Chapter 14
Principles of Neutralization Titrations

Like any titration, neutralization titrations depend on a chemical reaction between the **analyte** and a **standard reagent**.

The point of chemical equivalence is indicated by a *chemical indicator* or an *instrumental measurement*.

The discussion here focuses on the *types* of standard solutions and the chemical *indicators* that are used for neutralization titrations.

Standard Solutions

The standard solutions employed in neutralization titrations are strong acids or strong bases because these substances react more *completely* with an analyte than their weaker counterparts do and thus *yield sharper end points*.

Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.

Standard solutions of bases are ordinarily prepared from solid sodium or potassium and occasionally barium hydroxides. The concentrations of these bases must be established by standardization.

Acid/Base Indicators

Many substances display colors that depend on the pH of the solutions in which they are dissolved.

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

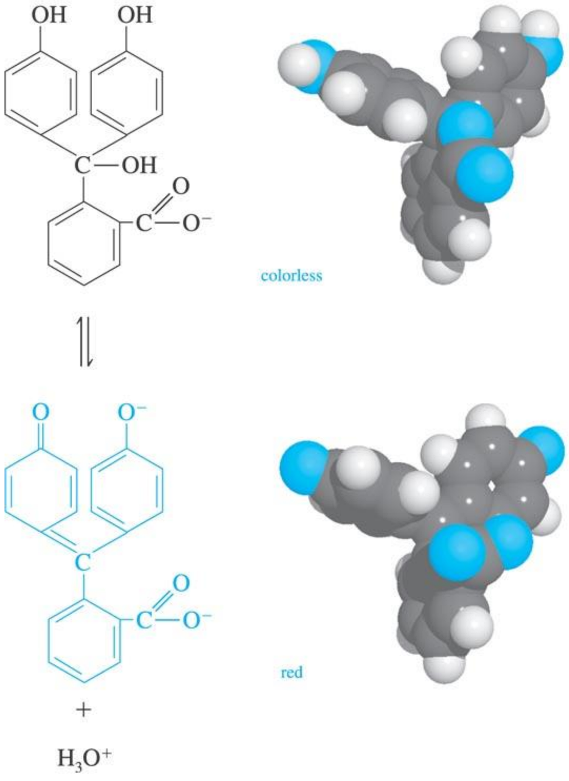
$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$

acid color — base color

The equilibrium for a base-type indicator, **In**, is

$$In + H_2O \rightleftharpoons InH^+ + OH^-$$

base color — acid color



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…continued…

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

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging leads to

$$[H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

The hydronium ion concentration determines the ratio of the acid to the conjugate base form of the indicator and thus determines the color developed by the solution.

…continued…

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In^-, particularly when the ratio [Hln/ln] is greater than about 10 or smaller than about 0.1.

The color imparted to a solution by a typical indicator appears to the average observer to change rapidly only within the limited concentration ratio of approximately **10** to **0.1**

The average indicator, Hln, exhibits its pure acid color when

$$\frac{[HIn]}{[In\quad]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[HIn]}{[In\quad]} \leq \frac{1}{10}$$

The color appears to be *intermediate* for ratios between these two values. These ratios vary considerably from indicator to indicator.

…continued…

For the full acid color,

$$[H_3O^+] = 10\ K_a$$

and similarly for the full base color,

$$[H_3O^+] = 0.1\ K_a$$

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

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

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

Indicator pH range = $pK_a \pm 1$

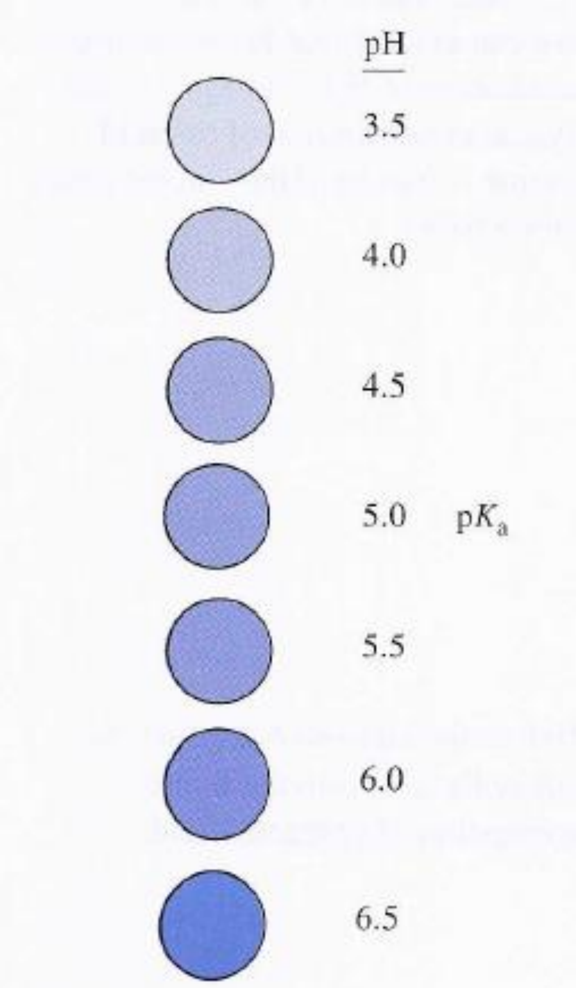

Figure 14-2 Indicator color as a function of pH ($pK_a = 5.0$).

Catalyst

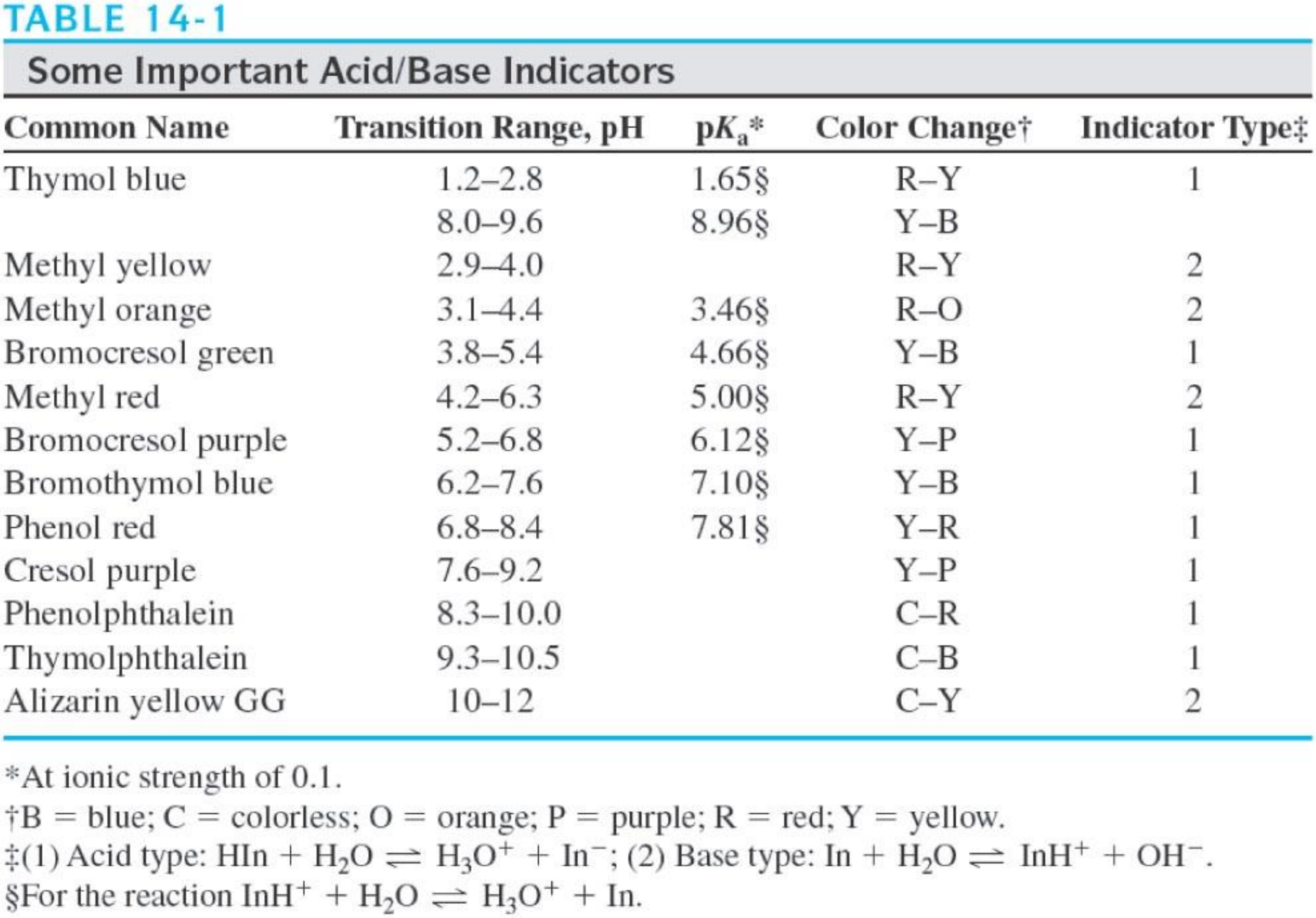

TABLE 14-1

Some Important Acid/Base Indicators

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

*At ionic strength of 0.1.

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

‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$.

§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$.

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CALCULATING pH IN TITRATIONS OF STRONG ACIDS AND STRONG BASES

The hydronium ions in an aqueous solution of a strong acid have two sources:

(1) the reaction of the acid with water and

(2) the dissociation of water itself.

In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent. Thus, for a solution of HCl with a concentration greater than about **10^{-6} M**, we can write

$$[H_3O^+] = c_{HCl} + [H_3O^+] \approx c_{HCl}$$

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

$$[OH^-] = c_{NaOH} + [OH^-] \approx c_{NaOH}$$

Titrating a Strong Acid with a Strong Base

We will be interested here, in calculating hypothetical titration curves of pH versus volume of titrant. Three types of calculation must be done to construct the hypothetical titration curve for titrating a solution of a strong acid with a strong base. Each calculation corresponds to a distinct stage in the titration:

1. Preequivalence
2. Equivalence
3. Postequivalence

In the **preequivalence** stage, we compute the concentration of the acid from its starting concentration and the amount of base that has been added.

At the **equivalence** point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration is derived directly from the ion-product constant for water.

In the **postequivalence** stage, the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration.

…continued…

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

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

$$= -\log [H_3O^+] - \log [OH^-]$$

$$pK_w = pH + pOH$$

$$-\log 10^{-14} = 14.00$$

$$= pH + pOH$$

EXAMPLE 14-1

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

Initial Point

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

$$pH = -\log[H_3O^+] = -\log 0.0500 = 1.30$$

After Addition of 10.00 mL of Reagent

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

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

$$[H_3O^+] = 2.500 \times 10^{-2} \text{ M}$$

$$\text{and } pH = -\log[H_3O^+] = -\log(2.500 \times 10^{-2}) = 1.60$$

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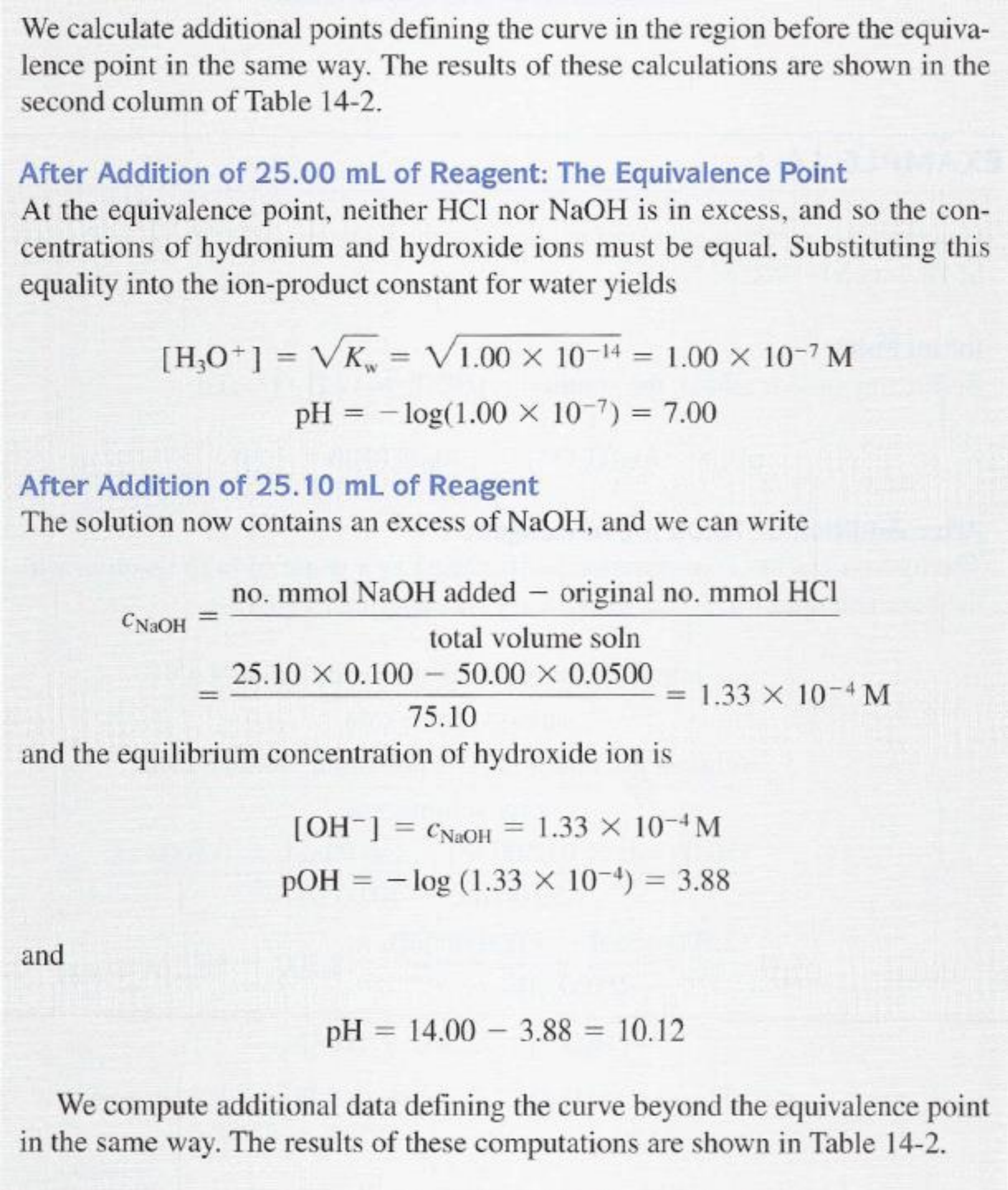

We calculate additional points defining the curve in the region before the equivalence point in the same way. The results of these calculations are shown in the second column of Table 14-2.

After Addition of 25.00 mL of Reagent: The Equivalence Point

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

$$[H_3O^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\,M$$

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

After Addition of 25.10 mL of Reagent

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

$$c_{NaOH} = \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\text{total volume soln}}$$

$$= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4}\,M$$

and the equilibrium concentration of hydroxide ion is

$$[OH^-] = c_{NaOH} = 1.33 \times 10^{-4}\,M$$

$$pOH = -\log(1.33 \times 10^{-4}) = 3.88$$

and

$$pH = 14.00 - 3.88 = 10.12$$

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

Catalyst

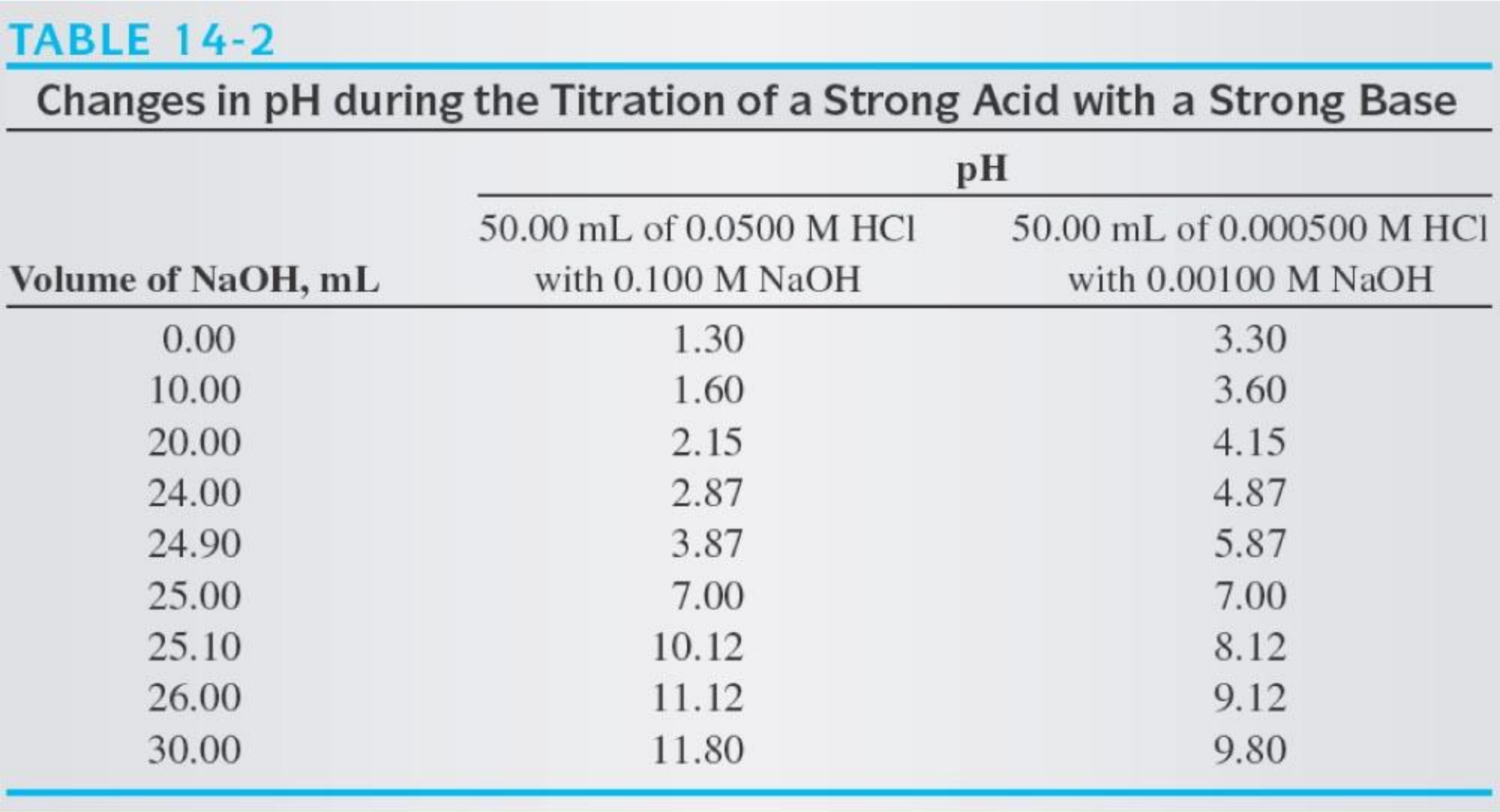

TABLE 14-2

Changes in pH during the Titration of a Strong Acid with a Strong Base

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

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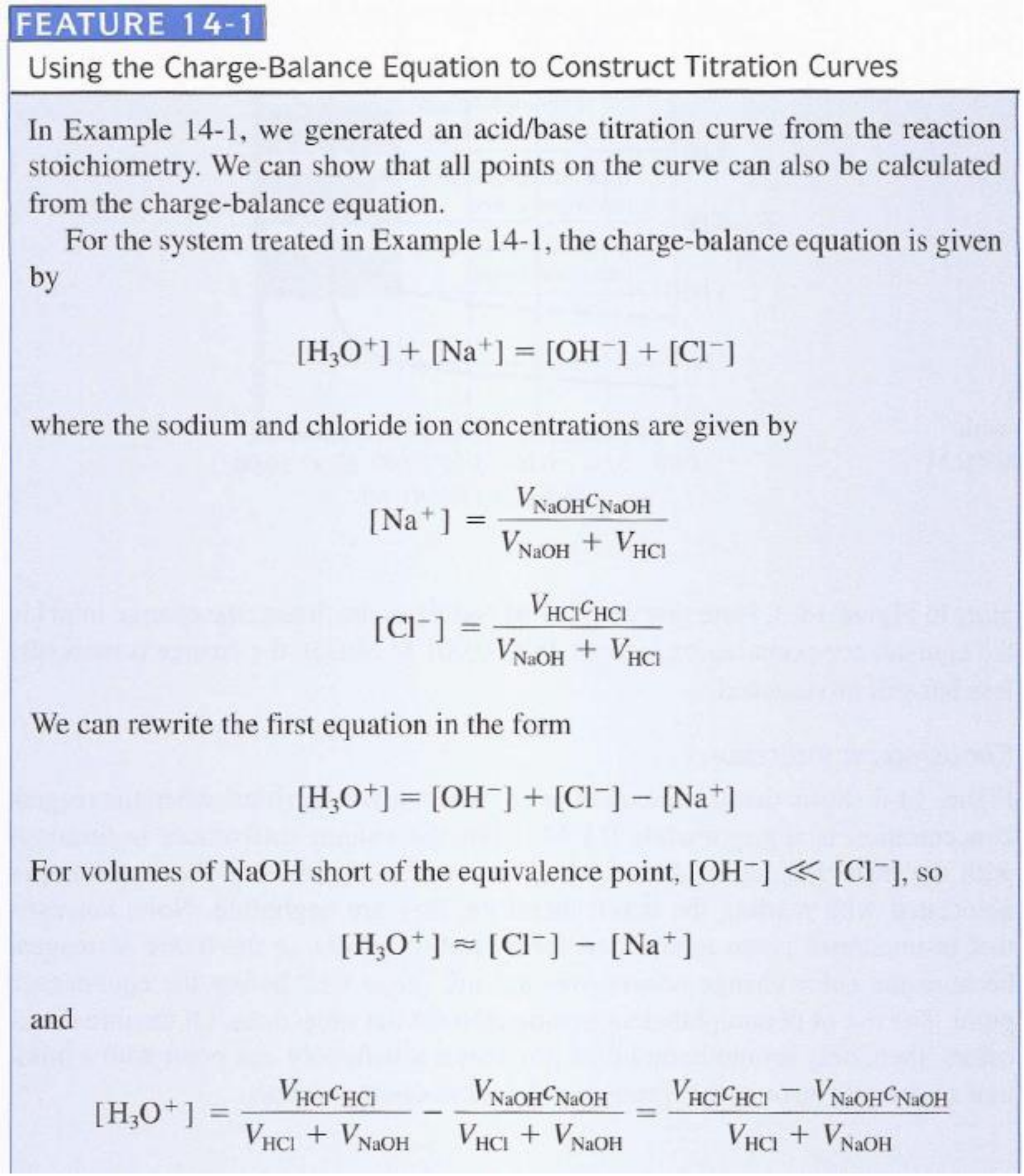

FEATURE 14-1

Using the Charge-Balance Equation to Construct Titration Curves

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

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

$$[H_3O^+] + [Na^+] = [OH^-] + [Cl^-]$$

where the sodium and chloride ion concentrations are given by

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

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

We can rewrite the first equation in the form

$$[H_3O^+] = [OH^-] + [Cl^-] - [Na^+]$$

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

$$[H_3O^+] \approx [Cl^-] - [Na^+]$$

and

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

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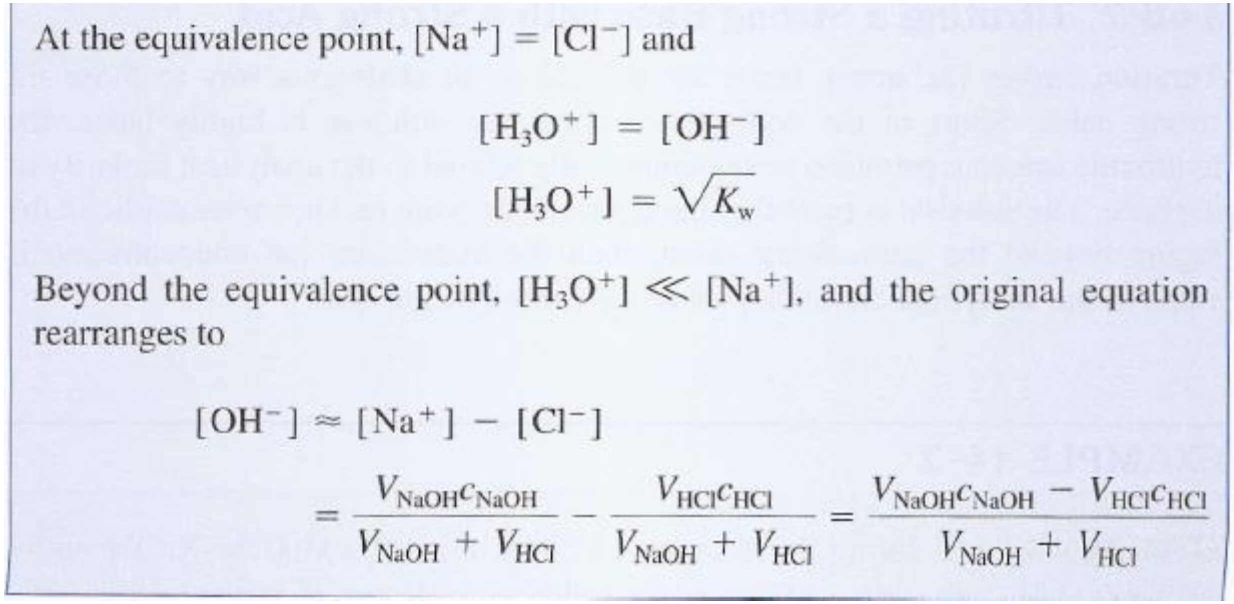


At the equivalence point, $[\mathrm{Na^+}] = [\mathrm{Cl^-}]$ and

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$$
$$[\mathrm{H_3O^+}] = \sqrt{K_w}$$

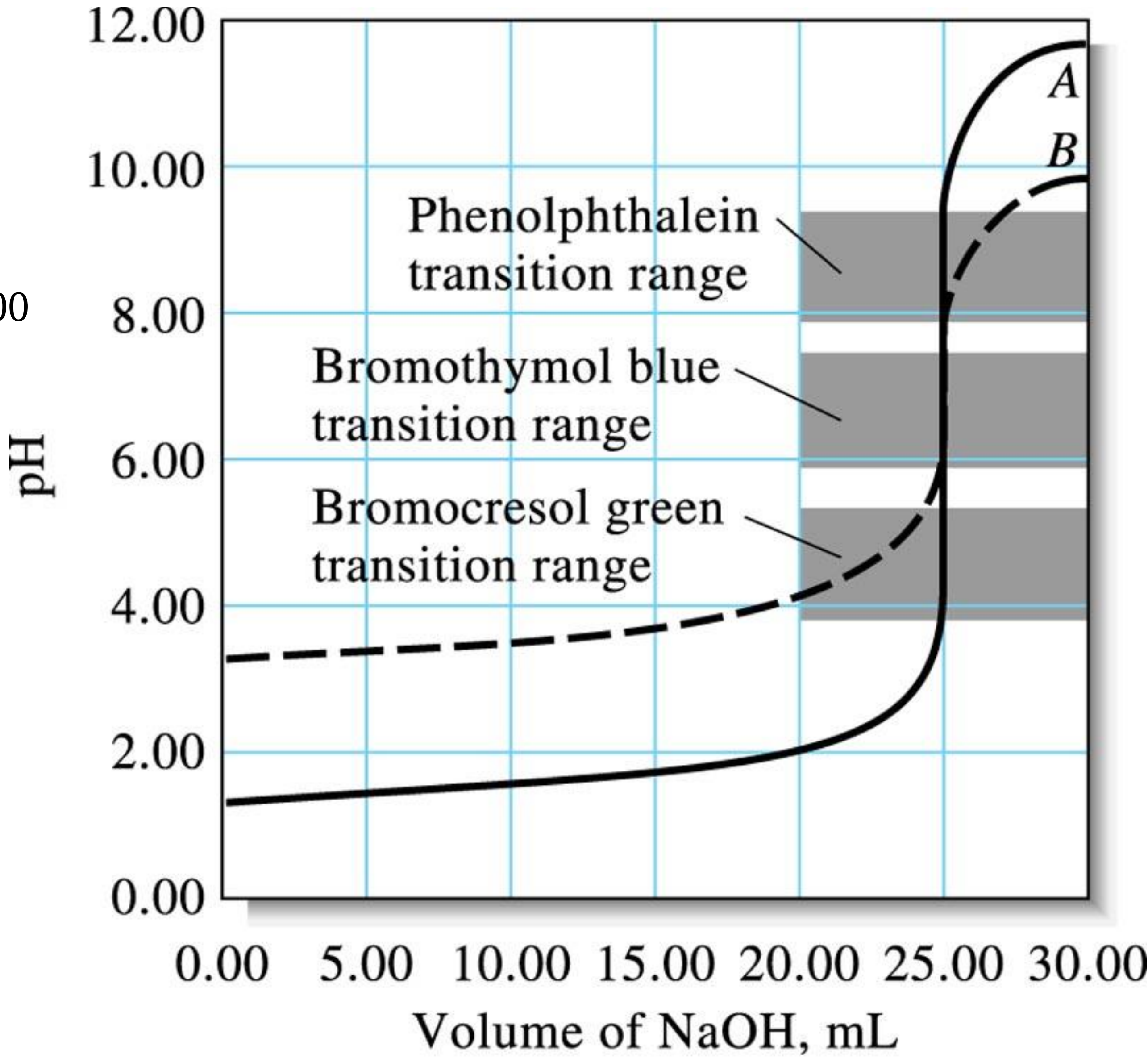
Beyond the equivalence point, $[\mathrm{H_3O^+}] \ll [\mathrm{Na^+}]$, and the original equation rearranges to

$$[\mathrm{OH^-}] \approx [\mathrm{Na^+}] - [\mathrm{Cl^-}]$$
$$= \frac{V_{\mathrm{NaOH}}c_{\mathrm{NaOH}}}{V_{\mathrm{NaOH}} + V_{\mathrm{HCl}}} - \frac{V_{\mathrm{HCl}}c_{\mathrm{HCl}}}{V_{\mathrm{NaOH}} + V_{\mathrm{HCl}}} = \frac{V_{\mathrm{NaOH}}c_{\mathrm{NaOH}} - V_{\mathrm{HCl}}c_{\mathrm{HCl}}}{V_{\mathrm{NaOH}} + V_{\mathrm{HCl}}}$$

The Effect of Concentration

Titration curves for HCl with NaOH.
Curve *A*: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.
Curve *B*: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.

