

Titrimetric Methods

titrimetry involves measuring the volume of a solution of known concentration that is needed to react essentially completely with analyte

1- **A standard solution** (or a standard titrant) is a reagent of exactly known concentration that is used in a titrimetric analysis.

Titration is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete .

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

reagent is slow or when the standard solution lacks stability

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

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 to reach the equivalence point .

13A-2 Primary Standards

A **primary standard** is a highly purified compound that serves as a reference material in volumetric and mass titrimetric methods. The accuracy of a method is critically dependent on the properties of this compound. Important requirements for a primary standard are the following:

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.

13B STANDARD SOLUTIONS

Standard solutions play a central role in all titrimetric methods of analysis. Therefore, we need to 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

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; and
4. undergo a selective reaction with the analyte that can be described by a balanced equation.

13C-1 Some Useful Algebraic Relationships

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

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}} \quad (13-1)$$

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} \quad (13-2)$$

The second pair is derived from the definition of molar concentration. That is,

$$\text{amount A (mmol)} = V (\text{mL}) \times c_A (\text{mmol A/mL}) \quad (13-3)$$

$$\text{amount A (mol)} = V (\text{L}) \times c_A (\text{mol A/L}) \quad (13-4)$$

where V is the volume of the solution.

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

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.

Since the volume is in liters, we base our calculations on the mole rather than the millimole. Thus, to obtain the amount of AgNO_3 needed, we write

$$\begin{aligned}\text{amount AgNO}_3 &= V_{\text{soln}}(\text{L}) \times c_{\text{AgNO}_3}(\text{mol/L}) \\ &= 2.000 \text{ L} \times \frac{0.0500 \text{ mol Na}_2\text{CO}_3}{\text{L}} = 0.1000 \text{ mol AgNO}_3\end{aligned}$$

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

$$\begin{aligned}\text{mass AgNO}_3 &= 0.1000 \text{ mol AgNO}_3 \times \frac{169.87 \text{ g AgNO}_3}{\text{mol AgNO}_3} \\ &= 16.98 \text{ g AgNO}_3\end{aligned}$$

Therefore, the solution is prepared by dissolving 16.98 g of AgNO_3 in water and diluting to exactly 2.000 L.

EXAMPLE 13-2

A standard 0.0100 M solution of Na^+ is required to calibrate a flame photometric method to determine the element. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mol).

We wish to compute the mass of reagent required to give a species molarity of 0.0100. Here, 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

$$\begin{aligned}\text{amount Na}_2\text{CO}_3 &= 500 \text{ mL} \times \frac{0.0100 \text{ mmol Na}^+}{\text{mL}} \times \frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol Na}^+} \\ &= 2.50 \text{ mmol}\end{aligned}$$

From the definition of millimole, we write

$$\text{mass Na}_2\text{CO}_3 = 2.50 \text{ mmol Na}_2\text{CO}_3 \times 0.10599 \frac{\text{g Na}_2\text{CO}_3}{\text{mmol Na}_2\text{CO}_3} = 0.265 \text{ g}$$

The solution is therefore 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?

The number of millimoles of Na^+ taken from the concentrated solution must equal the number in the diluted 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 rearranges to

$$V_{\text{concd}} = \frac{V_{\text{dil}} \times c_{\text{dil}}}{c_{\text{concd}}} = \frac{50.0 \text{ mL} \times 0.00500 \text{ mmol Na}^+/\text{mL}}{0.0100 \text{ mmol Na}^+/\text{mL}} = 25.0 \text{ mL}$$

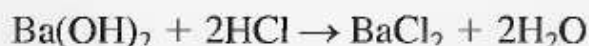
Thus, to produce 50.0 mL of 0.00500 M Na^+ , 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

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 solutions.

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 molarity of the HCl.

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



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 obtained by substituting into Equation 13-3:

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

To obtain the number of millimoles of HCl, we multiply this result by the stoichiometric ratio determined initially:

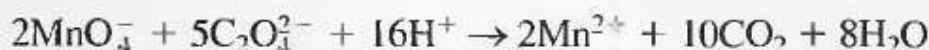
$$\text{amount HCl} = (29.71 \times 0.01963) \text{ mmol Ba(OH)}_2 \times \frac{2 \text{ mmol HCl}}{1 \text{ mmol Ba(OH)}_2}$$

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

$$\begin{aligned} c_{\text{HCl}} &= \frac{(29.71 \times 0.01963 \times 2) \text{ mmol HCl}}{50.0 \text{ mL HCl}} \\ &= 0.023328 \frac{\text{mmol HCl}}{\text{mL HCl}} = 0.02333 \text{ M} \end{aligned}$$

