Chapter 15

Complex Acid/Base Systems

➢ 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.
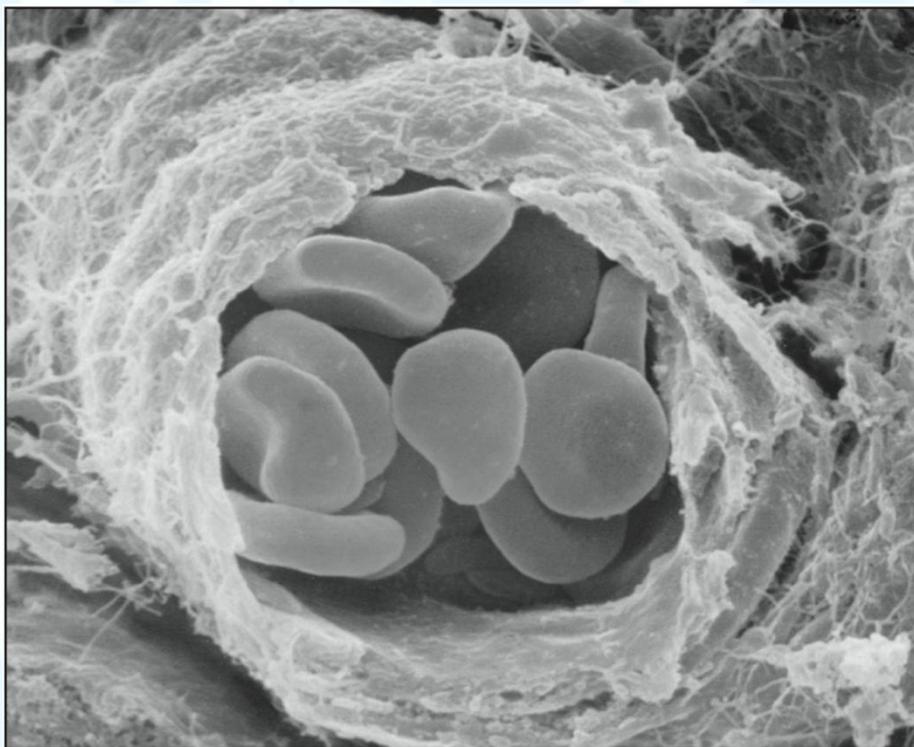
➢ Shown here is a scanning electron micrograph of red blood cells traveling through an artery.

➢ 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:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$
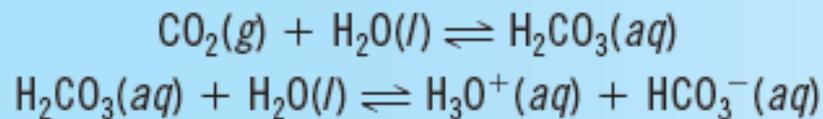
➢ This chapter describes polyfunctional acid and base systems including buffer solns.

➢ Calculations of pH and of titration curves are also described.

➢ Complex systems may be described as solutions made up of

(1) two acids or two bases of different strengths,

- a mixture containing a strong acid and a weak acid (or a strong base and a weak base)

(2) an acid or a base that has two or more acidic or basic functional groups, or

- polyfunctional acids or bases, H_3PO_4, H_2CO_3

(3) an amphiprotic substance, acting as both an acid and a base.

- sodium dihydrogen phosphate, disodium hydrogen phosphate, aminoacids etc.

There are several methods fro treating such complex systems.

1) two acids or two bases of different strengths,

15 A Mixtures of strong acids and weak acids or strong and weak bases

The composition of a mixture of a strong acid and a weak acid can be determined by titration with suitable indicators if ;

1. the weak acid has a dissociation constant that lies between 10^{-4} and 10^{-8} and

2. the concentrations of the two acids are of the same order of magnitude

EXAMPLE 15-1

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.

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

$$[H_3O^+] = c_{HCl}^0 + [A^-] = 0.1200 + [A^-]$$

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 $[A^-] \ll 0.1200$ 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

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

This expression can be rearranged to

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

Figure with curves labeled $K_a = 10^{-8}$ (D), $K_a = 10^{-6}$ (C), $K_a = 10^{-4}$ (B), $K_a = 10^{-2}$ (A); axes pH versus Volume of 0.1000 M NaOH, mL.
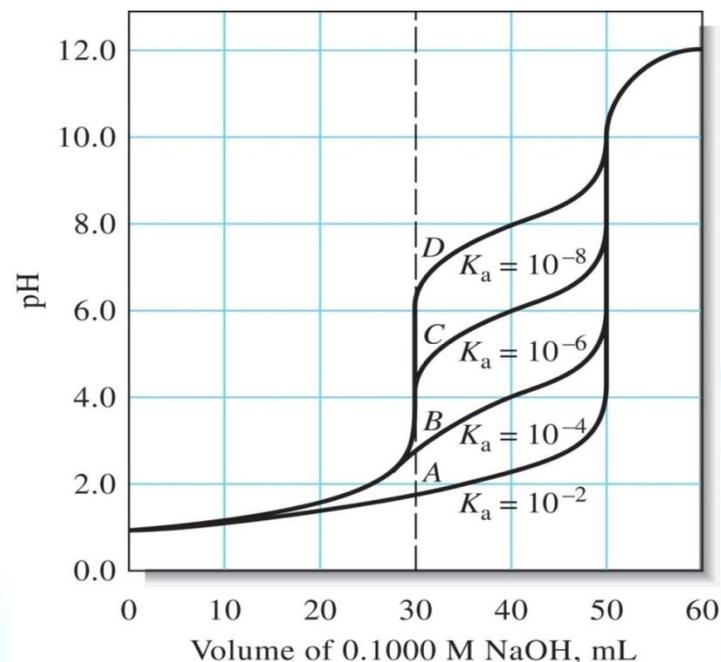
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From the concentration of the weak acid, we can write the mass-balance ex

