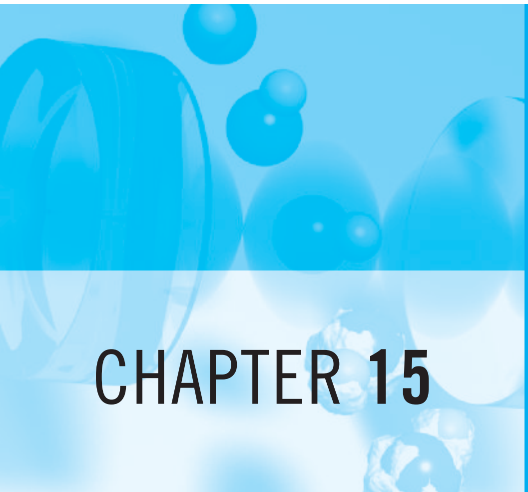
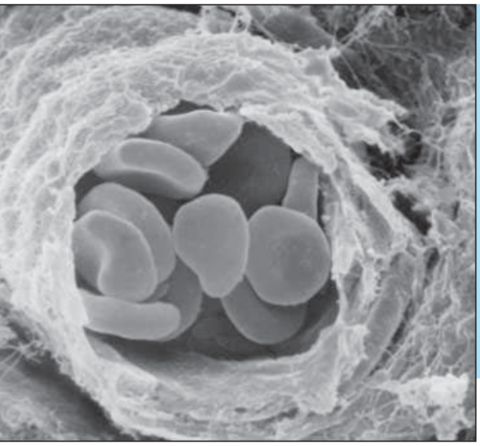


CHAPTER 15

Complex Acid/Base Systems



Professors Pietro M. Motta & Silvia Correr / Photo Researchers, Inc.

Polyfunctional acids and bases play important roles in many chemical and biological systems. The human body contains a complicated system of buffers within cells and within bodily fluids, such as human blood. Shown here is a scanning electron micrograph of red blood cells traveling through an artery. The pH of human blood is controlled to be within the range of 7.35 to 7.45, primarily by the carbonic acid-bicarbonate buffer system:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

This chapter describes polyfunctional acid and base systems including buffer solutions. Calculations of pH and of titration curves are also described.

In this chapter, we describe methods for treating complex acid/base systems, including the calculation of titration curves. We define complex systems as solutions made up of (1) two acids or two bases of different strengths, (2) an acid or a base that has two or more acidic or basic functional groups, or (3) an amphiprotic substance, which is capable of acting as both an acid and a base. For more than one equilibrium, chemical reactions and algebraic equations are required to describe the characteristics of any of these systems.

مخلوط اسید قوی و ضعیف
یا باز قوی و ضعیف

15A MIXTURES OF STRONG AND WEAK ACIDS OR STRONG AND WEAK BASES

Each of the components in a mixture containing a strong acid and a weak acid (or a strong base and a weak base) can be determined provided that the concentrations of the two are of the same order of magnitude and that the dissociation constant for the weak acid or base is somewhat less than about 10^{-4}. To demonstrate that this statement is true, Example 15-1 shows how a titration curve can be constructed for a solution containing roughly equal concentrations of HCl and HA, where HA is a weak acid with a dissociation constant of 10^{-4}.

دو شرط

EXAMPLE 15-1

تیتراسیون مخلوط HCl و اسید ضعیف HA با KOH

Calculate the pH of a mixture that is 0.1200 M in hydrochloric acid and 0.0800 M in the weak acid HA ($K_a = 1.00 \times 10^{-4}$) during its titration with 0.1000 M KOH. Compute results for additions of the following volumes of base: (a) 0.00 mL and (b) 5.00 mL.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Solution

(a) 0.00 mL KOH

The molar hydronium ion concentration in this mixture is equal to the concentration of HCl plus the concentration of hydronium ions that results from dissociation of HA and H_2O. In the presence of the two acids, however, we can be certain that the concentration of hydronium ions from the dissociation of water is extremely small. We, therefore, need to take into account only the other two sources of protons. Thus, we may write

$$\boxed{[H_3O^+] = c^0_{HCl} + [A^-] = 0.1200 + [A^-]}$$

Note that $[A^-]$ is equal to the concentration of hydronium ions from the dissociation of HA.

Now, assume that the presence of the strong acid so represses the dissociation of HA that $[A^-] << 0.1200$ M; then,

$$[H_3O^+] \approx 0.1200 \text{ M, and the pH is } 0.92$$

To check this assumption, the provisional value for $[H_3O^+]$ is substituted into the dissociation-constant expression for HA. When this expression is rearranged, we obtain

$$\frac{[A^-]}{[HA]} = \frac{K_a}{[H_3O^+]} = \frac{1.00 \times 10^{-4}}{0.1200} = 8.33 \times 10^{-4}$$

[A-] با استفاده از دو معادله دو مجهول به دست می آید و درستی تقریب امتحان می شود.

This expression can be rearranged to

$$[HA] = [A^-]/(8.33 \times 10^{-4})$$

From the concentration of the weak acid, we can write the mass-balance expression

$$c^0_{HA} = [HA] + [A^-] = 0.0800 \text{ M}$$

Substituting the value of [HA] from the previous equation gives

$$[A^-]/(8.33 \times 10^{-4}) + [A^-] \approx (1.20 \times 10^3)\,[A^-] = 0.0800 \text{ M}$$

$$[A^-] = 6.7 \times 10^{-5} \text{ M}$$

We see that $[A^-]$ is indeed much smaller than 0.1200 M, as assumed.

(b) 5.00 mL KOH

$$c_{HCl} = \frac{25.00 \times 0.1200 - 5.00 \times 0.100}{25.00 + 5.00} = 0.0833 \text{ M}$$

and we may write

$$[H_3O^+] = 0.0833 + [A^-] \approx 0.0833 \text{ M}$$

$$pH = 1.08$$

(continued)

To determine whether our assumption is still valid, we compute $[A^-]$ as we did in part (a), knowing that the concentration of HA is now $0.0800 \times 25.00/30.00 = 0.0667$, and find

$$[A^-] = 8.0 \times 10^{-5}\ \text{M}$$

which is still much smaller than 0.0833 M.

Example 15-1 demonstrates that hydrochloric acid suppresses the dissociation of the weak acid in the early stages of the titration to such an extent that we can assume that $[A^-] << c_{HCl}$ and $[H_3O^+] = c_{HCl}$. In other words, the hydronium ion concentration is simply the molar concentration of the strong acid.

The approximation used in Example 15-1 can be shown to apply until most of the hydrochloric acid has been neutralized by the titrant. Therefore, the curve in the early stages of the titration *is identical to that for a 0.1200 M solution of a strong acid by itself.* As shown by Example 15-2, however, the presence of HA must be taken into account as the first end point in the titration is approached.

EXAMPLE 15-2

Calculate the pH of the resulting solution after the addition of 29.00 mL of 0.1000 M NaOH to 25.00 mL of the solution described in Example 15-1.

Solution

In this case,

$$c_{HCl} = \frac{25.00 \times 0.1200 - 29.00 \times 0.1000}{25.00 + 29.00} = 1.85 \times 10^{-3}\ \text{M}$$

$$c_{HA} = \frac{25.00 \times 0.0800}{54.00} = 3.70 \times 10^{-2}\ \text{M}$$

As in the previous example, a provisional result based on the assumption that $[H_3O^+] = 1.85 \times 10^{-3}$ M yields a value of 1.90×10^{-3} M for $[A^-]$. We see that $[A^-]$ is no longer much smaller than $[H_3O^+]$, and we must write

$$\boxed{[H_3O^+] = c_{HCl} + [A^-] = 1.85 \times 10^{-3} + [A^-]} \tag{15-1}$$

In addition, from mass-balance considerations, we know that

$$[HA] + [A^-] = c_{HA} = 3.70 \times 10^{-2} \tag{15-2}$$

We rearrange the acid dissociation-constant expression for HA and obtain

$$[HA] = \frac{[H_3O^+][A^-]}{1.00 \times 10^{-4}}$$

Substitution of this expression into Equation 15-2 yields

$$\frac{[H_3O^+][A^-]}{1.00 \times 10^{-4}} + [A^-] = 3.70 \times 10^{-2}$$

$$[A^-] = \frac{3.70 \times 10^{-6}}{[H_3O^+] + 1.00 \times 10^{-4}}$$

Substitution for $[A^-]$ and c_{HCl} in Equation 15-1 yields

$$\boxed{[H_3O^+] = 1.85 \times 10^{-3} + \frac{3.70 \times 10^{-6}}{[H_3O^+] + 1.00 \times 10^{-4}}}$$

Multiplying through to clear the denominator and collecting terms gives

$$[H_3O^+]^2 - (1.75 \times 10^{-3})[H_3O^+] - 3.885 \times 10^{-6} = 0$$

Solving the quadratic equation gives

$$[H_3O^+] = 3.03 \times 10^{-3}\ M$$

$$pH = 2.52$$

Note that the contributions to the hydronium ion concentration from HCl (1.85×10^{-3} M) and HA (3.03×10^{-3} M $- 1.85 \times 10^{-3}$ M) are of comparable magnitude. Hence, we cannot make the assumption that we made in Example 15-1.

When the amount of base added is equivalent to the amount of hydrochloric acid originally present, the solution is identical in all respects to one prepared by dissolving appropriate quantities of the weak acid and sodium chloride in a suitable volume of water. The sodium chloride, however, has no effect on the pH (neglecting the increased ionic strength); thus, the remainder of the titration curve is identical to that for a dilute solution of HA.

The shape of the curve for a mixture of weak and strong acids, and hence the information that may be derived from it, depends in large measure on the strength of the weak acid. **Figure 15-1** illustrates the pH changes that occur during the titration of mixtures containing hydrochloric acid and several weak acids with different dissociation constants. Note that the rise in pH at the first equivalence point is small or essentially nonexistent when the weak acid has a relatively large dissociation constant (curves A and B). For titrations such as these, only the total number of millimoles of weak and strong acid can be determined accurately. Conversely, when the weak acid has a very small dissociation constant, only the strong acid content can be determined. For weak acids of intermediate strength (K_a somewhat less than 10^{-4} but greater than 10^{-8}), there are usually two useful end points.

It is also possible to determine the amount of each component in a mixture that contains a strong base and a weak base, subject to the constraints just described for the strong acid/weak acid system. The construction of titration curves for mixtures of bases is analogous to that for mixtures of acids.

The composition of a mixture of a strong acid and a weak acid can be determined by titration with suitable indicators if the weak acid has a dissociation constant that lies between 10^{-4} and 10^{-8} and the concentrations of the two acids are of the same order of magnitude.

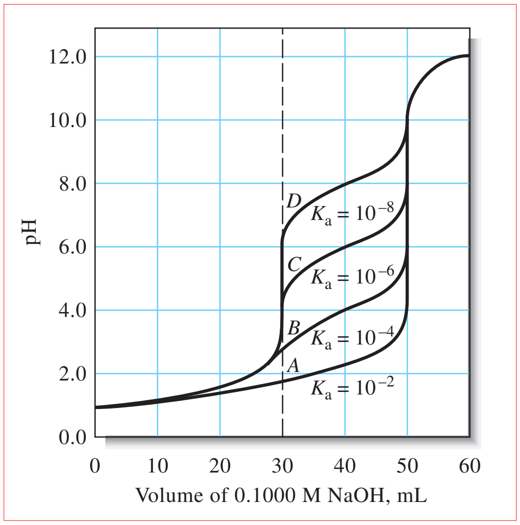


Figure 15-1 Curves for the titration of strong/weak acid mixtures with 0.1000 M NaOH. Each titration curve is for 25.00 mL of a solution that is 0.1200 M in HCl and 0.0800 M in the weak acid HA.