Choosing an Indicator



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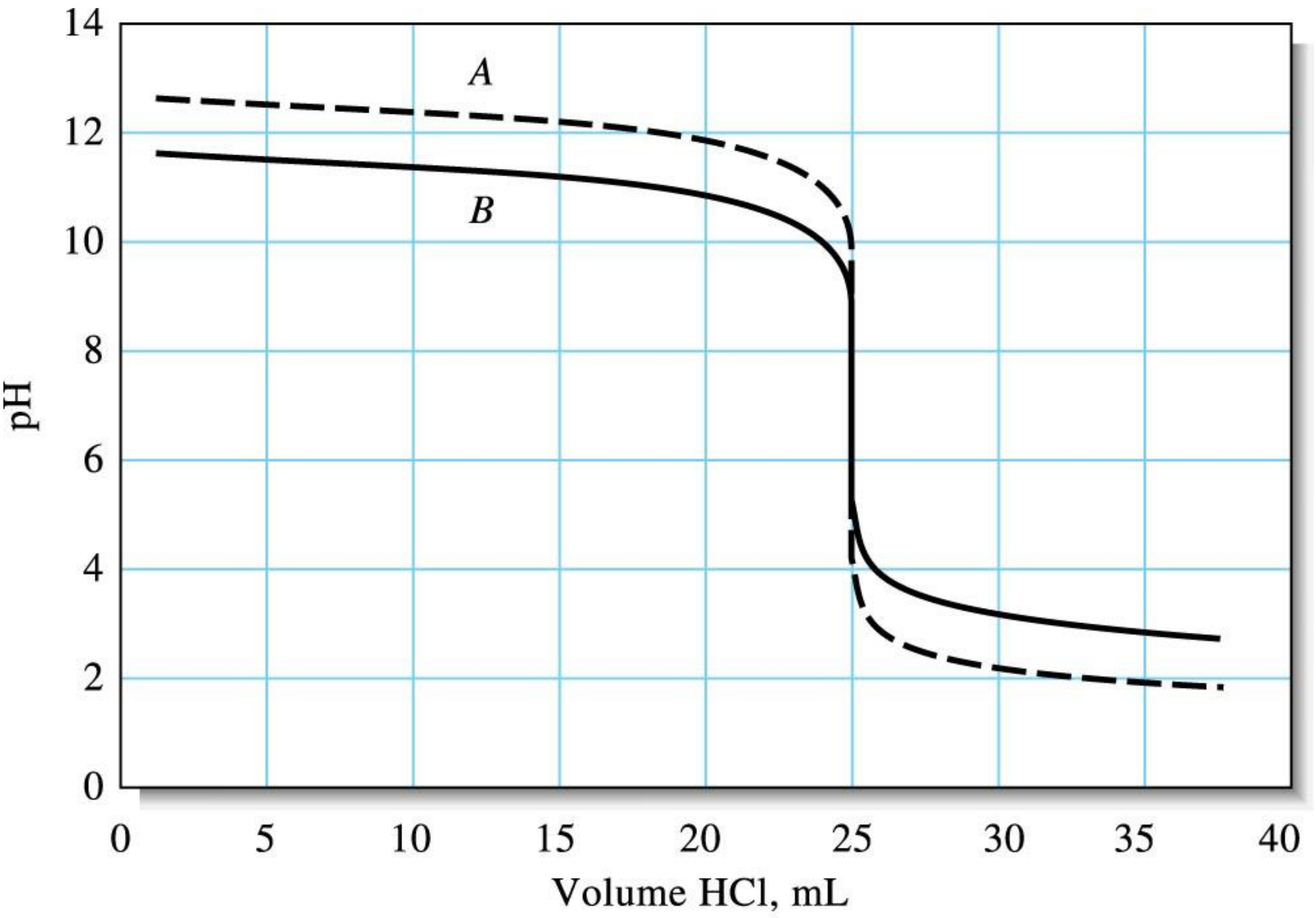
Titrating a Strong Base with a Strong Acid

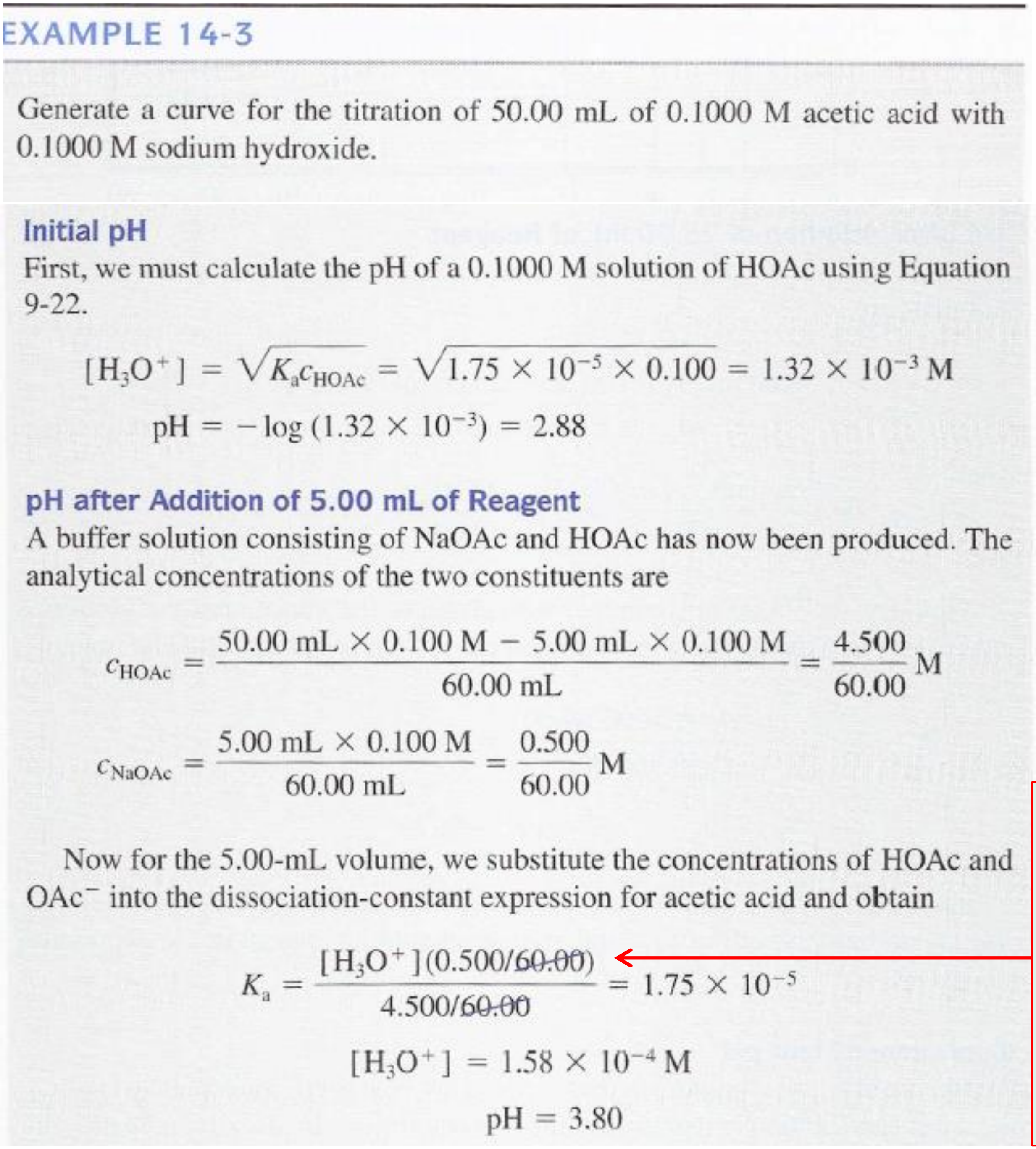


Catalyst

TITRATION CURVES FOR WEAK ACIDS

Four distinctly different types of calculations are needed to derive a titration curve for a weak acid (or a weak base):

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.
2. After various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of **buffers**. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the residual concentrations of the weak acid or base.
3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.
4. Beyond the equivalence point, the excess of strong acid or base titrant represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.



EXAMPLE 14-3

Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid with 0.1000 M sodium hydroxide.

Initial pH

First, we must calculate the pH of a 0.1000 M solution of HOAc using Equation 9-22.

$$[H_3O^+] = \sqrt{K_a c_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3}\ M$$

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

pH after Addition of 5.00 mL of Reagent

A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00\ mL \times 0.100\ M - 5.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{4.500}{60.00}\ M$$

$$c_{NaOAc} = \frac{5.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{0.500}{60.00}\ M$$

Now for the 5.00-mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](0.500/\cancel{60.00})}{4.500/\cancel{60.00}} = 1.75 \times 10^{-5}$$

$$[H_3O^+] = 1.58 \times 10^{-4}\ M$$

$$pH = 3.80$$

Note that the total volume of solution is present in both numerator and denominator and thus cancels in the expression for $[H_3O^+]$. Calculations similar to this provide points on the curve throughout the buffer region. Data from these calculations are presented in column 2 of Table 14-3.

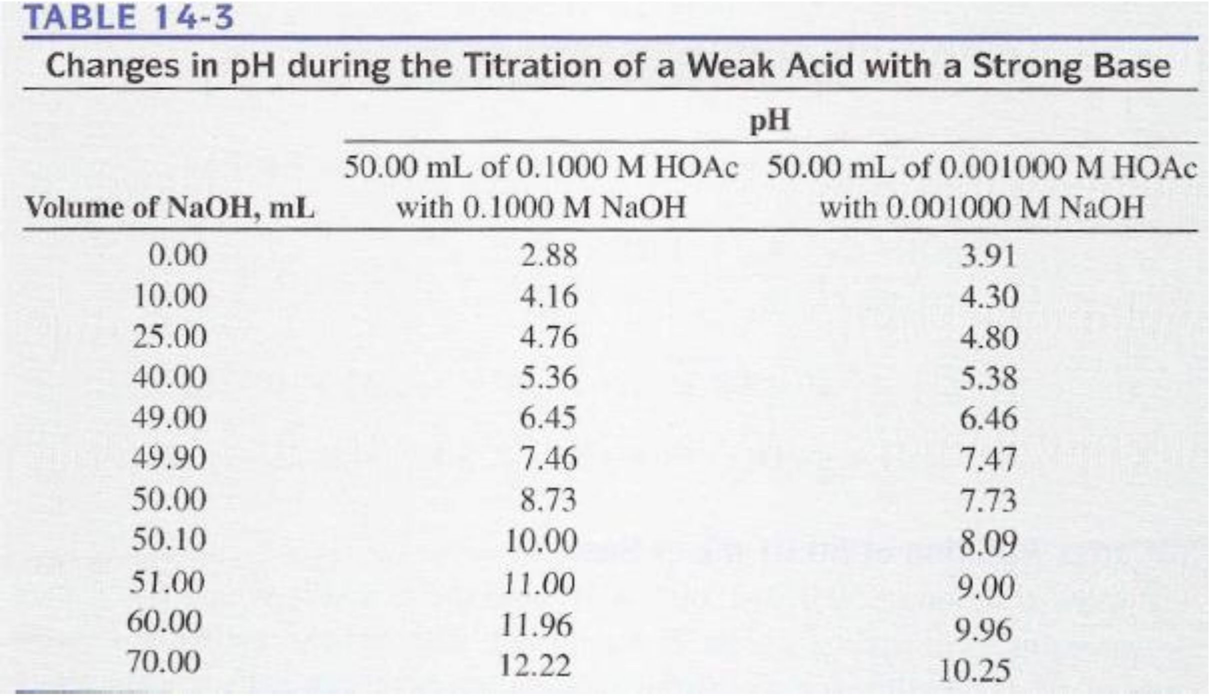
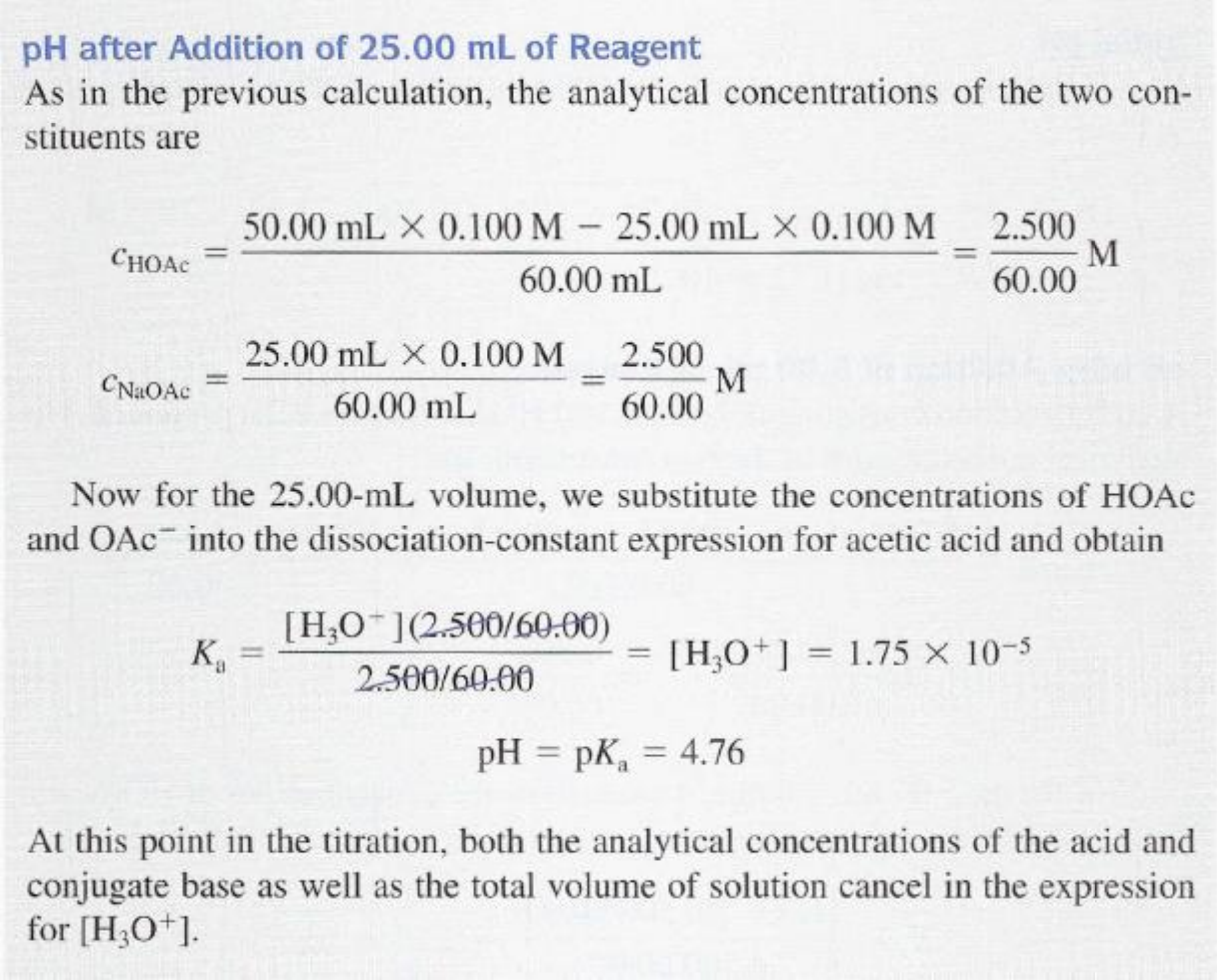


TABLE 14-3

Changes in pH during the Titration of a Weak Acid with a Strong Base

Volume of NaOH, mL	pH 50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH	 50.00 mL of 0.001000 M HOAc with 0.001000 M NaOH
0.00	2.88	3.91
10.00	4.16	4.30
25.00	4.76	4.80
40.00	5.36	5.38
49.00	6.45	6.46
49.90	7.46	7.47
50.00	8.73	7.73
50.10	10.00	8.09
51.00	11.00	9.00
60.00	11.96	9.96
70.00	12.22	10.25



pH after Addition of 25.00 mL of Reagent

As in the previous calculation, the analytical concentrations of the two constituents are

$$c_{\mathrm{HOAc}} = \frac{50.00\ \mathrm{mL} \times 0.100\ \mathrm{M} - 25.00\ \mathrm{mL} \times 0.100\ \mathrm{M}}{60.00\ \mathrm{mL}} = \frac{2.500}{60.00}\ \mathrm{M}$$

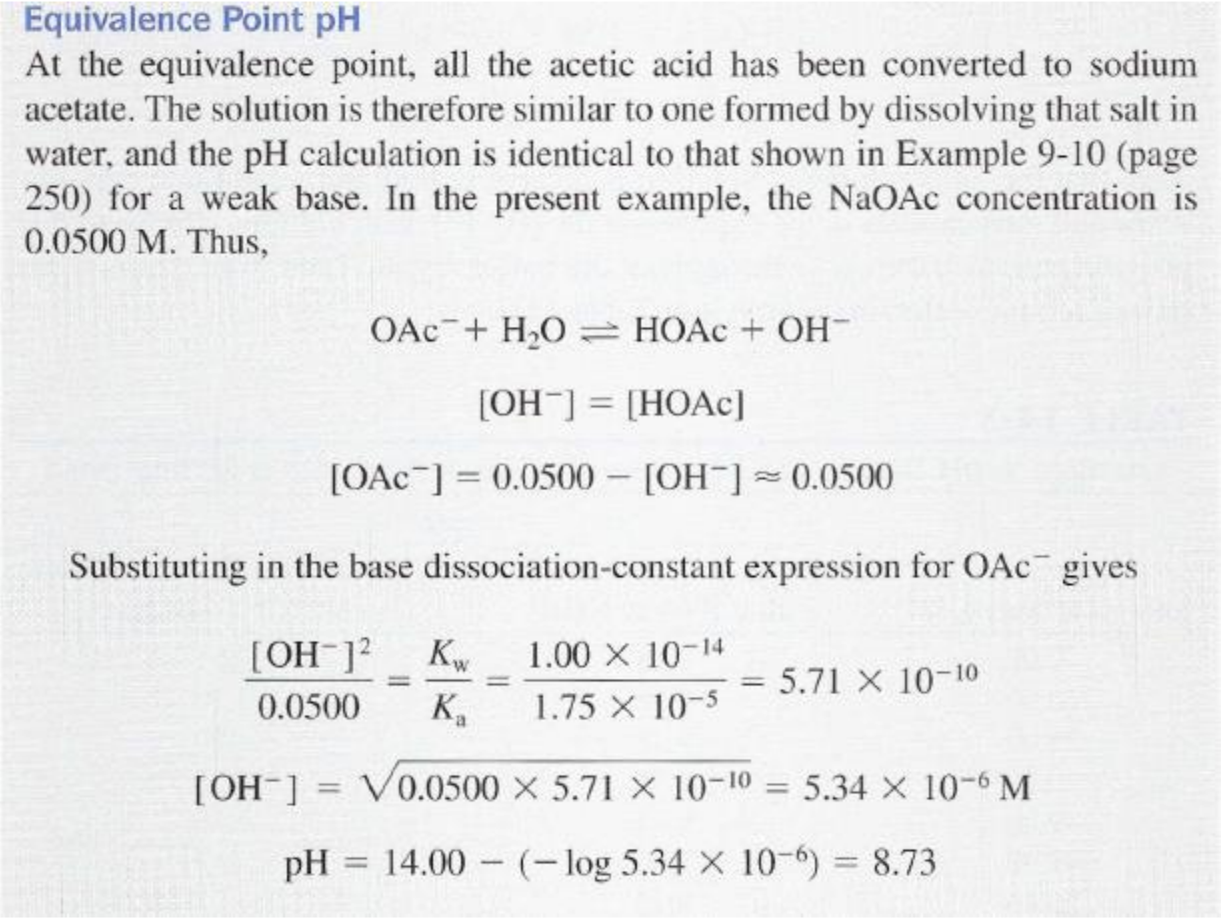
$$c_{\mathrm{NaOAc}} = \frac{25.00\ \mathrm{mL} \times 0.100\ \mathrm{M}}{60.00\ \mathrm{mL}} = \frac{2.500}{60.00}\ \mathrm{M}$$

Now for the 25.00-mL volume, we substitute the concentrations of HOAc and $\mathrm{OAc^-}$ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[\mathrm{H_3O^+}](\cancel{2.500}/\cancel{60.00})}{\cancel{2.500}/\cancel{60.00}} = [\mathrm{H_3O^+}] = 1.75 \times 10^{-5}$$

$$\mathrm{pH} = \mathrm{p}K_a = 4.76$$

At this point in the titration, both the analytical concentrations of the acid and conjugate base as well as the total volume of solution cancel in the expression for $[\mathrm{H_3O^+}]$.



Equivalence Point pH

At the equivalence point, all the acetic acid has been converted to sodium acetate. The solution is therefore similar to one formed by dissolving that salt in water, and the pH calculation is identical to that shown in Example 9-10 (page 250) for a weak base. In the present example, the NaOAc concentration is 0.0500 M. Thus,

$$\mathrm{OAc^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HOAc} + \mathrm{OH^-}$$

$$[\mathrm{OH^-}] = [\mathrm{HOAc}]$$

$$[\mathrm{OAc^-}] = 0.0500 - [\mathrm{OH^-}] \approx 0.0500$$

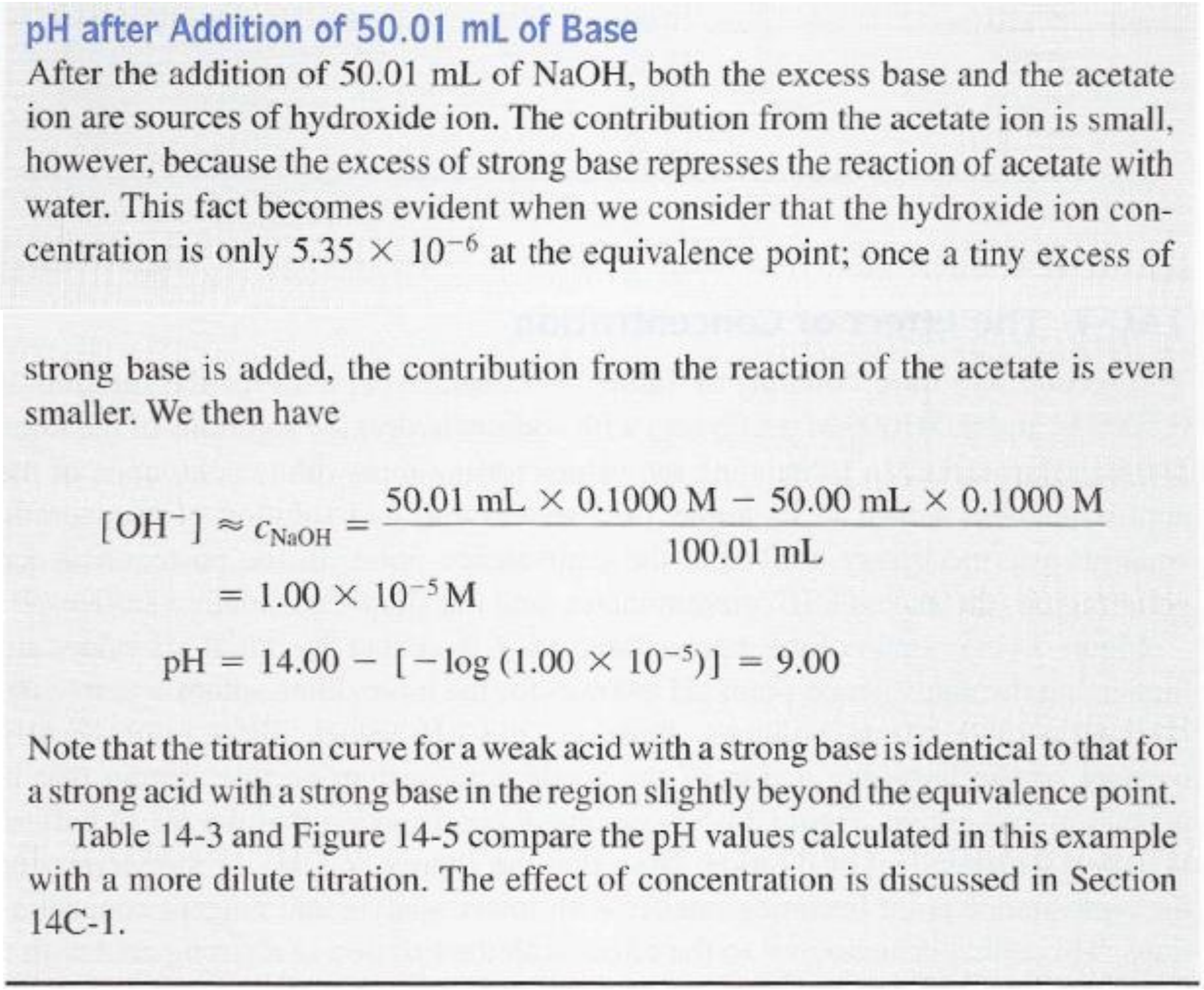
Substituting in the base dissociation-constant expression for $\mathrm{OAc^-}$ gives

$$\frac{[\mathrm{OH^-}]^2}{0.0500} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[\mathrm{OH^-}] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6}\ \mathrm{M}$$

$$\mathrm{pH} = 14.00 - (-\log 5.34 \times 10^{-6}) = 8.73$$

Catalyst



pH after Addition of 50.01 mL of Base

After the addition of 50.01 mL of NaOH, both the excess base and the acetate ion are sources of hydroxide ion. The contribution from the acetate ion is small, however, because the excess of strong base represses the reaction of acetate with water. This fact becomes evident when we consider that the hydroxide ion concentration is only 5.35×10^{-6} at the equivalence point; once a tiny excess of strong base is added, the contribution from the reaction of the acetate is even smaller. We then have

$$[\mathrm{OH^-}] \approx c_{\mathrm{NaOH}} = \frac{50.01\ \mathrm{mL} \times 0.1000\ \mathrm{M} - 50.00\ \mathrm{mL} \times 0.1000\ \mathrm{M}}{100.01\ \mathrm{mL}}$$

$$= 1.00 \times 10^{-5}\ \mathrm{M}$$

$$\mathrm{pH} = 14.00 - [-\log(1.00 \times 10^{-5})] = 9.00$$

Note that the titration curve for a weak acid with a strong base is identical to that for a strong acid with a strong base in the region slightly beyond the equivalence point.

Table 14-3 and Figure 14-5 compare the pH values calculated in this example with a more dilute titration. The effect of concentration is discussed in Section 14C-1.

- The analytical concentrations of acid and conjugate base are identical when an acid has been half neutralized.
- the buffer capacities of each of the solutions are at a maximum at this point. These points are often called the **half-titration points.**

➢ At the half-titration point in the titration of a weak acid,

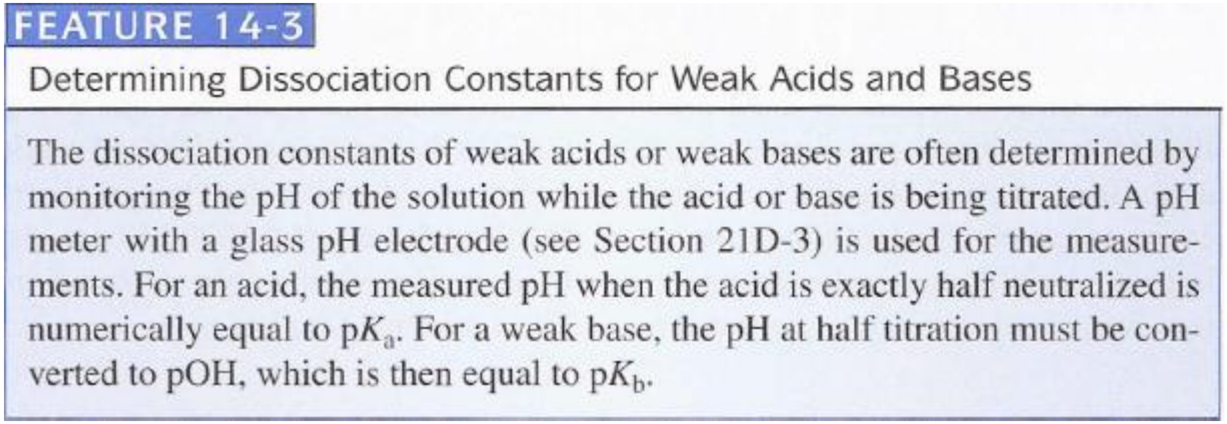
$[H3O^{+}] = Ka$ or

$pH = pKa$

➢ At the half-titration point in the titration of a weak base,

$[OH^{-}] = Kb$ or

$pOH = pKb$



FEATURE 14-3

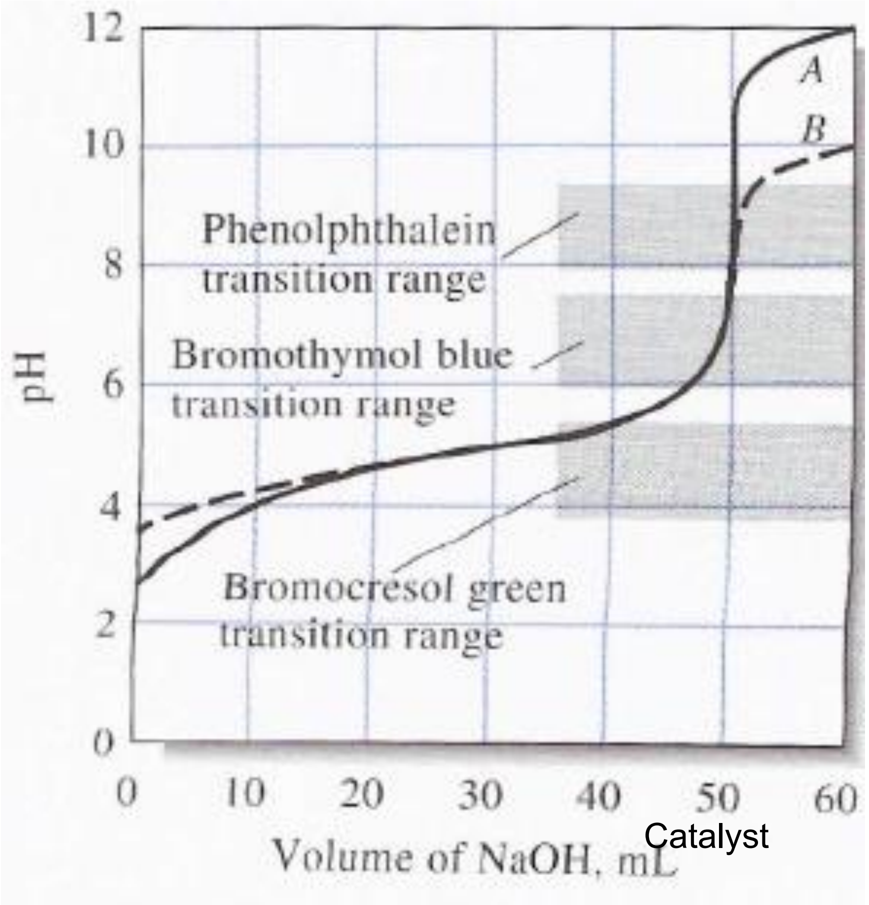
Determining Dissociation Constants for Weak Acids and Bases

The dissociation constants of weak acids or weak bases are often determined by monitoring the pH of the solution while the acid or base is being titrated. A pH meter with a glass pH electrode (see Section 21D-3) is used for the measurements. For an acid, the measured pH when the acid is exactly half neutralized is numerically equal to pK_a. For a weak base, the pH at half titration must be converted to pOH, which is then equal to pK_b.

The Effect of Concentration

- Note that the initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (curve *B*).
- At intermediate titrant volumes, however, the pH values differ only slightly because of the buffering action
- The pH of buffers is largely independent of dilution.

Choosing an Indicator: The Feasibility of Titration



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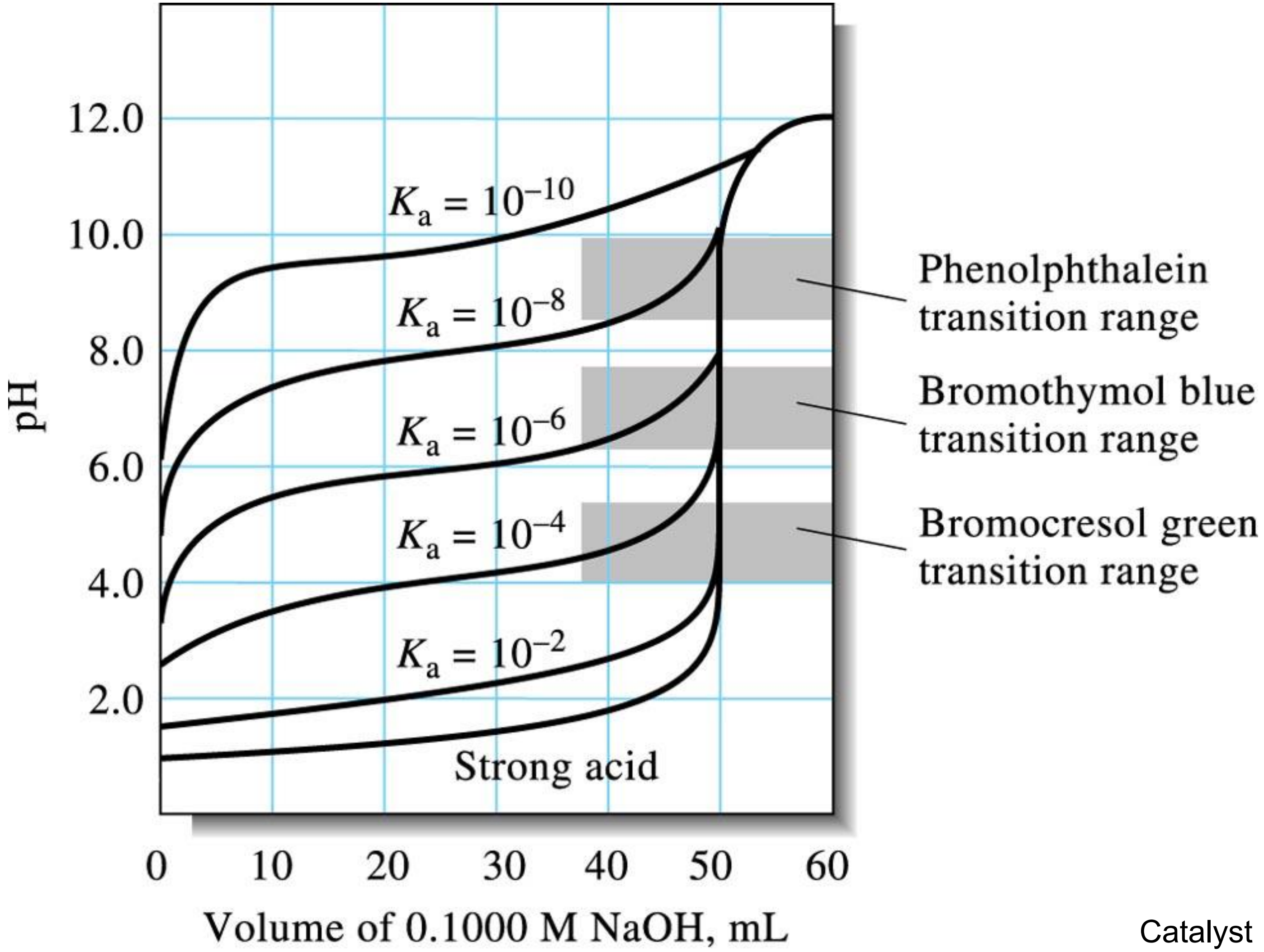
The Effect of Reaction Completeness

The pH change in the equivalence-point region becomes smaller as the acid becomes weaker-that is, as the reaction between the acid and the base becomes less complete.