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

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

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

$$pH = 1.08$$

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.
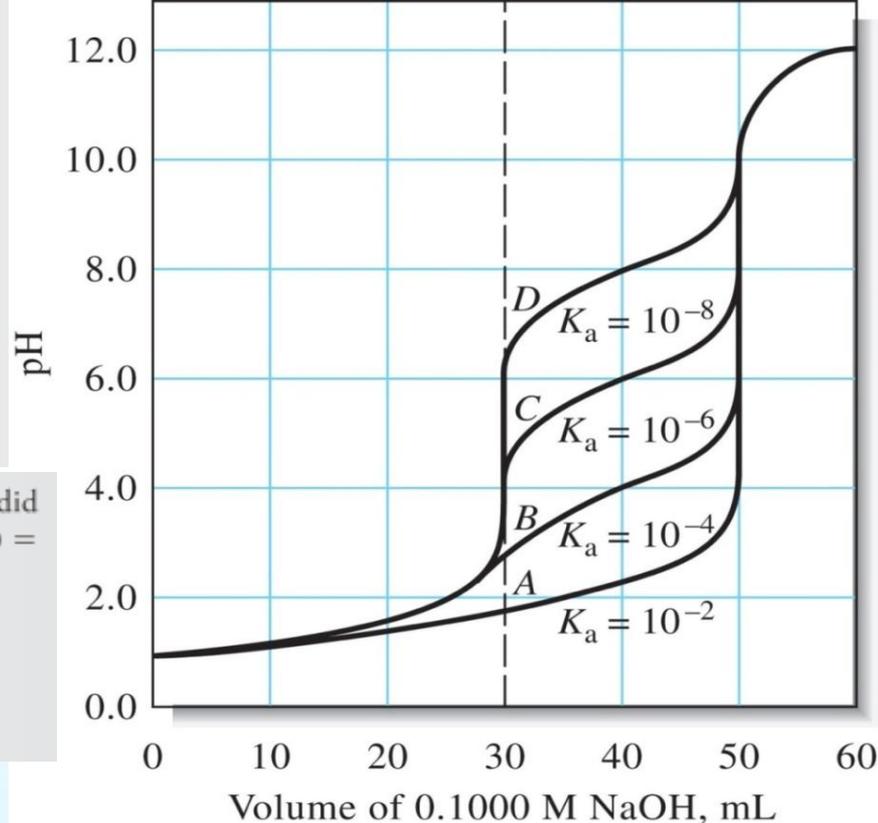
V $_{(NaOH)}$ (mL)	pH
10 ml	1.37
20 ml	1.65
25 ml	2.0
27	2.2
30	2.7
40	4.0
50	8.2
60	12.0

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

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

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

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

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

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

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

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

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

$$pH = 2.52$$

Note that the contributions to the hydronium ion concentration from HCl (1.85×10^{-3} M) and HA (3.03×10^{-3} M − 1.85×10^{-3} M) are of comparable magnitude.
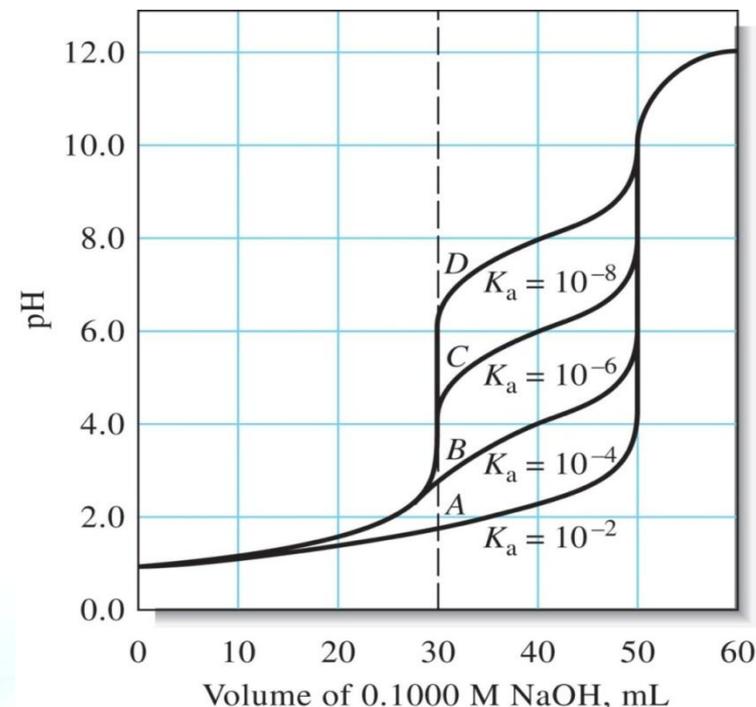
> The shape of the curve for a mixture of WA+SA and hence the information that may be derived from it, depends (in large measure) on the strength of the weak acid.

(curves A and B):
> The weak acid has a relatively large diss. const.
> The rise in pH at the first equivalence point is small or essentially nonexistent .
> 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 diss. const, only the strong acid content can be determined.

