14 Equilibria in Acid-Base Solutions

Blue delphinium petals contain an anthocyanin called delphinin. It changes from bluish red in acid to blue to violet in base. The delphiniums in the painting must be growing in soil with a basic pH.

The Metropolitan Museum of Art/Gift of Betty G. Newell, 1996

The meeting of two personalities is like the contact of two chemical substances: if there is any reaction, both are transformed.

—CARL JUNG
Modern Man in Search of a Soul

Chapter Outline

In Chapter 13 we dealt with the equilibrium established when a single solute, either a weak acid or a weak base, is added to water. This chapter focuses on the equilibrium established when two different solutes are mixed in water solution. These solutes may be

- ***a weak acid, HB, and its conjugate base, B^-.*** Solutions called *buffers* contain roughly equal amounts of these two species. The equilibria involved in buffer solutions are considered in Section 14-1.
- ***an acid and a base used in an acid-base titration.*** This type of reaction was discussed in Chapter 4. Section 14-3 examines the equilibria involved, the way pH changes during the titration, and the choice of indicator for the titration.

We will also consider the equilibrium involved in using an acid-base indicator to estimate pH (Section 14-2).

14-1 Buffers

Any solution containing appreciable amounts of both a weak acid and its conjugate base

- ***is highly resistant to changes in pH brought about by addition of strong acid or strong base.***
- ***has a pH close to the pK_a of the weak acid.***

A solution with these properties is called a **buffer** because it cushions the "shock" (i.e., the drastic change in pH) that occurs when a strong acid or strong base is added to water.

By definition, a buffer is any solution that resists a change in pH.

To prepare a buffer, we can mix solutions of a weak acid HB and the sodium salt of that acid NaB, which consists of Na^+ and B^- ions. This mixture can react with either a strong base

$$HB(aq) + OH^-(aq) \longrightarrow B^-(aq) + H_2O$$

or a strong acid

$$B^-(aq) + H^+(aq) \longrightarrow HB(aq)$$

These reactions have very large equilibrium constants, as we will see in Section 14-3, and so go virtually to completion. As a result, the added H^+ or OH^- ions are consumed and do not directly affect the pH. This is the principle of buffer action, which explains why a buffered solution is much more resistant to a change in pH than one that is unbuffered (Figure 14.1).

Buffers are widely used to maintain nearly constant pH in a variety of commercial products and laboratory procedures (Figure 14.2). For these applications