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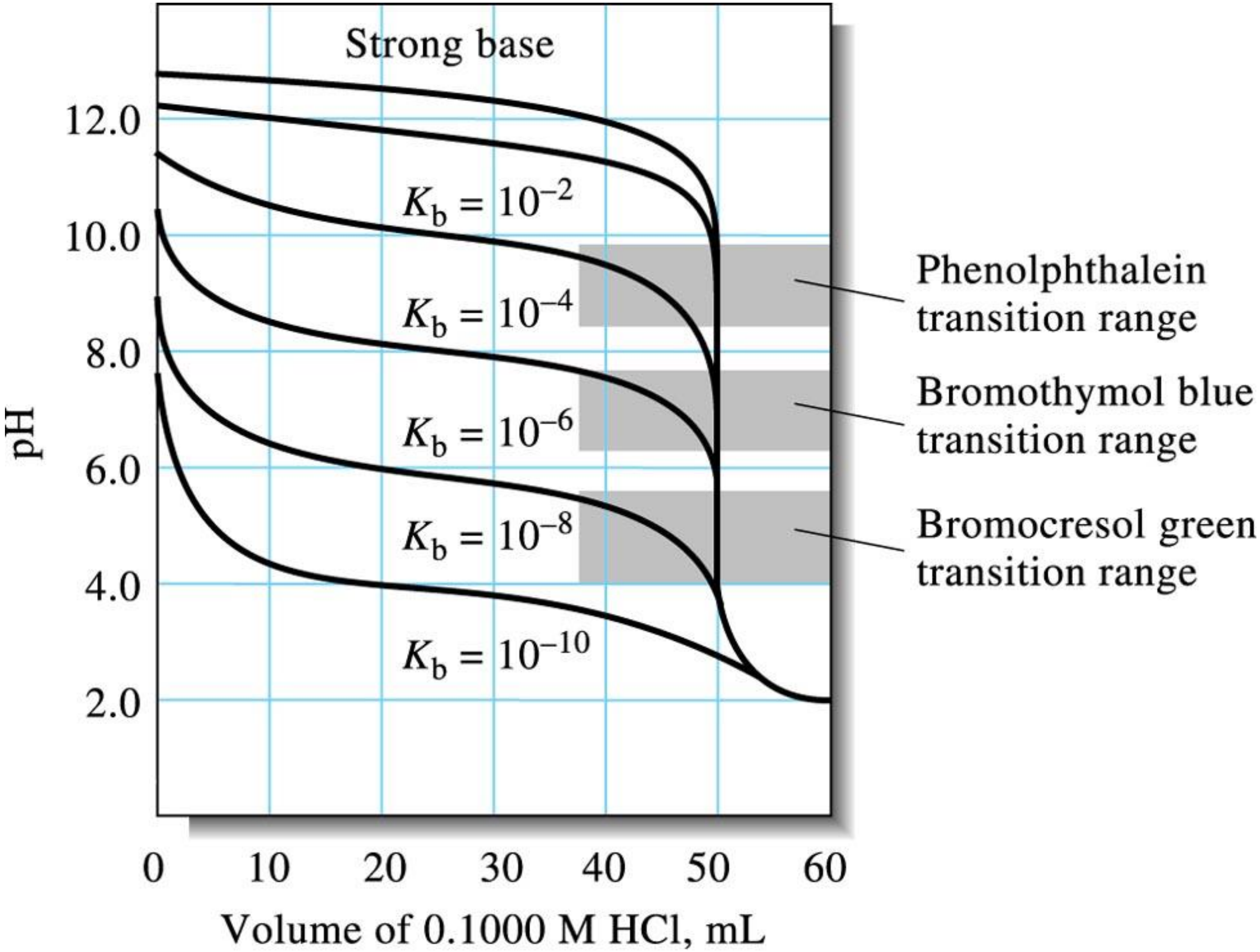
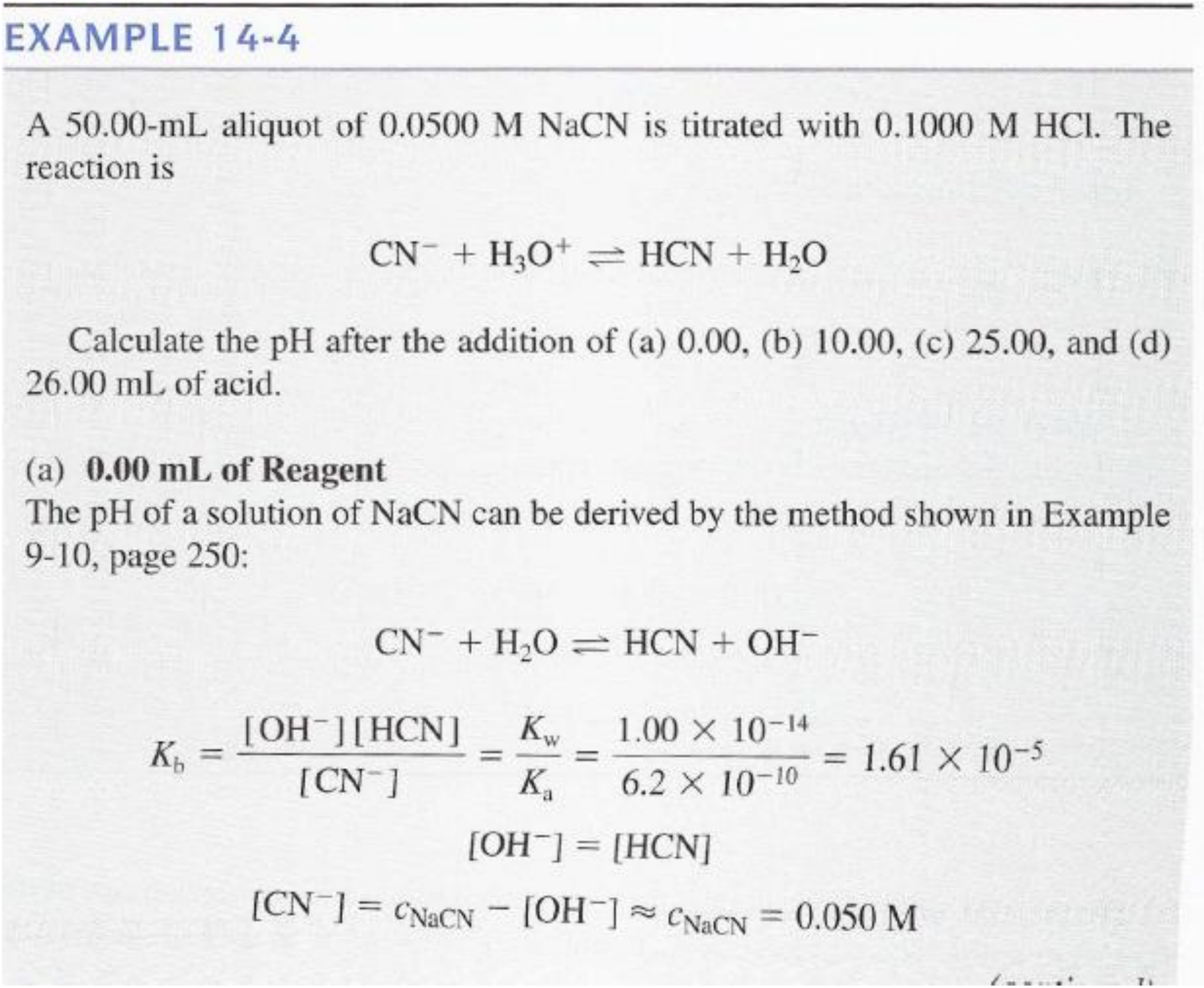
TITRATION CURVES FOR WEAK BASES





EXAMPLE 14-4

A 50.00-mL aliquot of 0.0500 M NaCN is titrated with 0.1000 M HCl. The reaction is

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.

(a) **0.00 mL of Reagent**

The pH of a solution of NaCN can be derived by the method shown in Example 9-10, page 250:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$[OH^-] = [HCN]$$

$$[CN^-] = c_{NaCN} - [OH^-] \approx c_{NaCN} = 0.050\ M$$

Substitution into the dissociation-constant expression gives, after rearrangement,

$$[OH^-] = \sqrt{K_b c_{NaCN}} = \sqrt{1.61 \times 10^{-5} \times 0.0500} = 8.97 \times 10^{-4}$$

$$pH = 14.00 - (-\log 8.97 \times 10^{-4}) = 10.95$$

(b) **10.00 mL of Reagent**

Addition of acid produces a buffer with a composition given by

$$c_{NaCN} = \frac{50.00 \times 0.0500 - 10.00 \times 0.1000}{60.00} = \frac{1.500}{60.00}\,M$$

$$c_{HCN} = \frac{10.00 \times 0.1000}{60.00} = \frac{1.000}{60.00}\,M$$

These values are then substituted into the expression for the acid dissociation constant of HCN to give $[H_3O^+]$ directly (see Margin Note):

$$[H_3O^+] = \frac{6.2 \times 10^{-10} \times (1.000/\cancel{60.00})}{1.500/\cancel{60.00}} = 4.13 \times 10^{-10}$$

$$pH = -\log(4.13 \times 10^{-10}) = 9.38$$

(c) **25.00 mL of Reagent**

This volume corresponds to the equivalence point, where the principal solute species is the weak acid HCN. Thus,

$$c_{\mathrm{HCN}} = \frac{25.00 \times 0.1000}{75.00} = 0.03333\ \mathrm{M}$$

Applying Equation 9-22 gives

$$[\mathrm{H_3O^+}] = \sqrt{K_a c_{\mathrm{HCN}}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.45 \times 10^{-6}\,\mathrm{M}$$

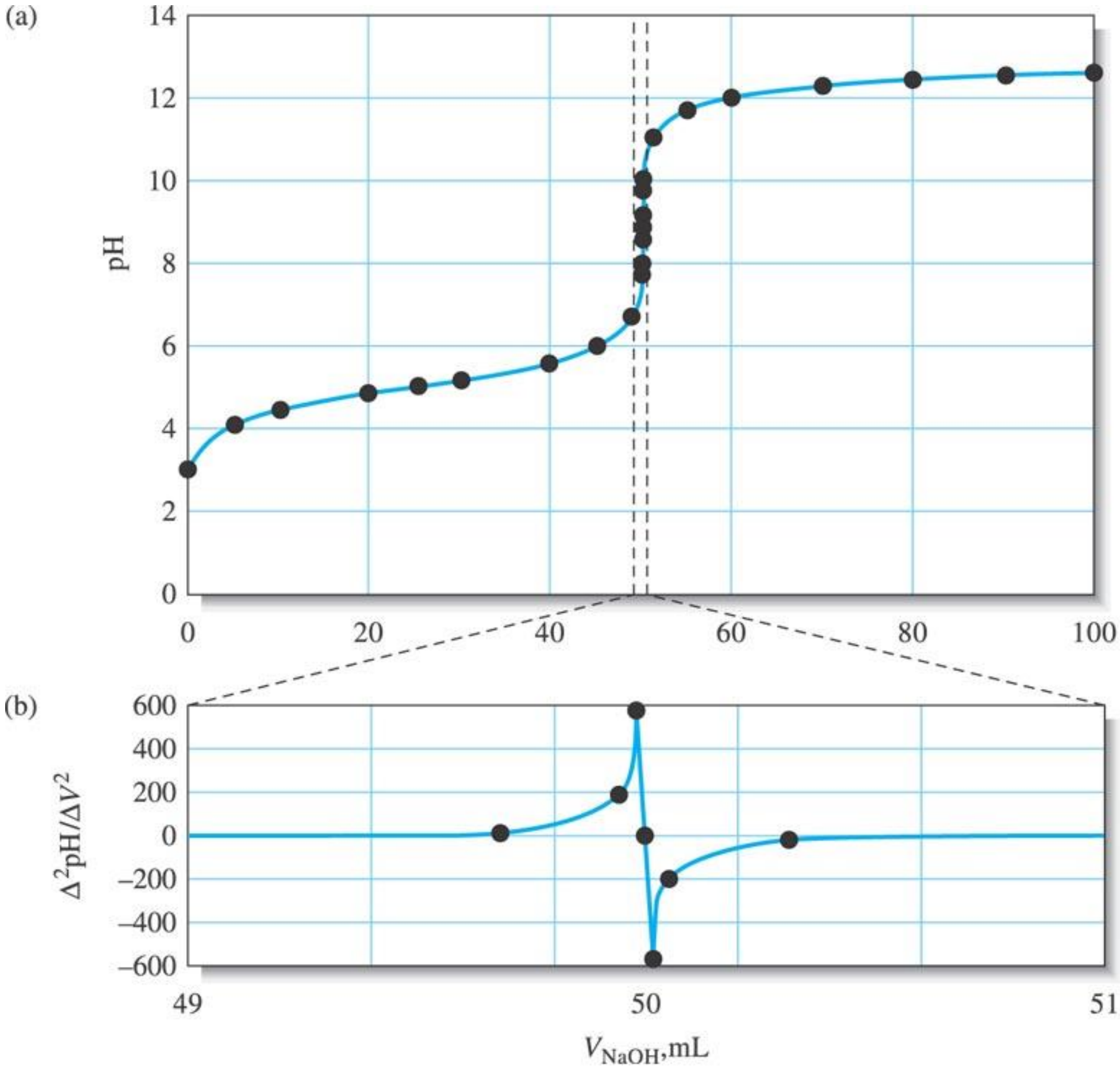
$$\mathrm{pH} = -\log(4.45 \times 10^{-6}) = 5.34$$

(d) **26.00 mL of Reagent**

The excess of strong acid now present represses the dissociation of the HCN to the point where its contribution to the pH is negligible. Thus,

$$[\mathrm{H_3O^+}] = c_{\mathrm{HCl}} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3}\,\mathrm{M}$$

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


(a)
14
12
10
8
6
4
2
0
pH
0
20
40
60
80
100
(b)
600
400
200
0
−200
−400
−600
Δ^2pH/ΔV^2
49
50
51
V_{NaOH},mL

Catalyst

Chapter 9

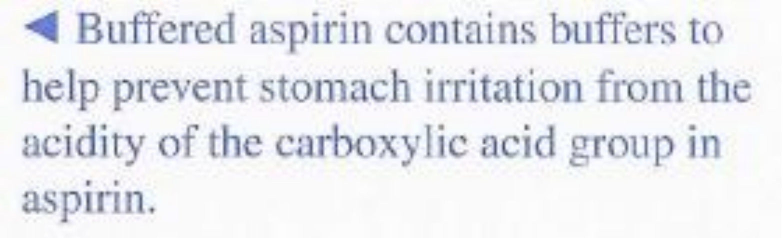
BUFFER SOLUTIONS

A buffer is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution.

Buffers are used in all types of chemistry whenever it is desirable to maintain the pH of a solution at a constant and predetermined level

What Are the Unique Properties of Buffer Solutions?

Buffers do not maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid or base are added.



◀ Buffered aspirin contains buffers to help prevent stomach irritation from the acidity of the carboxylic acid group in aspirin.

Catalyst

Calculating the pH of Buffer Solutions

Buffers Formed from a Weak Acid and Its Conjugate Base

A solution containing a weak acid, **HA** and its conjugate base **A^-**, may be acidic, neutral, or basic, depending on the position of two competitive equilibria:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad K_b = \frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]}$$

If the first equilibrium lies farther to the right than the second, the solution is acidic. If the second equilibrium is more favorable, the solution is basic.

Catalyst

The pH of a solution containing both an acid, **HA**, and its conjugate base, **A⁻**.

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

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

An examination of the two equilibria reveals that the first reaction decreases the concentration of HA by an amount equal to $[H_3O^+]$, whereas the second increases the HA concentration by an amount equal to $[OH^{-1}]$

$$[HA] = C_{HA} - [H_3O^+] + [OH^{-1}]$$

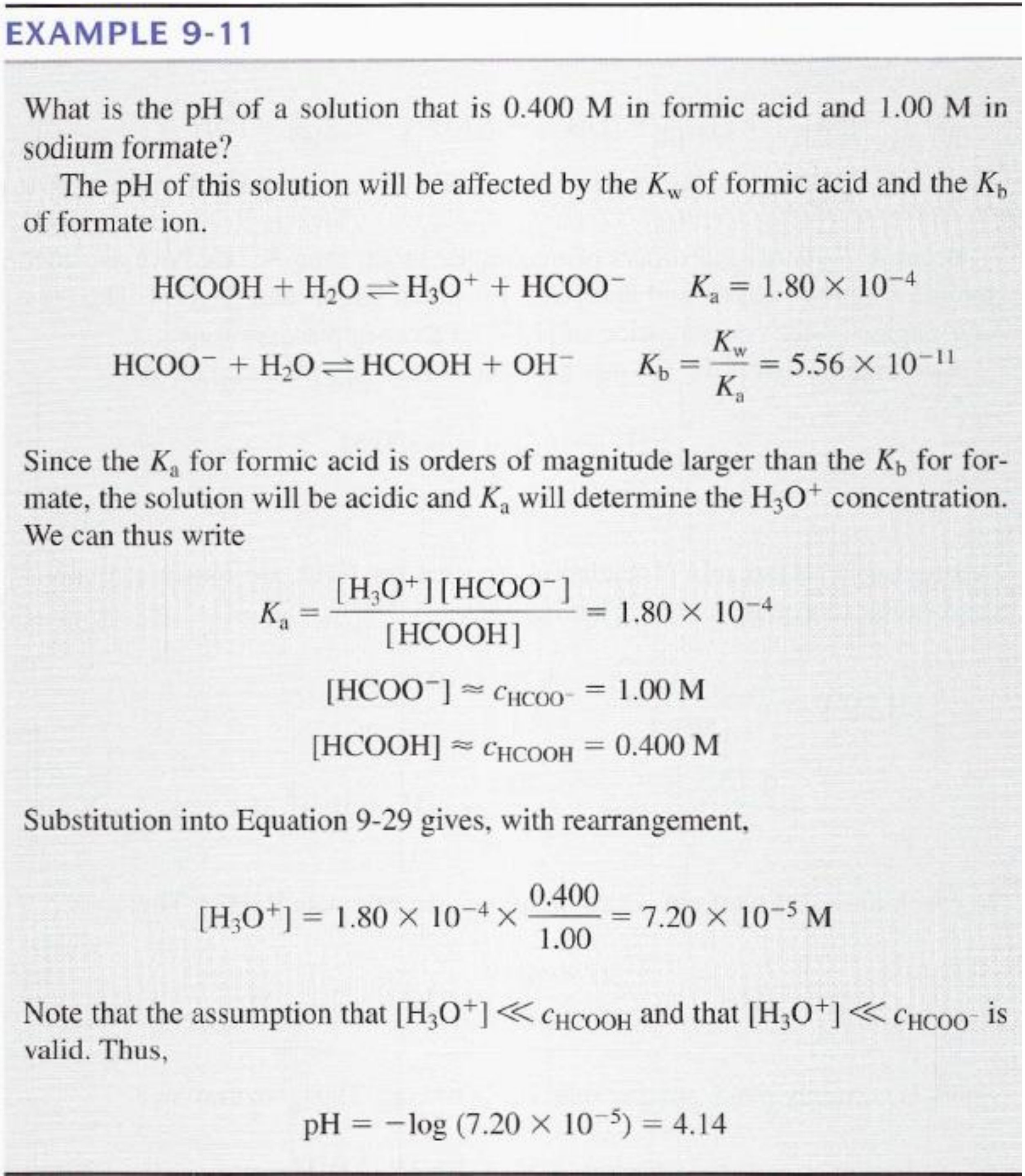
$$[A^-] = C_{A-} + [H_3O^+] - [OH^{-1}]$$

The difference in concentration between these two species is usually so small relative to the molar concentrations of acid and conjugate base

$$\mathbf{[HA] \approx C_{HA}} \quad \text{and} \quad \mathbf{[A^-] \approx C_{A-}}$$

$$[H_3O^+] = K_a \frac{C_{HA}}{C_{A-}} \Rightarrow -\log[H_3O^+] = -\log K_a - \log \frac{C_{HA}}{C_{A-}}$$

$$pH = pK_a + \log \frac{C_{A^-}}{C_{HA}}$$



EXAMPLE 9-11

What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate?

The pH of this solution will be affected by the K_w of formic acid and the K_b of formate ion.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^- \qquad K_a = 1.80 \times 10^{-4}$$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^- \qquad K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-11}$$

Since the K_a for formic acid is orders of magnitude larger than the K_b for formate, the solution will be acidic and K_a will determine the H_3O^+ concentration. We can thus write

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

$$[HCOO^-] \approx c_{HCOO^-} = 1.00 \text{ M}$$

$$[HCOOH] \approx c_{HCOOH} = 0.400 \text{ M}$$

Substitution into Equation 9-29 gives, with rearrangement,

$$[H_3O^+] = 1.80 \times 10^{-4} \times \frac{0.400}{1.00} = 7.20 \times 10^{-5} \text{ M}$$

Note that the assumption that $[H_3O^+] \ll c_{HCOOH}$ and that $[H_3O^+] \ll c_{HCOO^-}$ is valid. Thus,

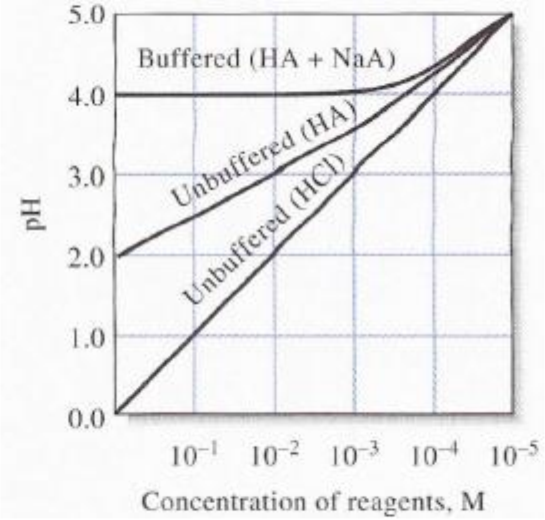
$$pH = -\log(7.20 \times 10^{-5}) = 4.14$$

Catalyst

Properties of Buffer Solutions

- *The Effect of Dilution*

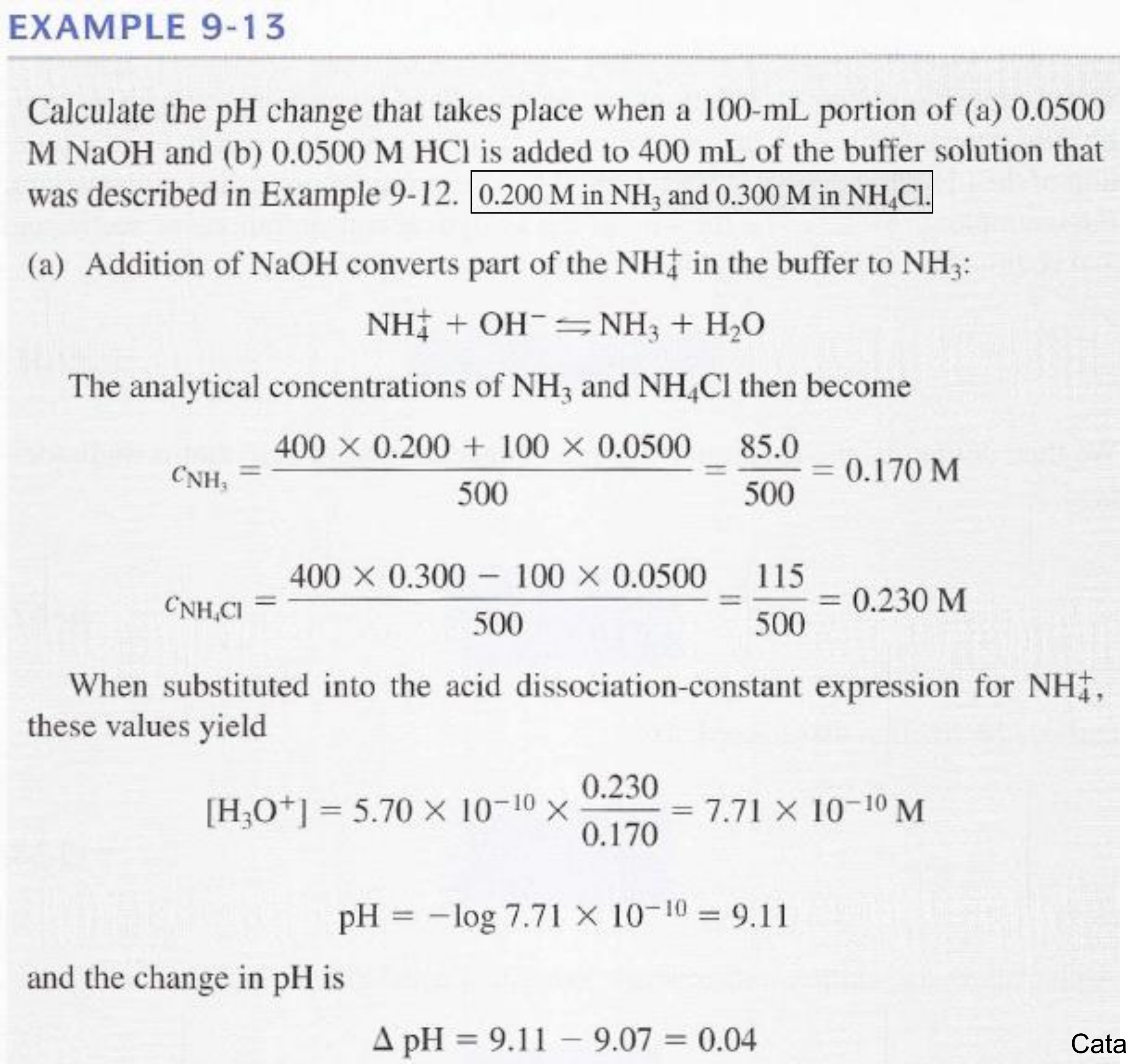
  The pH of a buffer solution remains essentially independent of dilution until the concentrations of the species it contains are decreased to the point where the approximations used to develop equations **[HA] ≈ C_{HA}** and **[A$^-$] ≈ C_{A^-}** become invalid



- *The Effect of Added Acids and Bases*

  Resistance to pH change after addition of small amounts of strong acids or bases.(*Ex. 9-13*)

Catalyst



EXAMPLE 9-13

Calculate the pH change that takes place when a 100-mL portion of (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400 mL of the buffer solution that was described in Example 9-12. 0.200 M in NH_3 and 0.300 M in NH_4Cl.

(a) Addition of NaOH converts part of the NH_4^+ in the buffer to NH_3:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

The analytical concentrations of NH_3 and NH_4Cl then become

$$c_{NH_3} = \frac{400 \times 0.200 + 100 \times 0.0500}{500} = \frac{85.0}{500} = 0.170 \text{ M}$$

$$c_{NH_4Cl} = \frac{400 \times 0.300 - 100 \times 0.0500}{500} = \frac{115}{500} = 0.230 \text{ M}$$

When substituted into the acid dissociation-constant expression for NH_4^+, these values yield

$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log 7.71 \times 10^{-10} = 9.11$$

and the change in pH is

$$\Delta \text{ pH} = 9.11 - 9.07 = 0.04$$

Buffer Capacity (*β*)

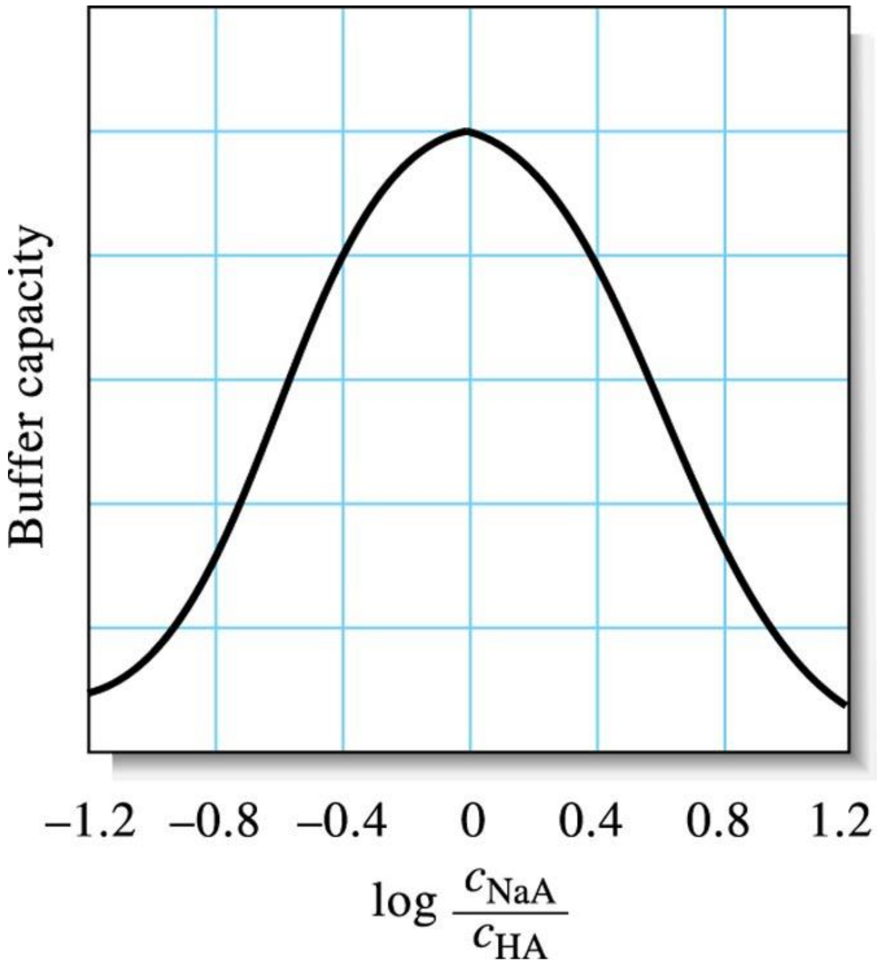
A solution containing a conjugate acid/base pair possesses remarkable resistance to changes in pH. The ability of a buffer to prevent a significant change in pH is directly related to the total concentration of the buffering species as well as to their concentration ratio.

The buffer capacity (***β***) of a solution is defined as the number of moles of a strong acid or a strong base that causes 1.00 L of the buffer to undergo a 1.00 unit change in pH.

$$\beta = \frac{dc_b}{d\mathrm{pH}} = -\frac{dc_a}{d\mathrm{pH}}$$

The capacity of a buffer depends not only on the total concentration of the two buffer components but also on their concentration ratio. Buffer capacity falls off moderately rapidly as the concentration ratio of acid to conjugate base departs from unity.

The pKa of the acid chosen for a given application should lie within: ±1 unit of the desired pH for the buffer to have a reasonable capacity.



Preparing Buffers

- In principle, a buffer solution of any desired pH can be prepared by combining calculated quantities of a suitable conjugate acid/base pair. In practice, however the pH values of buffers prepared from theoretically generated recipes differ from the predicted values. We prepare buffers by making up a solution of approximately the desired pH and then adjust by adding acid or conjugate base until the required pH is indicated by a pH meter.

- Buffers are of tremendous importance in biological and biochemical studies where a low but constant concentration of hydronium ions (10^{-6} to 10^{-10} M) must be maintained throughout experiments.

Chapter 15

Titration Curves for Complex Acid/Base Systems

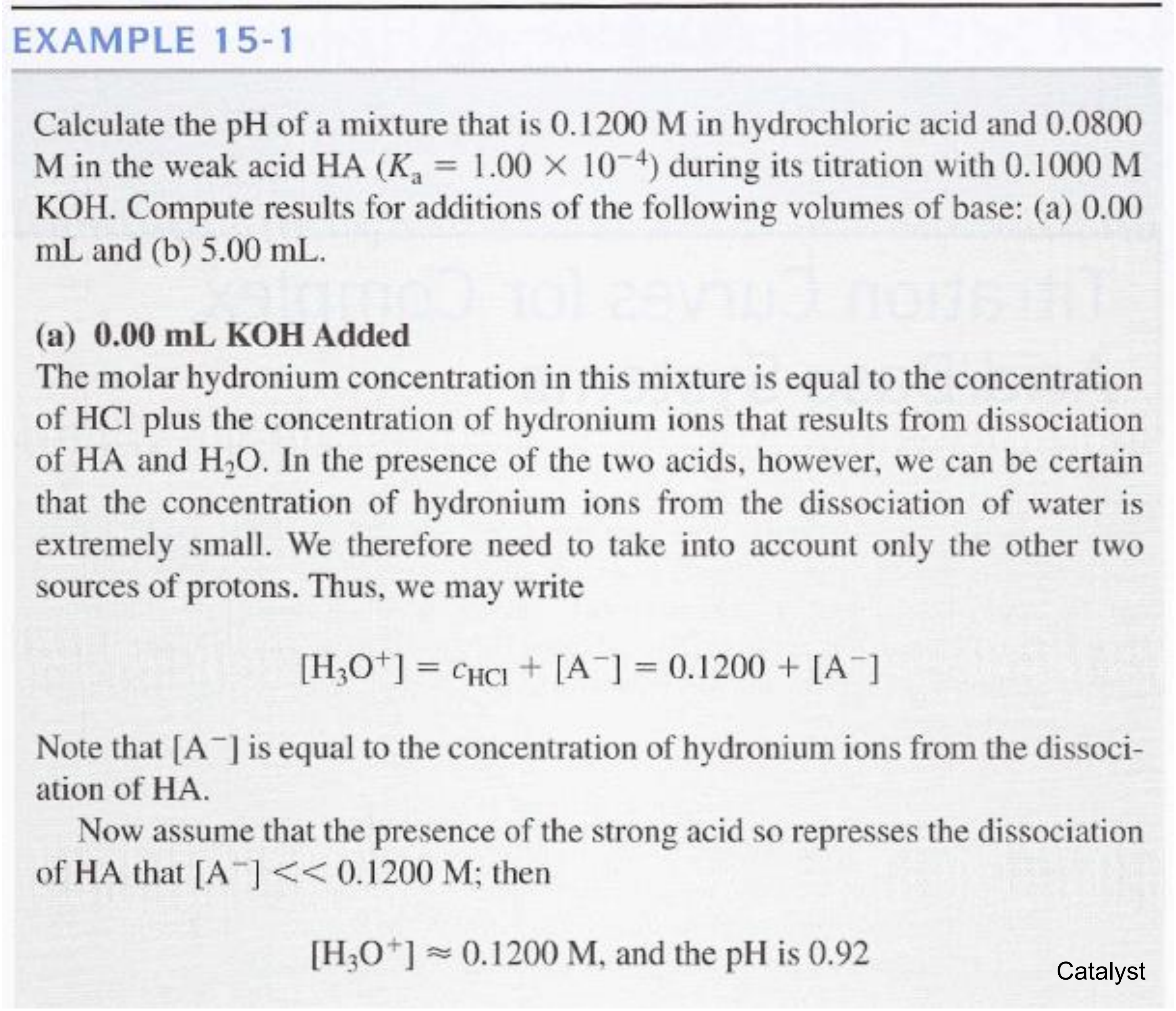
In this chapter; we describe methods for calculating titration curves for complex acid/base systems. For the purpose of this discussion, complex systems are defined as solutions made up of
(1) two acids or two bases of different strengths,
(2) an acid or a base that has two or more acidic or basic functional groups, or
(3) an amphiprotic substance, which is capable of acting as both an acid and a base.