(curves C and D):
> For weak acids of intermediate strength (K_a less than 10^{-4} but greater than 10^{-8}), there are usually two useful end points.
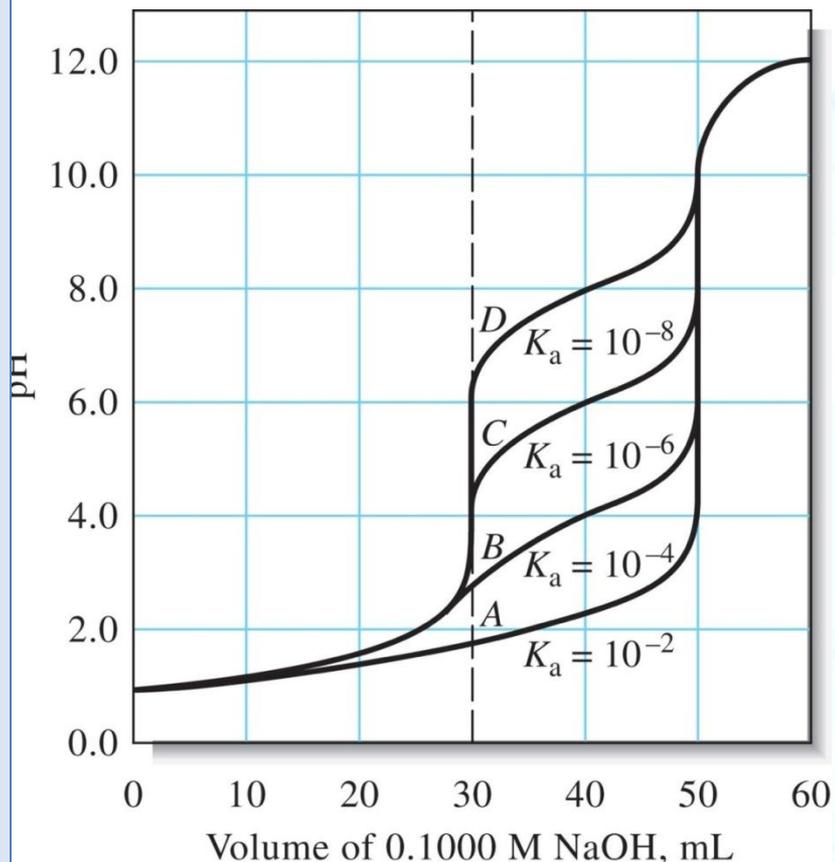
Figure 15-1 Curves for the titration of strong+weak acid mixtures with 0.1000 M NaOH. Each titration curve is for 25 mL of a solution that is 0.120 M in HCl and 0.080 M in the weak acid HA.

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:

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

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

$HPO_4^{-2} + H_2O \Leftrightarrow PO_4^{-3} + H_3O^+$ $\qquad K_{a3} = \dfrac{[H_3O^+][PO_4^{-3}]}{[HPO_4^{-2}]} = 4.5 \times 10^{-13}$
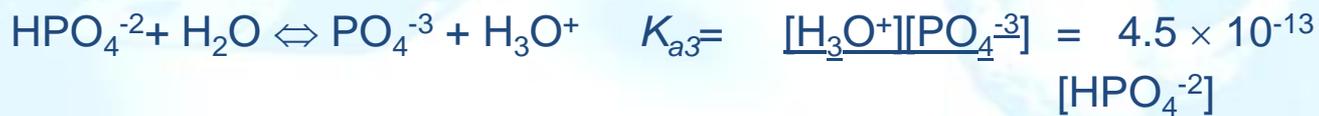
• K_{a1}, K_{a2} to represent the first and second dissociation constants of acids

and K_{b1}, K_{b2} *to represent the* stepwise constants of bases.

➤ Addition of two adjacent stepwise equilibria is followed by multiplication of the two equilibrium constants. Thus,

$$H_3PO_4 + 2H_2O \Leftrightarrow HPO_4^{-2} + 2H_3O^+ \qquad K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{-2}]}{[H_3PO_4]} = 4.49 \times 10^{-10}$$

Similarly,

$$H_3PO_4 + 3H_2O \Leftrightarrow PO_4^{-3} + 3H_3O^+ \qquad K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{-3}]}{[H_3PO_4]} = 2.0 \times 10^{-22}$$

15B-2   The Carbon Dioxide/Carbonic Acid System

When carbon dioxide is dissolved in water, a dibasic acid system is formed.

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

$$H_2CO_3 + H_2O \Leftrightarrow H_3O^+ + HCO_3^- \qquad K1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.5 \times 10^{-4}$$

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{-2} \qquad K1 = \frac{[H_3O^+][CO_3^{-2}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

✓ *The first reaction describes the hydration of aqueous CO_2 to form carbonic acid.*

✓ *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 the two,*

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

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{-2} \qquad K_{a2} = 4.69 \times 10^{-7}$$

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

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

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

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

We will then assume that

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

Therefore,

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

Substituting these approximations in Equation 15-6 leads to

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

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

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

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

$$CO_2(aq) + 2H_2O \Leftrightarrow H_3O^+ + HCO_3^-$$

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

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

$$K_{a2} = 4.69 \times 10^{-7}$$

15C Buffer solutions involving polyprotic acids

- 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.

- 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.

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.