اسیدها و بازهای چند عاملی

15B POLYFUNCTIONAL ACIDS AND BASES

There are several species of interest in analytical chemistry that have two or more acidic or basic functional groups. These species are said to exhibit polyfunctional acidic or basic behavior. Generally, with a polyfunctional acid such as phosphoric acid (H_3PO_4), the protonated species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}) differ enough in their dissociation constants that they exhibit multiple end points in a neutralization titration.

15B-1 The Phosphoric Acid System

Phosphoric acid is a typical polyfunctional acid. In aqueous solution, it undergoes the following three dissociation reactions:

Throughout the remainder of this chapter, we use K_{a1}, K_{a2} to represent the first and second dissociation constants of acids and K_{b1}, K_{b2} to represent the stepwise constants of bases.

Generally, $K_{a1} > K_{a2}$, often by a factor of 10^4 to 10^5 because of electrostatic forces. That is, the first dissociation involves separating a single positively charged hydronium ion from a singly charged anion. In the second step, the hydronium ion must be separated from a doubly charged anion, a process that requires considerably more energy.

A second reason that $K_{a1} > K_{a2}$ is a statistical one. In the first step, a proton can be removed from more locations than in the second and third steps.

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

When we add two adjacent stepwise equilibria, we multiply the two equilibrium constants to obtain the equilibrium constant for the resulting overall reaction. Thus, for the first two dissociation equilibria for H_3PO_4, we write

$$H_3PO_4 + 2H_2O \rightleftharpoons HPO_4^{2-} + 2H_3O^+ \qquad K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{2-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} = 4.49 \times 10^{-10}$$

Similarly, for the reaction

$$H_3PO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

we may write

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{3-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} \times 4.5 \times 10^{-13} = 2.0 \times 10^{-22}$$

15B-2 The Carbon Dioxide/Carbonic Acid System

When carbon dioxide is dissolved in water, a dibasic acid system is formed by the following reactions:

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \qquad K_{hyd} = \frac{[H_2CO_3]}{[CO_2(aq)]} = 2.8 \times 10^{-3} \qquad (15\text{-}3)$$

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.5 \times 10^{-4} \qquad (15\text{-}4)$$

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

$$K_2 = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \qquad (15\text{-}5)$$

The first reaction describes the hydration of aqueous CO_2 to form carbonic acid. Note that the magnitude of K_{hyd} indicates that the concentration of $CO_2(aq)$ is much larger than the concentration of H_2CO_3 (that is, $[H_2CO_3]$ is only about 0.3% that of $[CO_2(aq)]$). Thus, a more useful way of discussing the acidity of solutions of carbon dioxide is to combine Equation 15-3 and 15-4 to give

$$CO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[CO_2(aq)]} \qquad (15\text{-}6)$$

$$= 2.8 \times 10^{-3} \times 1.5 \times 10^{-4}$$

$$= 4.2 \times 10^{-7}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \qquad K_{a2} = 4.69 \times 10^{-11} \qquad (15\text{-}7)$$

EXAMPLE 15-3

Calculate the pH of a solution that is 0.02500 M CO_2.

Solution

The mass-balance expression for CO_2-containing species is

$$\boxed{c^0_{CO_2} = 0.02500 = [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}$$

The small magnitude of K_{hyd}, K_1, and K_2 (see Equations 15-3, 15-4, and 15-5) suggests that

$$([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]) \ll [CO_2(aq)]$$

and we may write

$$[CO_2(aq)] \approx c^0_{CO_2} = 0.02500 \text{ M}$$

The charge-balance equation is

$$\boxed{[H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]}$$

We will then assume that

$$2[CO_3^{2-}] + [OH^-] \ll [HCO_3^-]$$

Therefore,

$$[H_3O^+] \approx [HCO_3^-]$$

(continued)

Substituting these approximations in Equation 15-6 leads to

$$\boxed{\frac{[H_3O^+]^2}{0.02500} = K_{a1} = 4.2 \times 10^{-7}}$$

$$[H_3O^+] = \sqrt{0.02500 \times 4.2 \times 10^{-7}} = 1.02 \times 10^{-4}\ M$$

$$pH = -\log(1.02 \times 10^{-4}) = 3.99$$

Calculating values for $[H_2CO_3]$, $[CO_3^{2-}]$, and $[OH^-]$ indicates that the assumptions were valid.

CHALLENGE: Write a sufficient number of equations to make it possible to calculate the concentrations of all species in a solution containing known molar analytical concentrations of Na_2CO_3 and $NaHCO_3$.

The pH of polyfunctional systems, such as phosphoric acid or sodium carbonate, can be computed rigorously through use of the systematic approach to multiequilibrium problems described in Chapter 11. Manually solving the several simultaneous equations that are involved can be difficult and time consuming, but a computer can simplify the work dramatically.[1] In many cases, simplifying assumptions can be made when the successive equilibrium constants for the acid (or base) differ by a factor of about 10^3 or more. These assumptions can make it possible to compute pH data for titration curves by the techniques discussed in earlier chapters.

15C BUFFER SOLUTIONS INVOLVING POLYPROTIC ACIDS

محلول های بافری برگرفته
از اسیدهای چند ظرفیتی

Two buffer systems can be prepared from a weak dibasic acid and its salts. The first consists of free acid H_2A and its conjugate base NaHA, and the second makes use of the acid NaHA and its conjugate base Na_2A. The pH of the NaHA/Na_2A system is higher than that of the H_2A/NaHA system because the acid dissociation constant for HA^- is always less than that for H_2A.

We can write enough independent equations to permit a rigorous calculation of the hydronium ion concentration for either of these systems. Ordinarily, however, it is permissible to introduce the simplifying assumption that only one of the equilibria is important in determining the hydronium ion concentration of the solution. Thus, for a buffer prepared from H_2A and NaHA, the dissociation of HA^- to yield A^{2-} can usually be neglected so that the calculation is based only on the first dissociation. With this simplification, the hydronium ion concentration is calculated by the method described in Section 9C-1 for a simple buffer solution. As shown in Example 15-4, the validity of the assumption can be checked by calculating an approximate concentration of A^{2-} and comparing this value with the concentrations of H_2A and HA^-.

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[1] See S. R. Crouch and F. J. Holler, *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., Ch. 6, Belmont, CA: Brooks/Cole, 2014.

EXAMPLE 15-4

Calculate the hydronium ion concentration for a buffer solution that is 2.00 M in phosphoric acid and 1.50 M in potassium dihydrogen phosphate.

Solution

The principal equilibrium in this solution is the dissociation of H_3PO_4.

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

We assume that the dissociation of $H_2PO_4^-$ is negligible, that is, $[HPO_4^{2-}]$ and $[PO_4^{3-}] << [H_2PO_4^-]$ and $[H_3PO_4]$. Then,

$$[H_3PO_4] \approx c^0_{H_3PO_4} = 2.00\ M$$

$$[H_2PO_4^-] \approx c^0_{KH_2PO_4} = 1.50\ M$$

$$[H_3O^+] = \frac{7.11 \times 10^{-3} \times 2.00}{1.50} = 9.49 \times 10^{-3}\ M$$

We now use the equilibrium constant expression for K_{a2} to see if our assumption was valid.

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$$K_{a2} = 6.34 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{9.48 \times 10^{-3}[HPO_4^{2-}]}{1.50}$$

Solving this equation yields

$$[HPO_4^{2-}] = 1.00 \times 10^{-5}\ M$$

Since this concentration is much smaller than the concentrations of the major species, H_3PO_4 and $H_2PO_4^-$, our assumption is valid. Note that $[PO_4^{3-}]$ is even smaller than $[HPO_4^{2-}]$.

For a buffer prepared from NaHA and Na_2A, the second dissociation usually predominates, and the equilibrium

$$HA^- + H_2O \rightleftharpoons H_2A + OH^-$$

can be neglected. The concentration of H_2A is negligible compared with that of HA^- or A^{2-}. The hydronium ion concentration can then be calculated from the second dissociation constant by the techniques for a simple buffer solution. To test the assumption, we compare an estimate of the H_2A concentration with the concentrations of HA^- and A^{2-}, as in Example 15-5.

EXAMPLE 15-5

Calculate the hydronium ion concentration of a buffer that is 0.0500 M in potassium hydrogen phthalate (KHP) and 0.150 M in potassium phthalate (K_2P).

$$HP^- + H_2O \rightleftharpoons H_3O^+ + P^{2-} \qquad K_{a2} = \frac{[H_3O^+][P^{2-}]}{[HP^-]} = 3.91 \times 10^{-6}$$

Solution

We will make the assumption that the concentration of H_2P is negligible in this solution.
Therefore,

$$[HP^-] \approx c^0_{KHP} = 0.0500\ M$$

$$[P^{2-}] \approx c_{K_2P} = 0.150\ M$$

$$[H_3O^+] = \frac{3.91 \times 10^{-6} \times 0.0500}{0.150} = 1.30 \times 10^{-6}\ M$$

To check the first assumption, an approximate value for $[H_2P]$ is calculated by substituting numerical values for $[H_3O^+]$ and $[HP^-]$ into the K_{a1} expression:

$$K_{a1} = \frac{[H_3O^+][HP^-]}{[H_2P]} = 1.12 \times 10^{-3} = \frac{(1.30 \times 10^{-6})(0.0500)}{[H_2P]}$$

$$[H_2P] = 6 \times 10^{-5}\ M$$

Since $[H_2P] \ll [HP]$ and $[P^{2-}]$, our assumption that the reaction of HP^- to form OH^- is negligible is justified.

In all but a few situations, the assumption of a single principal equilibrium, as illustrated in Examples 15-4 and 15-5, provides a satisfactory estimate of the pH of buffer mixtures derived from polybasic acids. Appreciable errors occur, however, when the concentration of the acid or the salt is very low or when the two dissociation constants are numerically close. In these cases, a more rigorous calculation is needed.

15D CALCULATION OF THE pH OF SOLUTIONS OF NaHA

محاسبه pH محلول NaHA

We have not yet considered how to calculate the pH of solutions of salts that have both acidic and basic properties, that is, salts that are amphiprotic. Such salts are formed during neutralization titrations of polyfunctional acids and bases. For example, when 1 mol of NaOH is added to a solution containing 1 mol of the acid H_2A, 1 mol of NaHA is formed. The pH of this solution is determined by two equilibria established between HA^- and water:

$$\boxed{HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+}$$

and

$$\boxed{HA^- + H_2O \rightleftharpoons H_2A + OH^-}$$

If the first reaction predominates, the solution will be acidic. If the second predominates, the solution will be basic. The relative magnitudes of the equilibrium constants for these processes determine whether a solution of NaHA is acidic or basic.