Equations for more than one equilibrium are required to describe the characteristics of any of these systems.

Catalyst

MIXTURES OF STRONG AND WEAK ACIDS OR STRONG AND WEAK BASES

- Strong acid and a weak acid (or a strong base and a weak base)
  - the concentrations of the two are of the same order of magnitude and
  - the K_a or K_b for the weak acid or base is somewhat less than about 10^{-4}
  - Assume all $[H_2O^+]$ = comes from strong acid



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.

(a) 0.00 mL KOH Added

The molar hydronium 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

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

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

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

Catalyst

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

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

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

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

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) After Adding 5.00 mL of Base

$$c_{\mathrm{HCl}} = \frac{25.00 \times 0.1200 - 5.00 \times 0.1000}{25.00 + 5.00} = 0.0833\ \mathrm{M}$$

and we may write

$$[\mathrm{H_3O^+}] = 0.0833 + [\mathrm{A^-}] \approx 0.0833\ \mathrm{M}$$
$$\mathrm{pH} = 1.08$$

To determine whether our assumption is still valid, we compute $[\mathrm{A^-}]$ 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

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

which is still much smaller than 0.0833.

EXAMPLE 15-2

Calculate the pH of the solution that results when 29.00 mL of 0.1000 M NaOH is added to 25.00 mL of the solution described in Example 15-1.

Here,

$$c_{\mathrm{HCl}} = \frac{25.00 \times 0.1200 - 29.00 \times 0.1000}{54.00} = 1.85 \times 10^{-3}\ \mathrm{M}$$

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

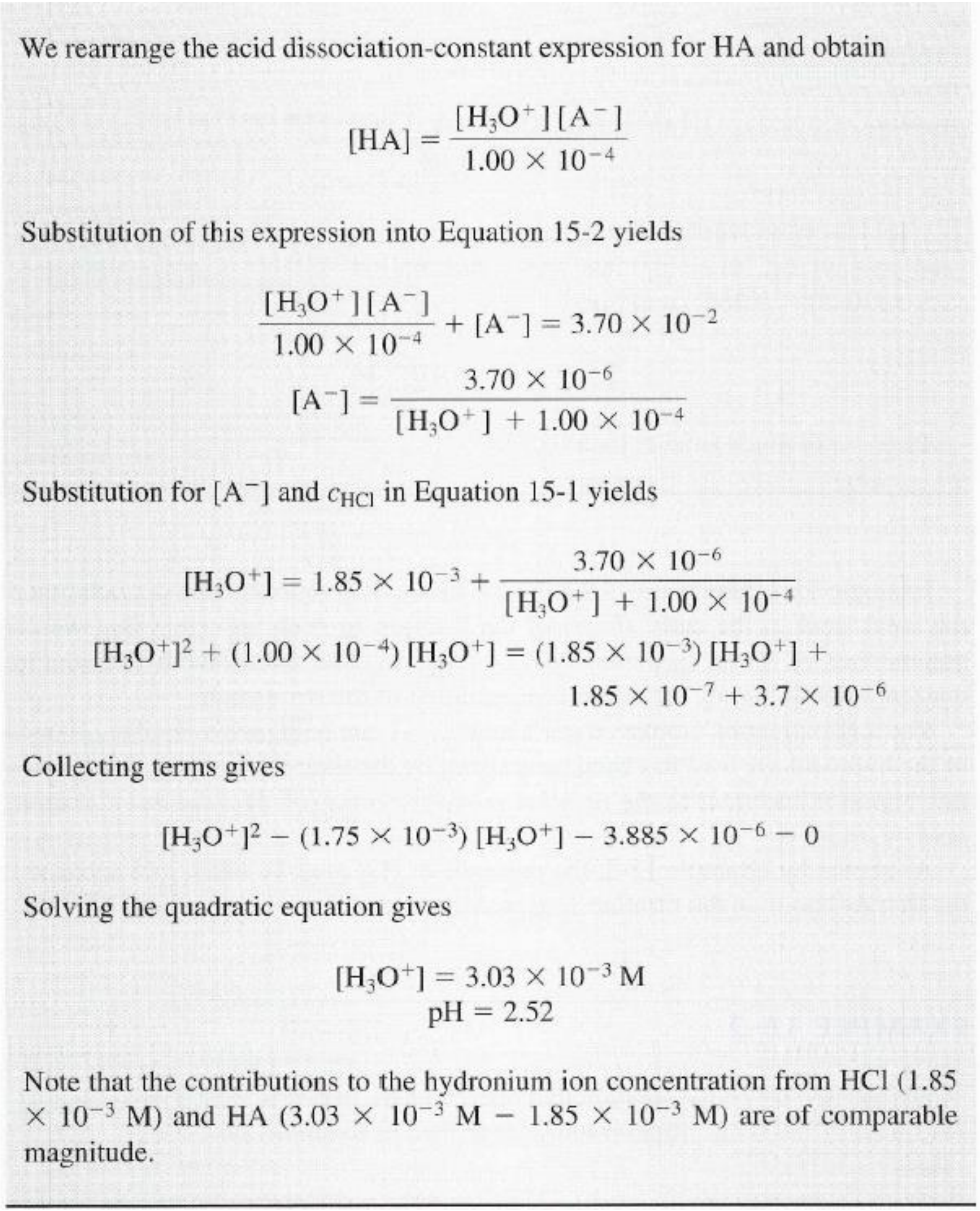
A provisional result based (as in the previous example) on the assumption that $[\mathrm{H_3O^+}] = 1.85 \times 10^{-3}$ yields a value of 1.90×10^{-3} for $[\mathrm{A^-}]$. Clearly, $[\mathrm{A^-}]$ is no longer much smaller than $[\mathrm{H_3O^+}]$, and we must write

$$[\mathrm{H_3O^+}] = c_{\mathrm{HCl}} + [\mathrm{A^-}] = 1.85 \times 10^{-3} + [\mathrm{A^-}] \qquad (15\text{-}1)$$

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

$$[\mathrm{HA}] + [\mathrm{A^-}] = c_{\mathrm{HA}} = 3.70 \times 10^{-2} \qquad (15\text{-}2)$$

(continued)



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

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

$$[H_3O^+]^2 + (1.00 \times 10^{-4})[H_3O^+] = (1.85 \times 10^{-3})[H_3O^+] + 1.85 \times 10^{-7} + 3.7 \times 10^{-6}$$

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 $-$ 1.85×10^{-3} M) are of comparable magnitude.

Catalyst

- assume that $[A^-] << C_{HCl}$ and $[H_3 0^+] = C_{HCl}$
- The approximation employed in Example 15-1 can be shown to apply until most of the **HCl** has been neutralized by the titrant.
  - the curve in this region *is identical to the titration curve for a solution of a strong acid by itself.*
- 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 solution that results when 29.00 mL of 0.1000 M NaOH is added to 25.00 mL of the solution described in Example 15-1.

Here,

$$c_{\mathrm{HCl}} = \frac{25.00 \times 0.1200 - 29.00 \times 0.1000}{54.00} = 1.85 \times 10^{-3}\ \mathrm{M}$$

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

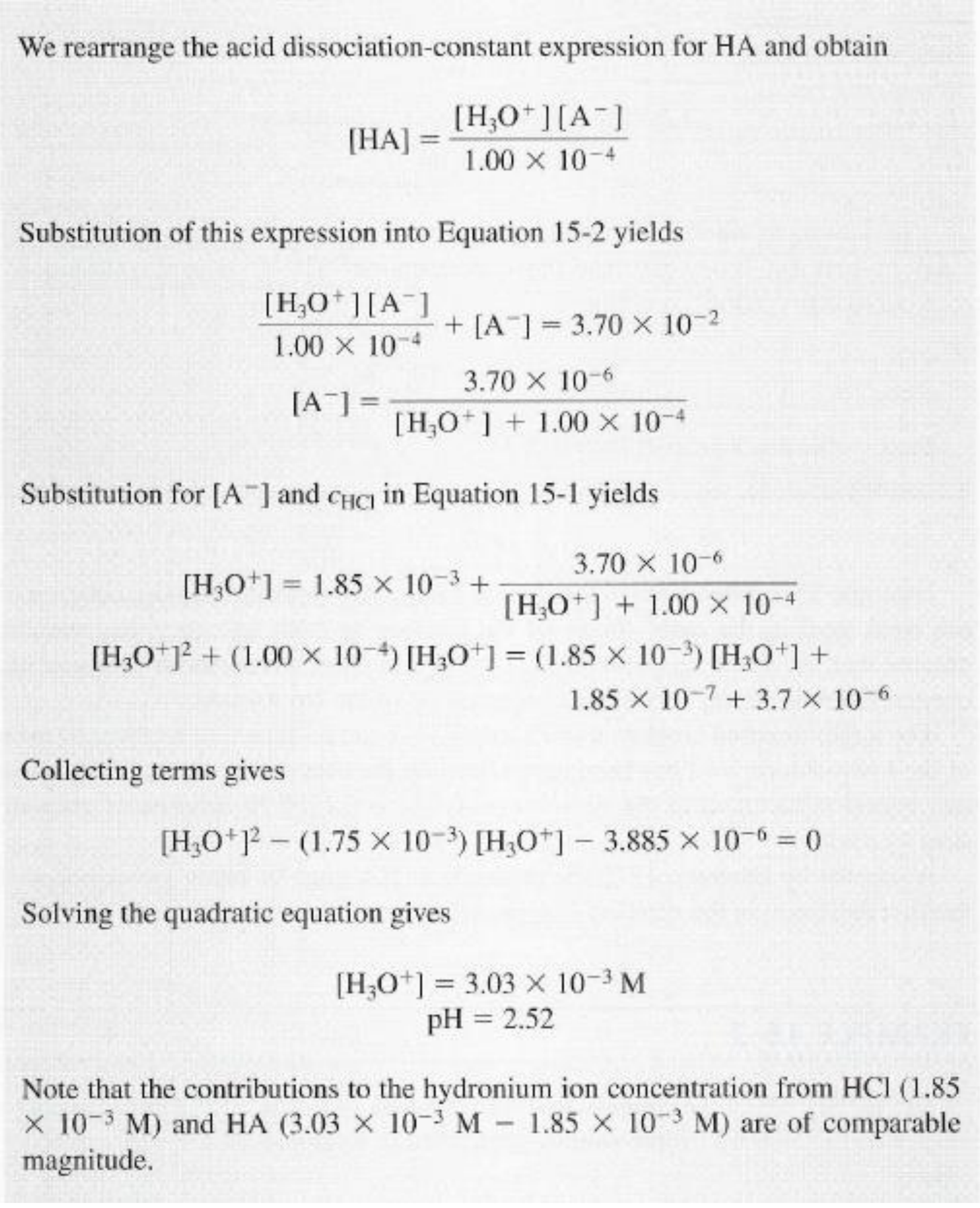
A provisional result based (as in the previous example) on the assumption that $[\mathrm{H_3O^+}] = 1.85 \times 10^{-3}$ yields a value of 1.90×10^{-3} for $[\mathrm{A^-}]$. Clearly, $[\mathrm{A^-}]$ is no longer much smaller than $[\mathrm{H_3O^+}]$, and we must write

$$[\mathrm{H_3O^+}] = c_{HCl} + [\mathrm{A^-}] = 1.85 \times 10^{-3} + [\mathrm{A^-}] \qquad (15\text{-}1)$$

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

$$[\mathrm{HA}] + [\mathrm{A^-}] = c_{\mathrm{HA}} = 3.70 \times 10^{-2} \qquad (15\text{-}2)$$

(continued)



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

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

$$[H_3O^+]^2 + (1.00 \times 10^{-4})[H_3O^+] = (1.85 \times 10^{-3})[H_3O^+] + 1.85 \times 10^{-7} + 3.7 \times 10^{-6}$$

Collecting terms gives

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

Solving the quadratic equation gives

$$[H_3O^+] = 3.03 \times 10^{-3}\ \text{M}$$
$$\text{pH} = 2.52$$

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.

Catalyst

The shape of the curve for a mixture of weak and strong acids, and hence the information obtainable from it, depends in large measure on the strength of the weak acid.

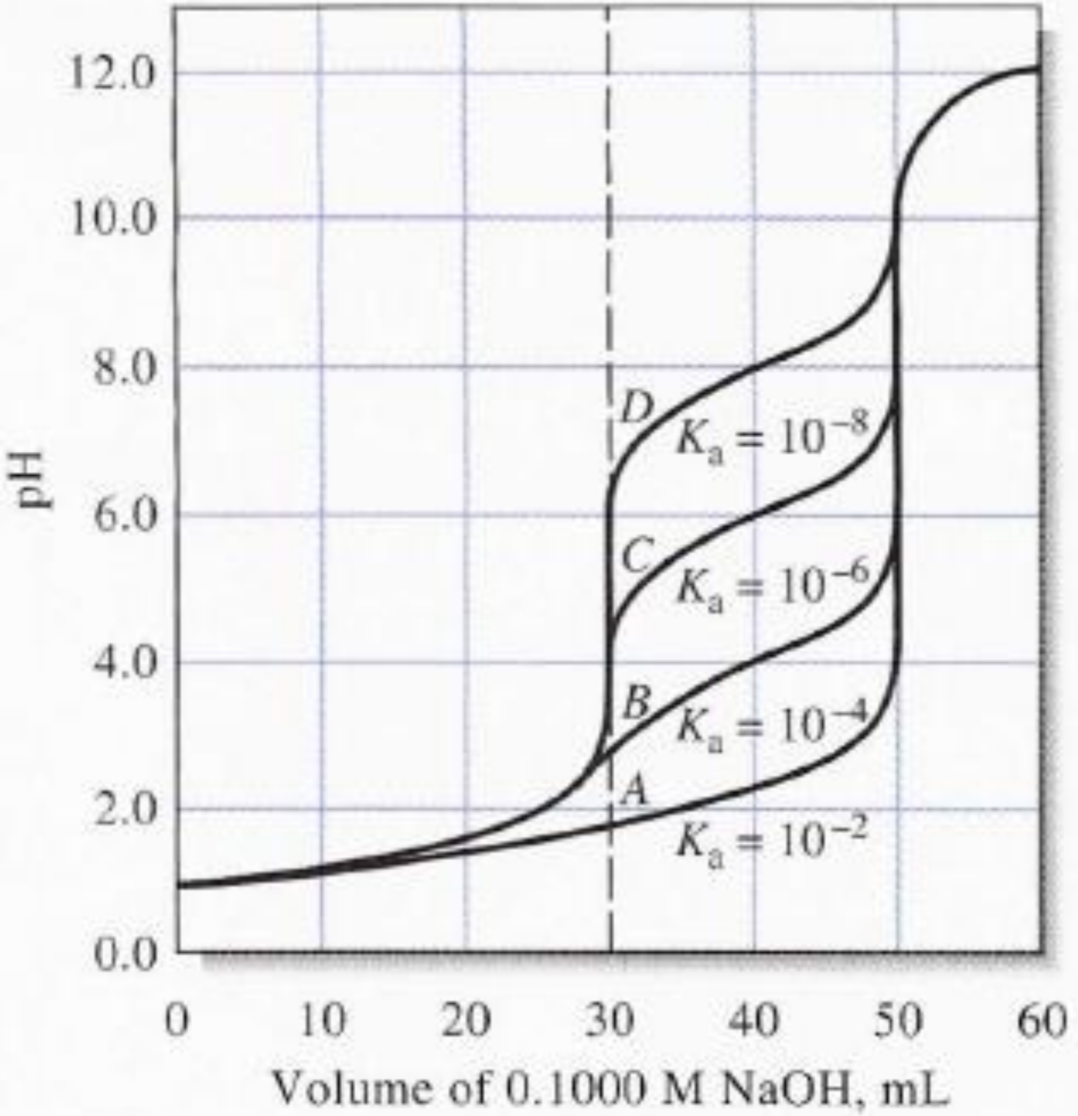


Figure 15-1 Curves for the titration of strong acid/weak acid mixtures with 0.1000 M NaOH. Each titration is on 25.00 mL of a solution that is 0.1200 M in HCl and 0.0800 M in HA.

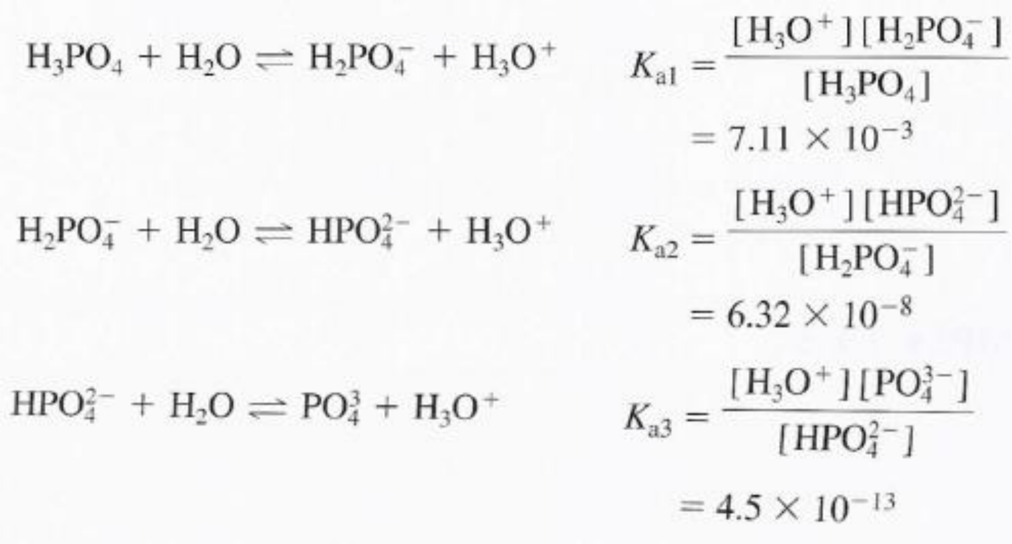
The composition of a mixture of a strong acid and a weak acid can be determined by titration with suitable indicators if the weak acid has a dissociation constant that lies between 10^{-4} and 10^{-8} and the concentrations of the two acids are of the same order of magnitude.

Catalyst

POLYFUNCTIONAL ACIDS AND BASES

- Several species are encountered in analytical chemistry that have two or more acidic or basic functional groups. Generally, the two groups differ in strength and, as a consequence, exhibit two or more end points in a neutralization titration.

The Phosphoric Acid System



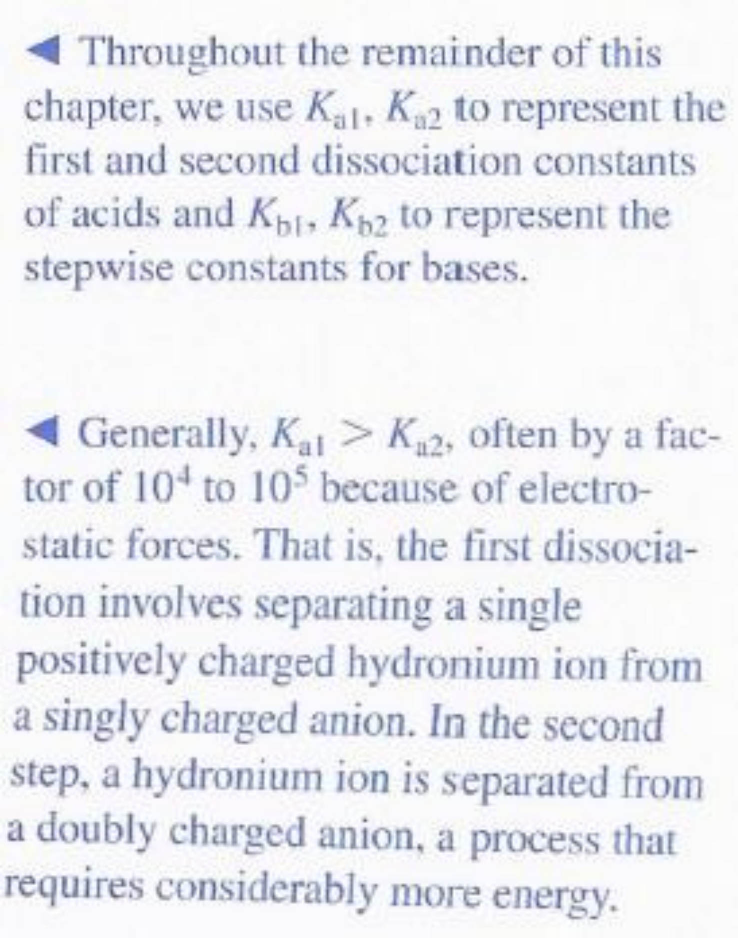
$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

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

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

With this acid, as with other *polyprotic* acids

$K_{a1} > K_{a2} > K_{a3}$.



◀ 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 for 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, a hydronium ion is separated from a doubly charged anion, a process that requires considerably more energy.

Catalyst

▶ A second reason that $K_{a1} > K_{a2}$ is a statistical one. In the first step, a proton can be removed from two locations; in the second step, only one can be removed. Thus, the first dissociation is twice as probable as the second.

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{2-}]}{[H_3PO_4]}$$
$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} = 4.49 \times 10^{-10}$$

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

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{3-}]}{H_3PO_4}$$
$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} \times 4.5 \times 10^{-13} = 2.0 \times 10^{-22}$$

The Carbon Dioxide Carbonic Acid System

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

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

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.5 \times 10^{-4}$$

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

$$K_2 = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

The first reaction describes the hydration of aqueous CO_2 to form carbonic acid. Note that the magnitude of Khyd 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 1st and 2nd Equations gives:

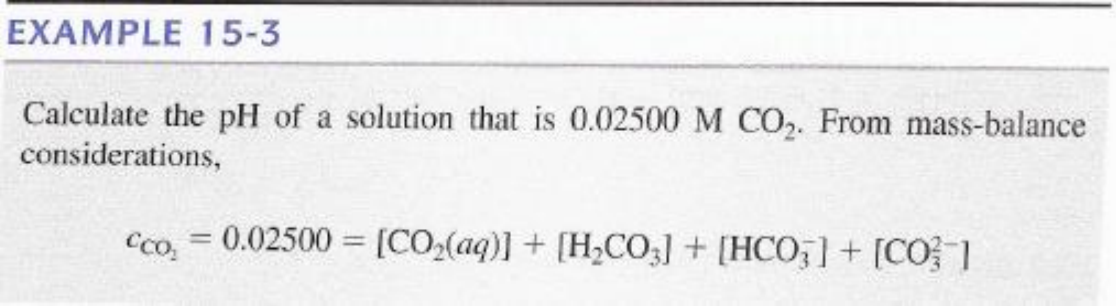
$$CO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[CO_2(aq)]}$$

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

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

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

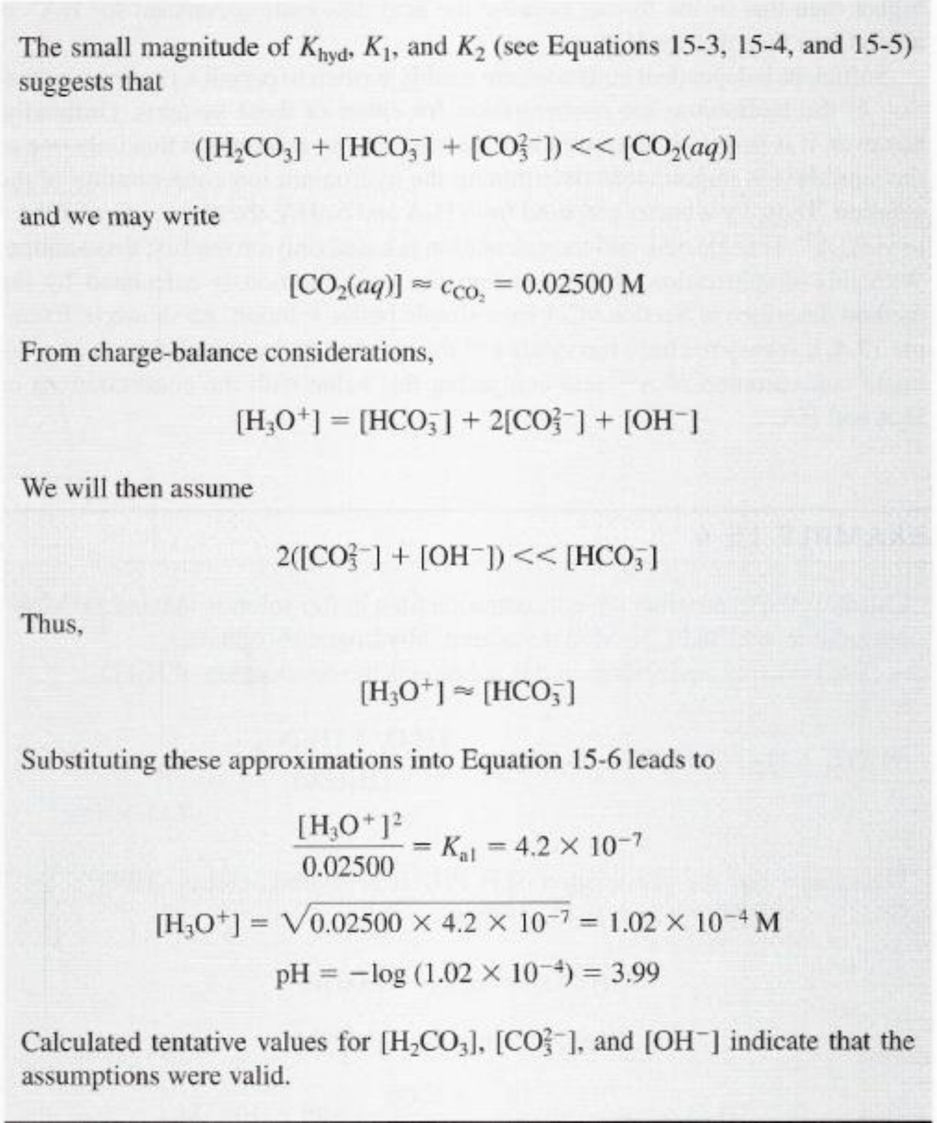
Catalyst



EXAMPLE 15-3

Calculate the pH of a solution that is 0.02500 M CO_2. From mass-balance considerations,

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



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

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

and we may write

$$[CO_2(aq)] \approx c_{CO_2} = 0.02500 \text{ M}$$

From charge-balance considerations,

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

We will then assume

$$2([CO_3^{2-}] + [OH^-]) << [HCO_3^-]$$

Thus,

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

Substituting these approximations into Equation 15-6 leads to

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

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

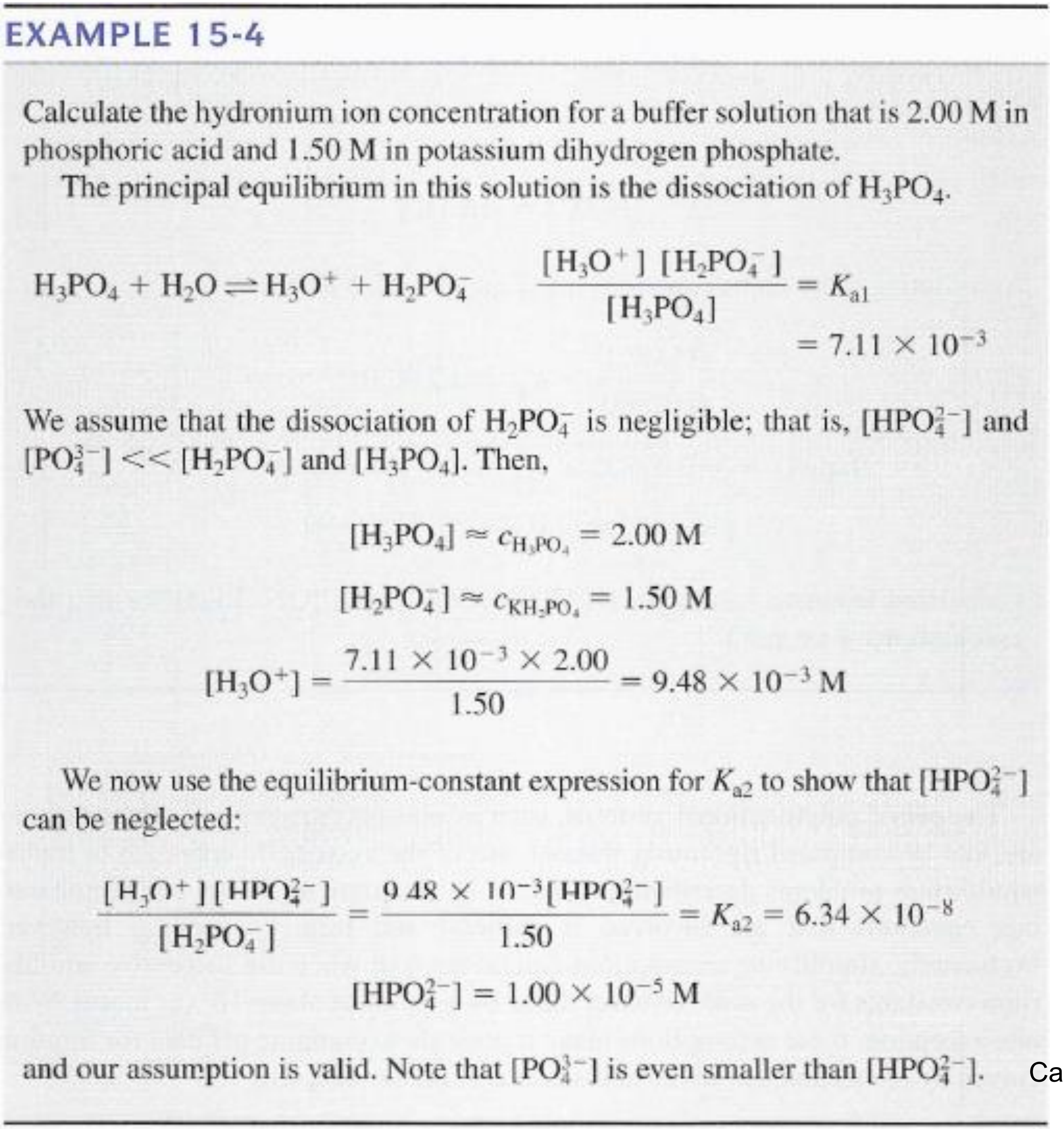
$$\text{pH} = -\log(1.02 \times 10^{-4}) = 3.99$$

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

Catalyst

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 latter system is higher than that of the former because the acid dissociation constant for HA^- is always less than that for H_2A.
- only one of the equilibria is important in determining the hydronium ion concentration of the solution.
- the dissociation of HA^- to yield A^{2-} is neglected.



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.