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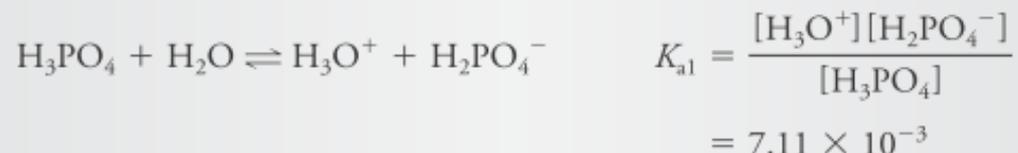
$$= 7.11 \times 10^{-3}$$

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

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

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

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

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

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

Solving this equation yields

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

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

For a buffer prepared from NaHA and Na$_2$A, the second dissociation usually predominates, and the equilibrium   HA$^-$ + H$_2$O $\Leftrightarrow$ H$_2$A + OH$^-$ can be neglected

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$_2$P).

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

Solution

We will make the assumption that the concentration of H$_2$P is negligible in this solution.
Therefore,

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

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

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

To check the first assumption, an approximate value for [H$_2$P] is calculated by substituting numerical values for [H$_3$O$^+$] and [HP$^-$] into the K_{a1} expression:

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

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

Since [H$_2$P] $\ll$ [HP] and [P^{2-}], our assumption that the reaction of HP$^-$ to form

15D Calculation of the pH of solutions of NaHA

➢ NaHA salts are amphiprotic substances that act as a base and an acid

$$HA^- + H_2O \Leftrightarrow A^{-2} + H_3O^+ \quad \text{and} \quad HA^- + H_2O \Leftrightarrow H_2A + OH^-$$

The relative magnitudes of the equilibrium constants for these processes determine whether a solution of NaHA is acidic or basic.

$$K_{a2} = \frac{[H_3O^+] + [A^{-2}]}{[HA^-]} \qquad\qquad K_{b2} = \frac{K_w}{K_{a1}} = \frac{[H_2A] + [OH^-]}{[HA^-]}$$

If K_{b2} is greater than K_{a2}, the solution is basic. It is acidic if K_{a2} exceeds K_{b2}.

➢ They are formed during neutralization titrations of polyfunctional acids and bases.

To derive an expression for the hydronium ion concentration of a solution of HA_2, we first *write the mass-balance equation:*

$$C_{NaHA} = [HA^-] + [H_2A] + [A^{-2}] \qquad MB$$

The charge-balance equation: $\qquad [Na^+] + [H_3O^+] = [HA^-] + 2[A^{-2}] + [OH^-] \qquad CB$

Since the sodium ion concentration is equal to the molar analytical concentration of NaHA,

$$C_{NaHA} + [H_3O^+] = [HA^-] + 2[A^{-2}] + [OH^-] \qquad \text{arranged CB}$$

Subtracting the mass-balance equation from the charge-balance equation.

$$C_{NaHA} + [H_3O^+] = [HA-] + 2[A^{-2}] + [OH^-] \qquad \text{charge balance}$$

$$C_{NaHA} = [H_2A] + [HA^-] + [A^{-2}] \qquad \text{mass balance}$$

$$\boxed{[H_3O^+] = [A^{-2}] + [OH^-] - [H_2A]}$$

Rearranging the acid-dissociation constant expressions for H_2A and A^{-2}

$$[H_2A] = \frac{[H_3O^+][HA^-]}{K_{a1}} \qquad\qquad [A^{-2}] = \frac{K_{a2}[HA^-]}{[H_3O^+]}$$

Substitution yields, $\qquad [H_3O^+] = \dfrac{Ka_2[HA^-]}{[H_3O^+]} + \dfrac{Kw}{[H_3O^+]} - \dfrac{[H_3O^+][HA^-]}{K_{a1}}$

Finally, we get $\qquad [H_3O^+] = \sqrt{\dfrac{K_{a2}[HA^-] + K_w}{1 + [HA^-]/K_{a1}}} = \sqrt{\dfrac{K_{a2}c_{NaHA} + K_w}{1 + c_{NaHA}/K_{a1}}}$

This simplifies to $\qquad [H_3O^+] = \sqrt{K_{a1}}\,\sqrt{K_{a2}}$

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

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

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:

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

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

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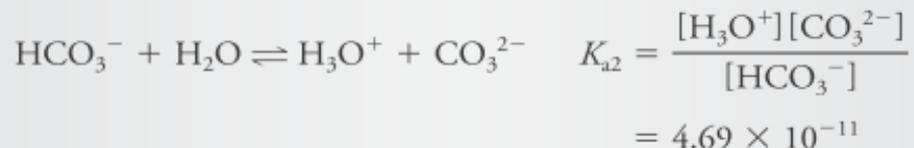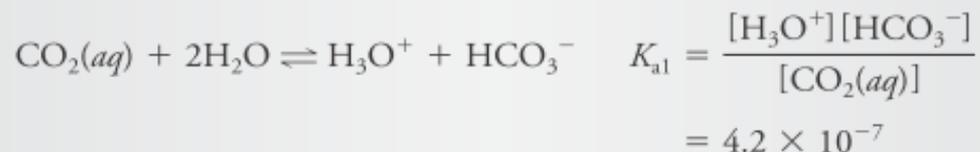
$$= 4.69 \times 10^{-11}$$

We note that $c_{NaHA}/K_{a1} \gg 1$ 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

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

➤ 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.

➤ If $Ka_1/Ka_2 > 10^3$, the theoretical titration curves can be calculated.