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \qquad (15\text{-}8)$$

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{[H_2A][OH^-]}{[HA^-]} \qquad (15\text{-}9)$$

where K_{a1} and K_{a2} are the acid dissociation constants for H_2A and K_{b2} is the basic dissociation constant for HA^-. If K_{b2} is greater than K_{a2}, the solution is basic. It is acidic if K_{a2} exceeds K_{b2}.

To derive an expression for the hydronium ion concentration of a solution of HA^-, we use the systematic approach described in Section 11A. We first write the mass-balance expression.

$$\boxed{c_{NaHA} = [HA^-] + [H_2A] + [A^{2-}]} \qquad (15\text{-}10)$$

The charge-balance equation is

$$[Na^+] + [H_3O^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

Since the sodium ion concentration is equal to the molar analytical concentration of NaHA, the last equation can be rewritten as

$$c_{NaHA} + [H_3O^+] = [HA^-] + 2[A^{2-}] + [OH^-] \qquad (15\text{-}11)$$

We now have four algebraic equations (Equations 15-10 and 15-11 and the two dissociation constant expressions for H_2A) and need one additional expression to solve for the five unknowns. The ion-product constant for water serves this purpose:

$$K_w = [H_3O^+][OH^-]$$

The rigorous solution of these five equations in five unknowns is somewhat difficult, but computer methods have made the task less formidable than previously.[2] A reasonable approximation, applicable to solutions of most acid salts, can be used, however, to simplify the problem. We first subtract the mass-balance equation from the charge-balance equation.

$$\begin{aligned} c_{NaHA} + [H_3O^+] &= [HA^-] + 2[A^{2-}] + [OH^-] && \text{charge balance} \\ c_{NaHA} &= [H_2A] + [HA^-] + [A^{2-}] && \text{mass balance} \\ \boxed{[H_3O^+] = [A^{2-}] + [OH^-] - [H_2A]} &&& (15\text{-}12) \end{aligned}$$

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[2] See S.R. Crouch and F. J. Holler, *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., Ch. 6, Belmont, CA: Brooks/Cole 2014.

We then rearrange the acid-dissociation constant expressions for H_2A and HA^- to give

$$[H_2A] = \frac{[H_3O^+][HA^-]}{K_{a1}}$$

$$[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]}$$

Substituting these expressions and that for K_w into Equation 15-12 yields

$$[H_3O^+] = \frac{K_{a2}[HA^-]}{[H_3O^+]} + \frac{K_w}{[H_3O^+]} - \frac{[H_3O^+][HA^-]}{K_{a1}}$$

Multiplying through by $[H_3O^+]$ gives

$$[H_3O^+]^2 = K_{a2}[HA^-] + K_w - \frac{[H_3O^+]^2[HA^-]}{K_{a1}}$$

We collect terms to obtain

$$[H_3O^+]^2\left(\frac{[HA^-]}{K_{a1}} + 1\right) = K_{a2}[HA^-] + K_w$$

This equation rearranges to

$$[H_3O^+] = \sqrt{\frac{K_{a2}[HA^-] + K_w}{1 + [HA^-]/K_{a1}}} \tag{15-13}$$

Under most circumstances, we can make the approximation that

$$[HA^-] \approx c_{NaHA} \tag{15-14}$$

Substituting this relationship into Equation 15-13 gives

تقريب

$$\boxed{[H_3O^+] = \sqrt{\frac{K_{a2}c_{NaHA} + \cancel{K_w}}{\cancel{1} + c_{NaHA}/K_{a1}}}} \tag{15-15}$$

The approximation shown as Equation 15-14 requires that $[HA^-]$ be much larger than any of the other equilibrium concentrations in Equations 15-10 and 15-11. This assumption is not valid for very dilute solutions of NaHA or in situations where K_{a2} or K_w/K_{a1} is relatively large.

Frequently, the ratio c_{NaHA}/K_{a1} is much larger than unity in the denominator of Equation 15-15, and $K_{a2}c_{NaHA}$ is considerably greater than K_w in the numerator. In this case, Equation 15-15 simplifies to

Always check the assumptions that are inherent in Equation 15-16. ❯

$$\boxed{[H_3O^+] = \sqrt{K_{a1}K_{a2}}} \tag{15-16}$$

Note that Equation 15-16 does not contain c_{NaHA}, which implies that the pH of solutions of this type remains constant over a considerable range of solution concentrations where the assumptions are valid.

EXAMPLE 15-6

Calculate the hydronium ion concentration of a 1.00×10^{-3} M Na_2HPO_4 solution.

Solution

The pertinent dissociation constants are K_{a2} and K_{a3}, which both contain $[HPO_4^{2-}]$. Their values are $K_{a2} = 6.32 \times 10^{-8}$ and $K_{a3} = 4.5 \times 10^{-13}$. In the case of a Na_2HPO_4 solution, Equation 15-15 can be written

هیدروژن فسفات گونه مشترک
بین K_2 و K_3 است

$$[H_3O^+] = \sqrt{\frac{K_{a3}c_{NaHA} + K_w}{1 + c_{NaHA}/K_{a2}}}$$

Note that we have used K_{a3} in place of K_{a2} in Equation 15-15 and K_{a2} in place of K_{a1} since these are the appropriate dissociation constants when Na_2HPO_4 is the salt.

If we consider again the assumptions that led to Equation 15-16, we find that the term $c_{NaHA}/K_{a2} = (1.0 \times 10^{-3})/(6.32 \times 10^{-8})$ is much larger than 1 so that the denominator can be simplified. In the numerator, however, $K_{a3}c_{NaHA} = 4.5 \times 10^{-13} \times 1.00 \times 10^{-3}$ is comparable to K_w so that no simplification can be made there. We, therefore, use a partially simplified version of Equation 15-15:

$$[H_3O^+] = \sqrt{\frac{K_{a3}c_{NaHA} + K_w}{c_{NaHA}/K_{a2}}}$$

$$= \sqrt{\frac{(4.5 \times 10^{-13})(1.00 \times 10^{-3}) + 1.00 \times 10^{-14}}{(1.00 \times 10^{-3})/(6.32 \times 10^{-8})}} = 8.1 \times 10^{-10}\text{ M}$$

The simplified Equation 15-15 gave 1.7×10^{-10} M, which is in error by a large amount.

EXAMPLE 15-7

Find the hydronium ion concentration of a 0.0100 M NaH_2PO_4 solution.

Solution

The two dissociation constants of importance (those containing $[H_2PO_4^{2-}]$ are $K_{a1} = 7.11 \times 10^{-3}$ and $K_{a2} = 6.32 \times 10^{-8}$). A test shows that the denominator of Equation 15-15 cannot be simplified, but the numerator reduces to $K_{a2}c_{NaH_2PO_4}$. Thus, Equation 15-15 becomes,

$$[H_3O^+] = \sqrt{\frac{(6.32 \times 10^{-8})(1.00 \times 10^{-2})}{1.00 + (1.00 \times 10^{-2})/(7.11 \times 10^{-3})}} = 1.62 \times 10^{-5}\text{ M}$$

EXAMPLE 15-8

Calculate the hydronium ion concentration of a 0.1000 M $NaHCO_3$ solution.

Solution

We assume, as we did earlier (page 353), that $[H_2CO_3] \ll [CO_2(aq)]$ and that the following equilibria describe the system:

$$CO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[CO_2(aq)]} = 4.2 \times 10^{-7}$$

(*continued*)

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \qquad K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$
$$= 4.69 \times 10^{-11}$$

We note that $c_{NaHA}/K_{a1} >> 1$ so that the denominator of Equation 15-15 can be simplified. In addition, $K_{a2}c_{NaHA}$ has a value of 4.69×10^{-12}, which is substantially greater than K_w. Thus, Equation 15-16 applies, and

$$[H_3O^+] = \sqrt{4.2 \times 10^{-7} \times 4.69 \times 10^{-11}} = 4.4 \times 10^{-9}\ M$$

15E TITRATION CURVES FOR POLYFUNCTIONAL ACIDS

Compounds with two or more acidic functional groups yield multiple end points in a titration if the functional groups differ sufficiently in strength as acids. The computational techniques described in Chapter 14 permit construction of reasonably accurate theoretical titration curves for polyprotic acids if the ratio K_{a1}/K_{a2} is somewhat greater than 10^3. If this ratio is smaller, the error becomes excessive, particularly in the region of the first equivalence point, and a more rigorous treatment of the equilibrium relationships is required.

Figure 15-2 shows the titration curve for a diprotic acid H_2A with dissociation constants of $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$. Because the K_{a1}/K_{a2} ratio is significantly greater than 10^3, we can calculate this curve (except for the first equivalence point) using the techniques developed in Chapter 14 for simple monoprotic weak acids. Thus, to calculate the initial pH (point *A*), we treat the system as if it contained a single monoprotic acid with a dissociation constant of $K_{a1} = 1.00 \times 10^{-3}$. In region *B*, we have the equivalent of a simple buffer solution consisting of the weak acid H_2A and its conjugate base NaHA. That is, we assume that the concentration of A^{2-} is negligible

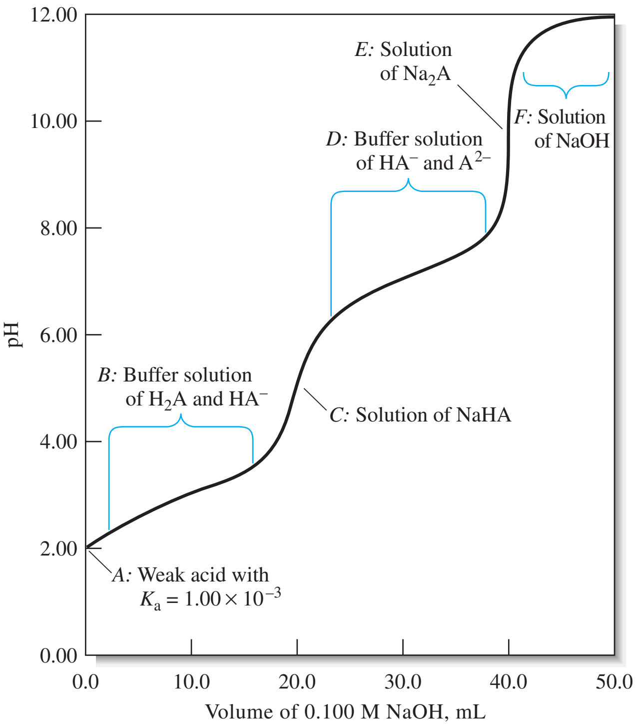

Figure 15-2 Titration of 20.00 mL of 0.1000 M H_2A with 0.1000 M NaOH. For H_2A, $K_{a1} = 1.00 \times 10^{-3}$, and $K_{a2} = 1.00 \times 10^{-7}$. The method of pH calculation is shown for several points and regions on the titration curve.