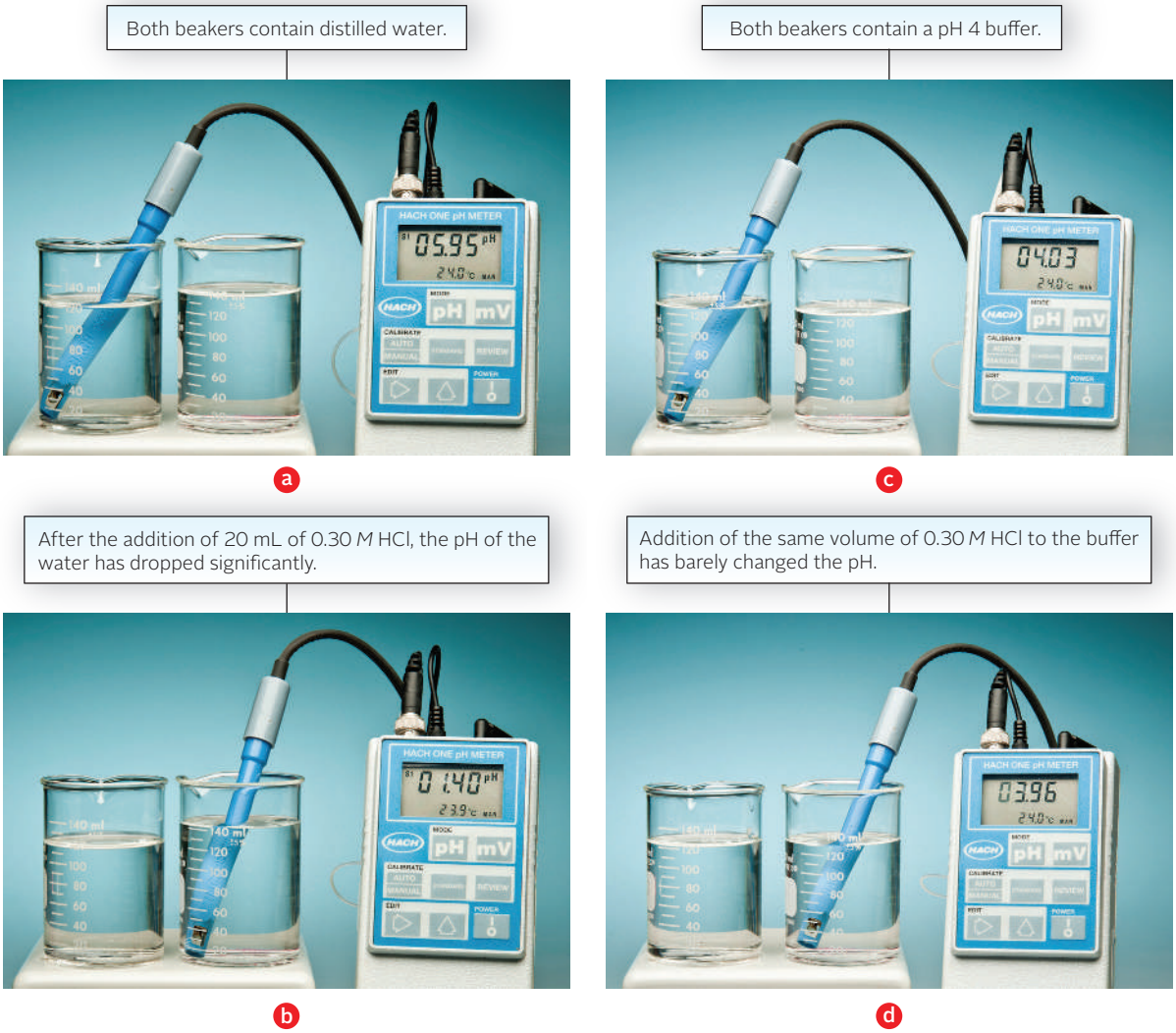

Figure 14.1 The effect of a buffer upon addition of acid. Note the reading on the pH meter.

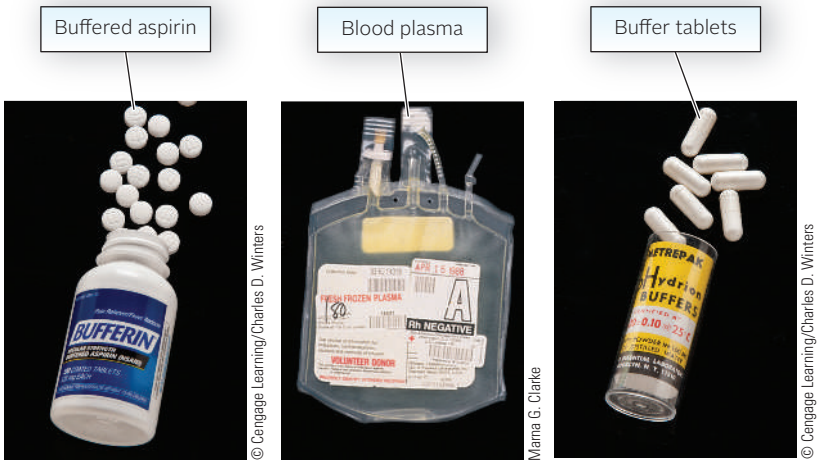

Figure 14.2 Some applications of buffers. Many products, including aspirin and blood plasma, are buffered. Buffer tablets are also available in the laboratory *(far right)* to make up a solution to a specified pH.

and others, it is essential to be able to determine

- the pH of a buffer system made by mixing a weak acid with its conjugate base.
- the appropriate buffer system to maintain a desired pH.
- the (small) change in pH that occurs when a strong acid or base is added to a buffer.
- the capacity of a buffer to absorb H^+ or OH^- ions.

Determination of $[H^+]$ in a Buffer System

The concentration of H^+ ion in a buffer can be calculated if you know the concentrations of the weak acid HB and its conjugate base B^-.◂ These three quantities are related through the acid equilibrium constant of HB:

B^- comes from adding a salt of the weak acid, such as NaB.

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq) \qquad K_a = \frac{[H^+][B^-]}{[HB]}$$

Solving for $[H^+]$,

$$[H^+] = K_a \times \frac{[HB]}{[B^-]} \tag{14.1}$$

By taking the logarithm of both sides of Equation 14.1 and multiplying through by -1, you can show that, for any buffer system,

$$pH = pK_a + \log_{10} \frac{[B^-]}{[HB]}$$

This relation, known as the *Henderson-Hasselbalch equation*, is often used in biology and biochemistry to calculate the pH of buffers. Historically, it was Henderson who "discovered" Equation 14.1 in 1908. Hasselbalch put it in logarithmic form eight years later.