EXAMPLE 13-5

Titration of 0.2121 g of pure $\text{Na}_2\text{C}_2\text{O}_4$ (134.00 g/mol) required 43.31 mL of KMnO_4 . What is the molarity of the KMnO_4 solution? The chemical reaction is



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 $\text{Na}_2\text{C}_2\text{O}_4$ is given by Equation 13-1:

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

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

$$\text{amount KMnO}_4 = \frac{0.2121}{0.1340} \text{ mmol Na}_2\text{C}_2\text{O}_4 \times \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}$$

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

$$c_{\text{KMnO}_4} = \frac{\left(\frac{0.2121}{0.13400} \times \frac{2}{5} \right) \text{ mmol KMnO}_4}{43.31 \text{ mL KMnO}_4} = 0.01462 \text{ M}$$

EXAMPLE 13-6

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



(a) stoichiometric ratio = $\frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$

$$\text{amount KMnO}_4 = 47.22 \text{ mL KMnO}_4 \times \frac{0.02242 \text{ mmol KMnO}_4}{\text{mL KMnO}_4}$$

$$\text{amount Fe}^{2+} = (47.22 \times 0.02242) \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

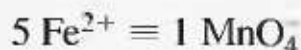
The mass of Fe^{2+} is then given by

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

The percent Fe^{2+} is

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

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



$$47.22 \text{ mL } \cancel{\text{KMnO}_4} \times \frac{0.02242 \text{ mmol } \cancel{\text{KMnO}_4}}{\text{mL } \cancel{\text{KMnO}_4}} \times \frac{5 \text{ mmol Fe}}{1 \text{ mmol } \cancel{\text{KMnO}_4}} \\ \times \frac{0.05585 \text{ g Fe}}{\text{mmol Fe}} \times \frac{1}{0.8040 \text{ g sample}} \times 100\% = 36.77\% \text{ Fe}$$

Therefore,



and

$$\text{stoichiometric ratio} = \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

As in part (a),

$$\text{amount KMnO}_4 = \frac{47.22 \text{ mL } \cancel{\text{KMnO}_4} \times 0.02242 \text{ mmol KMnO}_4}{\text{mL } \cancel{\text{KMnO}_4}}$$

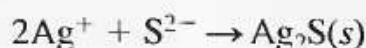
$$\text{amount Fe}_3\text{O}_4 = (47.22 \times 0.02242) \cancel{\text{mmol KMnO}_4} \times \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \cancel{\text{mmol KMnO}_4}}$$

$$\text{mass Fe}_3\text{O}_4 = \left(47.22 \times 0.02242 \times \frac{5}{3} \right) \cancel{\text{mmol Fe}_3\text{O}_4} \times 0.23154 \frac{\text{g Fe}_3\text{O}_4}{\cancel{\text{mmol Fe}_3\text{O}_4}}$$

$$\% \text{ Fe}_3\text{O}_4 = \frac{\left(47.22 \times 0.02242 \times \frac{5}{3} \right) \times 0.23154 \text{ g Fe}_3\text{O}_4}{0.8040 \text{ g sample}} \times 100\% = 50.81\%$$

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



Calculate the concentration of H_2S in the water in parts per million.
At the end point

$$\text{stoichiometric ratio} = \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

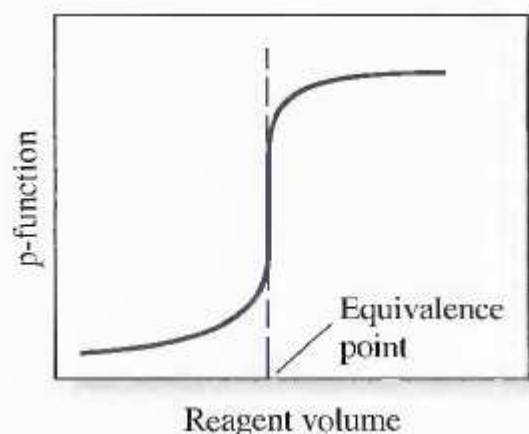
$$\text{amount AgNO}_3 = 16.47 \text{ mL AgNO}_3 \times 0.02310 \frac{\text{mmol AgNO}_3}{\text{mL AgNO}_3}$$

$$\text{amount AgNO}_3 = 16.47 \text{ mL AgNO}_3 \times 0.02310 \frac{\text{mmol AgNO}_3}{\text{mL AgNO}_3}$$

$$\text{amount H}_2\text{S} = (16.47 \times 0.02310) \text{ mmol AgNO}_3 \times \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