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

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

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,

$$[H_3PO_4] \approx c_{H_3PO_4} = 2.00\ \text{M}$$

$$[H_2PO_4^-] \approx c_{KH_2PO_4} = 1.50\ \text{M}$$

$$[H_3O^+] = \frac{7.11 \times 10^{-3} \times 2.00}{1.50} = 9.48 \times 10^{-3}\ \text{M}$$

We now use the equilibrium-constant expression for K_{a2} to show that $[HPO_4^{2-}]$ can be neglected:

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

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

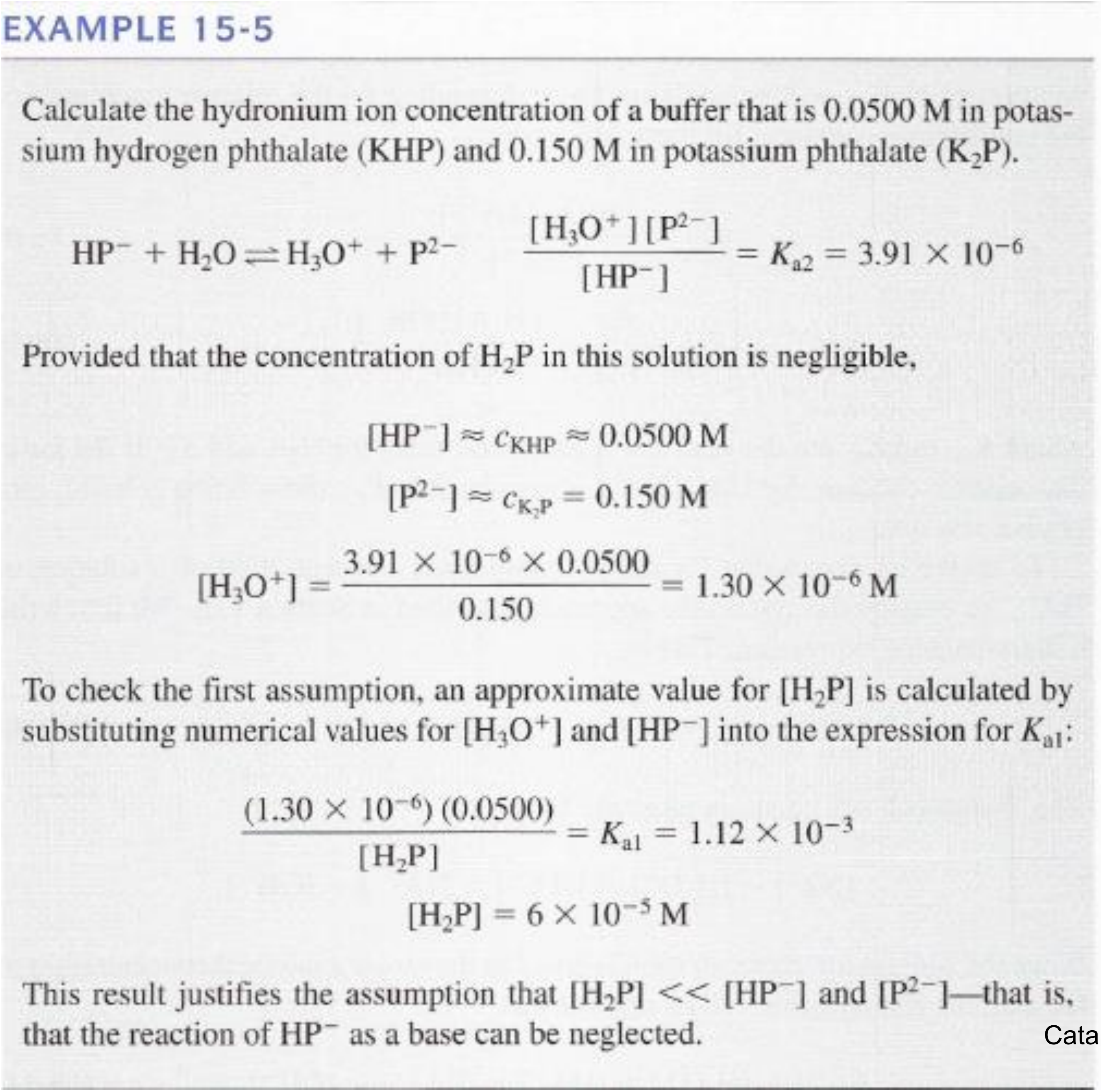
and our assumption is valid. Note that $[PO_4^{3-}]$ is even smaller than $[HPO_4^{2-}]$.

Catalyst

- For a buffer prepared from NaHA and Na_2A, the second dissociation will ordinarily predominate, and the equilibrium

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

is disregarded. The concentration of H_2A is negligible compared with that of HA^- or A^{2-}. The hydronium ion concentration can be calculated from the second dissociation constant, again employing 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-}.



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).

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

Provided that the concentration of H_2P in this solution is negligible,

$$[HP^-] \approx c_{KHP} \approx 0.0500\text{ M}$$

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

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

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

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

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

This result justifies the assumption that $[H_2P] << [HP^-]$ and $[P^{2-}]$—that is, that the reaction of HP^- as a base can be neglected.

Catalyst

CALCULATION OF THE pH OF SOLUTIONS OF **NaHA**

- Salts that have both acidic and basic properties (salts that are *amphiprotic).*
  - Salts are formed during neutralization titration of polyfunctional acids and bases
- 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:

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \longrightarrow K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \quad ①$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^- \longrightarrow K_{b2} = \frac{K_w}{K_{a1}} = \frac{[H_2A][OH^-]}{[HA^-]} \quad ②$$

Catalyst

- mass-balance expression.

$$c_{\mathrm{NaHA}} = [\mathrm{HA}^-] + [\mathrm{H_2A}] + [\mathrm{A}^{2-}] \qquad 3$$

- charge-balance equation

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

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

$$c_{\mathrm{NaHA}} + [\mathrm{H_3O}^+] = [\mathrm{HA}^-] + 2[\mathrm{A}^{2-}] + [\mathrm{OH}^-] \qquad 4$$

- We now have four algebraic equations (Equations 3 and 4 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:

$$K_w = [\mathrm{H_3O}^+][\mathrm{OH}^-]$$

- We first subtract the mass-balance equation from the charge-balance equation.

$$\begin{aligned} c_{\mathrm{NaHA}} + [\mathrm{H_3O}^+] &= [\mathrm{HA}^-] + 2[\mathrm{A}^{2-}] + [\mathrm{OH}^-] \\ c_{\mathrm{NaHA}} &= [\mathrm{H_2A}] + [\mathrm{HA}^-] + [\mathrm{A}^{2-}] \\ [\mathrm{H_3O}^+] &= [\mathrm{A}^{2-}] + [\mathrm{OH}^-] - [\mathrm{H_2A}] \end{aligned}$$

- We then rearrange the acid-dissociation constant expressions for H2A to obtain $[H_2A] = \frac{[H_3O^+][HA^-]}{K_{a1}}$ and for $HA^-$to give $[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]}$
- Substituting these expressions and the expression for *Kw* 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 $[H_30^+J$ gives

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

- We collect terms to obtain

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

- Finally, this equation rearranges to

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

5

- Under most circumstances, we can make the approximation that

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

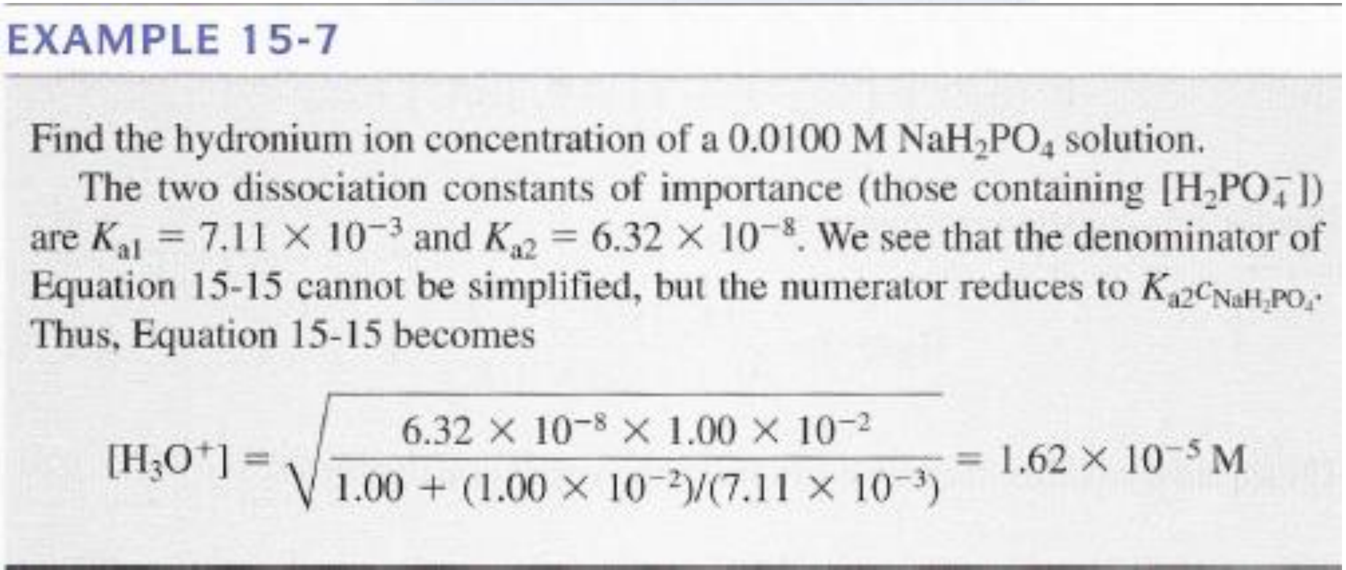
- Introduction of this relationship into Equation 5 gives

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

6

- The approximation shown as Equation 3 requires that [HA $^-$] be much larger than any of the other equilibrium concentrations in Equations 3 and 4 . This assumption is not valid for very dilute solutions of NaHA or when 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 6, and $K_{a2}C_{NaHA}$ is considerably greater than K_w in the numerator. With these assumptions, the equation simplifies to

$$[H_3O^+] \approx \sqrt{K_{a1}K_{a2}}$$



EXAMPLE 15-7

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

The two dissociation constants of importance (those containing $[H_2PO_4^-]$) are $K_{a1} = 7.11 \times 10^{-3}$ and $K_{a2} = 6.32 \times 10^{-8}$. We see 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

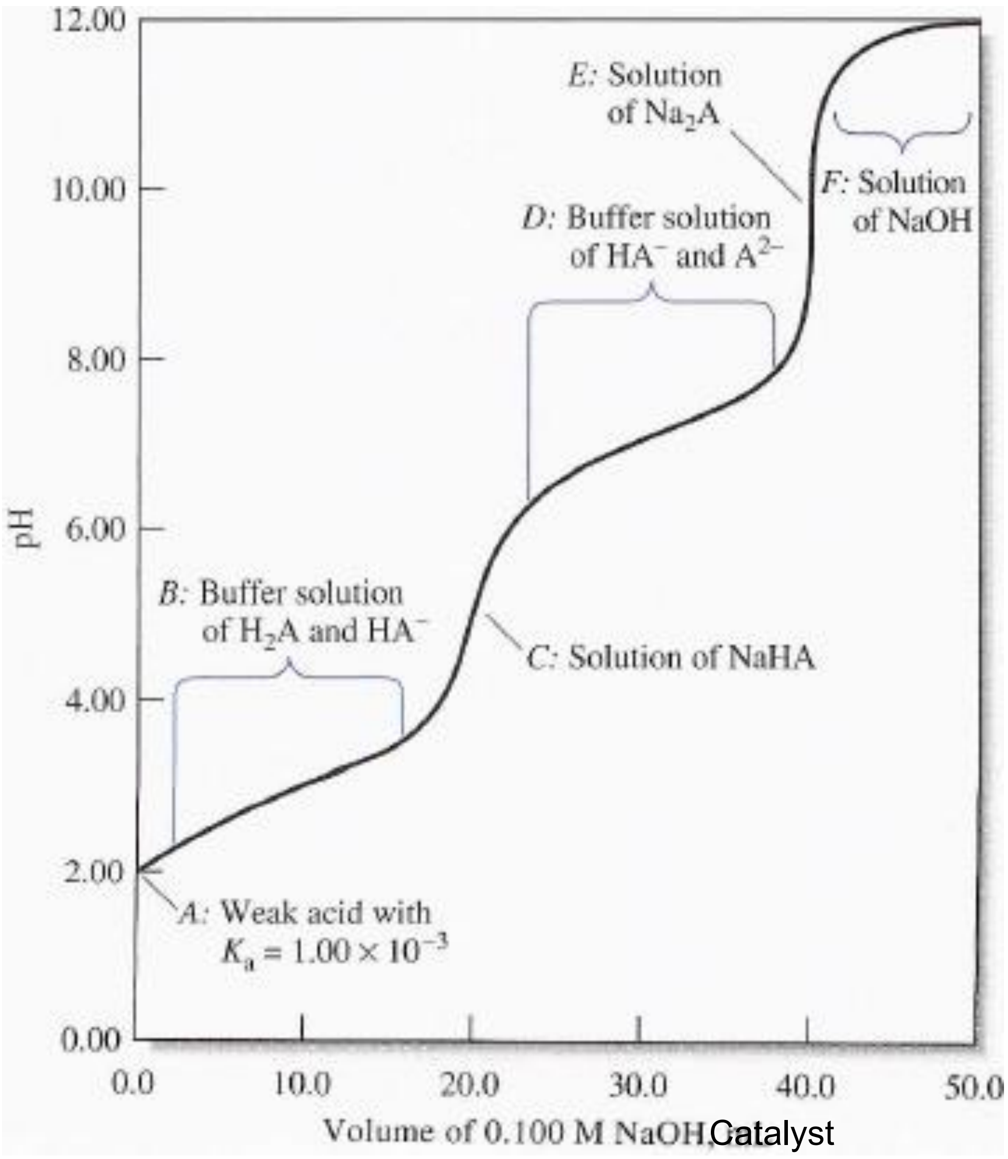
$$[H_3O^+] = \sqrt{\frac{6.32 \times 10^{-8} \times 1.00 \times 10^{-2}}{1.00 + (1.00 \times 10^{-2})/(7.11 \times 10^{-3})}} = 1.62 \times 10^{-5}\ M$$

Catalyst

TITRATION CURVES FOR POLYFUNCTIONAL ACIDS

- Compounds with two or more acid functional groups yield multiple end points in a titration provided that the functional groups differ sufficiently in strength as acids.

- **Figure 15-2** Titration of 20.00 mL of 0.1000 M H_2A with 0.1000 M NaOH.
  - For H_2A, $K_{a1} = 1.00 \text{ X } 10^{-3}$ and $Ka2 = 1.00 \text{ X } 10^{-7}$. The method of pH calculation is shown for several points and regions on the titration curve.



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.

Symbolizing the acid as H_2M, 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 proceed as just described.

Initial pH

Only the first dissociation makes an appreciable contribution to $[H_3O^+]$; thus,

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

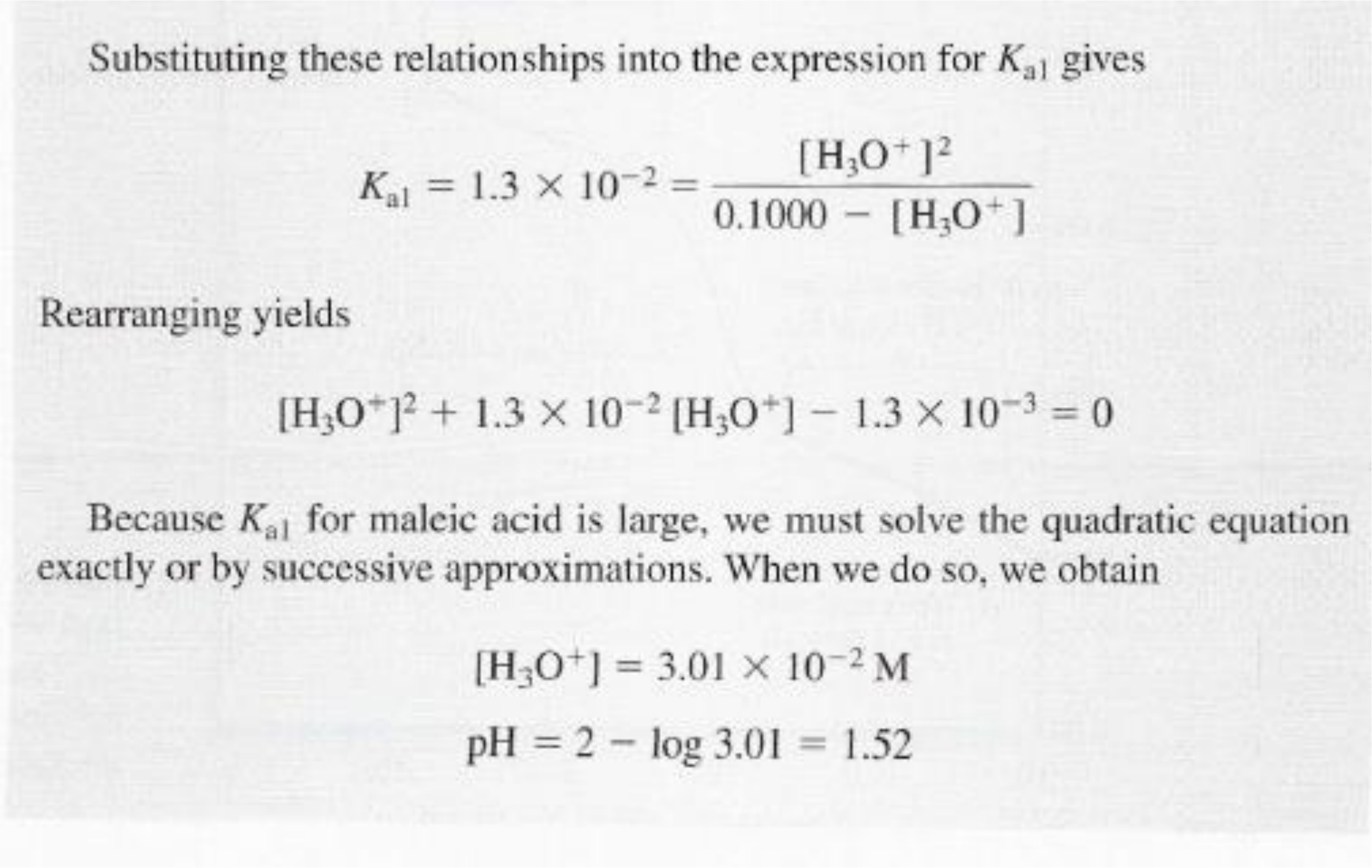
Mass balance requires that

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

or

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

Catalyst



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

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

Rearranging yields

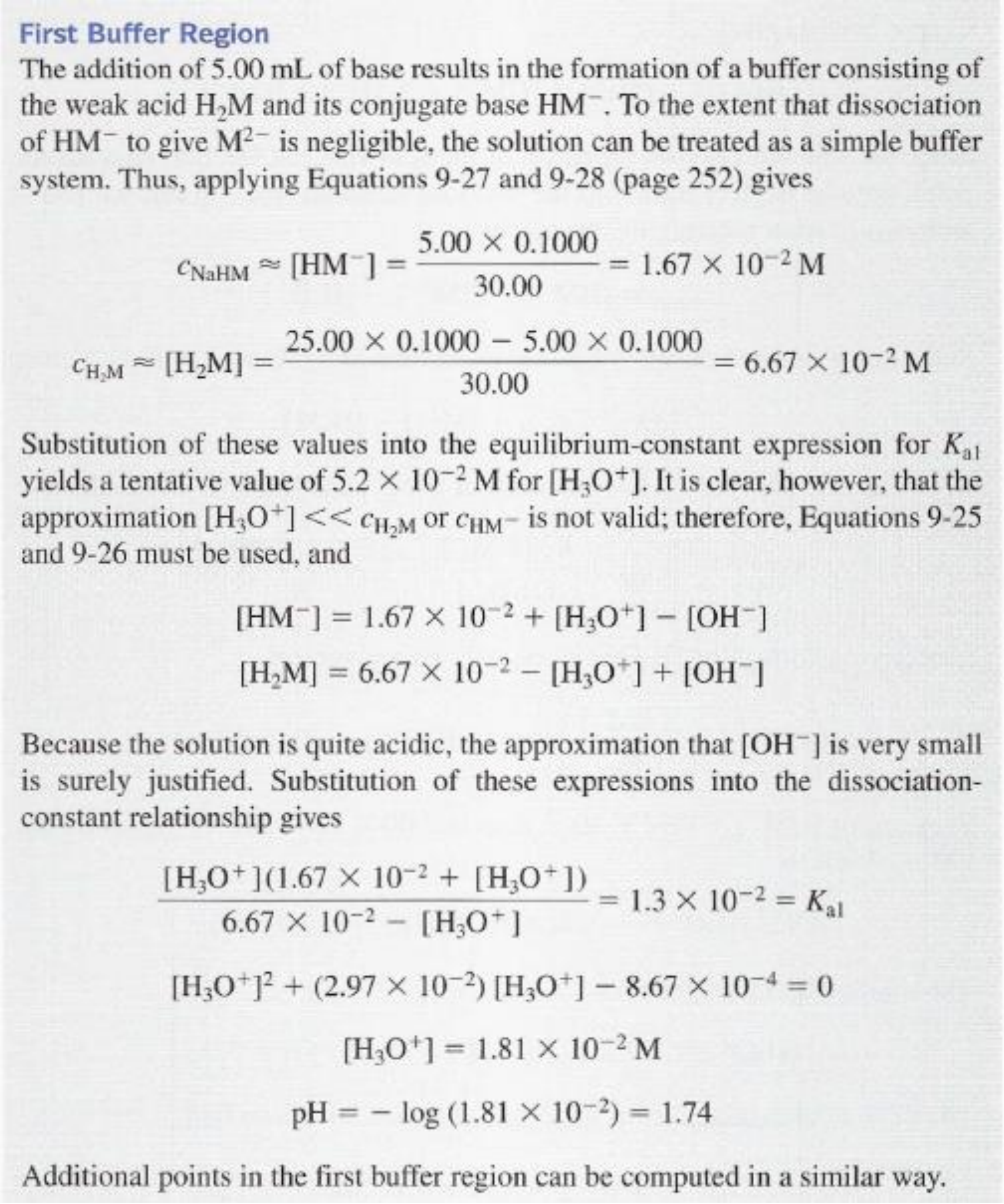
$$[H_3O^+]^2 + 1.3 \times 10^{-2}[H_3O^+] - 1.3 \times 10^{-3} = 0$$

Because K_{a1} for maleic acid is large, we must solve the quadratic equation exactly or by successive approximations. When we do so, we obtain

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

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

Catalyst



First Buffer Region

The addition of 5.00 mL of base 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 252) gives

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

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

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

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

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

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

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

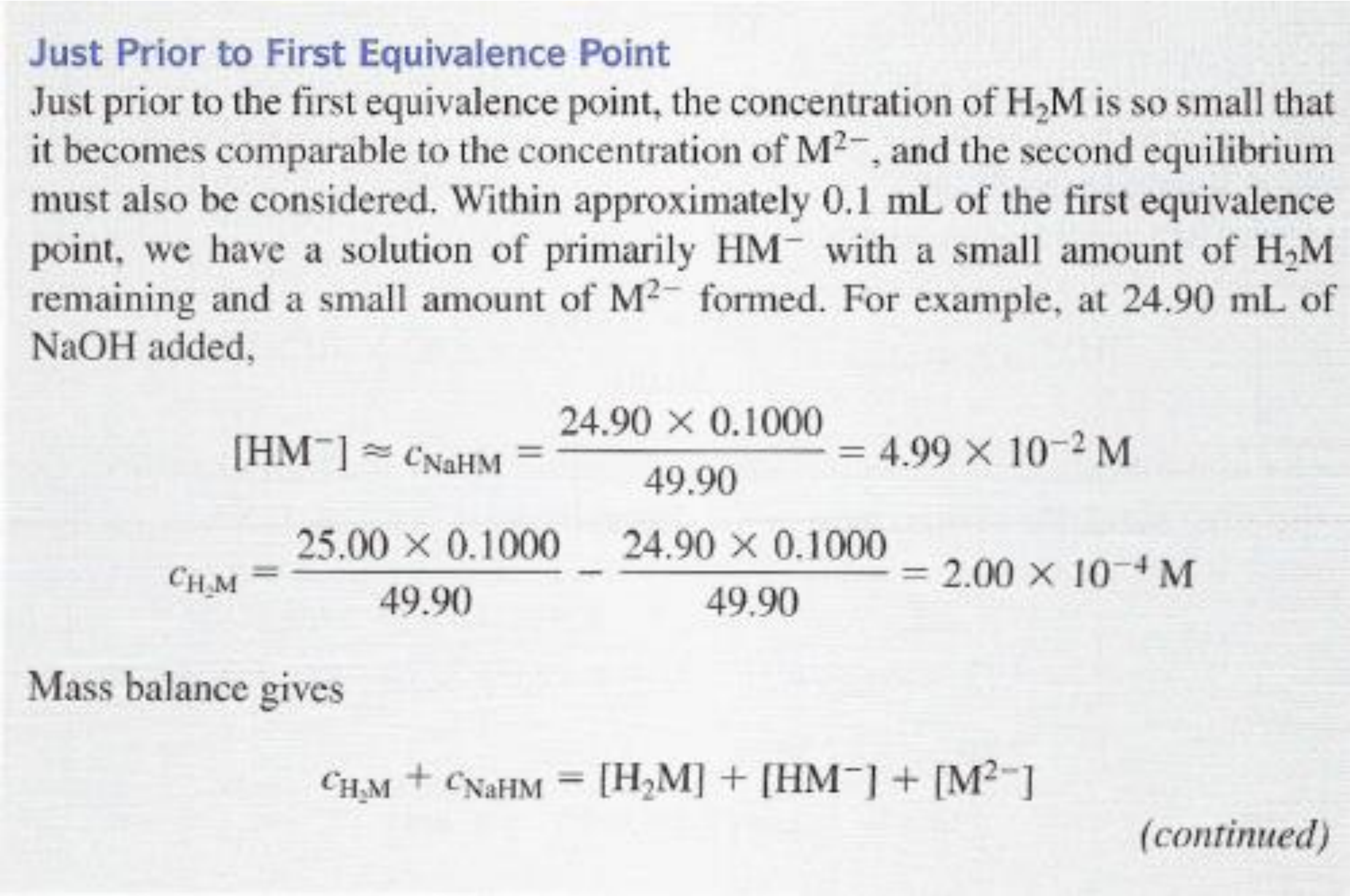
$$[\mathrm{H_3O^+}]^2 + (2.97 \times 10^{-2})\,[\mathrm{H_3O^+}] - 8.67 \times 10^{-4} = 0$$

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

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

Additional points in the first buffer region can be computed in a similar way.

Catalyst



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,

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

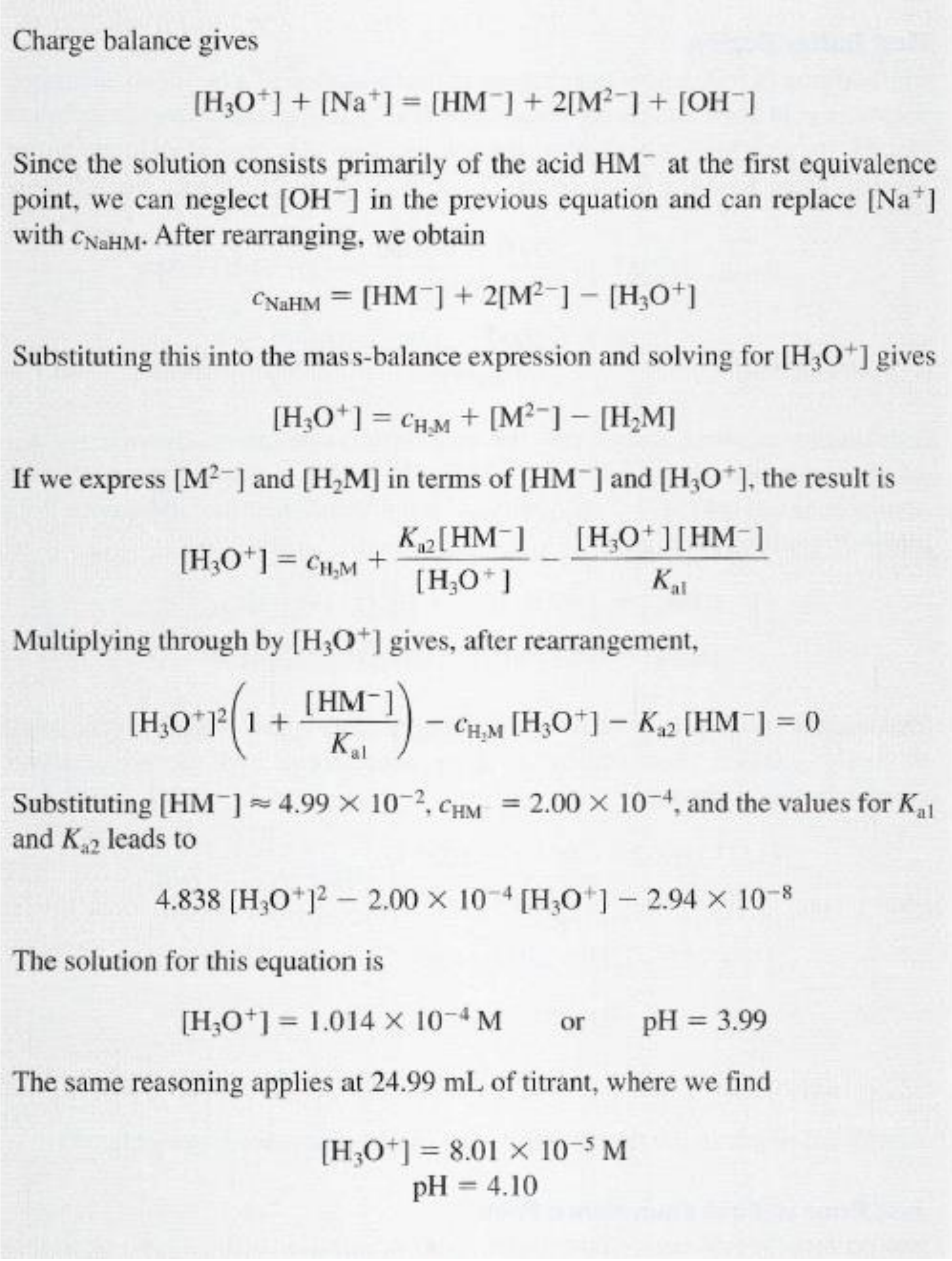
$$c_{\mathrm{H_2M}} = \frac{25.00 \times 0.1000}{49.90} - \frac{24.90 \times 0.1000}{49.90} = 2.00 \times 10^{-4}\ \mathrm{M}$$

Mass balance gives

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

(continued)

Catalyst



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 neglect $[OH^-]$ in the previous equation and can replace $[Na^+]$ with c_{NaHM}. After rearranging, we obtain

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

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

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

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

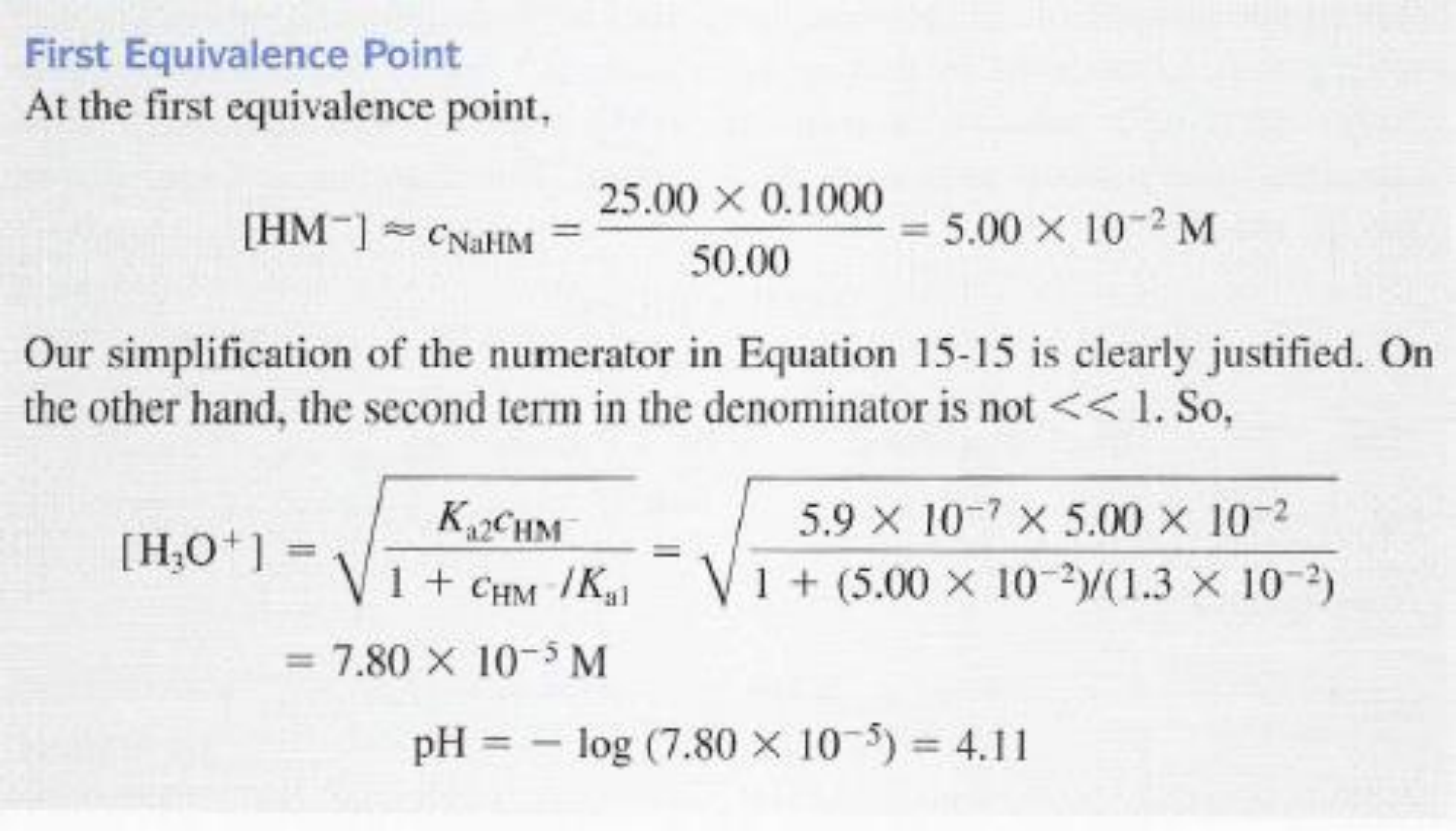
$$4.838\,[H_3O^+]^2 - 2.00 \times 10^{-4}\,[H_3O^+] - 2.94 \times 10^{-8}$$