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with respect to the other two A-containing species and use Equation 9-29 (page 220) to find $[H_3O^+]$. At the first equivalence point (point *C*), we have a solution of an acid salt and use Equation 15-15 or one of its simplifications to compute the hydronium ion concentration. In the region labeled *D*, we have a second buffer consisting of a weak acid HA^- and its conjugate base Na_2A, and we calculate the pH using the second dissociation constant, $K_{a2} = 1.00 \times 10^{-7}$. At point *E*, the solution contains the conjugate base of a weak acid with a dissociation constant of 1.00×10^{-7}. That is, we assume that the hydroxide concentration of the solution is determined solely by the reaction of A^{2-} with water to form HA^- and OH^-. Finally, in the region labeled *F*, we have excess NaOH and compute the hydroxide concentration from the molar concentration of the NaOH. The pH is then found from this quantity and the ion-product of water.

Example 15-9 illustrates a somewhat more complicated example, that of titrating the diprotic maleic acid (H_2M) with NaOH. Although the ratio of K_{a1}/K_{a2} is large enough to use the techniques just described, the value of K_{a1} is so large that some of the simplifications made in previous discussions do not apply, particularly in regions just prior to and just beyond the equivalence points.

EXAMPLE 15-9

Construct a curve for the titration of 25.00 mL of 0.1000 M maleic acid, HOOC—CH═CH—COOH, with 0.1000 M NaOH.

We can write the two dissociation equilibria as

$$H_2M + H_2O \rightleftharpoons H_3O^+ + HM^- \qquad K_{a1} = 1.3 \times 10^{-2}$$

$$HM^- + H_2O \rightleftharpoons H_3O^+ + M^{2-} \qquad K_{a2} = 5.9 \times 10^{-7}$$

Because the ratio K_{a1}/K_{a2} is large (2×10^{-4}), we can proceed using the techniques just described.

Solution

Initial pH

Initially, the solution is 0.1000 M H_2M. At this point, only the first dissociation makes an appreciable contribution to $[H_3O^+]$; thus,

$$[H_3O^+] \approx [HM^-]$$

Mass balance requires that

$$c^0_{H_2M} = [H_2M] + [HM^-] + [M^{2-}] = 0.1000 \text{ M}$$

Since the second dissociation is negligible, $[M^{2-}]$ is very small so that

$$c^0_{H_2M} \approx [H_2M] + [HM^-] = 0.1000 \text{ M}$$

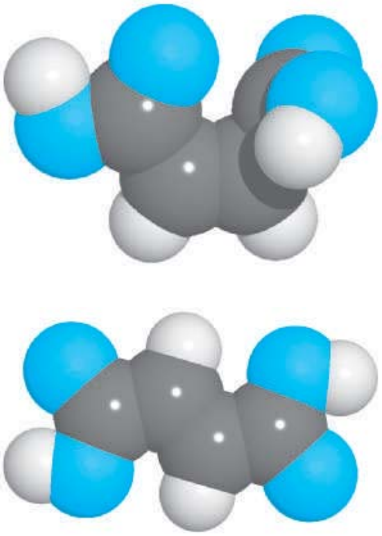
or

$$[H_2M] = 0.1000 - [HM^-] = 0.1000 - [H_3O^+]$$

Substituting these relationships into the expression for K_{a1} gives

$$\boxed{K_{a1} = 1.3 \times 10^{-2} = \frac{[H_3O^+][HM^-]}{[H_2M]} = \frac{[H_3O^+]^2}{0.1000 - [H_3O^+]}}$$

(*continued*)



Molecular models of maleic acid, or (Z)-butenedioic acid (top), and fumaric acid, or (E)-butenedioic acid (bottom). These geometric isomers exhibit striking differences in both their physical and their chemical properties. Because the *cis* isomer (maleic acid) has both carboxyl groups on the same side of the molecule, the compound eliminates water to form cyclic maleic anhydride, which is a very reactive precursor widely used in plastics, dyes, pharmaceuticals, and agrichemicals. Fumaric acid, which is essential to animal and vegetable respiration, is used industrially as an antioxidant to synthesize resins and to fix colors in dyeing. It is interesting to compare the pK_a values for the two acids; for fumaric acid, pK_{a1} = 3.05, and pK_{a2} = 4.49; for maleic acid, pK_{a1} = 1.89, and pK_{a2} = 6.23. CHALLENGE: Explain the differences in the pK_a values based on the differences in the molecular structures.

Rearranging yields

$$[H_3O^+]^2 + 1.3 \times 10^{-2}[H_3O^+] - 1.3 \times 10^{-3} = 0$$

Because K_{a1} for maleic acid is relatively large, we must solve the quadratic equation or find $[H_3O^+]$ by successive approximations. When we do so, we obtain

$$[H_3O^+] = 3.01 \times 10^{-2}\ M$$

$$pH = 2 - \log 3.01 = 1.52$$

First Buffer Region

The addition of base, for example 5.00 mL, results in the formation of a buffer consisting of the weak acid H_2M and its conjugate base HM^-. To the extent that dissociation of HM^- to give M^{2-} is negligible, the solution can be treated as a simple buffer system. Thus, applying Equations 9-27 and 9-28 (page 220) gives

$$c_{NaHM} \approx [HM^-] = \frac{5.00 \times 0.1000}{30.00} = 1.67 \times 10^{-2}\ M$$

$$c_{H_2M} \approx [H_2M] = \frac{25.00 \times 0.1000 - 5.00 \times 0.1000}{30.00} = 6.67 \times 10^{-2}\ M$$

Substitution of these values into the equilibrium-constant expression for K_{a1} yields a tentative value of 5.2×10^{-2} M for $[H_3O^+]$. It is clear, however, that the approximation $[H_3O^+] << c_{H_2M}$ or c_{HM^-} is not valid; therefore, Equations 9-25 and 9-26 must be used, and

$$[HM^-] = 1.67 \times 10^{-2} + [H_3O^+] - [OH^-]$$

$$[H_2M] = 6.67 \times 10^{-2} - [H_3O^+] - [OH^-]$$

Because the solution is quite acidic, the approximation that $[OH^-]$ is very small is surely justified. Substitution of these expressions into the dissociation-constant relationship gives

$$K_{a1} = \frac{[H_3O^+](1.67 \times 10^{-2} + [H_3O^+])}{6.67 \times 10^{-2} - [H_3O^+]} = 1.3 \times 10^{-2}$$

$$[H_3O^+]^2 + (2.97 \times 10^{-2})[H_3O^+] - 8.67 \times 10^{-4} = 0$$

$$[H_3O^+] = 1.81 \times 10^{-2}\ M$$

$$pH = -\log(1.81 \times 10^{-2}) = 1.74$$

Additional points in the first buffer region are computed in a similar way until just prior to the first equivalence point.

Just Prior to First Equivalence Point

Just prior to the first equivalence point, the concentration of H_2M is so small that it becomes comparable to the concentration of M^{2-}, and the second equilibrium must also be considered. Within approximately 0.1 mL of the first equivalence point, we have a solution of primarily HM^- with a small amount of H_2M

remaining and a small amount of M^{2-} formed. For example, at 24.90 mL of NaOH added,

$$[HM^-] \approx c_{NaHM} = \frac{24.90 \times 0.1000}{49.90} = 4.99 \times 10^{-2}\ M$$

$$c_{H_2M} = \frac{25.00 \times 0.1000}{49.90} - \frac{24.90 \times 0.1000}{49.90} = 2.00 \times 10^{-4}\ M$$

Mass balance gives

$$c_{H_2M} + c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}]$$

Charge balance gives

$$[H_3O^+] + [Na^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$

Since the solution consists primarily of the acid HM^- at the first equivalence point, we can safely neglect $[OH^-]$ in the previous equation and replace $[Na^+]$ with c_{NaHM}. After rearranging, we obtain

$$c_{NaHM} = [HM^-] + 2[M^{2-}] - [H_3O^+]$$

Substituting this equation into the mass-balance expression and solving for $[H_3O^+]$ give

$$[H_3O^+] = c_{H_2M} + [M^{2-}] - [H_2M]$$

If we express $[M^{2-}]$ and $[H_2M]$ in terms of $[HM^-]$ and $[H_3O^+]$, the result is

$$[H_3O^+] = c_{H_2M} + \frac{K_{a2}[HM^-]}{[H_3O^+]} - \frac{[H_3O^+][HM^-]}{K_{a1}}$$

Multiplying through by $[H_3O^+]$ gives, after rearrangement,

$$[H_3O^+]^2\left(1 + \frac{[HM^-]}{K_{a1}}\right) - c_{H_2M}[H_3O^+] - K_{a2}[HM^-] = 0$$

Substituting $[HM^-] = 4.99 \times 10^{-2}$, $c_{H_2M} = 2.00 \times 10^{-4}$, and the values for K_{a1} and K_{a2} leads to

$$4.838\,[H_3O^+]^2 - 2.00 \times 10^{-4}\,[H_3O^+] - 2.94 \times 10^{-8} = 0$$

The solution to this equation is

$$[H_3O^+] = 1.014 \times 10^{-4}\ M$$

$$pH = 3.99$$

The same reasoning applies at 24.99 mL of titrant, where we find

$$[H_3O^+] = 8.01 \times 10^{-5}\ M$$

$$pH = 4.10$$

(*continued*)

First Equivalence Point

At the first equivalence point,

$$[HM^-] \approx c_{NaHM} = \frac{25.00 \times 0.1000}{50.00} = 5.00 \times 10^{-2}\ M$$

Our simplification of the numerator in Equation 15-15 is certainly justified. On the other hand, the second term in the denominator is not << l. Hence,

$$[H_3O^+] = \sqrt{\frac{K_{a2}c_{NaHM}}{1 + c_{NaHM}/K_{a1}}} = \sqrt{\frac{5.9 \times 10^{-7} \times 5.00 \times 10^{-2}}{1 + (5.00 \times 10^{-2})/(1.3 \times 10^{-2})}}$$
$$= 7.80 \times 10^{-5}\ M$$

$$pH = -\log(7.80 \times 10^{-5}\ M) = 4.11$$

Just after the First Equivalence Point

Prior to the second equivalence point, we can obtain the analytical concentrations of NaHM and Na_2M from the titration stoichiometry. At 25.01 mL, for example, the values are

$$c_{NaHM} = \frac{\text{mmol NaHM formed} - (\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}}$$
$$= \frac{25.00 \times 0.1000 - (25.01 - 25.00) \times 0.1000}{50.01} = 0.04997\ M$$

$$c_{Na_2M} = \frac{(\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}} = 1.9996 \times 10^{-5}\ M$$

In the region a few tenths of a milliliter beyond the first equivalence point, the solution is primarily HM^- with some M^{2-} formed as a result of the titration. The mass balance at 25.01 mL added is

$$c_{Na_2M} + c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}] = 0.04997 + 1.9996 \times 10^{-5}$$
$$= 0.04999\ M$$

and the charge balance is

$$[H_3O^+] + [Na^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$

Again, the solution should be acidic, and so, we can neglect OH^- as an important species. The Na^+ concentration equals the number of millimoles of NaOH added divided by the total volume, or

$$[Na^+] = \frac{25.01 \times 0.1000}{50.01} = 0.05001\ M$$

Subtracting the mass balance from the charge balance and solving for $[H_3O^+]$ gives

$$[H_3O^+] = [M^{2-}] - [H_2M] + (c_{Na_2M} + c_{NaHM}) - [Na^+]$$

Expressing the $[M^{2-}]$ and $[H_2M]$ in terms of the predominant species HM^-, we have

$$[H_3O^+] = \frac{K_{a2}[HM^-]}{[H_3O^+]} - \frac{[H_3O^+][HM^-]}{K_{a1}} + (c_{Na_2M} + c_{NaHM}) - [Na^+]$$