Equation 14.1 is a completely general equation, applicable to all buffer systems. The calculation of $[H^+]$—and hence pH—can be simplified if you keep two points in mind:

1. ***You can always assume that equilibrium is established without appreciably changing the original concentrations of either HB or B⁻.*** That is,

$$[HB] = [HB]_o$$
$$[B^-] = [B^-]_o$$

To explain why these relations hold, consider, for example, what happens when the weak acid HB is added to water:

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$

We saw in Chapter 13 that under these conditions, it is usually a good approximation to take [HB] ≈ $[HB]_o$. The approximation is even more accurate when a considerable amount of B^- is added, as is the case with a buffer. By Le Châtelier's principle, the reverse reaction occurs, the ionization of HB is repressed, and [HB] = $[HB]_o$.

2. ***Because the two species HB and B^- are present in the same solution, the ratio of their concentrations is also their mole ratio.*** That is,

$$\frac{[HB]}{[B^-]} = \frac{\text{no. moles HB}/V}{\text{no. moles } B^-/V} = \frac{n_{HB}}{n_{B^-}}$$

where n = amount in moles and V = volume of solution. Hence Equation 14.1 can be rewritten as

$$[H^+] = K_a \times \frac{n_{HB}}{n_{B^-}} \qquad (14.2)$$

If you start with 0.20 mol HB and 0.10 mol B^-, $[H^+] = 2K_a$.

Frequently, Equation 14.2 is easier to work with than Equation 14.1.

EXAMPLE 14.1 GRADED

Lactic acid, $C_3H_6O_3$, is a weak organic acid present in both sour milk and buttermilk. It is also a product of carbohydrate metabolism and is found in the blood after vigorous muscular activity (Figure 14.3). A buffer is prepared by dissolving lactic acid, HLac ($K_a = 1.4 \times 10^{-4}$), and sodium lactate, $NaC_3H_5O_3$, NaLac.

a Calculate $[H^+]$ and the pH of the buffer made up of 1.00 mol of sodium lactate and 1.00 mol of lactic acid in enough water to form 550.0 mL of solution.

ANALYSIS

Information given:	K_a HLac (1.4×10^{-4}); n_{HLac} (1.00 mol); n_{Lac-} (1.00 mol) volume of solution (550.0 mL)
Asked for:	$[H^+]$ and pH of the buffer

STRATEGY

1. Substitute into Equation 14.2 to obtain $[H^+]$.

$$[H^+] = K_a \times \frac{n_{HB}}{n_{B-}}$$

2. Find pH: $pH = -\log_{10}[H^+]$

SOLUTION

1. $[H^+]$	$[H^+] = 1.4 \times 10^{-4} \times \frac{1.00}{1.00} = 1.4 \times 10^{-4}\ M$
2. pH	$pH = -\log_{10}(1.4 \times 10^{-4}) = 3.85$

b Calculate $[H^+]$ and the pH of the buffer made up of 34.6 g of NaLac dissolved in 550.0 mL of a 1.20 M aqueous solution of HLac. (Assume no volume change after addition of NaLac.)

ANALYSIS

Information given:	K_a HLac (1.4×10^{-4}); mass of NaLac (34.6 g); M HLac (1.20) volume of solution (550.0 mL)
Information implied:	MM NaLac
Asked for:	$[H^+]$ and pH of the buffer

STRATEGY

1. Find n_{HLac} in solution: $n = V \times M$
2. Find n_{Lac-} in solution. Recall 1 mol Lac^-/1 mol NaLac. Thus

$n_{NaLac} = n_{Lac-}$ = mass NaLac/MM NaLac

continued

3. Substitute into Equation 14.2 to find $[H^+]$.
4. $pH = -\log_{10}[H^+]$

SOLUTION

1. n_{HLac}	$n = 0.5500\ \text{L} \times 1.20\ \dfrac{\text{mol}}{\text{L}} = 0.660\ \text{mol}$
2. n_{Lac^-}	$n_{Lac^-} = n_{NaLac} = \dfrac{34.6\ \text{g NaLac}}{112.06\ \text{g/mol}} = 0.309\ \text{mol}$
3. $[H^+]$	$[H^+] = 1.4 \times 10^{-4} \times \dfrac{0.660}{0.309} = 3.0 \times 10^{-4}\ M$
4. pH	$pH = -\log_{10}(3.0 \times 10^{-4}) = 3.52$

END POINT

Looking back at part (a), note that when equal amounts of a weak acid and its conjugate base are present, $pH = pK_a$.