The solution for this equation is

$$[H_3O^+] = 1.014 \times 10^{-4}\ \text{M} \qquad \text{or} \qquad \text{pH} = 3.99$$

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

$$[H_3O^+] = 8.01 \times 10^{-5}\ \text{M}$$
$$\text{pH} = 4.10$$



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 clearly justified. On the other hand, the second term in the denominator is not << 1. So,

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

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

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

Catalyst

Just after the First Equivalence Point

Until the second equivalence point, we can obtain the analytical concentration of HM^- and M^{2-} from the titration stoichiometry. At 25.01 mL, the values are calculated as

$$c_{HM^-} = \frac{\text{mmol NaHM formed} - (\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}}$$

$$= \frac{25.00 \times 0.1000 - (25.01 - 25.00) \times 0.100}{50.01} = 0.04997$$

$$c_{M^{2-}} = \frac{(\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}} = 1.996 \times 10^{-5}$$

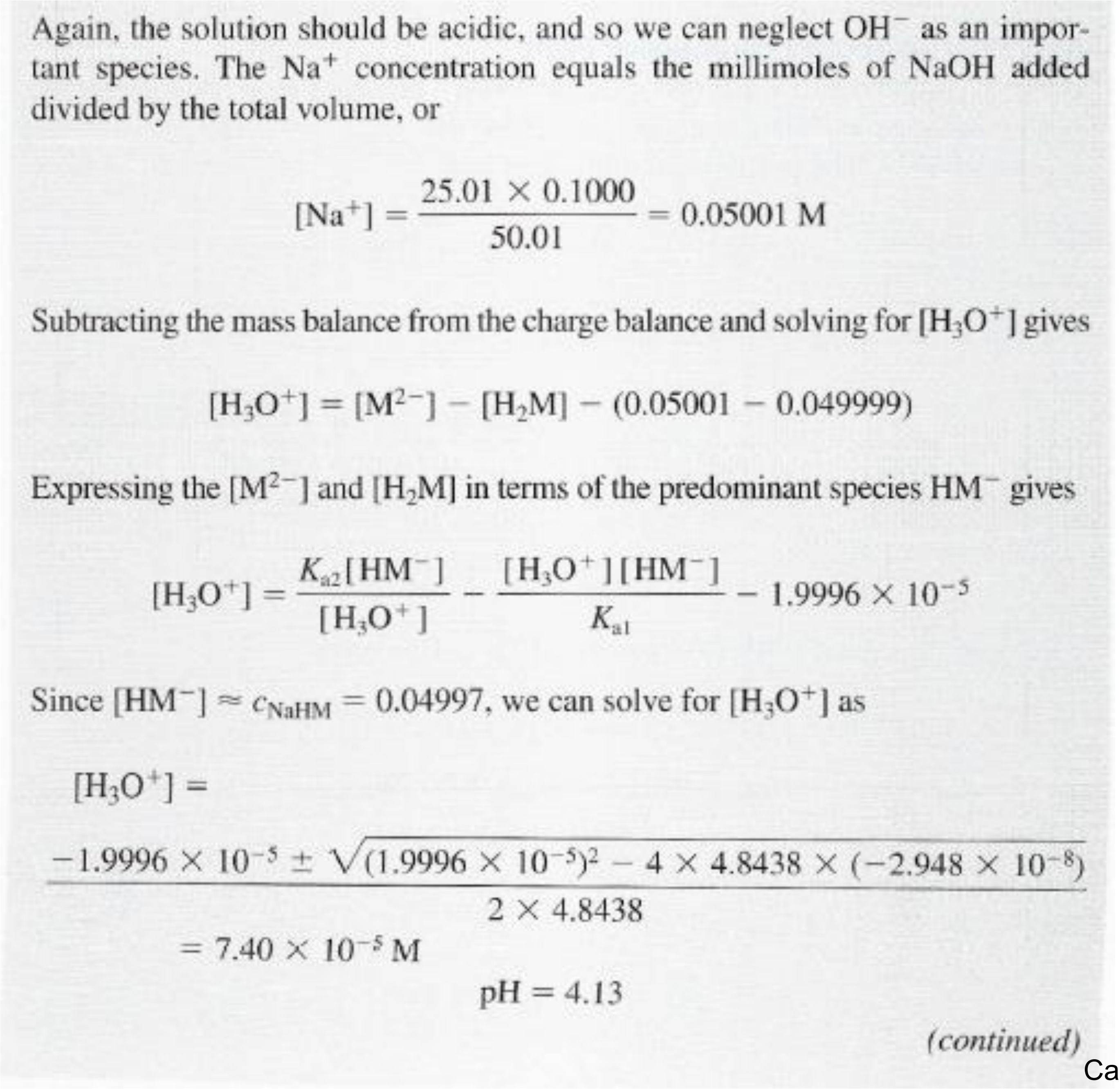
In the region of a few tenths of a milliliter beyond the first equivalence point, the solution is primarily HM^- with some M^{2-} formed as a result of the titration. So, the mass balance is

$$c_{Na_2M} + c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}] = 0.04997 + 1.996 \times 10^{-5}$$
$$= 0.049999$$

and the charge balance is

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

Catalyst



Again, the solution should be acidic, and so we can neglect OH^- as an important species. The Na^+ concentration equals the 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

$$[H_3O^+] = [M^{2-}] - [H_2M] - (0.05001 - 0.049999)$$

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

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

Since $[HM^-] \approx c_{NaHM} = 0.04997$, we can solve for $[H_3O^+]$ as

$$[H_3O^+] =$$

$$\frac{-1.9996 \times 10^{-5} \pm \sqrt{(1.9996 \times 10^{-5})^2 - 4 \times 4.8438 \times (-2.948 \times 10^{-8})}}{2 \times 4.8438}$$

$$= 7.40 \times 10^{-5}\ M$$

$$pH = 4.13$$

(continued)

Catalyst

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 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 is readily obtained from K_{a2}. When we introduce 25.50 mL of NaOH, for example,

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

and the molar concentration of NaHM is

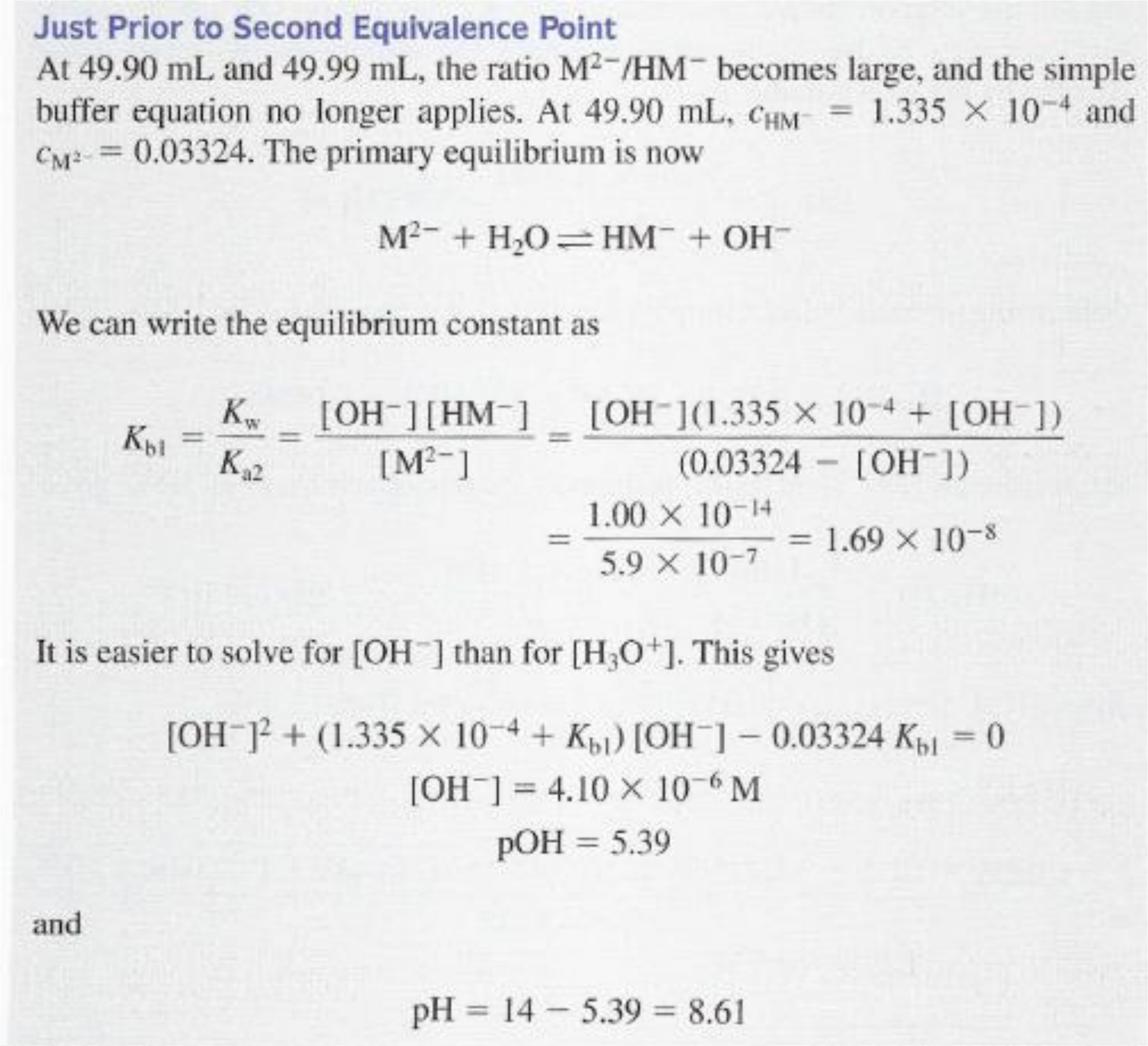
$$[HM^-] \approx c_{NaHM} \approx \frac{(25.00 \times 0.1000) - (25.50 - 25.00)(0.1000)}{50.50} = \frac{2.45}{50.50}\,M$$

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

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

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

The assumption that $[H_3O^+]$ is small relative to c_{HM^-} and $c_{M^{2-}}$ is valid, and pH = 4.54.



Just Prior to Second Equivalence Point

At 49.90 mL and 49.99 mL, the ratio M^{2-}/HM^- becomes large, and the simple buffer equation no longer applies. At 49.90 mL, $c_{HM^-} = 1.335 \times 10^{-4}$ and $c_{M^{2-}} = 0.03324$. The primary equilibrium is now

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

We can write the equilibrium constant as

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

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

It is easier to solve for $[OH^-]$ than for $[H_3O^+]$. This gives

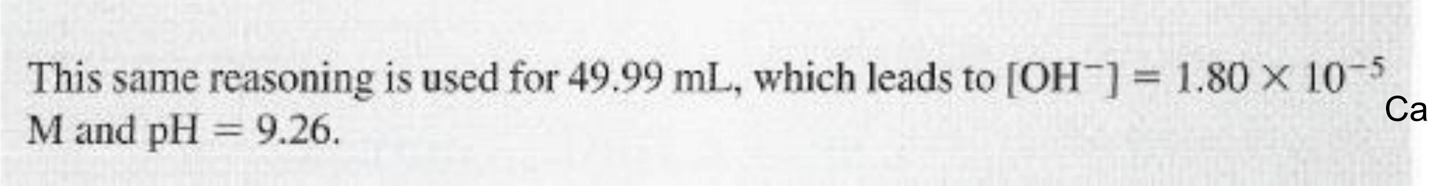
$$[OH^-]^2 + (1.335 \times 10^{-4} + K_{b1})\,[OH^-] - 0.03324\,K_{b1} = 0$$

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

$$\text{pOH} = 5.39$$

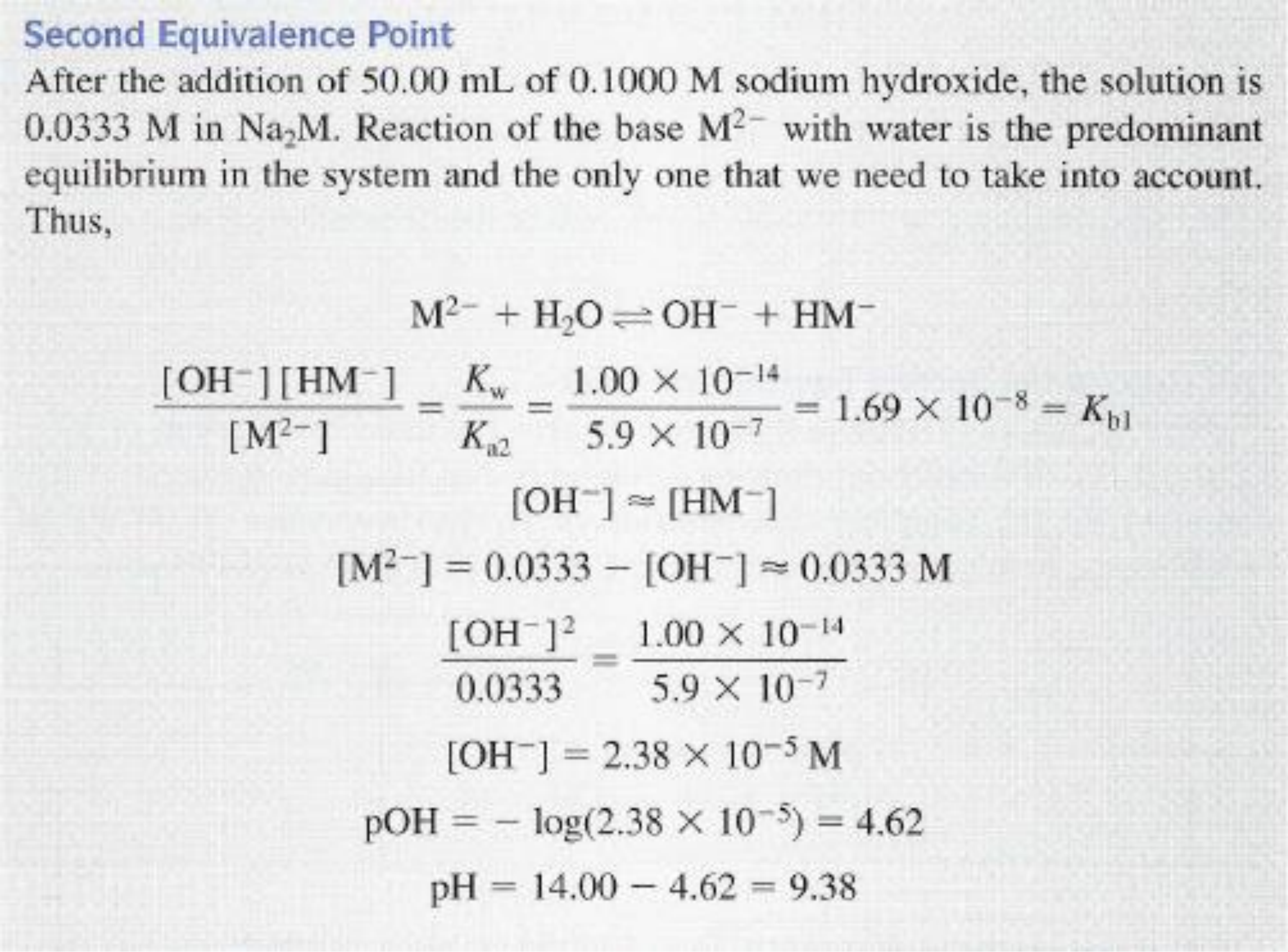
and

$$\text{pH} = 14 - 5.39 = 8.61$$



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

Catalyst



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. 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,

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

$$\frac{[OH^-][HM^-]}{[M^{2-}]} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{5.9 \times 10^{-7}} = 1.69 \times 10^{-8} = K_{b1}$$

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

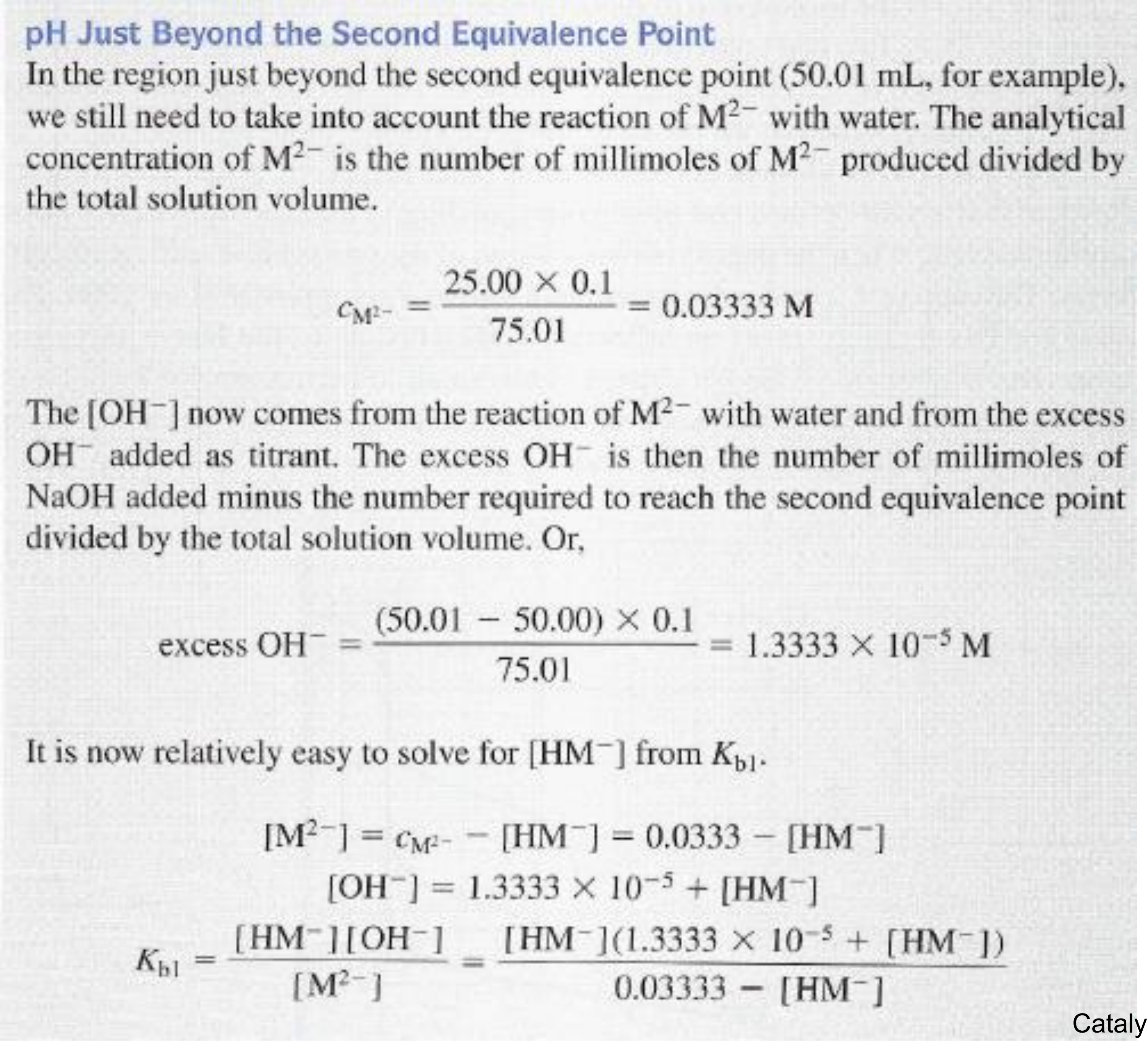
$$[M^{2-}] = 0.0333 - [OH^-] \approx 0.0333 \text{ M}$$

$$\frac{[OH^-]^2}{0.0333} = \frac{1.00 \times 10^{-14}}{5.9 \times 10^{-7}}$$

$$[OH^-] = 2.38 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(2.38 \times 10^{-5}) = 4.62$$

$$\text{pH} = 14.00 - 4.62 = 9.38$$



pH Just Beyond the 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. The analytical concentration of M^{2-} is the number of millimoles of M^{2-} produced divided by the total solution volume.

$$c_{M^{2-}} = \frac{25.00 \times 0.1}{75.01} = 0.03333\ M$$

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

$$\text{excess } OH^- = \frac{(50.01 - 50.00) \times 0.1}{75.01} = 1.3333 \times 10^{-5}\ M$$

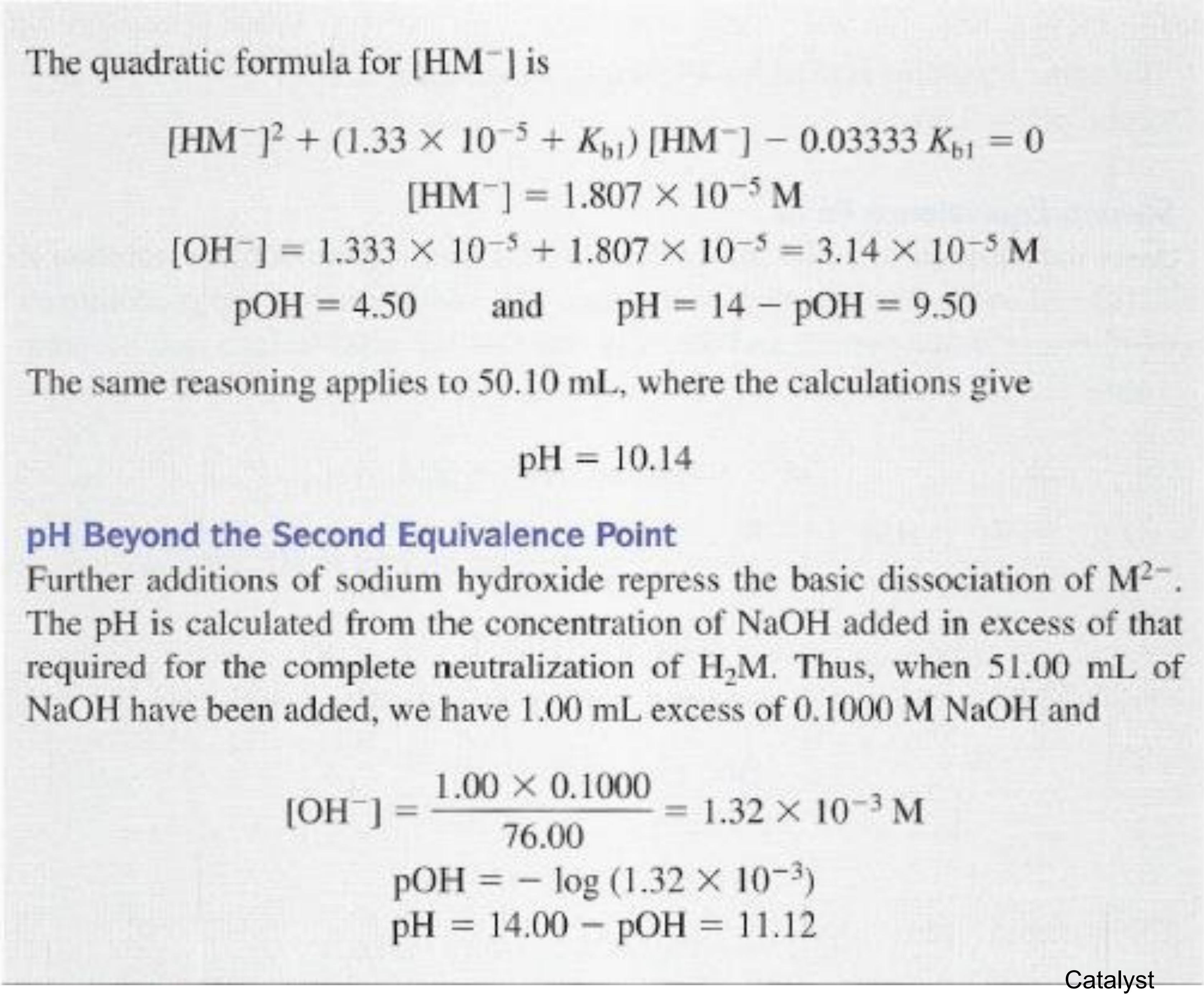
It is now relatively easy to solve for $[HM^-]$ from K_{b1}.

$$[M^{2-}] = c_{M^{2-}} - [HM^-] = 0.0333 - [HM^-]$$

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

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

Catalyst



The quadratic formula for $[HM^-]$ is

$$[HM^-]^2 + (1.33 \times 10^{-5} + K_{b1})\,[HM^-] - 0.03333\,K_{b1} = 0$$

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

$$[OH^-] = 1.333 \times 10^{-5} + 1.807 \times 10^{-5} = 3.14 \times 10^{-5}\ M$$

$$pOH = 4.50 \qquad \text{and} \qquad pH = 14 - pOH = 9.50$$

The same reasoning applies to 50.10 mL, where the calculations give

$$pH = 10.14$$

pH Beyond the Second Equivalence Point

Further additions of sodium hydroxide repress the basic dissociation of M^{2-}. The pH is 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

$$[OH^-] = \frac{1.00 \times 0.1000}{76.00} = 1.32 \times 10^{-3}\ M$$

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

$$pH = 14.00 - pOH = 11.12$$

Catalyst

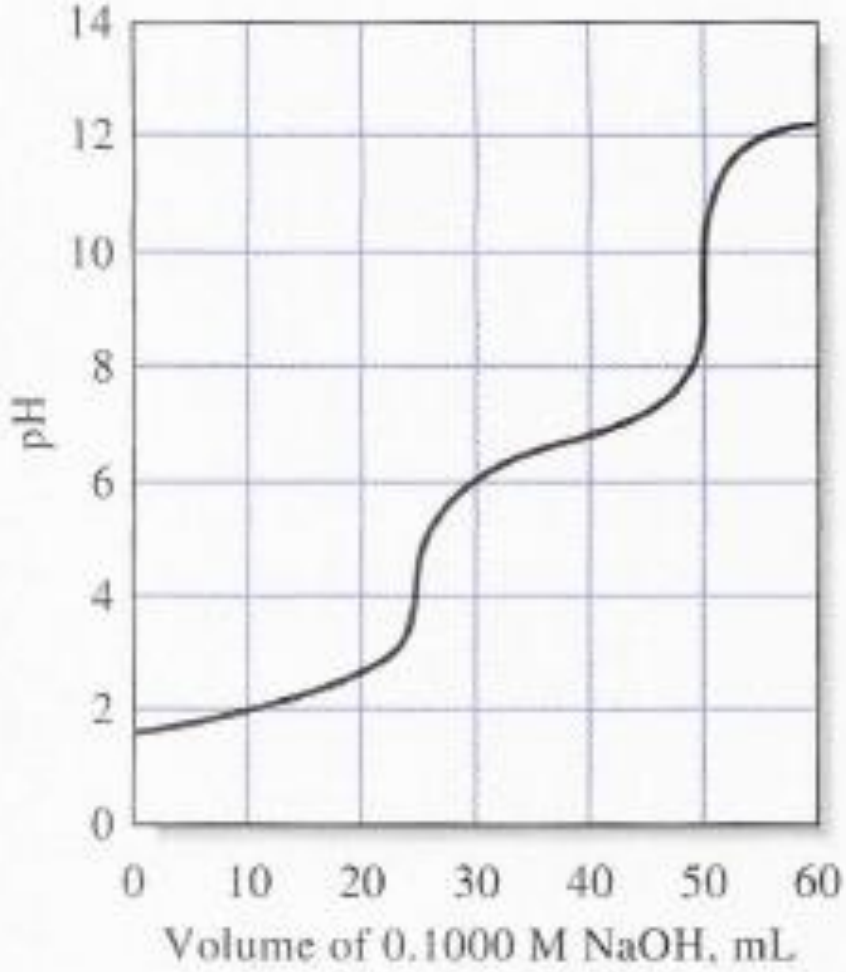


Figure 15-3 Titration curve for 25.00 mL of 0.1000 M maleic acid, H_2M, with 0.1000 M NaOH.

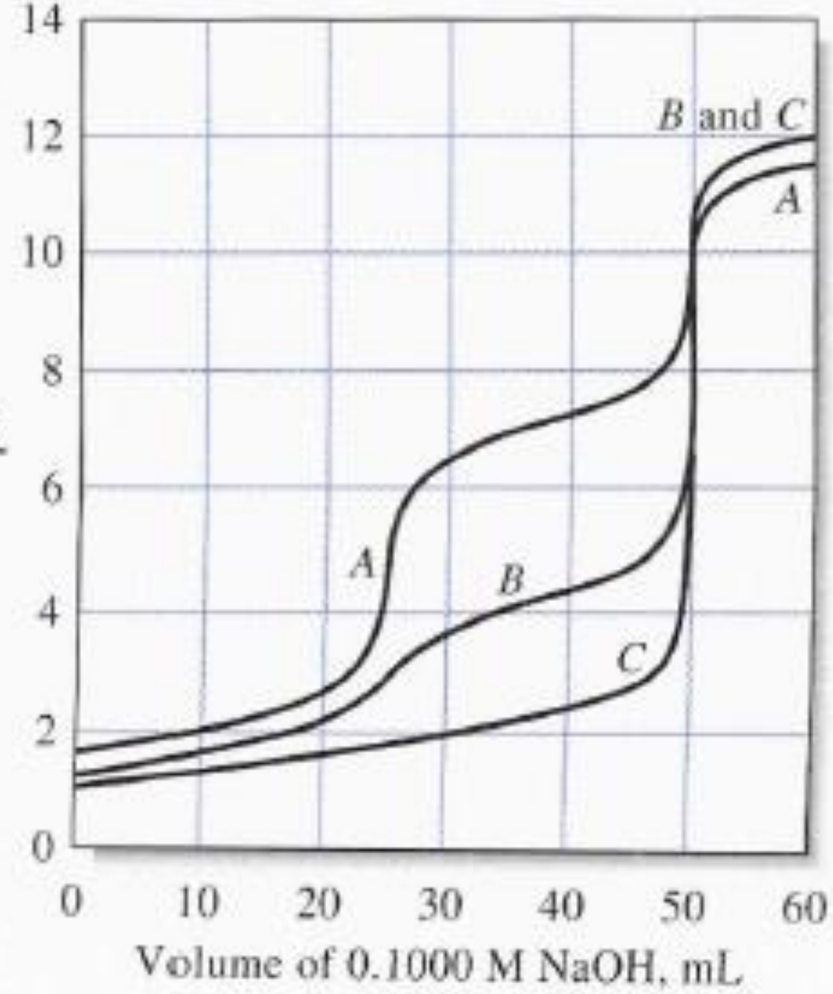
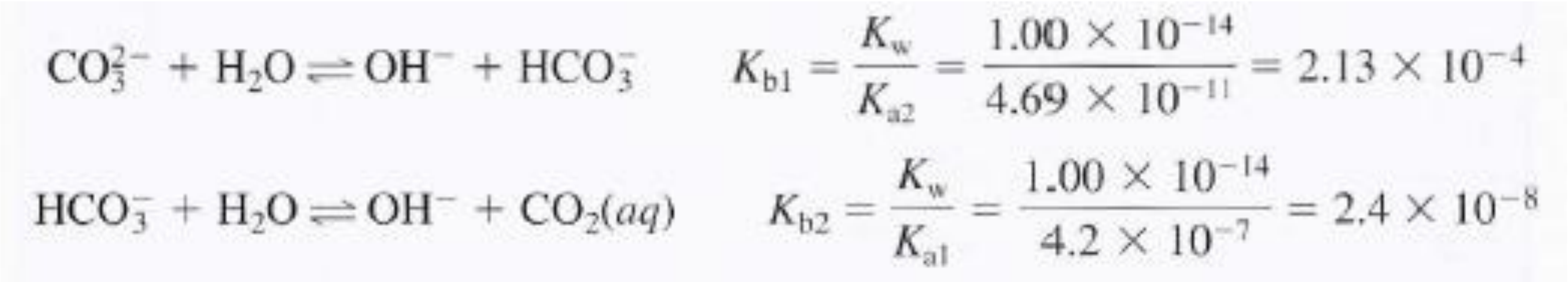


Figure 15-4 Curves for the titration of polyprotic acids. A 0.1000 M NaOH solution is used to titrate 25.00 mL of 0.1000 M H_3PO_4 (curve *A*), 0.1000 M oxalic acid (curve *B*), and 0.1000 M H_2SO_4 (curve *C*).