E: Solution of Na₂A
F: Solution of NaOH
D: Buffer solution of HA⁻ and A²⁻
B: Buffer solution of H₂A and HA⁻
C: Solution of NaHA
A: Weak acid with $K_a = 1.00 \times 10^{-3}$

pH
Volume of 0.100 M NaOH, mL
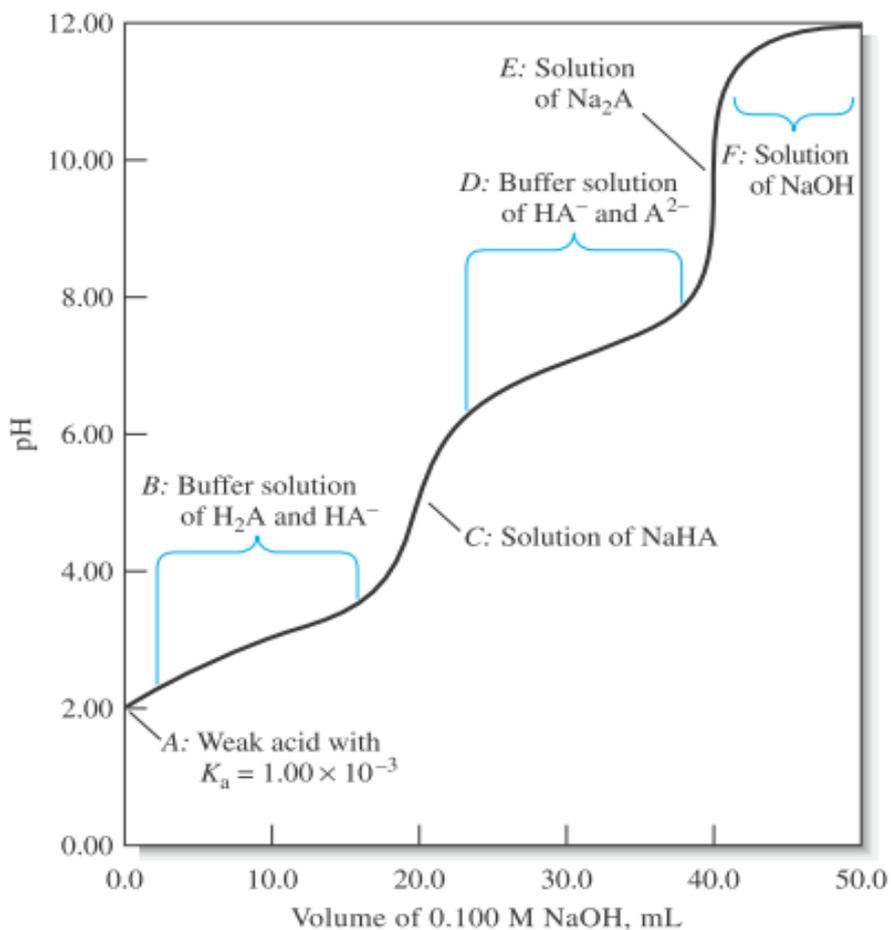
Point A: Weak acid H_2A, neglect the second dissociation

Point B: buffer solution H_2A – NaHA   use Ka1

Point C: First E.P. All H_2A converted to NaHA/ amphiprotic subst.

$$\sqrt{\frac{K_{a2}c_{NaHA} + K_w}{1 + c_{NaHA}/K_{a1}}}$$

Point D: Second buffer solution HA⁻ and A⁻² , Use K_{a2}

Point E: Second E.P. All HA⁻ converted to A⁻² . The hydroxide concentration of the solution is determined by the reaction of A⁻² with water to form HA⁻ and OH⁻ .

Point F: Excess NaOH.
Compute the hydroxide concentration from the molar concentration of the NaOH.

Figure 15-2Titration of 20 mL of 0.1 M H_2A with 0.1 M NaOH.
For H_2A, $Ka_1 = 1 \times 10^{-3}$, and $Ka_2 = 1.00 \times 10^{-7}$. The method of pH calculation is shown for several points and regions on

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

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

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

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

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

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

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

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

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

$$pH = 2 - \log 3.01 = 1.52$$
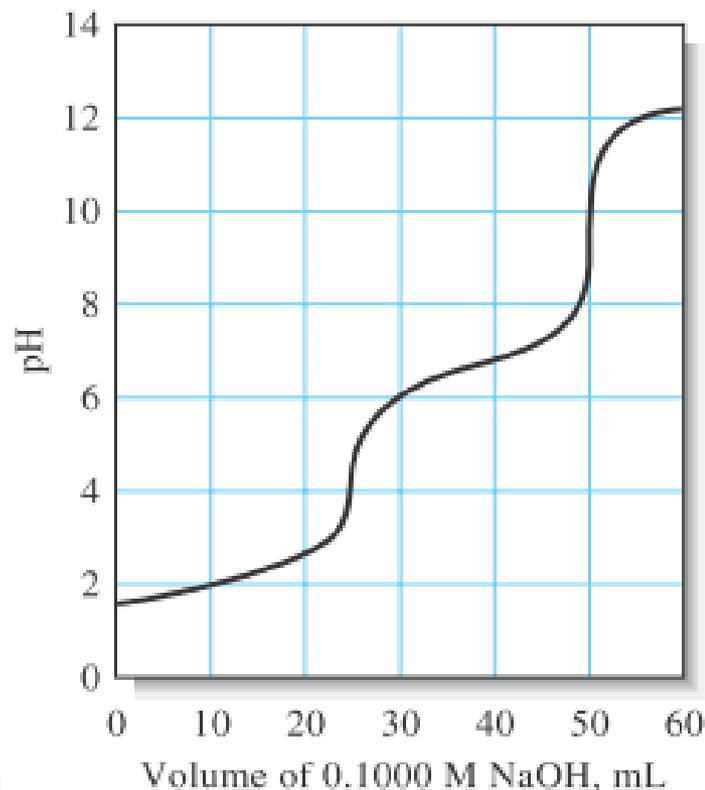
Figure 15-3   Titration curve for 25.00 mL of 0.1000 M maleic acid, H2M, titrated with 0.1000 M NaOH.