Since $[HM^-] \approx c_{NaHM} = 0.04997$. Therefore, if we substitute this value and numerical values for $c_{Na_2M} + c_{NaHM}$ and $[Na^+]$ into the previous equation, we have, after rearranging, the following quadratic equation:

$$[H_3O^+] = \frac{K_{a2}(0.04997)}{[H_3O^+]} - \frac{[H_3O^+](0.04997)}{K_{a1}} - 1.9996 \times 10^{-5}$$

$$K_{a1}[H_3O^+]^2 = 0.04997K_{a1}K_{a2} - 0.04997[H_3O^+]^2 - 1.9996 \times 10^{-5}K_{a1}[H_3O^+]$$

$$(K_{a1} + 0.04997)[H_3O^+]^2 + 1.9996 \times 10^{-5}K_{a1}[H_3O^+] - 0.04997K_{a1}K_{a2} = 0$$

This equation can then be solved for $[H_3O^+]$.

$$[H_3O^+] = 7.60 \times 10^{-5}\ M$$

$$pH = 4.12$$

Second Buffer Region

Further additions of base to the solution create a new buffer system consisting of HM^- and M^{2-}. When enough base has been added so that the reaction of HM^- with water to give OH^- can be neglected (a few tenths of a milliliter beyond the first equivalence point), the pH of the mixture may be calculated from K_{a2}. With the introduction of 25.50 mL of NaOH, for example,

$$[M^{2-}] \approx c_{Na_2M} = \frac{(25.50 - 25.00)(0.1000)}{50.50} = \frac{0.050}{50.50}\ M$$

and the molar concentration of NaHM is

$$[HM^-] \approx c_{NaHM} = \frac{(25.00 \times 0.1000) - (25.50 - 25.00)(0.1000)}{50.50} = \frac{2.45}{50.50}\ M$$

Substituting these values into the expression for K_{a2} gives

$$K_{a2} = \frac{[H_3O^+][M^{2-}]}{[HM^-]} = \frac{[H_3O^+](0.050/\cancel{50.50})}{2.45/\cancel{50.50}} = 5.9 \times 10^{-7}$$

$$[H_3O^+] = 2.89 \times 10^{-5}\ M$$

The assumption that $[H_3O^+]$ is small relative to c_{HM^-} and $c_{M^{2-}}$ is valid, and pH = 4.54. The other values in the second buffer region are calculated in a similar manner.

Just Prior to Second Equivalence Point

Just prior to the second equivalence point (49.90 mL and more), the ratio $[M^{2-}]/[HM^-]$ becomes large, and the simple buffer equation no longer applies. At 49.90 mL, $c_{HM^-} = 1.335 \times 10^{-4}$ M, and $c_{M^{2-}} = 0.03324$. The primary equilibrium is now

$$M^{2-} + H_2O \rightleftharpoons HM^- + OH^-$$

(continued)

We can write the equilibrium constant as

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{[OH^-][HM^-]}{[M^{2-}]} = \frac{[OH^-](1.335 \times 10^{-4} + [OH^-])}{(0.03324 - [OH^-])}$$

$$= \frac{1.00 \times 10^{-14}}{5.9 \times 10^{-7}} = 1.69 \times 10^{-8}$$

In this case, it is easier to solve for $[OH^-]$ than for $[H_3O^+]$. Solving the resulting quadratic equation gives

$$[OH^-] = 4.10 \times 10^{-6}\ M$$

$$pOH = 5.39$$

$$pH = 14.00 - pOH = 8.61$$

The same reasoning for 49.99 mL leads to $[OH^-] = 1.80 \times 10^{-5}$ M, and pH = 9.26.

Second Equivalence Point

After the addition of 50.00 mL of 0.1000 M sodium hydroxide, the solution is 0.0333 M in Na_2M (2.5 mmol/75.00 mL). Reaction of the base M^{2-} with water is the predominant equilibrium in the system and the only one that we need to take into account. Thus,

$$\boxed{M^{2-} + H_2O \rightleftharpoons OH^- + HM^-}$$

$$\boxed{K_{b1} = \frac{K_w}{K_{a2}} = \frac{[OH^-][HM^-]}{[M^{2-}]} = 1.69 \times 10^{-8}}$$

$$[OH^-] \cong [HM^-]$$

$$[M^{2-}] = 0.0333 - [OH^-] \cong 0.0333$$

$$\frac{[OH^-]^2}{0.0333} = 1.69 \times 10^{-8}$$

$$[OH^-] = 2.37 \times 10^{-5}\ M, \text{ and } pOH = -\log(2.37 \times 10^{-5}) = 4.62$$

$$pH = 14.00 - pOH = 9.38$$

pH Just beyond Second Equivalence Point

In the region just beyond the second equivalence point (50.01 mL, for example), we still need to take into account the reaction of M^{2-} with water to give OH^- since not enough OH^- has been added in excess to suppress this reaction. The analytical concentration of M^{2-} is the number of millimoles of M^{2-} produced divided by the total solution volume:

$$c_{M^{2-}} = \frac{25.00 \times 0.1000}{75.01} = 0.03333\ M$$

The OH^- now comes from the reaction of M^{2-} with water and from the excess OH^- added as titrant. The number of millimoles of excess OH^- is then the number of millimoles of NaOH added minus the number required to reach the second equivalence point. The concentration of this excess is the number of millimoles of excess OH^- divided by the total solution volume, or

$$[OH^-]_{excess} = \frac{(50.01 - 50.00) \times 0.1000}{75.01} = 1.333 \times 10^{-5}\ M$$

The concentration of HM^- can now be found from K_{b1}.

$$[M^{2-}] = c_{M^{2-}} - [HM^-] = 0.03333 - [HM^-]$$

$$[OH^-] = 1.3333 \times 10^{-5} + [HM^-]$$

$$K_{b1} = \frac{[HM^-][OH^-]}{[M^{2-}]} = \frac{[HM^-](1.3333 \times 10^{-5} + [HM^-])}{0.03333 - [HM^-]} = 1.69 \times 10^{-8}$$

Solving the quadratic equation for $[HM^-]$ gives

$$[HM^-] = 1.807 \times 10^{-5}\ M$$

and

$$[OH^-] = 1.3333 \times 10^{-5} + [HM^-] = 1.33 \times 10^{-5} + 1.807 \times 10^{-5} = 3.14 \times 10^{-5}\ M$$

$$pOH = 4.50 \text{ and } pH = 14.00 - pOH = 9.50$$

The same reasoning applies to 50.10 mL where the calculations give pH = 10.14

pH beyond the Second Equivalence Point

Addition of more than a few tenths of a milliliter of NaOH beyond the second equivalence point gives enough excess OH^- to repress the basic dissociation of M^{2-}. The pH is then calculated from the concentration of NaOH added in excess of that required for the complete neutralization of H_2M. Thus, when 51.00 mL of NaOH have been added, we have 1.00-mL excess of 0.1000 M NaOH, and

$$[OH^-] = \frac{1.00 \times 0.100}{76.00} = 1.32 \times 10^{-3}\ M$$

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

$$pH = 14.00 - pOH = 11.12$$

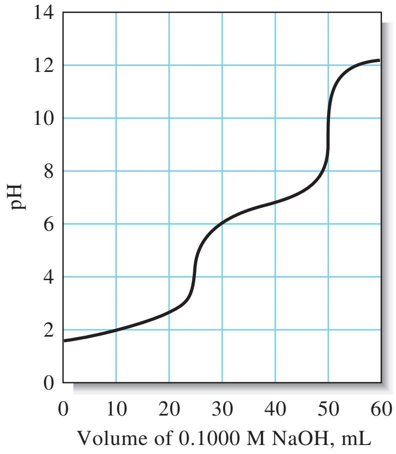


Figure 15-3 Titration curve for 25.00 mL of 0.1000 M maleic acid, H_2M, titrated with 0.1000 M NaOH.

Figure 15-3 is the titration curve for 0.1000 M maleic acid generated as shown in Example 15-9. Two end points are apparent, either of which could in principle be used as a measure of the concentration of the acid. The second end point is more satisfactory, however, because the pH change is more pronounced than in the first.

Figure 15-4 shows titration curves for three other polyprotic acids. These curves illustrate that a well-defined end point corresponding to the first equivalence point is observed only when the degree of dissociation of the two acids is sufficiently different. The ratio K_{a1}/K_{a2} for oxalic acid (curve *B*) is approximately 1000. The curve for this titration shows an inflection corresponding to the first equivalence point. The magnitude of the pH change is too small to permit precise location of the end point with an indicator. The second end point, however, can be used to accurately determine oxalic acid.

Curve *A* in Figure 15-4 is the theoretical titration curve for triprotic phosphoric acid. For this acid, the ratio K_{a1}/K_{a2} is approximately 10^5, as is K_{a2}/K_{a3}. This results in two well-defined end points, either of which is satisfactory for analytical purposes.

❮ In titrating a polyprotic acid or base, two usable end points appear if the ratio of dissociation constants is greater than 10^4 and if the weaker acid or base has a dissociation constant greater than 10^{-8}.

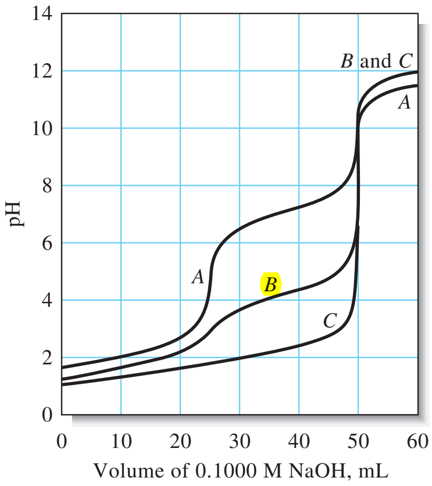


Figure 15-4 Curves for the titration of polyprotic acids. A 0.1000 M NaOH solution is used to titrate 25.00 mL of 0.1000 M H_3PO_4 (curve *A*), 0.1000 M oxalic acid (curve *B*), and 0.1000 M H_2SO_4 (curve *C*).

An acid-range indicator will provide a color change when 1 mol of base has been introduced for each mole of acid, and a base-range indicator will require 2 mol of base per mole of acid. The third hydrogen of phosphoric acid is so slightly dissociated ($K_{a3} = 4.5 \times 10^{-13}$) that no practical end point is associated with its neutralization. The buffering effect of the third dissociation is noticeable, however, and causes the pH for curve *A* to be lower than the pH for the other two curves in the region beyond the second equivalence point.

CHALLENGE: Construct a titration curve for 50.00 mL of 0.0500 M H_2SO_4 with 0.1000 M NaOH.

Curve *C* is the titration curve for sulfuric acid, a substance that has one fully dissociated proton and one that is dissociated to a relatively large extent ($K_{a2} = 1.02 \times 10^{-2}$). Because of the similarity in strengths of the two acids, only a single end point, corresponding to the titration of both protons, is observed. Calculation of the pH in sulfuric acid solutions is illustrated in Feature 15-1.