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Figure 14.3 An exhausted distance runner crouches in pain. Exertion beyond the point at which the body can clear lactic acid from the muscles causes the pain.

Notice in Example 14.1(a) that the total volume of solution is irrelevant. All that is required to solve for $[H^+]$ is the number of moles of lactic acid and sodium lactate. The pH of the buffer is 3.85 whether the volume of solution is 550 mL, 1 L, or even 10 L. This explains why *diluting a buffer with water does not change the pH.*

Choosing a Buffer System

Suppose you want to make up a buffer in the laboratory with a specified pH (e.g., 4.0, 7.0, 10.0, . . .). Looking at the equation

$$[H^+] = K_a \times \frac{[HB]}{[B^-]} = K_a \times \frac{n_{HB}}{n_{B^-}}$$

it is evident that the pH of the buffer depends on two factors:

1. ***The acid equilibrium constant of the weak acid, K_a.*** The value of K_a has the greatest influence on buffer pH. Because HB and B^- are likely to be present in nearly equal amounts,

$$[H^+] \approx K_a \qquad pH \approx pK_a$$

Thus to make up a buffer with a pH close to 7, you should use a conjugate weak acid–weak base pair in which K_a of the weak acid is about 10^{-7}.

2. ***The ratio of the concentrations or amounts of HB and B^-.*** Small variations in pH can be achieved by adjusting this ratio. To obtain a slightly more acidic buffer, add more weak acid, HB; addition of more weak base, B^-, will make the buffer a bit more basic.

EXAMPLE 14.2 GRADED

Suppose you need to prepare a buffer with a pH of 9.00.

a Which of the buffer systems in Table 14.1 would you choose?

STRATEGY AND SOLUTION

Check the K_a values in Table 14.1. Find the buffer system with a pK_a value closest to 9.00. The clear choice is the NH_4^+/NH_3 system with a pK_a of 9.25.

continued

b What should be the ratio of the concentration of weak acid, HB, to its conjugate base, B^-?

ANALYSIS

Information given:	pH (9.00); from part (a): buffer system (NH_4^+/NH_3)
Information implied:	K_a of NH_4^+
Asked for:	$[NH_4^+]/[NH_3]$

STRATEGY

1. Find $[H^+]$.
2. Substitute into Equation 14.1 where [HB] is $[NH_4^+]$ and B^- is $[NH_3]$.

SOLUTION

1. $[H^+]$ — $\text{pH} = -\log_{10} 9.00 = 1.0 \times 10^{-9}\ M$
2. $\dfrac{NH_4^+}{NH_3}$ — $[H^+] = K_a \times \dfrac{NH_4^+}{NH_3} \longrightarrow \dfrac{NH_4^+}{NH_3} = \dfrac{[H^+]}{K_a} = \dfrac{1.0 \times 10^{-9}}{5.6 \times 10^{-10}} = 1.8$

c What mass in grams of B^- should be added to 245 mL of 0.880 *M* HB to give a pH of 9.00?

ANALYSIS

Information given:	from part (a): buffer system (NH_4^+/NH_3) from part (b): $[H^+]$ (1.0×10^{-9} *M*); NH_4^+/NH_3 (1.8) NH_4^+ solution: *V* (0.245 L); *M* (0.880)
Information implied:	molar mass of NH_3
Asked for:	mass of NH_3 required to prepare a buffer with pH 9.0.

STRATEGY

1. Find mol NH_4^+.

   $n = V \times M$

2. Since there is only one solution, $[NH_4^+]/[NH_3]$ = mol NH_4^+/mol NH_3 = 1.8. Substitute mol NH_4^+ and find mol NH_3.
3. Find the mass of NH_3 required using its molar mass.