In the titration curve for 0.1000 M maleic acid, two end points are apparent, the second end point is more satisfactory because the pH change is more pronounced here.

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 $5.2 \times 10^{-2}\ M$ for $[H_3O^+]$. It is clear, however, that the approximation $[H_3O^+] \ll c_{H_2M}$ 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.

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 $\ll 1$. Hence,

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

$$= 7.80 \times 10^{-5} \; M$$

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

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

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

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

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.

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,

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

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

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

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

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

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

$$pH = 14.00 - pOH = 9.38$$

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:

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

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

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

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

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

and

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

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

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

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

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

$$pH = 14.00 - pOH = 11.12$$

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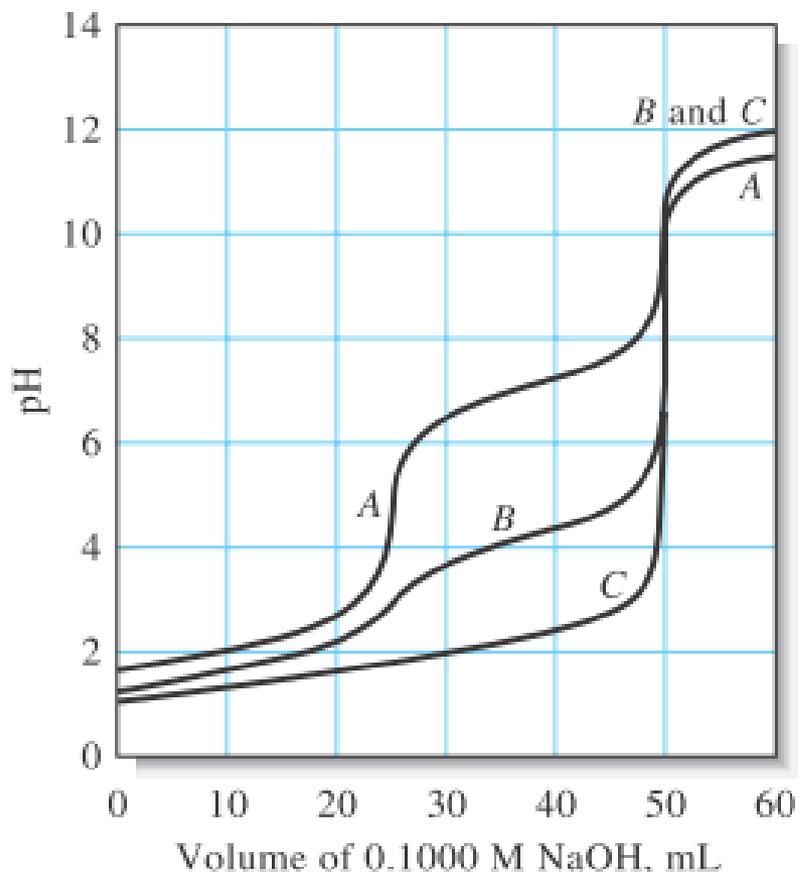
Figure 15-4 Curves for the titration of polyprotic acids. A 0.1000 M NaOH solution is used to titrate 25.00 mL of 0.1000 M H_3PO_4 (curve A), 0.1000 M oxalic acid (curve B), and 0.1000 M H_2SO_4 (curve C).

- 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}.

Phosphoric acid:
• The ratio K_{a1}/K_{a2} is 10^5, as is K_{a2}/K_{a3}.
• *This results* in two well-defined end points, either of which is satisfactory for analytical purposes.
• 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

Oxalic Acid:
* The ratio Ka_1/Ka_2 for oxalic acid (curve B) is $10^3 < 10^4$. 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.

Sulfuric acid:
* Has one fully dissociated proton and one that is dissociated to a relatively large extent ($Ka_2 = 1.02 \times 10^{-2}$).
Because of the similarity in strengths of the two acids, only a single end point, corresponding to the titration of both protons, is observed.

15F Titration curves for polyfunctional bases
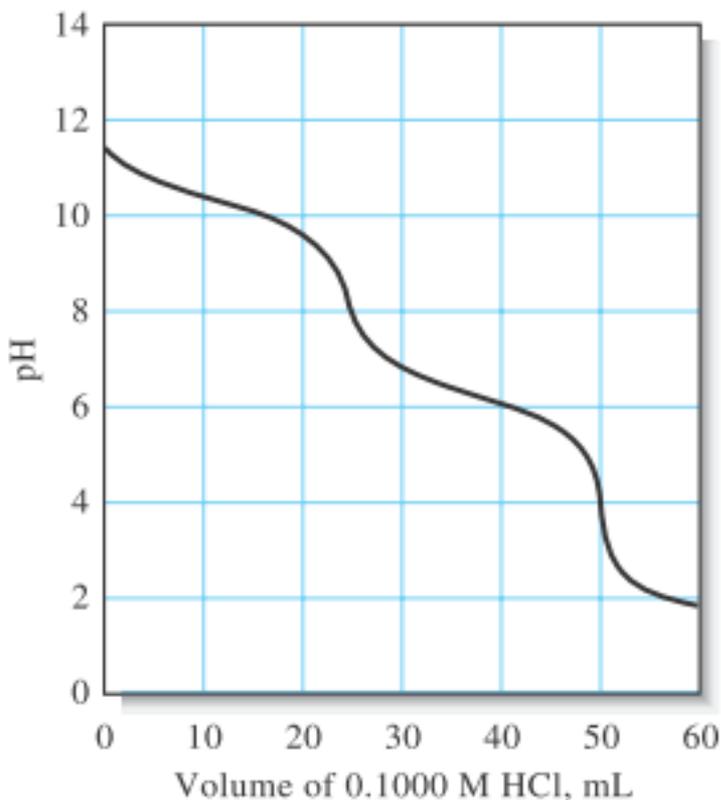
Figure 15-5   Curve for the titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl.