In general, the titration of acids or bases that have two reactive groups yields individual end points that are of practical value only when the ratio between the two dissociation constants is at least 10^4. If the ratio is much smaller than this 10^4, the pH change at the first equivalence point will prove less satisfactory for an analysis.

FEATURE 15-1

The Dissociation of Sulfuric Acid

Sulfuric acid is unusual in that one of its protons behaves as a strong acid in water and the other as a weak acid ($K_{a2} = 1.02 \times 10^{-2}$). Let us consider how the hydronium ion concentration of sulfuric acid solutions is computed using a 0.0400 M solution as an example.

We will first assume that the dissociation of HSO_4 is negligible because of the large excess of H_3O^+ resulting from the complete dissociation of H_2SO_4. Therefore,

$$[H_3O^+] \approx [HSO_4^-] \approx 0.0400\ M$$

An estimate of $[SO_4^{2-}]$ based on this approximation and the expression for K_{a2} reveals that

$$\frac{\cancel{0.0400}\,[SO_4^{2-}]}{\cancel{0.0400}} = 1.02 \times 10^{-2}$$

We see that $[SO_4^{2-}]$ is *not* small relative to $[HSO_4^-]$, and a more rigorous solution is required.

From stoichiometric considerations, it is necessary that

$$[H_3O^+] = 0.0400 + [SO_4^{2-}]$$

The first term on the right is the concentration of H_3O^+ resulting from dissociation of the H_2SO_4 to HSO_4^-. The second term is the contribution of the dissociation of HSO_4^-. Rearrangement yields

$$[SO_4^{2-}] = [H_3O^+] - 0.0400$$

Mass-balance considerations require that

$$c_{H_2SO_4} = 0.0400 = [HSO_4^-] + [SO_4^{2-}]$$

Combining the last two equations and rearranging yield

$$[HSO_4^-] = 0.0800 - [H_3O^+]$$

By introducing these equations for $[SO_4^{2-}]$ and HSO_4^- into the expression for K_{a2}, we find that

$$\frac{[H_3O^+]([H_3O^+] - 0.0400)}{0.0800 - [H_3O^+]} = 1.02 \times 10^{-2}$$

Solving the quadratic equation for $[H_3O^+]$ yields

$$[H_3O^+] = 0.0471 \text{ M}$$

Spreadsheet Summary In Chapter 8 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., we extend the treatment of neutralization titration curves to polyfunctional acids. Both a stoichiometric approach and a master equation approach are used for the titration of maleic acid with sodium hydroxide.

15F TITRATION CURVES FOR POLYFUNCTIONAL BASES

The same principles just described for constructing titration curves for polyfunctional acids can be applied to titration curves for polyfunctional bases. To illustrate, consider the titration of a sodium carbonate solution with standard hydrochloric acid. The important equilibrium constants are

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^- \qquad K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{4.69 \times 10^{-11}} = 2.13 \times 10^{-4}$$

$$\boxed{HCO_3^- + H_2O \rightleftharpoons OH^- + CO_2(aq) \quad K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}}$$

The reaction of carbonate ion with water governs the initial pH of the solution, which can be found by the method shown for the second equivalence point in Example 15-9. With the first additions of acid, a carbonate/hydrogen carbonate buffer is established. In this region, the pH can be determined from *either* the hydroxide ion concentration calculated from K_{b1} *or* the hydronium ion concentration calculated from K_{a2}. Because we are usually interested in calculating $[H_3O^+]$ and pH, the expression for K_{a2} is easier to use.

CHALLENGE: Show that either K_{b2} or K_{a1} can be used to calculate the pH of a buffer that is 0.100 M in Na_2CO_3 and 0.100 M in $NaHCO_3$.

Sodium hydrogen carbonate is the principal solute species at the first equivalence point, and Equation 15-16 is used to compute the hydronium ion concentration (see Example 15-8). With the addition of more acid, a new buffer consisting of sodium hydrogen carbonate and carbonic acid (from $CO_2(aq)$ as shown in Equation 15-3) is formed. The pH of this buffer is easily calculated from either K_{b2} or K_{a1}.

At the second equivalence point, the solution consists of $CO_2(aq)$ (carbonic acid) and sodium chloride. The $CO_2(aq)$ can be treated as a simple weak acid having a dissociation constant K_{a1}. Finally, after excess hydrochloric acid has been introduced, the dissociation of the weak acid is repressed to a point where the hydronium ion concentration is essentially that of the molar concentration of the strong acid.

Figure 15-5 illustrates that two end points appear in the titration of sodium carbonate, the second being appreciably sharper than the first. This suggests that the individual components in mixtures of sodium carbonate and sodium hydrogen carbonate can be determined by neutralization methods.

Spreadsheet Summary The titration curve for a difunctional base being titrated with strong acid is developed in Chapter 8 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. In the example studied, ethylene diamine is titrated with hydrochloric acid. A master equation approach is explored, and the spreadsheet is used to plot pH versus fraction titrated.

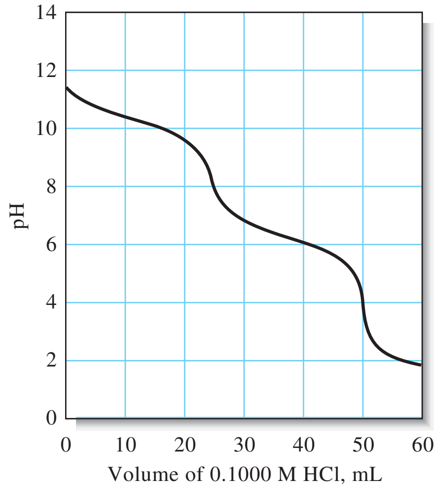


Figure 15-5 Curve for the titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl.

15G TITRATION CURVES FOR AMPHIPROTIC SPECIES

An amphiprotic substance when dissolved in a suitable solvent behaves both as a weak acid and as a weak base. If either of its acidic or basic characters predominates, titration of the substance with a strong base or a strong acid may be feasible. For example, in a sodium dihydrogen phosphate solution, the principal equilibria are:

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a2} = 6.32 \times 10^{-8}$$

$$H_2PO_4^- + H_2O \rightleftharpoons OH^- + H_3PO_4 \qquad K_{b3} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}}$$

$$= 1.41 \times 10^{-12}$$

Note that K_{b3} is much too small to permit titration of $H_2PO_4^-$ with an acid, but K_{a2} is large enough for a successful titration of dihydrogen phosphate with a standard base solution.

A different situation prevails in solutions containing disodium hydrogen phosphate for which the pertinent equilibria are

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a3} = 4.5 \times 10^{-13}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons OH^- + H_2PO_4^- \qquad K_{b2} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{6.32 \times 10^{-8}}$$

$$= 1.58 \times 10^{-7}$$

The magnitude of the constants indicates that HPO_4^{2-} can be titrated with standard acid but not with standard base.

Amino acids are amphiprotic.

FEATURE 15-2

Acid/Base Behavior of Amino Acids

The simple amino acids are an important class of amphiprotic compounds that contain both a weak acid and a weak base functional group. In an aqueous solution of a typical amino acid, such as glycine, three important equilibria operate:

$$NH_2CH_2COOH \rightleftharpoons NH_3^+CH_2COO^- \qquad (15\text{-}17)$$

$$NH_3^+CH_2COO^- + H_2O \rightleftharpoons$$
$$NH_2CH_2COO^- + H_3O^+ \qquad K_a = 2 \times 10^{-10} \qquad (15\text{-}18)$$

$$NH_3^+CH_2COO^- + H_2O \rightleftharpoons$$
$$NH_3^+CH_2COOH + OH^- \qquad K_b = 2 \times 10^{-12} \qquad (15\text{-}19)$$

The first equilibrium constitutes a kind of internal acid/base reaction and is analogous to the reaction one would observe between a carboxylic acid and an amine:

$$R_1NH_2 + R_2COOH \rightleftharpoons R_1NH_3^+ + R_2COO^- \qquad (15\text{-}20)$$

The typical aliphatic amine has a base dissociation constant of 10^{-4} to 10^{-5} (see Appendix 3), while many carboxylic acids have acid dissociation constants of about the same magnitude. As a result, both Reactions 15-18 and 15-19 proceed far to the right, with the product or products being the predominant species in the solution.

(*continued*)

A **zwitterion** is an ionic species that has both a positive and a negative charge.

The **isoelectric** point of a species is the pH at which no net migration occurs in an electric field.

The amino acid species in Equation 15-17, which bears both a positive and a negative charge, is called a **zwitterion**. As shown by Equations 15-18 and 15-19, the zwitterion of glycine is stronger as an acid than as a base. Thus, an aqueous solution of glycine is somewhat acidic.

The zwitterion of an amino acid, which contains both a positive and a negative charge, has no tendency to migrate in an electric field, although the singly charged anionic and cationic species are attracted to electrodes of opposite polarity. No net migration of the amino acid occurs in an electric field when the pH of the solvent is such that the concentrations of the anionic and cationic forms are identical. The pH at which no net migration occurs is called the **isoelectric point** and is an important physical constant for characterizing amino acids. The isoelectric point is readily related to the ionization constants for the species. Thus, for glycine,

$$K_a = \frac{[NH_2CH_2COO^-][H_3O^+]}{[NH_3^+CH_2COO^-]}$$

$$K_b = \frac{[NH_3^+CH_2COOH][OH^-]}{[NH_3^+CH_2COO^-]}$$

At the isoelectric point,

$$[NH_2CH_2COO^-] = [NH_3^+CH_2COOH]$$

Therefore, if we divide K_a by K_b and substitute this relationship, we obtain for the isoelectric point

$$\frac{K_a}{K_b} = \frac{[H_3O^+][NH_2CH_2COO^-]}{[OH^-][NH_3^+CH_2COOH]} = \frac{[H_3O^+]}{[OH^-]}$$

If we substitute $K_w/[H_3O^+]$ for $[OH^-]$ and rearrange, we get

$$[H_3O^+] = \sqrt{\frac{K_aK_w}{K_b}}$$

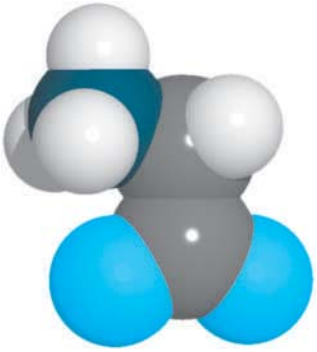
The isoelectric point for glycine occurs at a pH of 6.0, that is

$$[H_3O^+] = \sqrt{\frac{(2 \times 10^{-10})(1 \times 10^{-14})}{2 \times 10^{-12}}} = 1 \times 10^{-6}\ M$$

For simple amino acids, K_a and K_b are generally so small that their determination by direct neutralization is impossible. Addition of formaldehyde removes the amine functional group, however, and leaves the carboxylic acid available for titration with a standard base. For example, with glycine,

$$NH_3^+CH_2COO^- + CH_2O \rightarrow CH_2C{=}NCH_2COOH + H_2O$$

The titration curve for the product is that of a typical carboxylic acid.