Catalyst

TITRATION CURVES FOR POLYFUNCTIONAl BASES



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

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

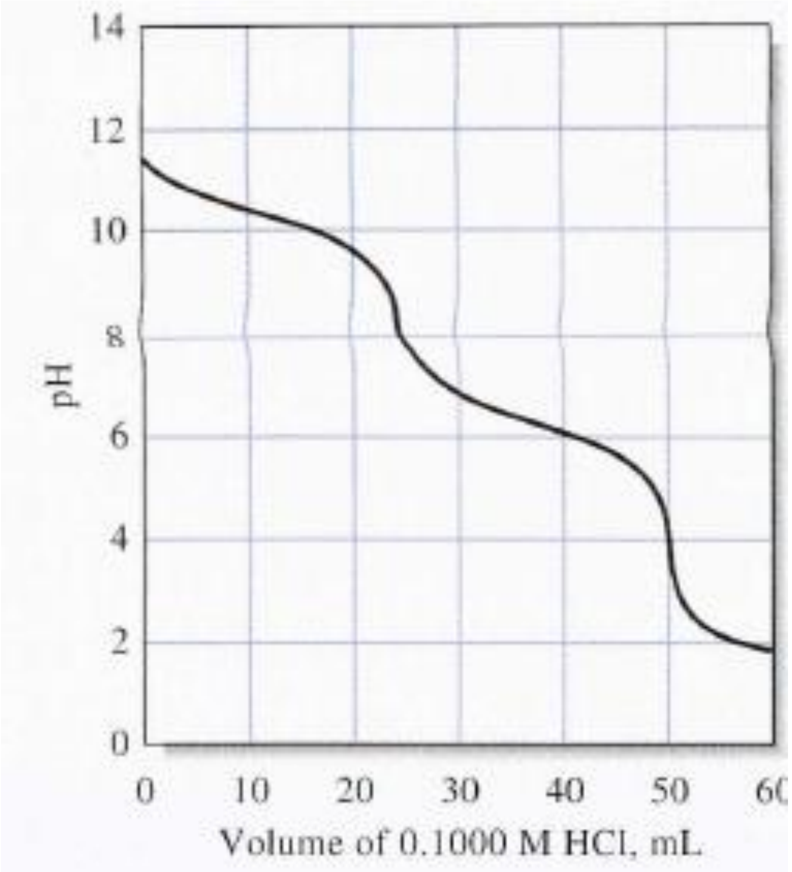
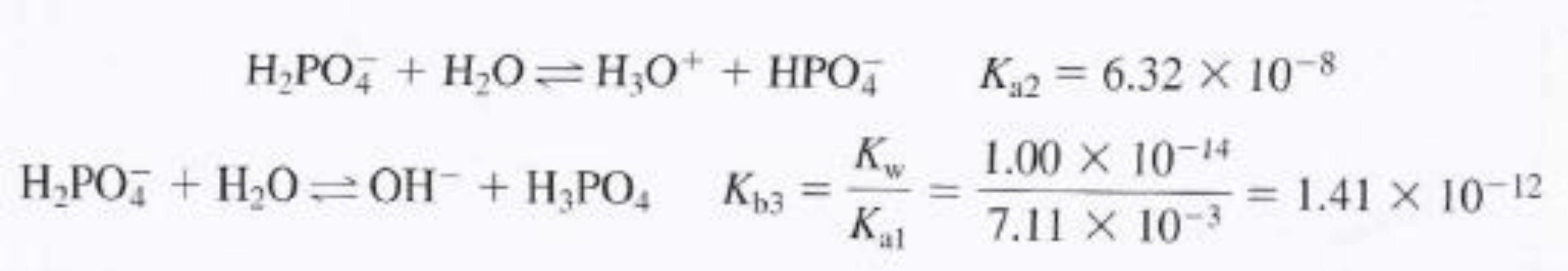


Figure 15-5 Curve for the titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl.

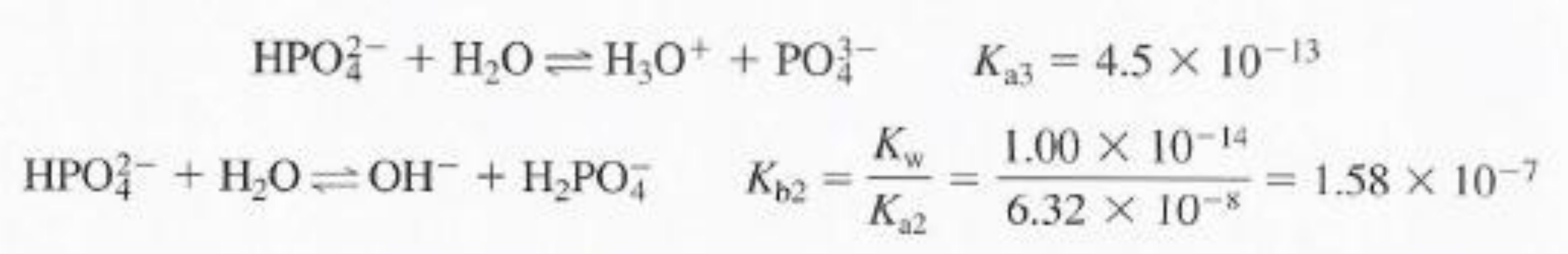
Catalyst

TITRATION CURVES FOR AMPHIPROTIC SPECIES



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

$$H_2PO_4^- + H_2O \rightleftharpoons OH^- + H_3PO_4 \qquad K_{b3} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$$



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

$$HPO_4^{2-} + H_2O \rightleftharpoons OH^- + H_2PO_4^- \qquad K_{b2} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{6.32 \times 10^{-8}} = 1.58 \times 10^{-7}$$

Chapter 17

Complexation Reactions and Titrations

Complex-formation reactions are widely used in analytical chemistry. One of the first uses of these reagents was for titrating cations. In addition, many complexes are colored or absorb ultraviolet radiation; the formation of these complexes is often the basis for spectrophotometric determinations. Some complexes are sparingly soluble and can be used in gravimetric analysis. Complexes are also widely used for extracting cations from one solvent to another and for dissolving insoluble precipitates. The most useful complex forming reagents are organic compounds that contain several electron donor groups that form multiple covalent bonds with metal ions.

Catalyst

FORMING COMPLEXES

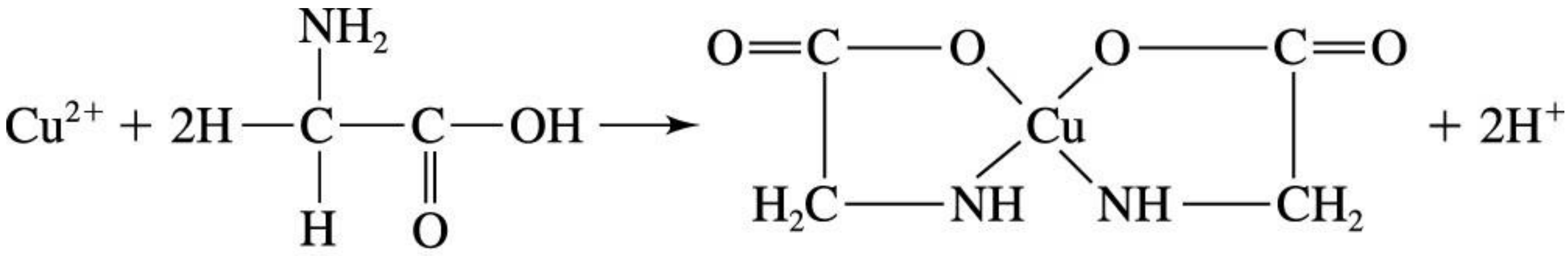
Most metal ions react with electron-pair donors to form coordination compounds or complexes.

The donor species, or ligand is an ion or a molecule that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons that are then shared by the two.

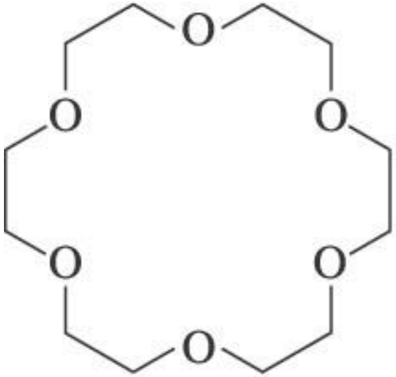
The number of covalent bonds that a cation tends to form with electron donors is its **coordination number**. Typical values for coordination numbers are two, four, and six. The species formed as a result of coordination can be electrically positive, neutral, or negative.

A ligand that has a single donor group, such as ammonia, is called **unidentate** (single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called **bidenate**. **Tridentate**, **tetradentate**, **pentadentate**, and **hexadentate** chelating agents are also known.

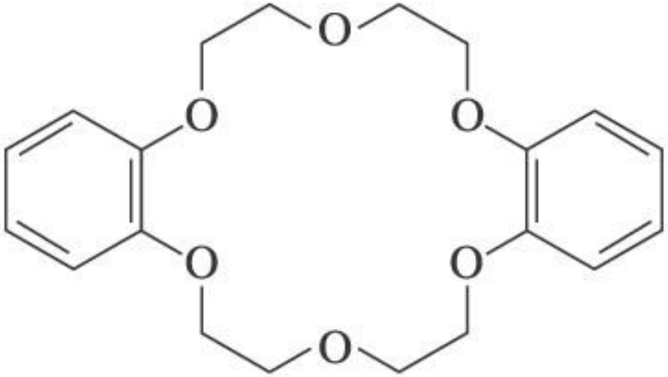
Another important type of complex, **a macrocycle**, is formed between a metal ion and a cyclic organic compound. The selectivity of a ligand for one metal ion over another relates to the stability of the complexes formed. The higher the formation constant of a metal-ligand complex, the better the selectivity of the ligand for the metal relative to similar complexes formed with other metals.



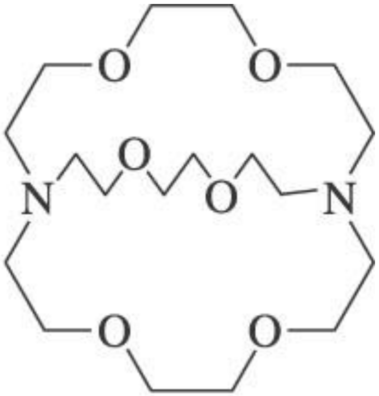
Glycine



18-crown-6



dibenzo-18-crown-6



cryptand 2,2,2

Catalyst

Producing Soluble Compelxes

Complexation reactions involve a metal ion M reacting with a ligand L to form a complex ML.

$$M + L \rightleftharpoons ML$$

Complexation reactions occur in a stepwise fashion, and the reaction above is often followed by additional reactions:

$$ML + L \rightleftharpoons ML_2$$

$$ML_2 + L \rightleftharpoons ML_3$$

$$ML_{n-1} + L \rightleftharpoons ML_n$$

Unidentate ligands invariably add in a series of steps. With multidentate ligands, the maximum coordination number of the cation may be satisfied with only one or a few added ligands.

The equilibrium constants for complex formation reactions are generally written as formation constants.

$M + 2L \rightleftharpoons ML_2$	$M + 3L \rightleftharpoons ML_3$	$M + nL \rightleftharpoons ML_n$
$\beta_2 = \frac{[ML_2]}{[M][L]} = K_1K_2$	$\beta_3 = \frac{[ML_3]}{[M][L]} = K_1K_2K_3$	$\beta_n = \frac{[ML_n]}{[M][L]} = K_1K_2....K_n$

The overall formation constants are products of the stepwise formation constants for the individual steps leading to the product.

Forming Insoluble Species

The addition of ligands to a metal ion may result in insoluble species, such as the familiar nickel-dimethylglyoxime precipitate.

In many cases, the intermediate uncharged complexes in the stepwise formation scheme may be sparingly soluble, whereas the addition of more ligand molecules may result in soluble species. AgCl is insoluble, but addition of large excess of Cl^- produces soluble $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$.

In contrast to complexation equilibria, which are most often treated as formation reactions, solubility equilibria are usually treated as dissociation reactions

$$M_xA_y(s) \rightleftharpoons xM^{y+}(aq) + yA^{x-}(aq) \qquad K_{sp} = [M^{y+}]^x[A^{x-}]^y$$

where, K_{sp} = solubility product. Hence, for BiI_3, the solubility product is written $K_{sp} = [Bi^{3+}][I^-]^3$.

The formation of soluble complexes can be used to control the concentration of free metal ions in solution and thus control their reactivity.

TITRATION WITH INORGANIC COMPLEXING AGENTS

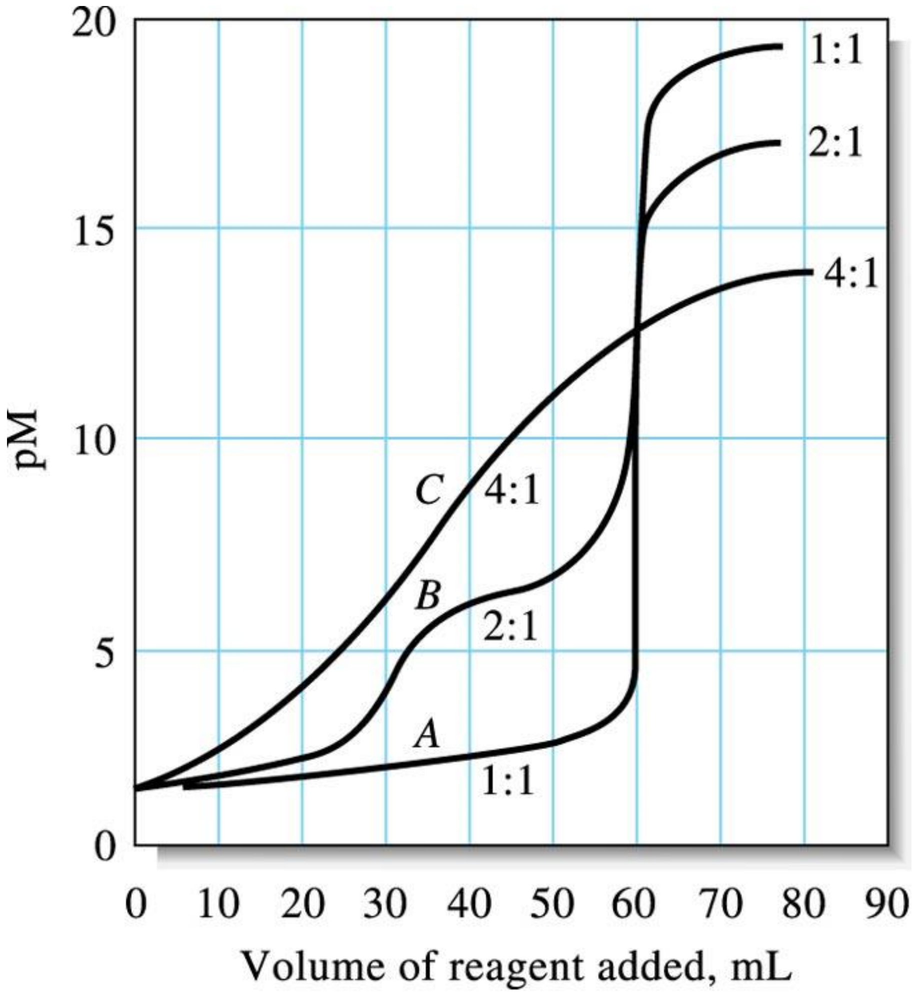
Complexation reactions have many uses in analytical chemistry, but their classical application is in complexometric titrations. Here, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or a suitable instrumental method. The formation of soluble inorganic complexes is not widely used for titration but the formation of precipitates is the basis for many important determinations.

Complexation Titrations

The progress of a complexometric titration is generally illustrated by a titration curve, which is usually a plot of pM= -log[M] as a function of the volume of titrant added.

Most often in complexometric titrations the ligand is the titrant and the metal ion the analyte, although occasionally the reverse is true.

Many precipitation titrations use the metal ion as the titrant. Most simple inorganic ligands are unidentate, which can lead to low complex stability and indistinct titration end points.



As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantages over their unidentate counterparts. **First**, they generally react more completely with cations and thus provide sharper end points. **Second**, they ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands usually involves two or more intermediate species.

Precipitation Titratons (Chapter 13)

Precipitation titrimetry, which is based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques. The slow rate of formation of most precipitates, however, limits the number of precipitating agents that can be used in titrations to a handful.

The most widely used and important precipitating reagent, silver nitrate, which is used for the determination of the halogens, the halogen-like anions. Titrations with silver nitrate are sometimes called **argentometric titrations**.

ORGANIC COMPLEXING AGENTS

(Chapter 17)

Many different organic complexing agents have become important in analytical chemistry because of their inherent sensitivity and potential selectivity in reacting with metal ions. Such reagents are particularly useful in precipitating metal and in extracting metal from one solvent to another. The most useful organic reagents form chelate complexes with metal ions.

Reagents for Precipitating Metals

One important type of reaction involving an organic complexing agent is that in which an insoluble, uncharged complex is formed. Usually, it is necessary to consider stepwise formation of soluble species in addition to the formation of the insoluble species. Thus, a metal ion M^{n+} reacts with a complexing agent X^- to form $MX^{(n-1)+}$, $MX_2^{(n-2)+}$, MX_{n-1}^{+}, and MX_n(soln).

$$M^{n+} + nX^- \rightleftharpoons MX_n(\text{soln})$$

$$\boxed{\beta_n = \frac{[MX_n]}{[M^{n+}][X^-]^n} = K_1K_2 \ldots K_n}$$

$$MX_n(\text{solid}) \rightleftharpoons MX_n(\text{soln}) \qquad \mathbf{K_{eq} = [MX_n]}$$

Solubility product expression is:

$$\mathbf{K_{sp} = [M^{n+}][X^-]^n = K_{eq} / \beta_n}$$

Forming Soluble Complexes for Extractions

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

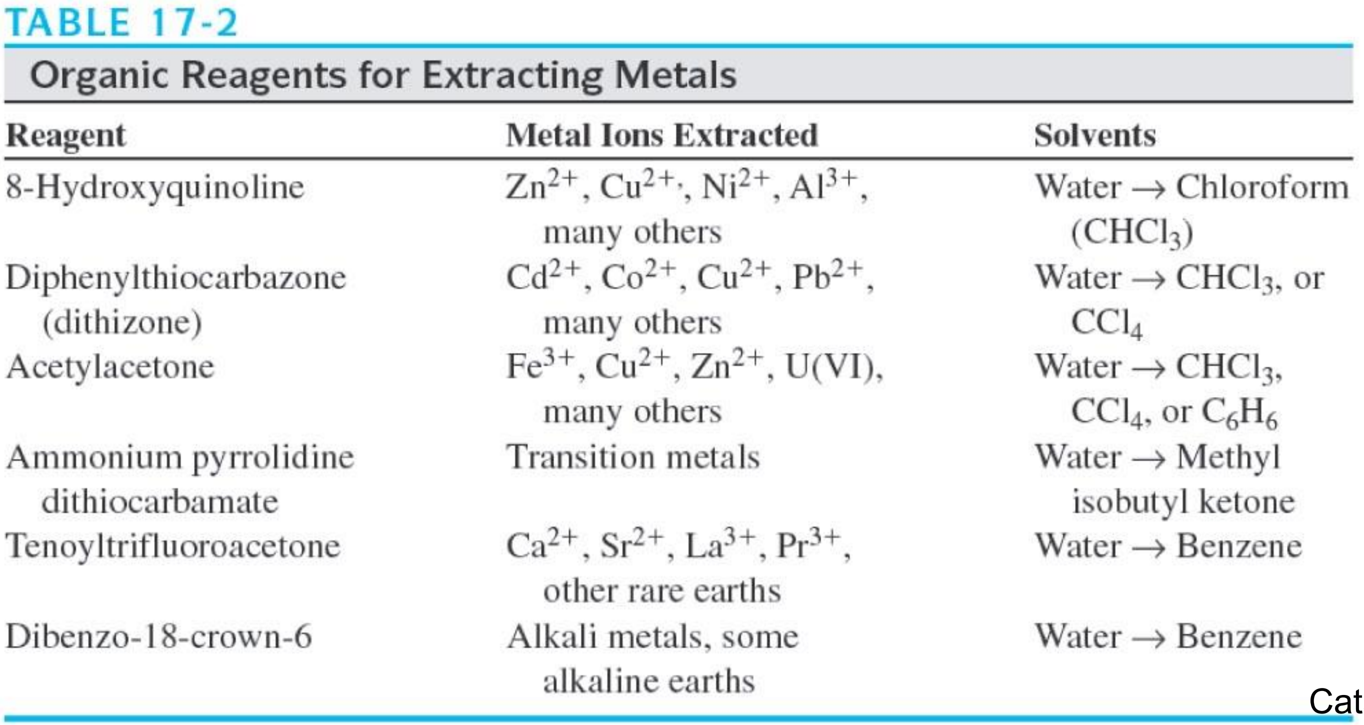


TABLE 17-2

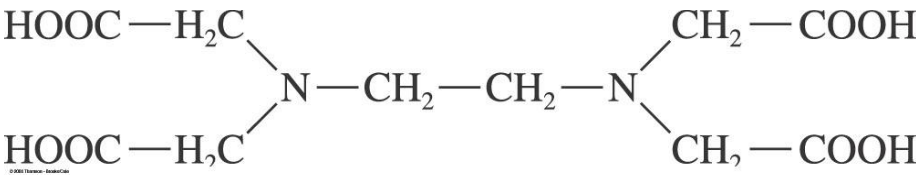
Organic Reagents for Extracting Metals

Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Water → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Water → $CHCl_3$, or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Water → $CHCl_3$, CCl_4, or C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+}, other rare earths	Water → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water → Benzene

Catalyst

Ethylenediaminetetraacetic Acid (EDTA)

Ethylenediaminetetraacetic acid [also called (ethylenedinitrilo)tetraacetic acid], which is commonly shortened to **EDTA**, is the most widely used complexometric titrant. Fully protonated EDTA has the structure



The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

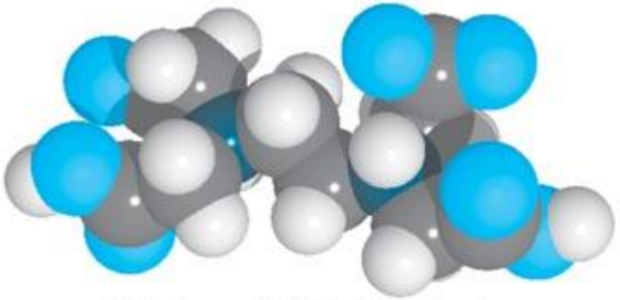
EDTA Is a Tetrabasic Acid

The dissociation constants for the acidic groups in EDTA are $K_1 = 1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$, and $K_4 = 5.50 \times 10^{-11}$. It is of interest that the first two constants are of the same order of magnitude, which suggests that the two protons involved dissociate from opposite ends of the long molecule. As a consequence of their physical separation, the negative charge created by the first dissociation does not greatly affect the removal of the second proton. The various EDTA species are often abbreviated H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}.

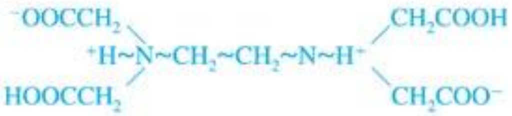
Reagents for EDTA Titrations

The free acid **H_4Y** and the dihydrate of the sodium salt, $Na_2H_2Y.2H_2O$, are commercially available in reagent quality.

Under normal atmospheric conditions, the dihydrate, $Na_2H_2Y.2H_2O$, contains 0.3% moisture in excess of the stoichiometric amount. This excess is sufficiently reproducible to permit use of a corrected weight of the salt in the direct preparation of a standard solution. The pure dihydrate can be prepared by drying at 80°C for several days in an atmosphere of 50% relative humidity.

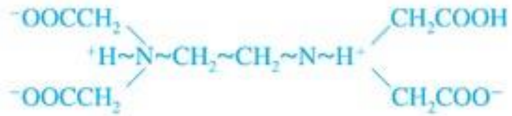


Molecular model of the H_4Y zwitterion.



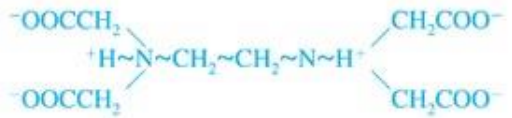
$$\begin{array}{lcr} {}^{-}OOCCH_2 & & CH_2COOH \\ & {}^{+}H\sim N\sim CH_2\sim CH_2\sim N\sim H^{+} & \\ HOOCCH_2 & & CH_2COO^{-} \end{array}$$

(a) H_4Y



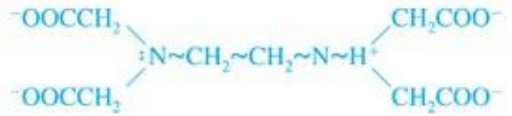
$$\begin{array}{lcr} {}^{-}OOCCH_2 & & CH_2COOH \\ & {}^{+}H\sim N\sim CH_2\sim CH_2\sim N\sim H^{+} & \\ {}^{-}OOCCH_2 & & CH_2COO^{-} \end{array}$$

(b) H_3Y^{-}



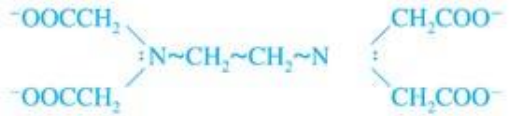
$$\begin{array}{lcr} {}^{-}OOCCH_2 & & CH_2COO^{-} \\ & {}^{+}H\sim N\sim CH_2\sim CH_2\sim N\sim H^{+} & \\ {}^{-}OOCCH_2 & & CH_2COO^{-} \end{array}$$

(c) H_2Y^{2-}



$$\begin{array}{lcr} {}^{-}OOCCH_2 & & CH_2COO^{-} \\ & :N\sim CH_2\sim CH_2\sim N\sim H^{+} & \\ {}^{-}OOCCH_2 & & CH_2COO^{-} \end{array}$$

(d) HY^{3-}



$$\begin{array}{lcr} {}^{-}OOCCH_2 & & CH_2COO^{-} \\ & :N\sim CH_2\sim CH_2\sim N\;: & \\ {}^{-}OOCCH_2 & & CH_2COO^{-} \end{array}$$

(e) Y^{4-}

Catalyst

The Nature of EDTA Complexes with Metal Ions

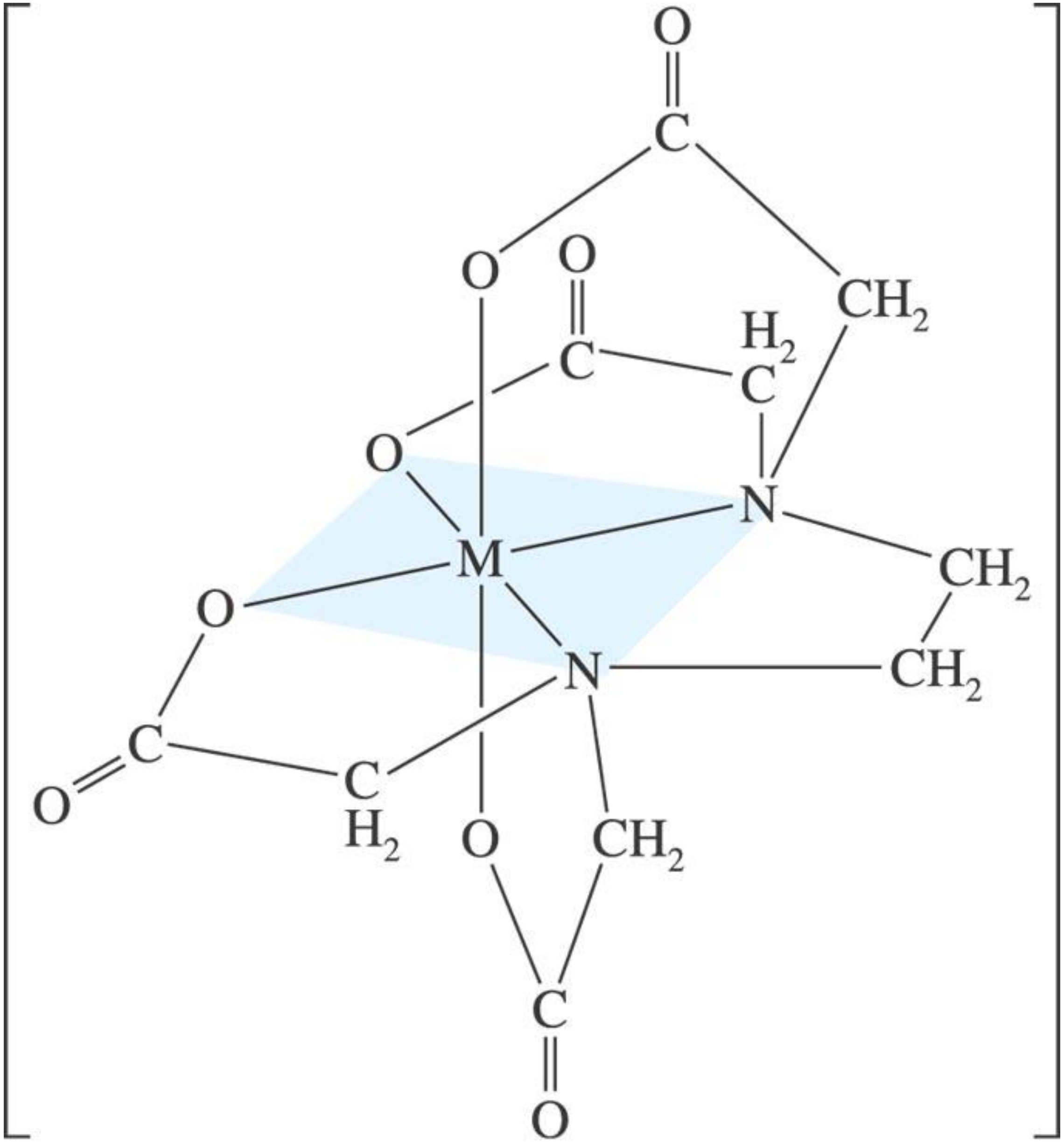
Solutions of EDTA are valuable as titrants because the reagent combines with metal ions in a 1:1 ratio regardless of the charge on the cation.

$$Ag^{+} + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^{-}$$

EDTA is a remarkable reagent not only because it forms chelates with all cation but also because most of these chelates are sufficiently stable for titrations. This great stability undoubtedly results from the several complexing sites within the molecule that give rise to a **cagelike** structure in which the cation is effectively surrounded and isolated from solvent molecules.

The ability of EDTA to complex metals is responsible for its widespread use as a preservative in foods and in biological samples.



Catalyst

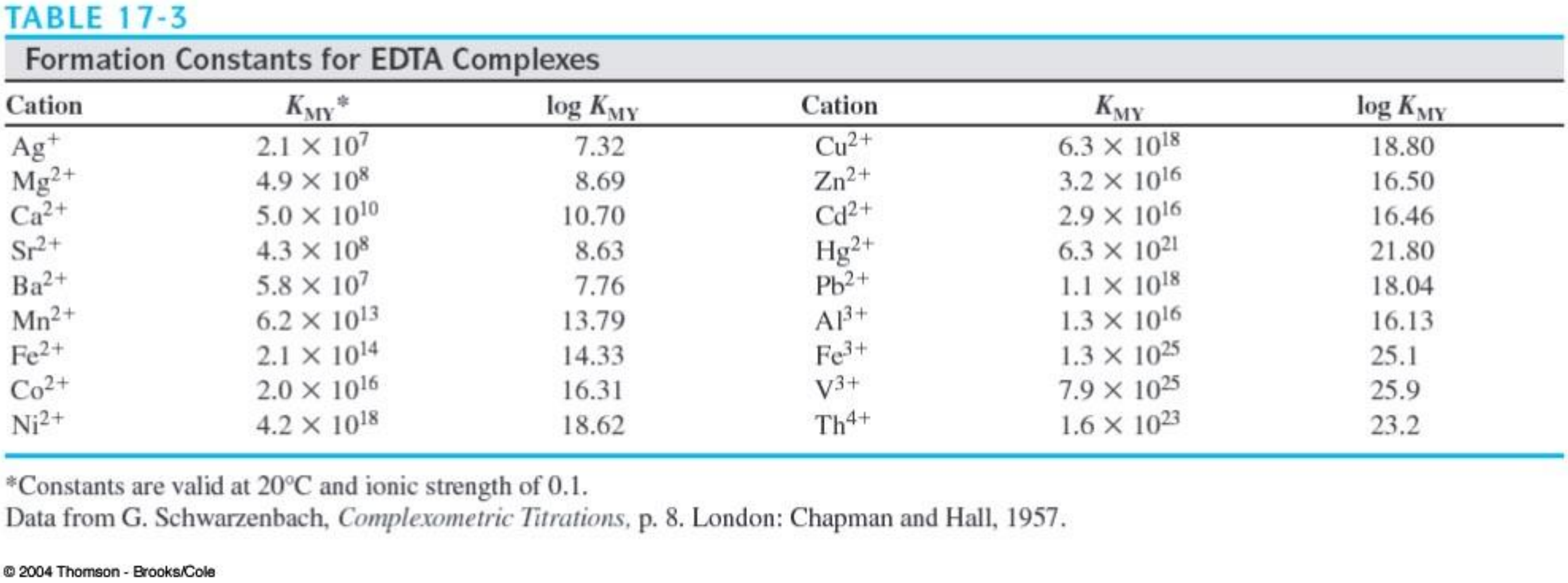


TABLE 17-3

Formation Constants for EDTA Complexes

Cation	K_{MY}*	log K_{MY}	Cation	K_{MY}	log K_{MY}
Ag^+	2.1×10^7	7.32	Cu^{2+}	6.3×10^{18}	18.80
Mg^{2+}	4.9×10^8	8.69	Zn^{2+}	3.2×10^{16}	16.50
Ca^{2+}	5.0×10^{10}	10.70	Cd^{2+}	2.9×10^{16}	16.46
Sr^{2+}	4.3×10^8	8.63	Hg^{2+}	6.3×10^{21}	21.80
Ba^{2+}	5.8×10^7	7.76	Pb^{2+}	1.1×10^{18}	18.04
Mn^{2+}	6.2×10^{13}	13.79	Al^{3+}	1.3×10^{16}	16.13
Fe^{2+}	2.1×10^{14}	14.33	Fe^{3+}	1.3×10^{25}	25.1
Co^{2+}	2.0×10^{16}	16.31	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

*Constants are valid at 20°C and ionic strength of 0.1.