- Two end points appear in the titration.
- The important equilibrium constants are

$$CO_3^{-2} + H_2O \Leftrightarrow OH^- + HCO_3^- \quad K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{4.69 \times 10^{-11}} = 2.13 \times 10^{-4}$$

$$HCO_3^- + H_2O \Leftrightarrow OH^- + CO_{2(aq)} \quad K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}$$

- initially V_{HCl}=0 mL /weak base/ use first equilibrium/pH= 11.66

- V_{HCl}=10 mL/ CO_3^- - HCO_3^- buffer/ pH= 10.50

- V_{HCl}=12.5 mL / half eq-point/ $P_{OH} = pK_{b1}$ / pH= 10.32

- V_{HCl}=25 mL / 1st E.P / HCO_3^- amphiprotic subst. / pH=8.35

- V_{HCl}=30 mL / HCO_3^- - $H_2CO_3^-$ buffer/ pH= 6.98

- V_{HCl}=40 mL / HCO_3^- - H_2CO_3 buffer/ pH= 6.2

- V_{HCl}=50 mL / 2nd E.P / weak acid H_2CO_3 / pH= 3.84

- V_{HCl}=60 mL / excess HCl / pH= 1.94

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.

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

$$H_2PO_4^- + H_2O \Leftrightarrow OH^- + H_3PO_4 \qquad K_{b3} = \frac{K_w}{Ka_1} = \frac{1 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$$

-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

$$HPO_4^{-2} + H_2O \Leftrightarrow PO_4^{-3} + H_3O^+ \qquad K_{a3} = 4.5 \times 10^{-13}$$
$$HPO_4^{-2} + H_2O \Leftrightarrow H_2PO_4^- + OH^- \qquad K_{b2} = 1.58 \times 10^{-7}$$

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

15H Composition of polyprotic acid solutions as a function of pH

➢ Alpha values are useful in visualizing the changes in the concentration of various species that occur in a titration of a monoprotic weak acid.

➢ Let c_T be the sum of the molar concentrations of the maleate-containing species in the solution throughout the titration, then the *alpha value for the free acid α_0* is defined as

$$\alpha_0 = \frac{[H_2M]}{c_T}$$
Where $c_T = [H_2M] + [HM^-] + [M^{-2}]$

$$\alpha_1 + \alpha_2 + \alpha_3 = 1$$

The alpha values for HM^- and M^{-2} are:

$$\alpha_1 = \frac{[HM^-]}{c_T} \qquad \alpha_2 = \frac{[M^{2-}]}{c_T}$$

We may express the alpha values for the maleic acid system very neatly in terms of $[H_3O]$, K_{a1}, and K_{a2}.

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

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

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}$$
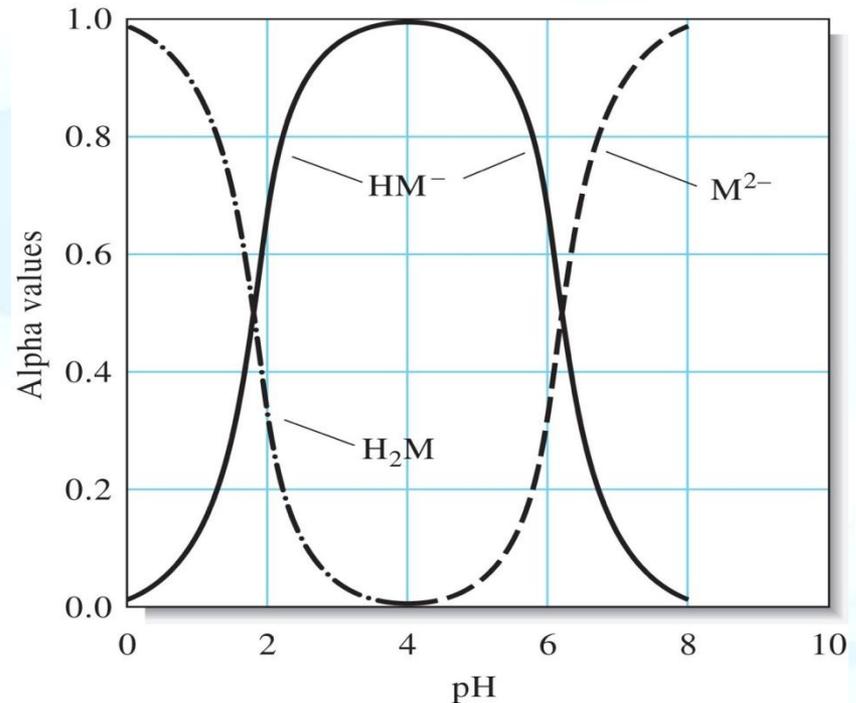
Figure 15-6 Composition of H_2M solutions as a function of pH. Alpha values for each maleate-containing species

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 $[OH^-]$.