$$\begin{aligned} \text{mass H}_2\text{S} &= \left(16.47 \times 0.02310 \times \frac{1}{2} \right) \text{ mmol H}_2\text{S} \times 0.034802 \frac{\text{g H}_2\text{S}}{\text{mmol H}_2\text{S}} \\ &= 6.620 \times 10^{-3} \text{ g H}_2\text{S} \end{aligned}$$

$$\begin{aligned} \text{concd H}_2\text{S} &= \frac{6.620 \times 10^{-3} \text{ g H}_2\text{S}}{100.0 \text{ mL sample} \times 1.000 \text{ g sample/mL sample}} \times 10^6 \text{ ppm} \\ &= 6.62 \text{ ppm H}_2\text{S} \end{aligned}$$



◀ Titration curves are plots of a concentration-related variable as a function of reagent volume.

Principles of Neutralization Titrations

14A SOLUTIONS AND INDICATORS FOR ACID/BASE TITRATIONS

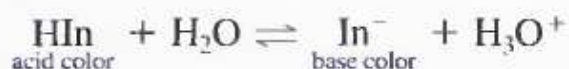
Like all titrations, neutralization titrations depend on a chemical reaction between the analyte and a standard reagent. The point of chemical equivalence is indicated by a chemical indicator or an instrumental method. The discussion here focuses on the types of standard solutions and the chemical indicators that are used for neutralization titrations.

◀ The standard reagents used in acid/base titrations are always strong acids or strong bases, most commonly HCl , HClO_4 , H_2SO_4 , NaOH , and KOH . Weak acids and bases are never used as standard reagents because they react incompletely with analytes.

14A-2 Acid/Base Indicators

Many substances, both naturally occurring and synthetic, display colors that depend on the pH of the solutions in which they are dissolved. Some of these substances, which have been used for centuries to indicate the acidity or alkalinity of water, are still employed as acid/base indicators.

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form. For example, the behavior of an acid-type indicator, HIn , is described by the equilibrium



Here, internal structural changes accompany dissociation and cause the color change (Figure 14-1). The equilibrium for a base-type indicator, In , is



base color

acid color

In the paragraphs that follow, we focus on the behavior of acid-type indicators. The principles, however, can be easily extended to base-type indicators as well.

The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad (14-1)$$

Rearranging leads to

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HIn}]}{[\text{In}^-]} \quad (14-2)$$

We then see that the hydronium ion concentration determines the ratio of the acid to the conjugate base form of the indicator, which in turn controls the color of the solution.

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In^- , particularly when the ratio $[\text{HIn}]/[\text{In}^-]$ is greater than about 10 or smaller than about 0.1. Consequently, the color change detected by an average observer occurs within a limited range of concentration ratios from about

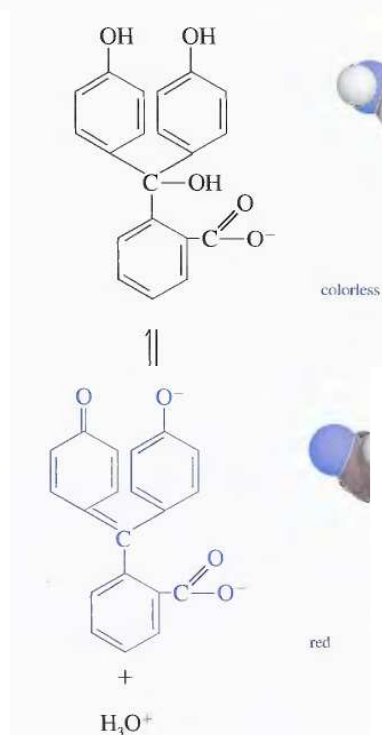


Figure 14-1 Color change and molecular model for phenolphthalein.

10 to about 0.1. At greater or smaller ratios, the color appears essentially constant to the eye and is independent of the ratio. As a result, we can write that the average indicator, HIn, exhibits its pure acid color when

$$\frac{[\text{HIn}]}{[\text{In}^-]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[\text{HIn}]}{[\text{In}^-]} \leq \frac{1}{10}$$

The color appears to be intermediate for ratios between these two values. These ratios vary considerably from indicator to indicator, of course. Furthermore, people differ significantly in their ability to distinguish between colors; indeed a color-blind person may be unable to distinguish any color change at all.