The molecular structure of the glycine zwitterion, $NH_3^+CH_2COO^-$. Glycine is one of the so-called nonessential amino acids; it is nonessential in the sense that it is synthesized in the bodies of mammals and so is not generally essential in the diet. Because of its compact structure, glycine acts as a versatile building block in protein synthesis and in the biosynthesis of hemoglobin. A significant fraction of the collagen—or the fibrous protein constituent of bone, cartilage, tendon, and other connective tissue in the human body—is made up of glycine. Glycine is also an inhibitory *neurotransmitter* and, as a result, has been suggested as a possible therapeutic agent for diseases of the central nervous system such as multiple sclerosis and epilepsy. Glycine is also used in treating schizophrenia, stroke, and benign prostatic hyperplasia.

Spreadsheet Summary The final exercise in Chapter 8 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., considers the titration of an amphiprotic species, phenylalanine. A spreadsheet is developed to plot the titration curve of this amino acid, and the isoelectric pH is calculated.

15H COMPOSITION OF POLYPROTIC ACID SOLUTIONS AS A FUNCTION OF pH

In Section 14E, we showed how alpha values are useful in visualizing the changes in the concentration of various species that occur in a titration of a monoprotic weak acid. Alpha values provide an excellent way of thinking about the properties of polyfunctional acids and bases. For example, if we let c_T be the sum of the molar concentrations of the maleate-containing species in the solution throughout the titration described in Example 15-9, the alpha value for the free acid α_0 is defined as

$$\alpha_0 = \frac{[H_2M]}{c_T}$$

where

$$c_T = [H_2M] + [HM^-] + [M^{2-}] \tag{15-21}$$

The alpha values for HM^- and M^{2-} are given by similar equations

$$\alpha_1 = \frac{[HM^-]}{c_T}$$

$$\alpha_2 = \frac{[M^{2-}]}{c_T}$$

As noted in Section 9C-2, the sum of the alpha values for a system must equal one:

$$\alpha_0 + \alpha_1 + \alpha_2 = 1$$

We may express the alpha values for the maleic acid system very neatly in terms of $[H_3O^+]$, K_{a1}, and K_{a2}. To find the appropriate expressions, we follow the method used to derive Equations 9-35 and 9-36 in Section 9C-2 and obtain the following equations:

CHALLENGE: Derive Equations 15-22, 15-23, and 15-24.

$$\alpha_0 = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \tag{15-22}$$

$$\alpha_1 = \frac{K_{a1}[H_3O^+]}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \tag{15-23}$$

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \tag{15-24}$$

Notice that the denominator is the same for each expression. A somewhat surprising result is that the fractional amount of each species is fixed at a given pH and is *absolutely independent* of the total concentration, c_T. A general expression for the alpha values is given in Feature 15-3.

FEATURE 15-3

A General Expression for Alpha Values

For the weak acid H_nA, the denominator D in all alpha-value expressions takes the form:

$$D = [H_3O^+]^n + K_{a1}[H_3O^+]^{(n-1)} + K_{a1}K_{a2}[H_3O^+]^{(n-2)} + \cdots K_{a1}K_{a2}\cdots K_{an}$$

The numerator for α_0 is the first term in the denominator, and for α_1, it is the second term, and so forth. Thus, $\alpha_0 = [H_3O^+]^n/D$, and $\alpha_1 = K_{a1}[H_3O^+]^{(n-1)}/D$.

Alpha values for polyfunctional bases are generated in an analogous way, with the equations being written in terms of base dissociation constants and $[OH^-]$.

The three curves plotted in **Figure 15-6** show the alpha values for each maleate-containing species as a function of pH. The solid curves in **Figure 15-7** depict the same alpha values but now plotted as a function of volume of sodium hydroxide as the acid is titrated. The titration curve is also shown by the dashed line in Figure 15-7. These curves give a comprehensive picture of all concentration changes that occur during the titration. For example, Figure 15-7 reveals that before the addition of any base, α_0 for H_2M is roughly 0.7, and α_1 for HM^- is approximately 0.3. For all practical purposes, α_2 is zero. Thus, initially, approximately 70% of the maleic acid exists as H_2M and 30% as HM^-. With addition of base, the pH rises, as does the fraction of HM^-. At the first equivalence point ($pH = 4.11$), essentially all of the maleate is present as HM^- ($\alpha_1 \rightarrow 1$). When we add more base, beyond the first equivalence point, HM^- decreases and M^{2-} increases. At the second equivalence point ($pH = 9.38$) and beyond, essentially all of the maleate is in the M^{2-} form.

Another way to visualize polyfunctional acid and base systems is by using logarithmic concentration diagrams, as illustrated in Feature 15-4.

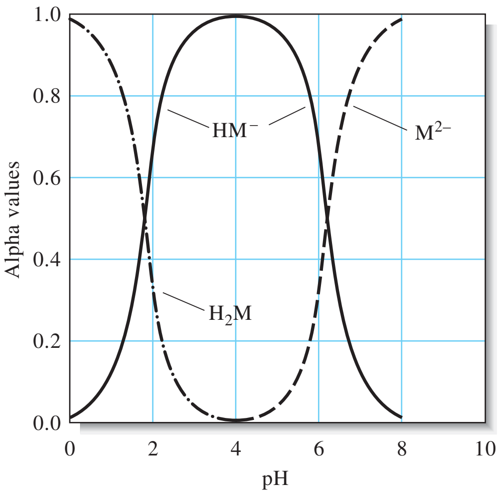


Figure 15-6 Composition of H_2M solutions as a function of pH.

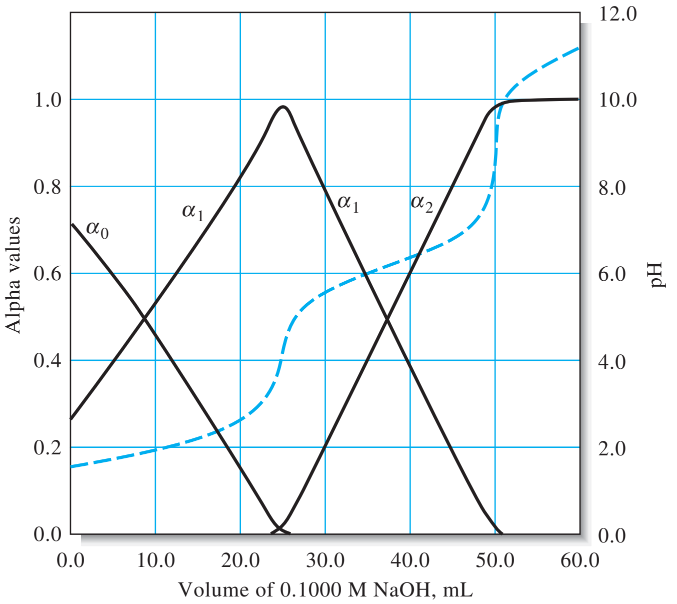


Figure 15-7 Titration of 25.00 mL of 0.1000 M maleic acid with 0.1000 M NaOH. The solid curves are plots of alpha values as a function of titrant volume. The broken curve is the titration curve of pH as a function of volume.

FEATURE 15-4

Logarithmic Concentration Diagrams

A logarithmic concentration diagram is a plot of log concentration versus a master variable such as pH. Such diagrams are useful because they express the concentrations of all species in a polyprotic acid solution as a function of pH. This type of diagram allows us to observe at a glance the species that are important at a particular pH. The logarithmic scale is used because the concentrations can vary over many orders of magnitude.

The logarithmic concentration diagram only applies for a specific acid and for a particular initial concentration of acid. We may calculate results to construct logarithmic concentration diagrams from the distribution diagrams previously discussed. The details of constructing logarithmic concentration diagrams are given in Chapter 8 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed.

Logarithmic concentration diagrams can be computed from the concentration of acid and the dissociation constants. We use as an example the maleic acid system discussed previously. The diagram shown in **Figure 15F-1** is a logarithmic concentration diagram for a maleic acid concentration of 0.10M (c_T = 0.10 M maleic acid). The diagram expresses the concentrations of all forms of maleic acid, H_2M, HM^-, and M^{2-} as a function of pH. We usually include the H_3O^+ and OH^- concentrations as well. The diagram is based on the mass-balance condition and the acid-dissociation constants. The changes in slope in the diagram for the maleic acid species occur near what are termed **system points**. These are defined by the total acid concentration, 0.10 M in our case, and the pK_a values. For maleic acid, the first system point occurs at $\log c_T = -1$ and $\text{pH} = \text{p}K_{a1} = -\log(1.30 \times 10^{-2}) = 1.89$, while the second system point is at $\text{pH} = \text{p}K_{a2} = -\log(5.90 \times 10^{-7}) = 6.23$ and $\log c_T = -1$. Note that when pH = pK_{a1}, the concentrations of H_2M and HM^- are equal as shown by the crossing of the lines indicating these concentrations. Also, note that at this first system point $[M^{2-}] << [HM^-]$ and $[M^{2-}] << [H_2M]$. Near this first system point we can thus neglect the unprotonated maleate ion and express the mass balance as $c_T \approx [H_2M] + [HM^-]$.

To the left of this first system point, $[H_2M] >> [HM^-]$, and so $c_T \approx [H_2M]$. This is indicated on the diagram by the slope of 0 for the H_2M line between pH values of 0 to about 1. In this same region, the HM^- concentration is steadily increasing with increasing pH since protons are removed from H_2M as the pH increases. From the K_{a1} expression we can write,

$$[HM^-] = \frac{[H_2M]K_{a1}}{[H_3O^+]} \approx \frac{c_T K_{a1}}{[H_3O^+]}$$

Taking the logarithms of both sides of this equation gives

$$\log [HM^-] = \log c_T + \log K_{a1} - \log [H_3O^+]$$
$$= \log c_T + \log K_{a1} + \text{pH}$$

Hence, to the left of the first system point (region A), a plot of $\log [HM^-]$ versus pH is a straight line of slope +1.

Using similar reasoning we conclude that to the right of the first system point, $c_T \approx [HM^-]$, and

$$[H_2M] \approx \frac{c_T[H_3O^+]}{K_{a1}}$$

(*continued*)

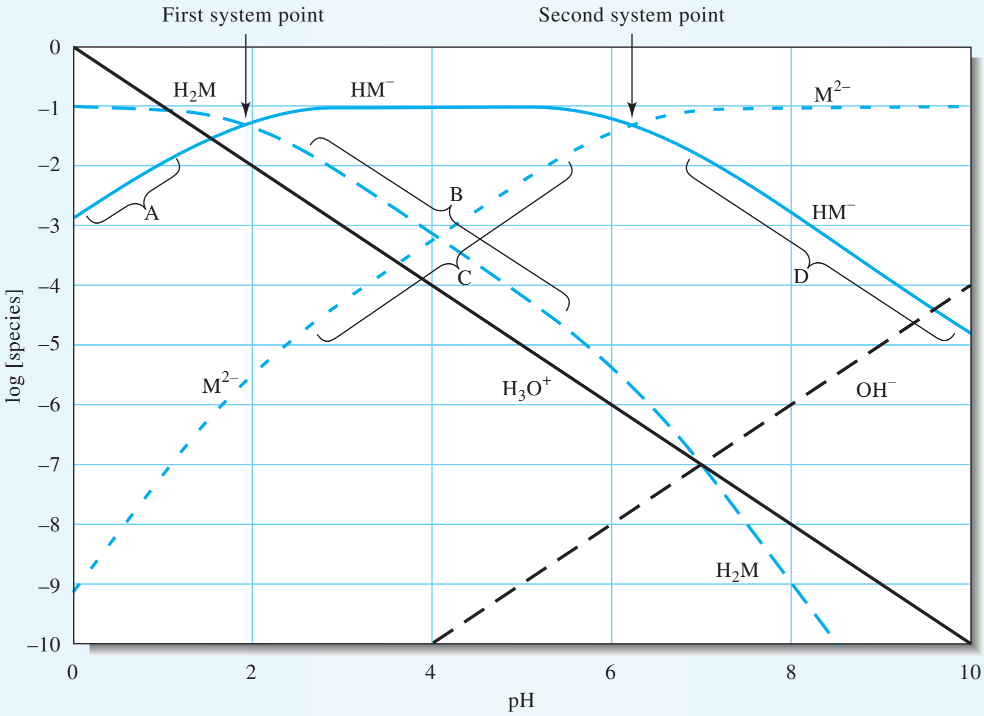


Figure 15F-1 Logarithmic concentration diagram for 0.10 M maleic acid.