SOLUTION

1. mol NH_4^+ — $n = (0.245\ \text{L})(0.880\ \text{mol/L}) = 0.216\ \text{mol}$
2. mol NH_3 — $\dfrac{0.216}{\text{mol } NH_3} = 1.8 \longrightarrow \text{mol } NH_3 = 0.12$
3. mass NH_3 — $\text{mass} = (0.12\ \text{mol})(17.03\ \text{g/mol}) = 2.0\ \text{g}$

As Example 14.2 suggests, the most common way to prepare buffers is by mixing a weak acid and its conjugate base. However, a somewhat different approach is also possible: partial neutralization of a weak acid or a weak base gives a buffer. To illustrate, suppose that 0.18 mol of HCl is added to 0.28 mol of NH_3. The following reaction occurs:

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

Table 14.1 Buffer Systems at Different pH Values

	Buffer System			
Desired pH	**Weak Acid**	**Weak Base**	**K_a (Weak Acid)**	**pK_a**
4	Lactic acid (HLac)	Lactate ion (Lac^-)	1.4×10^{-4}	3.85
5	Acetic acid ($HC_2H_3O_2$)	Acetate ion ($C_2H_3O_2^-$)	1.8×10^{-5}	4.74
6	Carbonic acid (H_2CO_3)	Hydrogen carbonate ion (HCO_3^-)	4.4×10^{-7}	6.36
7	Dihydrogen phosphate ion ($H_2PO_4^-$)	Hydrogen phosphate ion (HPO_4^{2-})	6.2×10^{-8}	7.21
8	Hypochlorous acid (HClO)	Hypochlorite ion (ClO^-)	2.8×10^{-8}	7.55
9	Ammonium ion (NH_4^+)	Ammonia (NH_3)	5.6×10^{-10}	9.25
10	Hydrogen carbonate ion (HCO_3^-)	Carbonate ion (CO_3^{2-})	4.7×10^{-11}	10.32

The limiting reactant, H^+, is consumed. Hence we have

	n_{H^+}	n_{NH_3}	$n_{NH_4^+}$
Original	0.18	0.28	0.00
Change	−0.18	−0.18	+0.18
Final	0.00	0.10	0.18

The solution formed contains appreciable amounts of both NH_4^+ and NH_3. It is a buffer. As we saw in Example 14.2, when the ratio $[NH_4^+]/[NH_3]$ is 1.8, the pH of the buffer is 9.00.

Note that complete neutralization would not produce a buffer; only NH_4^+ ions would be present.

In buffers, the limiting reactant is always the reactant with the smaller number of moles because the ratio of reactants to products is always 1.

EXAMPLE 14.3

The food industry uses the acetic acid/sodium acetate buffer to control the pH of some prepared foods. When NaOH is added to acetic acid (HAc) to prepare the buffer, the following reaction occurs:

$$HAc(aq) + OH^-(aq) \longrightarrow Ac^-(aq) + H_2O$$

a Show by calculation whether a solution made up of 0.300 mol of NaOH and 0.500 mol of $HC_2H_3O_2$ is a buffer.

ANALYSIS

Information given:	mol NaOH = mol OH^- (0.300); mol HAc (0.500)
Information implied:	K_a for HAc (Table 13.2)
Asked for:	Is the solution a buffer?

STRATEGY

1. Fill in a table like the one shown in the preceding discussion.
2. Recall that for a solution to be a buffer, the solution must have a weak acid and its conjugate base.

continued

SOLUTION

1. Table

	n_{OH^-}	n_{HAc}	n_{Ac^-}
Original	0.300	0.500	0
Change	−0.300	−0.300	+0.300
Final	0	0.200	0.300

2. Buffer? There are 0.200 mol HAc and 0.300 mol Ac^- after reaction. The solution is a buffer.

b Is a buffer produced when 25.00 mL of 0.100 *M* NaOH is added to 35.00 mL of 0.125 *M* $HC_2H_3O_2$?

ANALYSIS

Information given:	NaOH: *V* (25.00 mL); *M* (0.100) HAc: *V* (35.00 mL); *M* (0.125)
Information implied:	K_a for HAc
Asked for:	Is the solution a buffer?

STRATEGY

1. Find mol OH^-.
2. Find mol HAc.
3. Make a table as in part (a).
4. Check for the presence of the weak acid (HAc) and its conjugate base (Ac^-) after reaction is complete.

SOLUTION

1. mol OH^- $(0.02500\ L)(0.100\ mol/L) = 2.50 \times 10^{-3}$ mol

2. mol HAc $(0.03500\ L)(0.125\ mol/L) = 4.38 \times 10^{-3}$ mol

3. Table

	n_{OH^-}	n_{HAc}	n_{Ac^-}
Original	2.50×10^{-3}	4.38×10^{-3}	0
Change	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final	0	1.88×10^{-3}	2.50×10^{-3}

4. Buffer? There are 2.50×10^{-3} mol Ac^- and 1.88×10^{-3} mol HAc after reaction. The solution is a buffer.

c When 5.00 g of NaOH are added to 150.0 mL of 0.500 *M* $HC_2H_3O_2$ (without a volume change), is the resulting solution a buffer?