Data from G. Schwarzenbach, *Complexometric Titrations,* p. 8. London: Chapman and Hall, 1957.

Catalyst

Indicators for EDTA Titrations

Indicators are organic dyes that form colored chelates with metal ions in a **pM** range that is characteristic of the particular cation and dye. The complexes are often intensely colored and are discernible to the eye at concentrations in the range of 10^{-6} to 10^{-7} M.

Eriochrome Black T is a typical metal-ion indicator used in the titration of several common cations.

$H_2O + H_2In^- \rightleftharpoons HIn^{2-} + H_3O^+ \qquad K_1 = 5 \text{ X } 10^{-7}$

red blue

$H_2O + HIn^{2-} \rightleftharpoons In^{3-} + H_3O^+ \qquad K_2 = 2.8 \text{ X } 10^{-12}$

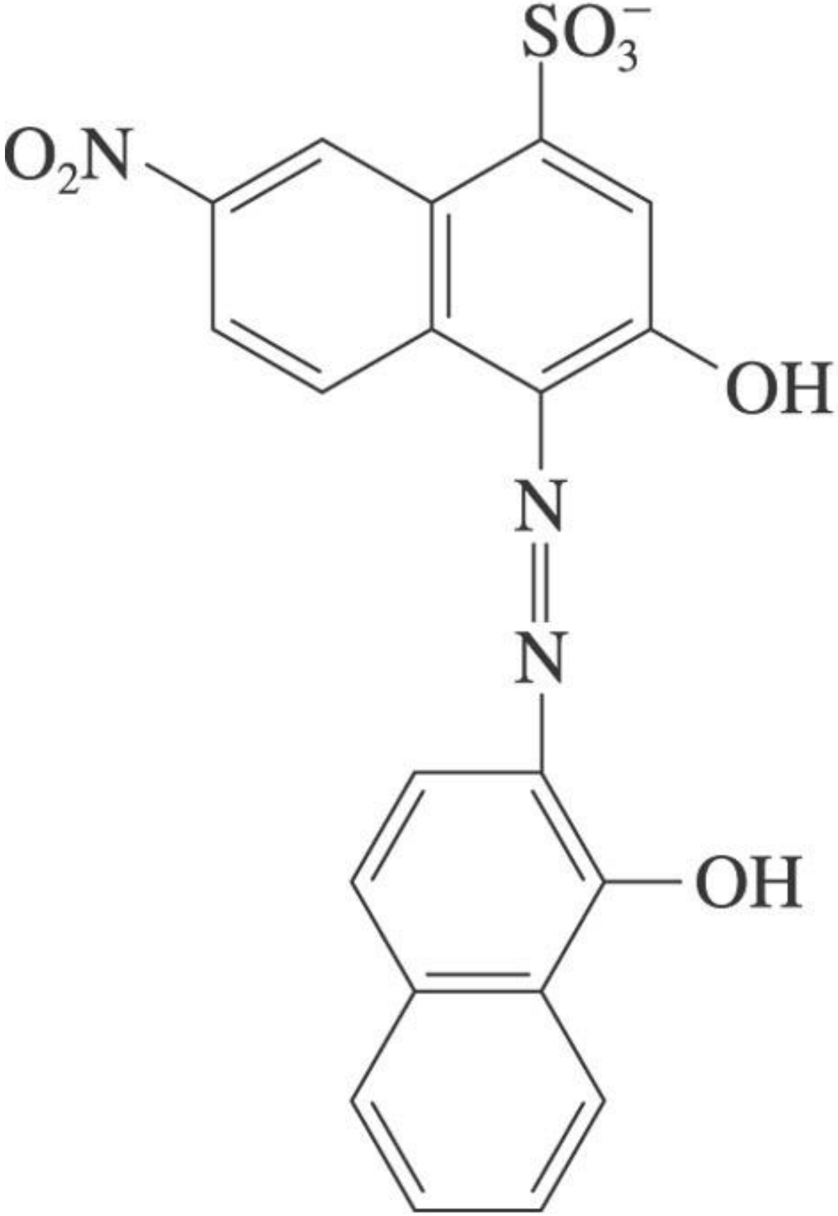
blue orange

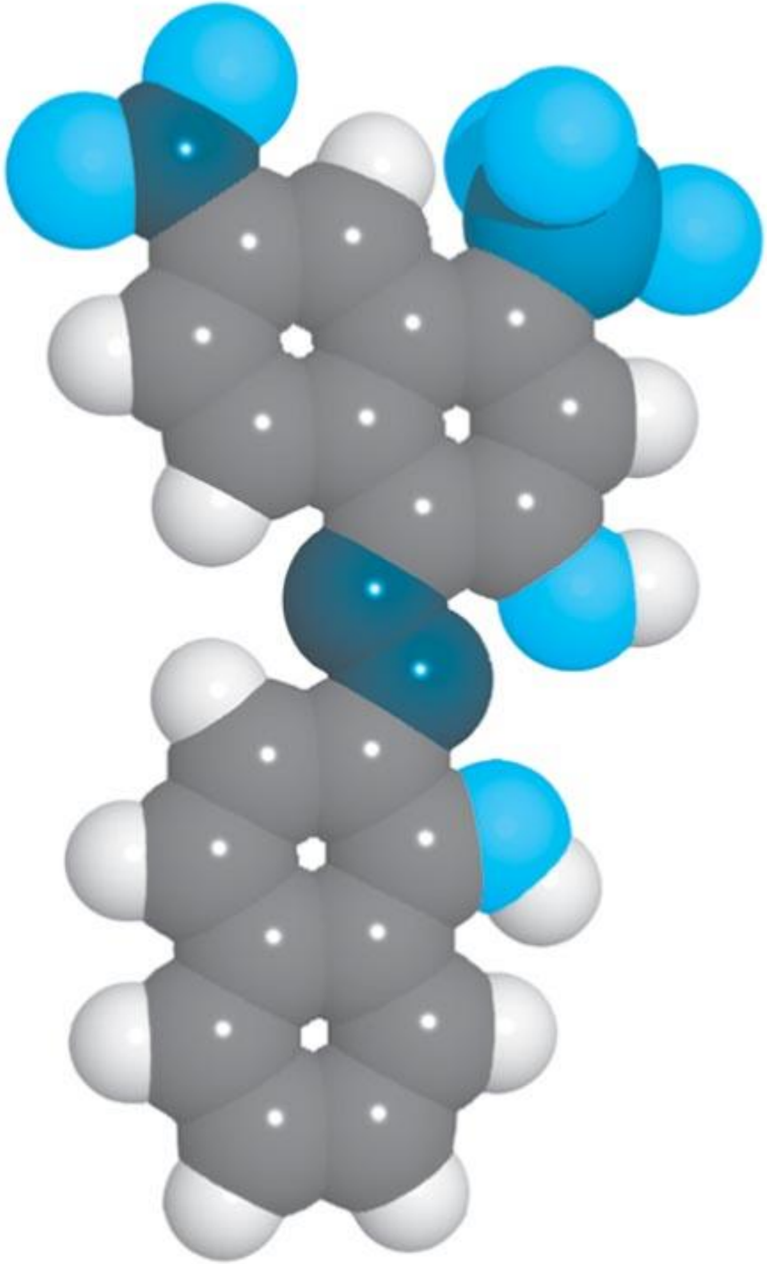
The acids and their conjugate bases have different colors.

The metal complexes of Eriochrome Black T are generally red, as is H_2In^-. Thus, for metal-ion detection, it is necessary to adjust the pH to 7 or above so that the blue form of the species, HIn^{2-}, predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is red. With the first slight excess of **EDTA**, the solution turns blue as a consequence of the reaction

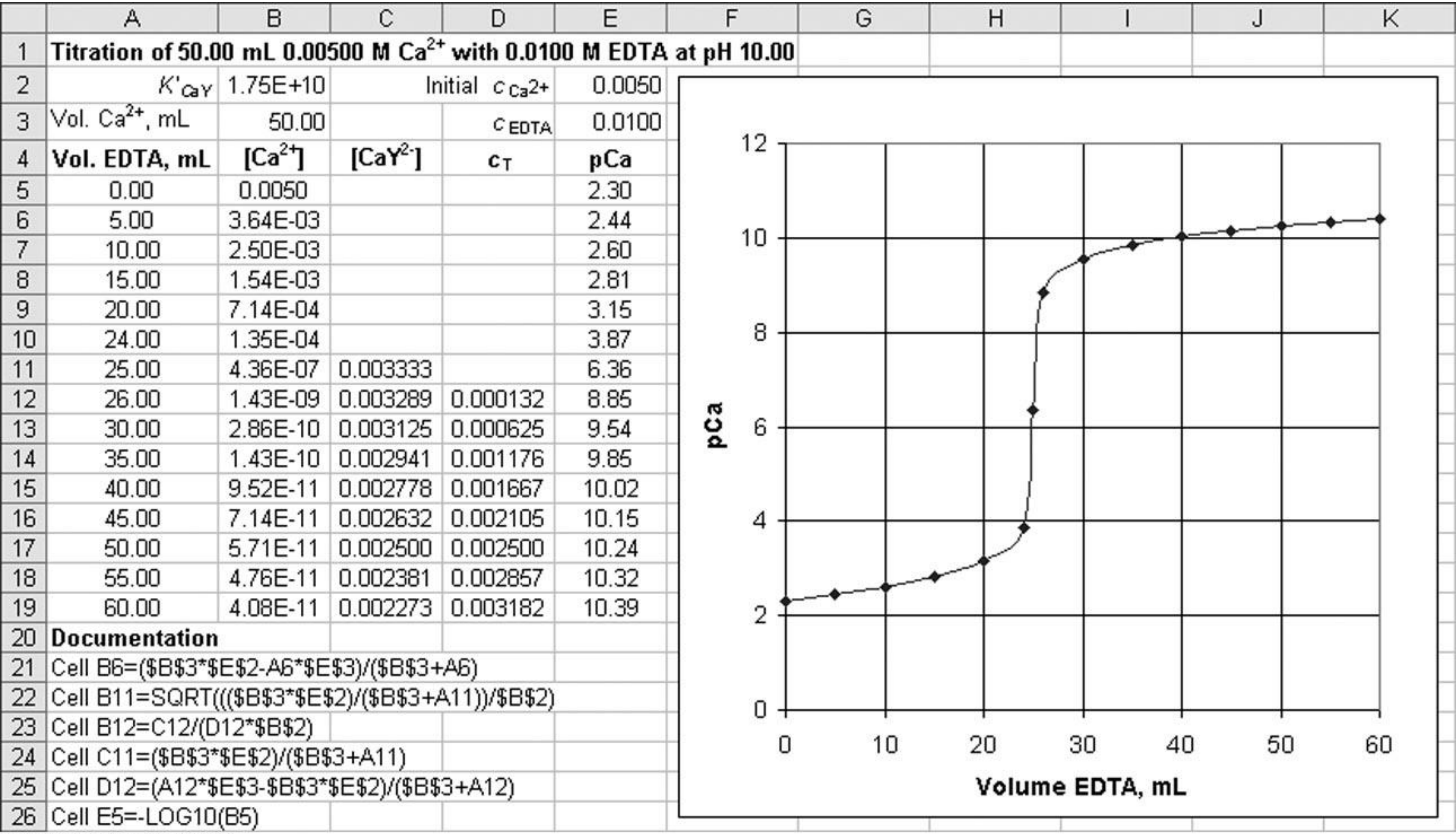
$MIn^- + HY^{3-} \rightleftharpoons HIn^{2-} + MY^{2-}$

red blue

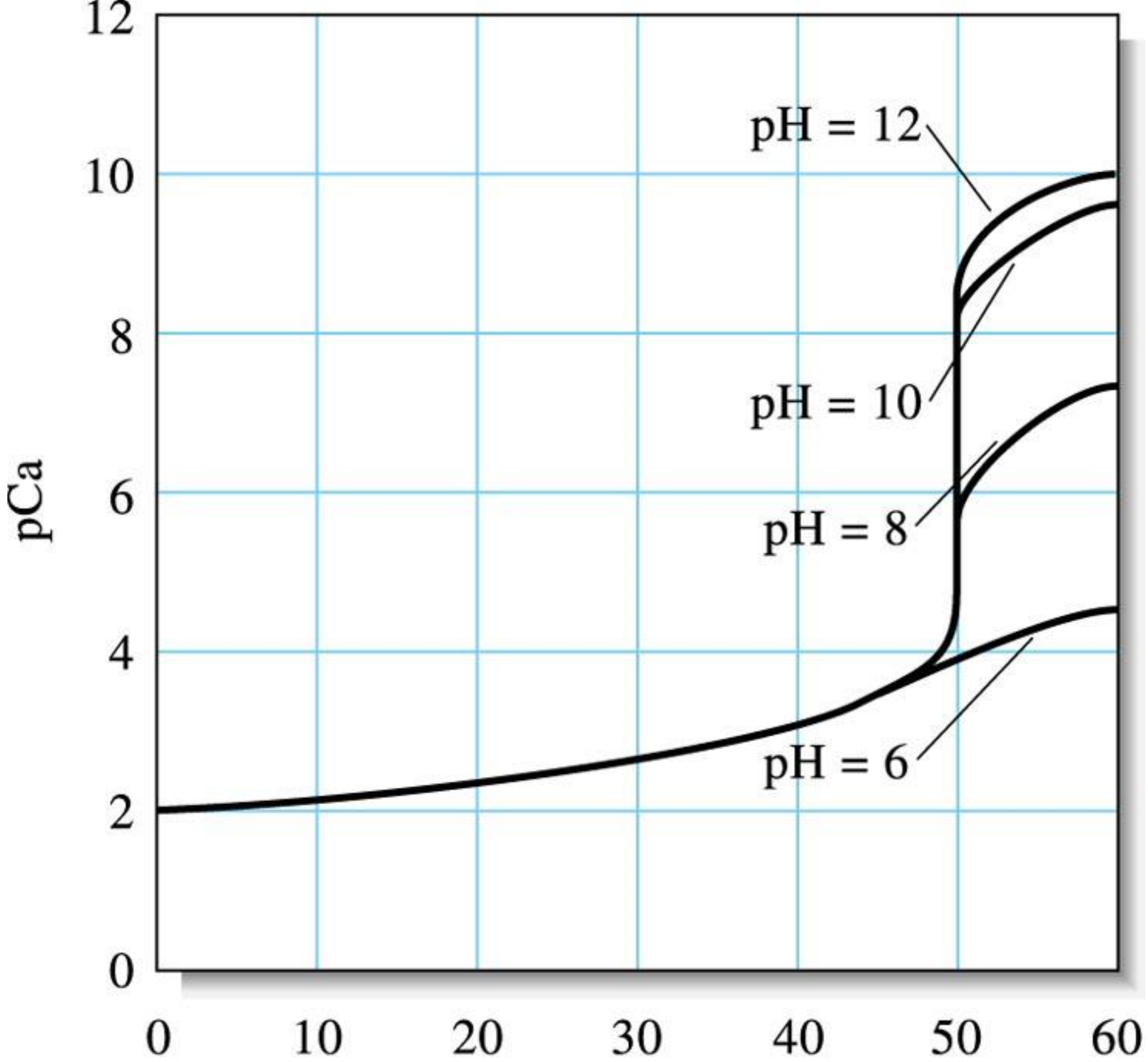




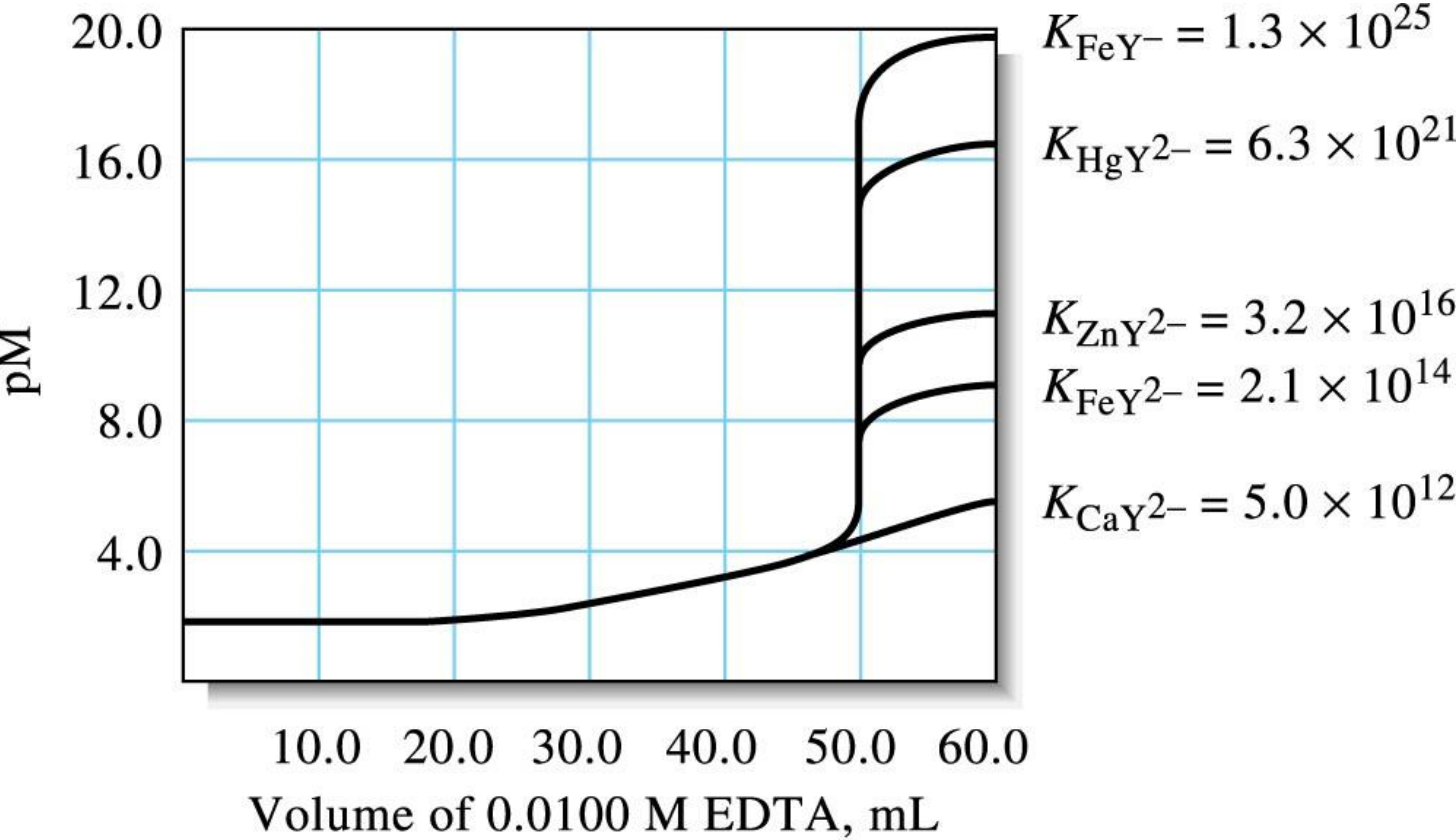
Catalyst

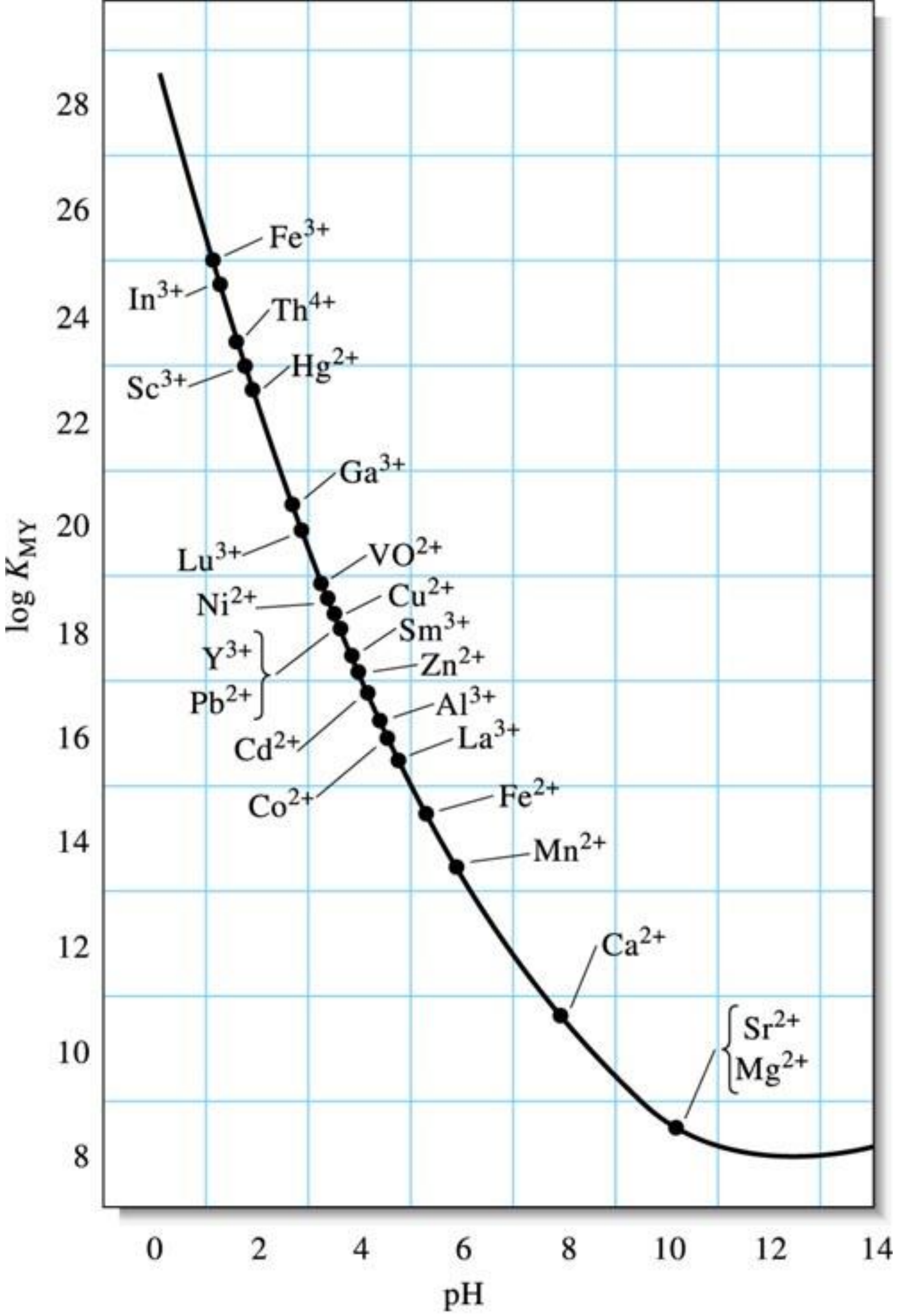


	A	B	C	D	E
1	**Titration of 50.00 mL 0.00500 M Ca^{2+} with 0.0100 M EDTA at pH 10.00**				
2	K'_{CaY}	1.75E+10	Initial	$c_{Ca^{2+}}$	0.0050
3	Vol. Ca^{2+}, mL	50.00		c_{EDTA}	0.0100
4	**Vol. EDTA, mL**	**$[Ca^{2+}]$**	**$[CaY^{2-}]$**	**c_T**	**pCa**
5	0.00	0.0050			2.30
6	5.00	3.64E-03			2.44
7	10.00	2.50E-03			2.60
8	15.00	1.54E-03			2.81
9	20.00	7.14E-04			3.15
10	24.00	1.35E-04			3.87
11	25.00	4.36E-07	0.003333		6.36
12	26.00	1.43E-09	0.003289	0.000132	8.85
13	30.00	2.86E-10	0.003125	0.000625	9.54
14	35.00	1.43E-10	0.002941	0.001176	9.85
15	40.00	9.52E-11	0.002778	0.001667	10.02
16	45.00	7.14E-11	0.002632	0.002105	10.15
17	50.00	5.71E-11	0.002500	0.002500	10.24
18	55.00	4.76E-11	0.002381	0.002857	10.32
19	60.00	4.08E-11	0.002273	0.003182	10.39
20	**Documentation**				
21	Cell B6=(B3*E2-A6*E3)/(B3+A6)				
22	Cell B11=SQRT(((B3*E2)/(B3+A11))/B2)				
23	Cell B12=C12/(D12*B2)				
24	Cell C11=(B3*E2)/(B3+A11)				
25	Cell D12=(A12*E3-B3*E2)/(B3+A12)				
26	Cell E5=-LOG10(B5)				


pCa
0
2
4
6
8
10
12
0
10
20
30
40
50
60
Volume of 0.0100 M EDTA, mL
pH = 12
pH = 10
pH = 8
pH = 6

Catalyst


20.0
16.0
12.0
8.0
4.0
pM
10.0
20.0
30.0
40.0
50.0
60.0
Volume of 0.0100 M EDTA, mL
$K_{FeY^-} = 1.3 \times 10^{25}$
$K_{HgY^{2-}} = 6.3 \times 10^{21}$
$K_{ZnY^{2-}} = 3.2 \times 10^{16}$
$K_{FeY^{2-}} = 2.1 \times 10^{14}$
$K_{CaY^{2-}} = 5.0 \times 10^{12}$


log K_{MY}
28
26
24
22
20
18
16
14
12
10
8
pH
0
2
4
6
8
10
12
14
Fe^{3+}
In^{3+}
Th^{4+}
Sc^{3+}
Hg^{2+}
Ga^{3+}
Lu^{3+}
VO^{2+}
Ni^{2+}
Cu^{2+}
Y^{3+}
Pb^{2+}
Sm^{3+}
Zn^{2+}
Al^{3+}
Cd^{2+}
La^{3+}
Co^{2+}
Fe^{2+}
Mn^{2+}
Ca^{2+}
Sr^{2+}
Mg^{2+}

Catalyst

Titration Methods Employing EDTA

Direct Titration: Many of the metals in the periodic table can be determined by titration with standard EDTA solution. Some methods are based on indicators that respond to the analyte itself, whereas others are based on an added metal ion.

Methods Based on Indicators for an Added metal Ion: In case where a good, direct indicator for the analyte is unavailable, a small amount of a metal ion for which a good indicator is available can be added. The metal ion must form a complex that is less stable than the analyte complex.

Potentionmetric Methods: Potential measurements can be used for end-point detection in the EDTA titration of those metal ion for which specific ion electrodes are available.

Spectrophotometric Methods: Measurement of UV/visible absorption can also be used to determine the end points of titrations. In these cases, an instrument responds to the color change in the titration rather than relying on a visual determination of the end point.

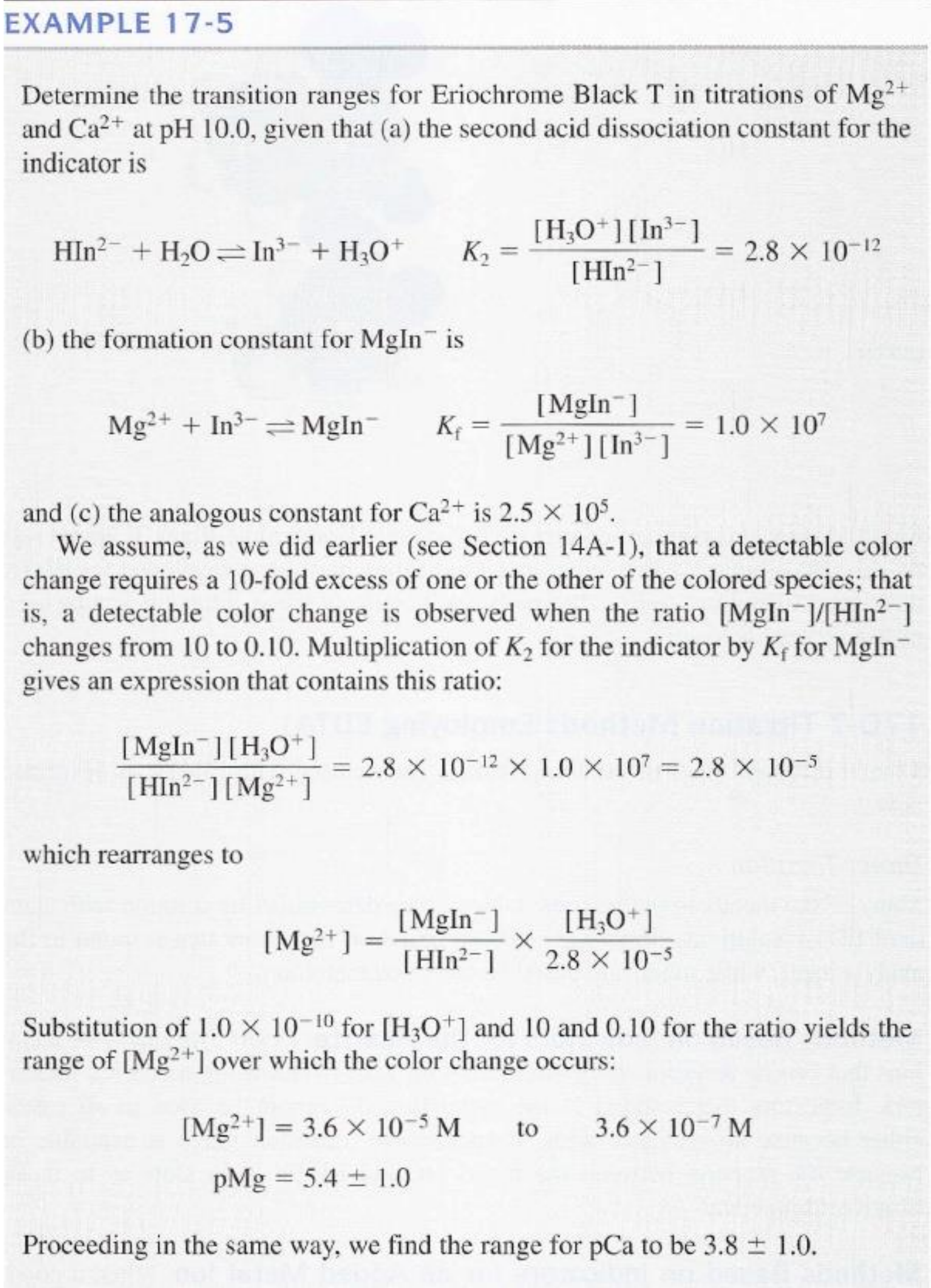
…continued…

Back-Titration Methods: Back-titrations are useful for the determination of cations that form stable EDTA complexes and for which a satisfactory indicator is not available; the determination of thallium is an extreme example. The method is also useful for cations such as Cr(III) and Co(III) that react only slowly with EDTA. A measured excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution to an Eriochrome Black T or Calmagite end point.

Displacement methods: In displacement titrations, an unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is introduced into the analyte solution. If the analyte forms a more stable complex than that of magnesium or zinc, the following displacement reaction occurs:

$$MgY^{2-} + M^{2+} \rightleftharpoons MY^{2-} + Mg^{2+}$$

where M^{2+} represents the analyte cation. The liberated Mg^{2+} or, in some cases Zn^{2+} is then titrated with a standard EDTA solution. Displacement titrations are used when no indicator for an analyte is available.



EXAMPLE 17-5

Determine the transition ranges for Eriochrome Black T in titrations of Mg^{2+} and Ca^{2+} at pH 10.0, given that (a) the second acid dissociation constant for the indicator is

$$HIn^{2-} + H_2O \rightleftharpoons In^{3-} + H_3O^+ \qquad K_2 = \frac{[H_3O^+][In^{3-}]}{[HIn^{2-}]} = 2.8 \times 10^{-12}$$

(b) the formation constant for $MgIn^-$ is

$$Mg^{2+} + In^{3-} \rightleftharpoons MgIn^- \qquad K_f = \frac{[MgIn^-]}{[Mg^{2+}][In^{3-}]} = 1.0 \times 10^7$$

and (c) the analogous constant for Ca^{2+} is 2.5×10^5.

We assume, as we did earlier (see Section 14A-1), that a detectable color change requires a 10-fold excess of one or the other of the colored species; that is, a detectable color change is observed when the ratio $[MgIn^-]/[HIn^{2-}]$ changes from 10 to 0.10. Multiplication of K_2 for the indicator by K_f for $MgIn^-$ gives an expression that contains this ratio:

$$\frac{[MgIn^-][H_3O^+]}{[HIn^{2-}][Mg^{2+}]} = 2.8 \times 10^{-12} \times 1.0 \times 10^7 = 2.8 \times 10^{-5}$$

which rearranges to

$$[Mg^{2+}] = \frac{[MgIn^-]}{[HIn^{2-}]} \times \frac{[H_3O^+]}{2.8 \times 10^{-5}}$$

Substitution of 1.0×10^{-10} for $[H_3O^+]$ and 10 and 0.10 for the ratio yields the range of $[Mg^{2+}]$ over which the color change occurs:

$$[Mg^{2+}] = 3.6 \times 10^{-5}\ \text{M} \qquad \text{to} \qquad 3.6 \times 10^{-7}\ \text{M}$$

$$\text{pMg} = 5.4 \pm 1.0$$

Proceeding in the same way, we find the range for pCa to be 3.8 ± 1.0.

Catalyst