Taking the logarithms of both sides of this equation reveals that a plot of log [H_2M] versus pH (region B) should be linear with a slope of −1. This relationship holds until we get near the second system point that occurs at pH = pK_{a2} = −log (5.90×10^{-7}) = 6.23 and log c_T = −1.

At the second system point, the HM^- and M^{2-} concentrations are equal. Note that to the left of the second system point, [HM^-] ≈ c_T, and log [M^{2-}] increases with increasing pH with a slope of +1 (region C). To the right of the second system point, [M^{2-}] ≈ c_T, and log [HM^-] decreases with increasing pH with a slope of −1 (region D). The H_3O^+ lines and the OH^- lines are easy to draw since

$$\log [H_3O^+] = -\,\text{pH}, \text{ and } \log [OH^-] = \text{pH} - 14.$$

We can draw a logarithmic concentration diagram easily by noting the relationships given above. An easier method is to modify the distribution diagram so that it produces the logarithmic concentration diagram. This is the method illustrated in *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., Chapter 8. Note that the plot is specific for a total analytical concentration of 0.10 M and for maleic acid since the acid dissociation constants are included.

Estimating Concentrations at a Given pH Value

The log concentration diagram can be very useful in making more exact calculations and in determining which species are important at a given pH. For example, if we are interested in calculating concentrations at pH 5.7, we can use the diagram in Figure 15F-1 to tell us which species to include in the calculation. At pH 5.7, the concentrations of the maleate containing species are [H_2M] ≈ 10^{-5} M, [HM^-] ≈ 0.07 M, and [M^{2-}] ≈ 0.02 M. Hence, the only maleate species of importance at this pH are HM^- and M^{2-}. Since [OH^-] is four orders of magnitude lower than [H_3O^+], we could carry out a more accurate calculation than the above estimates by considering only three species. If we do so, we find the following concentrations: [H_2M] ≈ 1.18×10^{-5} M, [HM^-] ≈ 0.077 M, and [M^{2-}] = 0.023 M.

Finding pH Values

If we do not know the pH, the logarithmic concentration diagram can also be used to give us an approximate pH value. For example, find the pH of a 0.10 M maleic acid solution. Since the log concentration diagram expresses mass balance and the equilibrium constants, we need only one additional equation such as charge balance to solve the problem exactly. The charge-balance equation for this system is

$$[H_3O^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$

The pH is found by graphically superimposing the charge-balance equation on the log concentration diagram. Beginning with a pH of 0, move from left to right along the H_3O^+ line until it intersects a line representing one of the species on the right hand side of the charge-balance equation. We see that the H_3O^+ line first intersects the HM^- line at a pH of approximately 1.5. At this point, [H_3O^+] = [HM^-]. We also see that the concentrations of the other negatively charged species M^{2-} and OH^- are negligible compared to the HM^- concentration. Hence, the pH of a 0.10 M solution of maleic acid is approximately 1.5. A more accurate calculation using the quadratic formula gives pH = 1.52.

We can ask another question: "What is the pH of a 0.10 M solution of NaHM?" In this case, the charge-balance equation is

$$[H_3O^+] + [Na^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$

The Na^+ concentration is just the total concentration of maleate-containing species:

$$[Na^+] = c_T = [H_2M] + [HM^-] + [M^{2-}]$$

Substituting this latter equation into the charge-balance equation gives

$$[H_3O^+] + [H_2M] = [M^{2-}] + [OH^-]$$

Now, we superimpose this equation on the log concentration diagram. If we again begin on the left at pH 0 and move along either the H_3O^+ line or the H_2M line, we see that, at pH values greater than about 2, the concentration of H_2M exceeds the H_3O^+ concentration by about an order of magnitude. Hence, we move along the H_2M line until it intersects either the M^{2-} line or the OH^- line. We see that it intersects the M^{2-} line first at pH ≈ 4.1. Thus, $[H_2M] \approx [M^{2-}]$, and the concentrations of the $[H_3O^+]$ and $[OH^-]$ are relatively small compared to H_2M and M^{2-}. Therefore, we conclude that the pH of a 0.10 M NaHM solution is approximately 4.1. A more exact calculation using the quadratic formula reveals that the pH of this solution is 4.08.

Finally, we will find the pH of a 0.10 M solution of Na_2M. The charge-balance equation is the same as before:

$$[H_3O^+] + [Na^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$

Now, however, the Na^+ concentration is given by

$$[Na^+] = 2c_T = 2[H_2M] + 2[HM^-] + 2[M^{2-}]$$

Substituting this equation into the charge-balance equation gives

$$[H_3O^+] + 2[H_2M] + [HM^-] = [OH^-]$$

In this case, it is easier to find the OH^- concentration. This time we move down the OH^- line from right to left until it intersects the HM^- line at a pH of approximately 9.7. Since $[H_3O^+]$ and $[H_2M]$ are negligibly small at this intersection, $[HM^-] \approx [OH^-]$, and we conclude that pH 9.7 is the approximate pH of a 0.10 M solution of Na_2M. A more exact calculation using the quadratic formula gives the pH as 9.61.

Spreadsheet Summary In the first exercise in Chapter 8 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., we investigate the calculation of distribution diagrams for polyfunctional acids and bases. The alpha values are plotted as a function of pH. The plots are used to find concentrations at a given pH and to infer which species can be neglected in more extensive calculations. A logarithmic concentration diagram is constructed. The diagram is used to estimate concentrations at a given pH and to find the pH for various starting conditions with a weak acid system.

WEB WORKS

Go to **www.cengage.com/chemistry/skoog/fac9**, choose Chapter 15 and go to the Web Works. Click on the link to the Virtual Titrator. Click on the indicated frame to invoke the Virtual Titrator Java applet and display two windows: the Menu Panel and the Virtual Titrator main window. To begin, click on Acids on the main window menu bar and select the diprotic acid *o*-phthalic acid. Examine the titration curve that results. Then, click on Graphs/Alpha Plot vs. pH and observe the result. Click on Graphs/Alpha Plot vs. mL base. Repeat the process for several monoprotic and polyprotic acids and note the results.

QUESTIONS AND PROBLEMS

*15-1. As its name implies, NaHA is an "acid salt" because it has a proton available to donate to a base. Briefly explain why a pH calculation for a solution of NaHA differs from that for a weak acid of the type HA.

15-2. Explain the origin and significance of each of the terms on the right side of Equation 15-12. Does the equation make intuitive sense? Why or why not?

15-3. Briefly explain why Equation 15-15 can only be used to calculate the hydronium ion concentration of solutions in which NaHA is the only solute that determines the pH.

*15-4. Why is it impossible to titrate all three protons of phosphoric acid in aqueous solution?

15-5. Indicate whether an aqueous solution of the following compounds is acidic, neutral, or basic. Explain your answer.

*(a) NH_4OAc
(b) $NaNO_2$
*(c) $NaNO_3$
(d) $NaHC_2O_4$
*(e) $Na_2C_2O_4$
(f) Na_2HPO_4
*(g) NaH_2PO_4
(h) Na_3PO_4

*15-6. Suggest an indicator that could be used to provide an end point for the titration of the first proton in H_3AsO_4.

15-7. Suggest an indicator that would give an end point for the titration of the first two protons in H_3AsO_4.

*15-8. Suggest a method for determining the amounts of H_3PO_4 and NaH_2PO_4 in an aqueous solution.

15-9. Suggest a suitable indicator for a titration based on each of the following reactions. Use 0.05 M if an equivalence point concentration is needed.

*(a) $H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$
(b) $H_2P + 2NaOH \rightarrow Na_2P + 2H_2O$ (H_2P = *o*-phthalic acid)
*(c) $H_2T + 2NaOH \rightarrow Na_2T + 2H_2O$ (H_2T = tartaric acid)
(d) $NH_2C_2H_4NH_2 + HCl \rightarrow NH_2C_2H_4NH_3Cl$
*(e) $NH_2C_2H_4NH_2 + 2HCl \rightarrow ClNH_3C_2H_4NH_3Cl$
(f) $H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O$
*(g) $H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 + 2H_2O$

15-10. Calculate the pH of a solution that is 0.0400 M in

*(a) H_3PO_4.
(b) $H_2C_2O_4$.
*(c) H_3PO_3.
(d) H_2SO_3.
*(e) H_2S.
(f) $H_2NC_2H_4NH_2$.

15-11. Calculate the pH of a solution that is 0.0400 M in

*(a) NaH_2PO_4.
(b) $NaHC_2O_4$.
*(c) NaH_2PO_3.
(d) $NaHSO_3$.
*(e) NaHS.
(f) $H_2NC_2H_4NH_3^+Cl^-$.

15-12. Calculate the pH of a solution that is 0.0400 M in

*(a) Na_3PO_4.
(b) $Na_2C_2O_4$.
*(c) Na_2HPO_3.
(d) Na_2SO_3.
*(e) Na_2S.
(f) $C_2H_4(NH_3^+Cl^-)_2$.

15-13. Calculate the pH of a solution that contains the following analytical concentrations:

(a) 0.0500 M in H_3PO_4 and 0.0200 M in NaH_2PO_4.
(b) 0.0300 M in NaH_2AsO_4 and 0.0500 M in Na_2HAsO_4.
(c) 0.0600 M in Na_2CO_3 and 0.0300 M in $NaHCO_3$.
(d) 0.0400 M in H_3PO_4 and 0.0200 M in Na_2HPO_4.
(e) 0.0500 M in $NaHSO_4$ and 0.0400 M in Na_2SO_4.

*15-14. Calculate the pH of a solution that contains the following analytical concentrations:

(a) 0.225 M in H_3PO_4 and 0.414 M in NaH_2PO_4.
(b) 0.0670 M in Na_2SO_3 and 0.0315 M in $NaHSO_3$.
(c) 0.640 M in $HOC_2H_4NH_2$ and 0.750 M in $HOC_2H_4NH_3Cl$.
(d) 0.0240 in $H_2C_2O_4$ (oxalic acid) and 0.0360 M in $Na_2C_2O_4$.
(e) 0.0100 M in $Na_2C_2O_4$ and 0.0400 M in $NaHC_2O_4$.