ANALYSIS

Information given:	NaOH: mass (5.00 g) HAc: *V* (150.0 mL); *M* (0.500)
Information implied:	K_a for HAc
Asked for:	Is the solution a buffer?

STRATEGY

1. Find mol OH^-.
2. Find mol HAc.
3. Make a table as in part (a).
4. Check for the presence of the weak acid (HAc) and its conjugate base (Ac^-) after reaction is complete.

continued

SOLUTION

1. mol OH^-

$$\text{mol NaOH} = \frac{5.00\text{ g}}{40.0\text{ g/mol}} = 0.125\text{ mol} = \text{mol } OH^-$$

2. mol HAc

$$(0.1500\text{ L})(0.500\text{ mol/L}) = 0.0750\text{ mol}$$

3. Table

	n_{OH^-}	n_{HAc}	n_{Ac^-}
Original	0.125	0.0750	0
Change	−0.0750	−0.0750	+0.0750
Final	0.050	0	0.0750

4. Buffer?

There are 0.0750 mol Ac^- and no mol HAc after reaction. The solution is not a buffer.

END POINT

To make a buffer from a strong base and a weak acid (or a strong acid and a weak base), the strong base (or strong acid) must be the limiting reactant (the reactant with the smaller number of moles).

Effect of Added H^+ or OH^- on Buffer Systems

The pH of a buffer does change slightly on addition of moderate amounts of a strong acid or strong base (Figure 14.4). Addition of H^+ ions converts an equal amount of weak base B^- to its conjugate acid HB:

$$H^+(aq) + B^-(aq) \longrightarrow HB(aq)$$

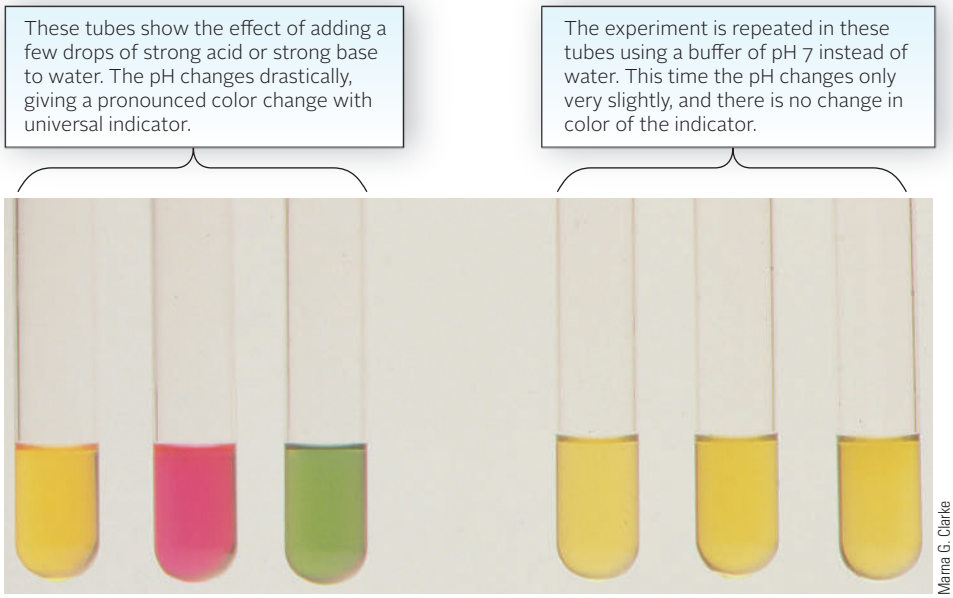
By the same token, addition of OH^- ions converts an equal amount of weak acid to its conjugate base B^-:

$$HB(aq) + OH^-(aq) \longrightarrow B^-(aq) + H_2O$$

In either case, the ratio n_{HB}/n_{B^-} changes. This in turn changes the H^+ ion concentration and pH of the buffer. The effect ordinarily is small, as Example 14.4 illustrates.

A buffer "works" because it contains species (HB and B^-) that react with both H^+ and OH^-.

Figure 14.4 Comparison of pH changes in water and a buffer solution.



EXAMPLE 14.4

Consider the buffer described in Example 14.1, where $n_{HLac} = n_{Lac^-} = 1.00$ mol (K_a HLac $= 1.4 \times 10^{-4}$). You will recall that in this buffer the pH is 3.85.

a Calculate the pH after addition of 0.08 mol of HCl.