If the two concentration ratios are substituted into Equation 14-2, the range of hydronium ion concentrations needed to change the indicator color can be evaluated. So, for the full acid color,

$$[\text{H}_3\text{O}^+] = 10K_a$$

and in the same way, for the full base color,

$$[\text{H}_3\text{O}^+] = 0.1K_a$$

To obtain the indicator pH range, we take the negative logarithms of the two expressions:

$$\text{pH}(\text{acid color}) = -\log(10K_a) = \text{p}K_a + 1$$

$$\text{pH}(\text{basic color}) = -\log(0.1K_a) = \text{p}K_a - 1$$

$$\text{indicator pH range} = \text{p}K_a \pm 1 \quad (14-3)$$

Titration Errors with Acid/Base Indicators

We find two types of titration errors in acid/base titrations. The first is a determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point. This type of error can usually be minimized by choosing the indicator carefully or by making a blank correction.

The second type is an indeterminate error that originates from the limited ability of the eye to distinguish reproducibly the intermediate color of the indicator. The magnitude of this error depends on the change in pH per milliliter of reagent at the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors. On the average, the visual uncertainty with an acid/base indicator is in the range of ± 0.5 to ± 1 pH unit. This uncertainty can often be decreased to as little as ± 0.1 pH unit by matching the color of the solution being titrated to that of a reference standard containing a similar amount of indicator at the appropriate pH. These uncertainties are of course approximations that vary considerably from indicator to indicator as well as from person to person.

Variables That Influence the Behavior of Indicators

The pH interval over which a given indicator exhibits a color change is influenced by temperature, by the ionic strength of the medium, and by the presence of organic solvents and colloidal particles. Some of these effects, particularly the last two, can cause the transition range to shift by one or more pH units.¹

The Common Acid/Base Indicators

The list of acid/base indicators is large and includes a number of organic compounds. Indicators are available for almost any desired pH range. A few common indicators and their properties are listed in Table 14-1. Note that the transition ranges vary from 1.1 to 2.2, with the average being about 1.6 units. These indicators and several more are shown along with their transition ranges in the color chart inside the front cover of this book.

TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK _a [*]	Color Change [†]	Indicator Type [‡]
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

^{*}At ionic strength of 0.1.

[†]B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

[‡](1) Acid type: $\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-$; (2) Base type: $\text{In} + \text{H}_2\text{O} \rightleftharpoons \text{InH}^+ + \text{OH}^-$.

[§]For the reaction $\text{InH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}$.

TITRATION OF STRONG ACIDS AND STRONG BASES

14B

The hydronium ions in an aqueous solution of a strong acid have two sources: (1) the reaction of the acid with water and (2) the dissociation of water itself. In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent. So, for a solution of HCl with a concentration greater than about 10^{-6} M, we can write

$$[\text{H}_3\text{O}^+] = c_{\text{HCl}} + [\text{OH}^-] \approx c_{\text{HCl}}$$

where $[\text{OH}^-]$ represents the contribution of hydronium ions from the dissociation of water. An analogous relationship applies for a solution of a strong base, such as sodium hydroxide. That is,

$$[\text{OH}^-] = c_{\text{NaOH}} + [\text{H}_3\text{O}^+] \approx c_{\text{NaOH}}$$

14B-1 Titrating a Strong Acid with a Strong Base

We are interested here, and in the next several chapters, in calculating *hypothetical* titration curves of pH versus volume of titrant. We distinguish between the curves constructed by computing the values of pH and the *experimental* titration curves observed in the laboratory. Three types of calculations must be done to construct the hypothetical curve for titrating a solution of a strong acid with a strong base. Each of these corresponds to a distinct stage in the titration: (1) preequivalence, (2) equivalence, and (3) postequivalence. In the preequivalence stage, we compute the concentration of the acid from its starting concentration and the amount of base

added. At the equivalence point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration is derived directly from the ion-product constant for water. In the postequivalence stage, the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration. Our approach is analogous to the method that we used in the silver chloride titration in Example 13-10.

A convenient way of converting hydroxide concentration to pH is to take the negative logarithm of both sides of the ion-product constant expression for water. Thus,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$-\log K_w = -\log[\text{H}_3\text{O}^+][\text{OH}^-] = -\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

$$-\log 10^{-14} = \text{pH} + \text{pOH} = 14.00$$

EXAMPLE 14-1

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.

