] = \frac{50.00 \times 0.0800 + 50.00 \times 0.0500 - 30.00 \times 0.100}{50.00 + 30.00} = 0.0438\,\text{M}$$

In this expression, the first two terms in the numerator give the number of millimoles of chloride and iodide, respectively, and the third term is the number of millimoles of titrant. Therefore,

$$[\text{Ag}^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}\ \text{M}$$

$$\text{pAg} = 8.38$$

The remainder of the data points for this curve can be computed in the same way as for a curve of chloride by itself.

Curve *A* in Figure 17-4, which is the titration curve for the chloride/iodide mixture just considered, is a composite of the individual curves for the two anionic species. Two equivalence points are evident. Curve *B* is the titration curve for a mixture of bromide and chloride ions. Note that the change associated with the first equivalence point becomes less distinct as the solubilities of the two precipitates approach one another. In the bromide/chloride titration, the initial pAg values are lower than they are in the iodide/chloride titration because the solubility of silver bromide exceeds that of silver iodide. Beyond the first equivalence point, however, where chloride ion is being titrated, the two titration curves are identical.

Titration curves similar to those in Figure 17-4 can be obtained experimentally by measuring the potential of a silver electrode immersed in the analyte solution (see Section 21C). These curves can then be use to determine the concentration of each of the ions in mixtures of two halide ions.

استفاده عملی در تعیین مخلوط آنیون ها با
به دست آوردن نقاط اکی والان در منحنی
با روش تیتراسیون پتانسیومتری

End Points for Argentometric Titrations

Chemical, potentiometric, and amperometric [illegible] silver nitrate. In this section, we describe one of the chemical indicator methods. In potentiometric titrations, the potential difference between a silver electrode and a reference electrode is measured as a function of titrant volume. Titration curves similar to those shown in Figures 17-2, 17-3, and 17-4 are obtained. Potentiometric titrations are discussed in Section 21C. In amperometric titrations, the current generated between a pair of silver electrodes is measured and plotted as a function of titrant volume. Amperometric methods are considered in Section 23B-4.

شناساگر بایستی دردامنه
محدودی از pAg درناحیه
تیز منحنی تغییر رنگ دهد.

Chemical indicators produce a color change or occasionally the appearance or disap[illegible]arance of turbidity in the solution being titrated. The requirements for an indicator for precipitation titration are that (1) the color change should occur over a limited range in p-function of the titrant or the analyte and (2) the color change should take place within the steep portion of the titration curve for the analyte. For example, in Figure 17-3, we see that the titration of iodide with any indicator providing a signal in the pAg range of about 4.0 to 12.0 should give a satisfactory end point. Note that, in contrast, the end-point signal for the titration of chloride would be limited to a pAg of about 4.0 to 6.0.

The Volhard Method. The Volhard method is one of the most common argentometric methods. In this method, silver ions are titrated with a standard solution of thiocyanate ion:

تیتران

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

Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion due to the formation of Fe(SCN)^{2+}.

The most important application of the Volhard method is the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution. The strongly acidic environment of the Volhard titration is a distinct advantage over other titrations of halide ions because such ions as carbonate, oxalate, and arsenate do not interfere. The silver salts of these ions are soluble in acidic media but only slightly soluble in neutral media.

Silver chloride is more soluble than silver thiocyanate. As a result, in chloride determinations using the Volhard method, the reaction

$$\text{AgCl}(s) + \text{SCN}^- \rightleftharpoons \text{AgSCN}(s) + \text{Cl}^-$$

occurs to a significant extent near the end of the back-titration. This reaction causes the end point to fade and results in overconsumption of thiocyanate ion. The resulting low results for chloride can be overcome by filtering the silver chloride before undertaking the back-titration. Filtration is not required for other halides because they form silver salts that are less soluble than silver thiocyanate.

تیتران Ag^+ است

Other Argentometric Methods. In the **Mohr method**, sodium chromate serves as the indicator for the argentometric titration of chloride, bromide, and cyanide ions. Silver ions react with chromate to form the brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region. The Mohr method is now rarely used because Cr(VI) is a carcinogen.

The **Fajans method** uses an **adsorption indicator**, an organic compound that adsorbs onto or desorbs from the surface of the solid in a precipitation titration. Ideally, the adsorption or desorption occurs near the equivalence point and results not only in a color change but also in the transfer of color from the solution to the solid or vice versa.

تیتران Ag^+ است

Adsorption indicators were first described by K. Fajans, a Polish chemist in 1926. Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the few precipitation titrations that form colloidal precipitates rapidly.

Spreadsheet Summary In Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., we plot a curve for the titration of NaCl with $AgNO_3$. A stoichiometric approach is first used and then a master equation approach is explored. Finally, the problem is inverted, and the volume needed to achieve a given pAg value is computed.

17C ORGANIC COMPLEXING AGENTS

Several different organic complexing agents have become important in analytical chemistry because of their inherent sensitivity and potential selectivity in reacting with metal ions. Organic reagents are particularly useful in precipitating metals, in binding metals so as to prevent interferences, in extracting metals from one solvent to another, and in forming complexes that absorb light for spectrophotometric determinations. The most useful organic reagents form chelate complexes with metal ions.

Many organic reagents are useful in converting metal ions into forms that can be readily extracted from water into an immiscible organic phase. Extractions are widely used to separate metals of interest from potential interfering ions and for achieving a concentrating effect by transfer of the metal into a phase of smaller volume. Extractions are applicable to much smaller amounts of metals than precipitations, and they avoid problems associated with coprecipitation. Separations by extraction are considered in Section 31C.

Several of the most widely used organic complexing agents for extractions are listed in Table 17-3. Some of these same reagents normally form insoluble species