ANALYSIS

Information given:	mol HLac (1.00); mol Lac^- (1.00); mol HCl = mol H^+ (0.08) pH of the buffer (3.85) K_a for HLac (1.4×10^{-4})
Asked for:	pH of the buffer after the addition of acid

STRATEGY

1. Write the reaction between the strong acid H^+ and the conjugate base, Lac^-.
2. Adding H^+ uses up the conjugate base in a 1:1 stoichiometric ratio.
   mol Lac^- after addition = mol Lac^- − mol H^+
3. Adding H^+ produces more weak acid in a 1:1 stoichiometric ratio.
   mol HLac after addition = mol HLac + mol H^+
4. Substitute into Equation 14.2 to find $[H^+]$ and pH.

SOLUTION

1. Reaction	$Lac^-(aq) + H^+(aq) \longrightarrow HLac\ (aq)$
2. mol Lac^- after H^+ addition	mol $Lac^- = 1.00 - 0.08 = 0.92$ mol
3. mol HLac after H^+ addition	mol HLac $= 1.00 + 0.08 = 1.08$ mol
4. $[H^+]$; pH	$[H^+] = 1.4 \times 10^{-4} \times \frac{1.08}{0.92} = 1.6 \times 10^{-4}$ $pH = -\log_{10}(1.6 \times 10^{-4}) = 3.80$

b Calculate the pH after addition of 0.08 mol of NaOH.

ANALYSIS

Information given:	mol HLac (1.00); mol Lac^- (1.00); mol NaOH = mol OH^- (0.08) pH of the buffer (3.85) K_a for HLac (1.4×10^{-4})
Asked for:	pH of the buffer after the addition of strong base

STRATEGY

1. Write the reaction between the strong base OH^- and the weak acid, HLac.
2. Adding OH^- uses up the weak acid in a 1:1 stoichiometric ratio.
   mol HLac after addition = mol HLac − mol OH^-
3. Adding OH^- produces more conjugate base in a 1:1 stoichiometric ratio.
   mol Lac^- after addition = mol Lac^- + mol OH^-
4. Substitute into Equation 14.2 to find $[H^+]$ and pH.

SOLUTION

1. Reaction	$HLac(aq) + OH^-(aq) \longrightarrow Lac^-(aq) + H_2O$
2. mol HLac after OH^- addition	mol HLac $= 1.00 - 0.08 = 0.92$ mol
3. mol Lac^- after OH^- addition	mol $Lac^- = 1.00 + 0.08 = 1.08$ mol

continued

4. $[H^+]$; pH	$[H^+] = 1.4 \times 10^{-4} \times \frac{0.92}{1.08} = 1.2 \times 10^{-4}$ $pH = -\log_{10}(1.2 \times 10^{-4}) = 3.92$

END POINTS

1. Adding a strong acid to a buffer
- increases the number of moles of the weak acid.
- decreases the number of moles of the conjugate base.
- decreases the pH by a small amount. (In this case: 3.85 ⟶ 3.80)

2. Adding a strong base to a buffer
- increases the number of moles of the conjugate base.
- decreases the number of moles of the weak acid.
- increases the pH by a small amount. (In this case: 3.85 ⟶ 3.92)

3. One cannot add an unlimited amount of strong acid or base. When the weak acid or its conjugate base becomes the limiting reactant, then the buffer is destroyed and only H^+ and the weak acid are present (if H^+ is added) or OH^- and the weak base are left (if OH^- is added).

Example 14.4 shows, among other things, how effectively a buffer "soaks up" H^+ or OH^- ions. That can be important. Suppose you are carrying out a reaction whose rate is first-order in H^+. If the pH increases from 5 to 7, perhaps by the absorption of traces of ammonia from the air, the rate will decrease by a factor of 100. A reaction that should have been complete in three hours will still be going on when you come back ten days later. Small wonder that chemists frequently work with buffered solutions to avoid disasters of that type.

Buffer Capacity and Buffer Range

A buffer has a limited capacity to react with H^+ or OH^- ions without undergoing a drastic change in pH. To see why this is the case, consider Figure 14.5, which applies to the H_2CO_3–HCO_3^- buffer system ($K_a\,H_2CO_3 = 4 \times 10^{-7}$).