Initial Point

Before any base is added, the solution is 0.0500 M in H_3O^+ , and

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0500 = 1.30$$

After Addition of 10.00 mL of Reagent

The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So the analytical concentration of HCl is

$$\begin{aligned} c_{\text{HCl}} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\ &= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\ &= \frac{(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})}{50.00 \text{ mL} + 10.00 \text{ mL}} \\ &= \frac{(2.500 \text{ mmol} - 1.000 \text{ mmol})}{60.00 \text{ mL}} = 2.500 \times 10^{-2} \text{ M} \end{aligned}$$

$$[\text{H}_3\text{O}^+] = 2.500 \times 10^{-2} \text{ M}$$

$$\text{and pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.500 \times 10^{-2}) = 1.60$$

After Addition of 25.00 mL of Reagent: The Equivalence Point

At the equivalence point, neither HCl nor NaOH is in excess, and so the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

TABLE 14-2**Changes in pH during the Titration of a Strong Acid with a Strong Base**

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

After Addition of 25.10 mL of Reagent

The solution now contains an excess of NaOH, and we can write

$$\begin{aligned}c_{\text{NaOH}} &= \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\text{total volume soln}} \\&= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}\end{aligned}$$

and the equilibrium concentration of hydroxide ion is

$$\begin{aligned}[\text{OH}^-] &= c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M} \\ \text{pOH} &= -\log(1.33 \times 10^{-4}) = 3.88\end{aligned}$$

and

$$\text{pH} = 14.00 - 3.88 = 10.12$$

We compute additional data defining the curve beyond the equivalence point in the same way. The results of these computations are shown in Table 14-2.

FEATURE 14-1

Using the Charge-Balance Equation to Construct Titration Curves

In Example 14-1, we generated an acid/base titration curve from the reaction stoichiometry. We can show that all points on the curve can also be calculated from the charge-balance equation.

For the system treated in Example 14-1, the charge-balance equation is given by

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

where the sodium and chloride ion concentrations are given by

$$[\text{Na}^+] = \frac{V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{NaOH}} + V_{\text{HCl}}}$$

$$[\text{Cl}^-] = \frac{V_{\text{HCl}}c_{\text{HCl}}}{V_{\text{NaOH}} + V_{\text{HCl}}}$$

We can rewrite the first equation in the form

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Cl}^-] - [\text{Na}^+]$$

For volumes of NaOH short of the equivalence point, $[\text{OH}^-] \ll [\text{Cl}^-]$, so

$$[\text{H}_3\text{O}^+] \approx [\text{Cl}^-] - [\text{Na}^+]$$

and

$$[\text{H}_3\text{O}^+] = \frac{V_{\text{HCl}}c_{\text{HCl}}}{V_{\text{HCl}} + V_{\text{NaOH}}} - \frac{V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{HCl}} + V_{\text{NaOH}}} = \frac{V_{\text{HCl}}c_{\text{HCl}} - V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{HCl}} + V_{\text{NaOH}}}$$

At the equivalence point, $[\text{Na}^+] = [\text{Cl}^-]$ and

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_w}$$

Beyond the equivalence point, $[\text{H}_3\text{O}^+] \ll [\text{Na}^+]$, and the original equation rearranges to

$$= \frac{V_{\text{NaOH}}C_{\text{NaOH}}}{V_{\text{NaOH}} + V_{\text{HCl}}} - \frac{V_{\text{HCl}}C_{\text{HCl}}}{V_{\text{NaOH}} + V_{\text{HCl}}} = \frac{V_{\text{NaOH}}C_{\text{NaOH}} - V_{\text{HCl}}C_{\text{HCl}}}{V_{\text{NaOH}} + V_{\text{HCl}}}$$

The Effect of Concentration

The effects of reagent and analyte concentrations on the neutralization titration curves for strong acids are shown by the two sets of data in Table 14-2, and the

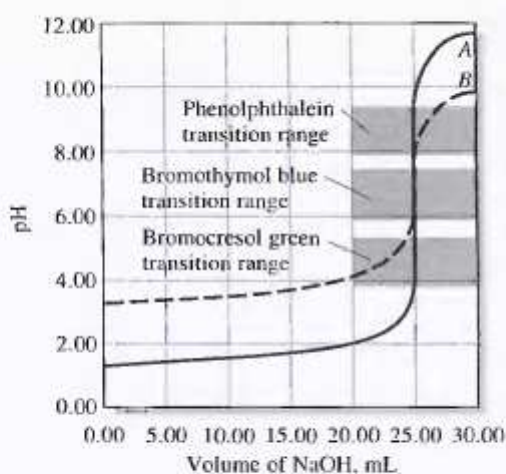


Figure 14-3 Titration curves for HCl with NaOH. Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve B: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.

plots in Figure 14-3. Note that with 0.1 M NaOH as the titrant, the change in pH in the equivalence-point region is large. With 0.001 M NaOH, the change is markedly less but still pronounced.