Example: End of book question 15-31- a) Phthalic acid, components at pH= 2,6,10

- H_2P K_{a1}: 1.12×10^{-2} K_{a2}: 3.91×10^{-6}

pH	α_1	α_2	α_3
2	0.899	0.101	3.94x10-5
6	1.82x10-4	0.204	0.796
10	2.28x10-12	2.56x10-5	1
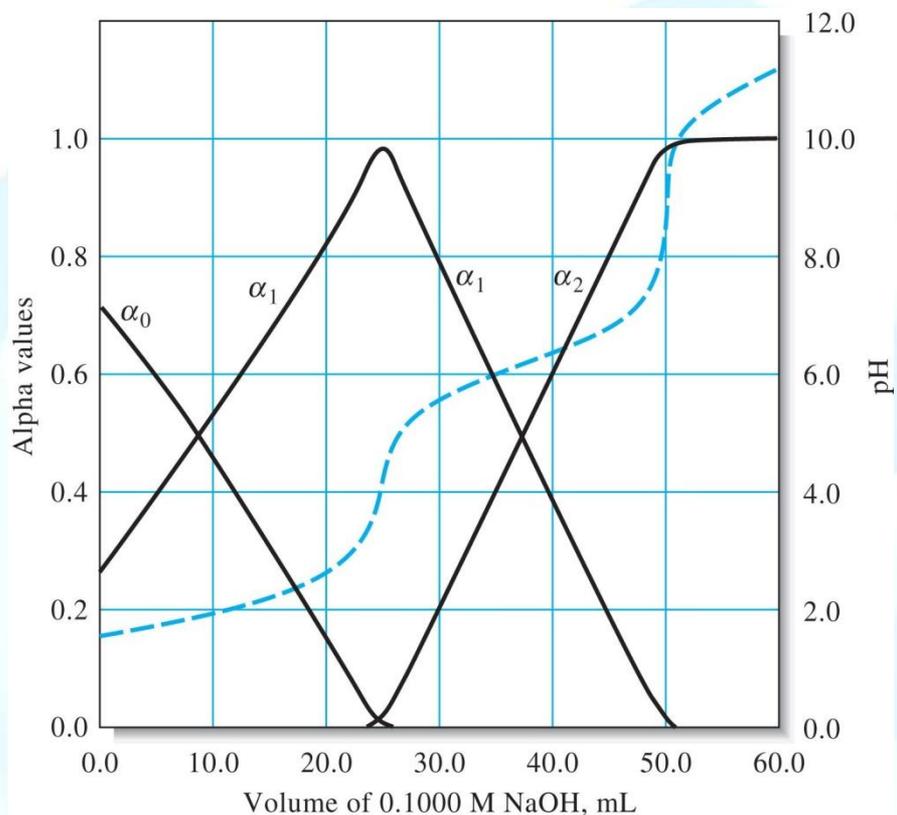
Figure 15-7 Titration of 25.00 mL of 0.1000 M maleic acid with 0.1000 M NaOH.
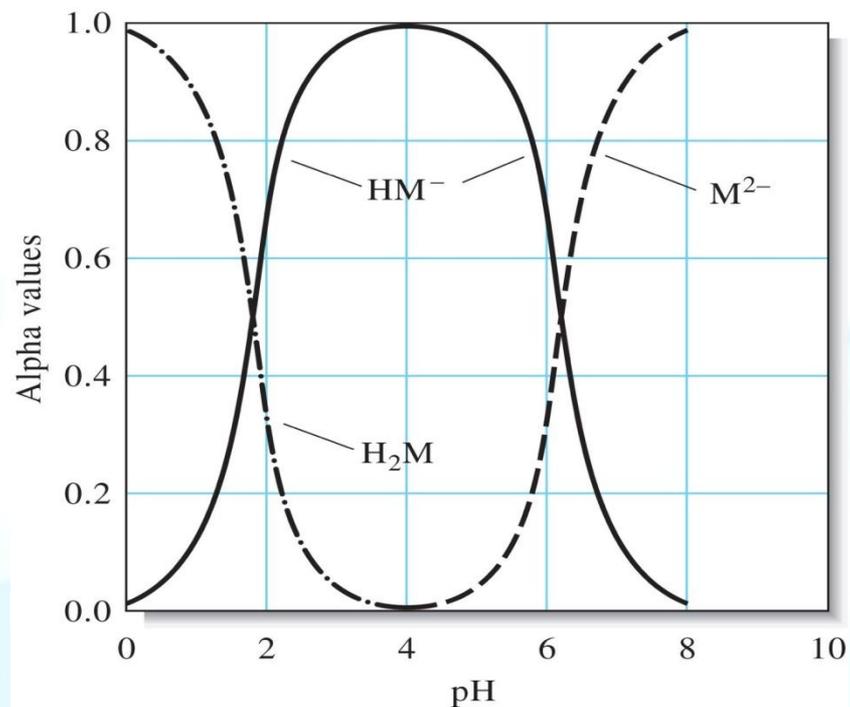
- The solid curves depict the same alpha values but now plotted as a function of volume of sodium hydroxide as the acid is titrated.
- These curves give a comprehensive picture of all concentration changes that occur during the titration.