To interpret Figure 14.5, it is important to realize that the **buffer capacity** *to absorb added OH^- or H^+ ions is inversely related to the slope of the curve.* Notice that

- at point A where

$$pH = pK_a\,H_2CO_3 = 6.4$$

the slope is very small and the buffer has its maximum capacity to absorb OH^- or H^+ ions without a drastic change in pH.
- at point B, where

$$pH = 7.4; \qquad [HCO_3^-] = 10 \times [H_2CO_3]$$

the slope is very large. Very few H_2CO_3 molecules are left, so the buffer has lost its capacity to absorb more OH^- ions.
- at point C, where

$$pH = 5.4; \qquad [H_2CO_3] = 10 \times [HCO_3^-]$$

the pH is dropping off precipitously. Very few HCO_3^- ions are left, so the buffer has lost its capacity to absorb added H^+ ions.

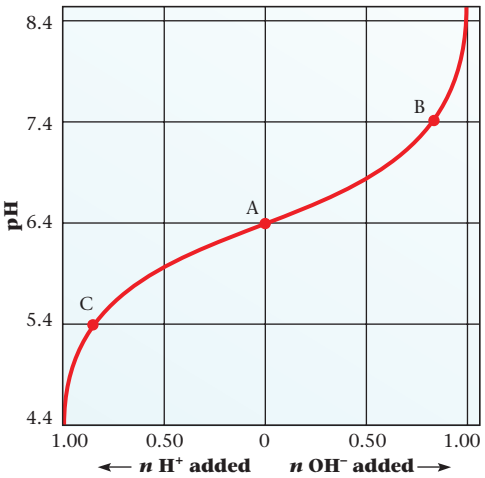


Figure 14.5 Variation of pH of an H_2CO_3–HCO_3^- buffer with addition of strong acid or base. Starting with one mole of both H_2CO_3 and HCO_3^- at point A, the curve to the left shows how pH decreases when H^+ is added. The curve to the right shows how pH increases as OH^- is added.

Blood is buffered at pH 7.4, in part by the H_2CO_3–HCO_3^- system. As you can see from Figure 14.5 and the above discussion, that puts us at point B on the curve. We conclude that blood has very little capacity to absorb OH^- ions (moving to the right of point B) but a large capacity to absorb H^+ ions (moving to the left of point B). This is indeed fortunate because life processes produce many more H^+ ions than OH^- ions.

The *buffer range* is the pH range over which the buffer is effective. It is related to the ratio of concentrations of the weak acid and its conjugate base. The further the ratio is from 1, the less effective the buffering action. Ideally, the acid/base ratio should be between 0.1 and 10. Since $\log_{10} 10 = 1$ and $\log_{10} 0.1 = -1$, buffers are most useful within ± 1 pH unit of the pK_a of the weak acid.

EXAMPLE 14.5 CONCEPTUAL

Consider the buffer system shown in the box below. The symbol ● represents a mole of the weak acid; the symbol ● represents a mole of its conjugate base. The pH of the buffer is 6.0. What is K_a of the weak acid?

ANALYSIS

Information given:	mol HB (3); mol B^- (2) pH (6.0)
Asked for:	K_a for HB

STRATEGY

1. Find $[H^+]$.
2. Substitute into Equation 14.2.

SOLUTION

1. $[H^+]$ $\quad 6.0 = -\log_{10}[H^+] \longrightarrow [H^+] = 1 \times 10^{-6}\ M$
2. K_a $\quad 1.0 \times 10^{-6} = K_a \times \frac{3}{2} \longrightarrow K_a = 7 \times 10^{-7}$

14-2 Acid-Base Indicators

As pointed out in Chapter 4, an *acid-base indicator* is useful in determining the **equivalence point** of an acid-base titration. This is the point at which reaction is complete; equivalent quantities of acid and base have reacted. If the indicator is chosen properly, the point at which it changes color (its **end point**) coincides with the equivalence point. To understand how and why an indicator changes color, we need to understand the equilibrium principle involved.

It's called an end point because that's when you stop the titration.

An acid-base indicator (Figure 14.6) is derived from a weak acid HIn:

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq) \qquad K_a = \frac{[H^+] \times [In^-]}{[HIn]}$$

where the weak acid HIn and its conjugate base In^- have different colors (Figure 14.7). The color that you see when a drop of indicator solution is added in an acid-base titration depends on the ratio

$$\frac{[HIn]}{[In^-]}$$

Three cases can be distinguished:

1. If $\frac{[HIn]}{[In^-]} \geq 10$
   the principal species is HIn; you see the "acid" color, that of the HIn molecule.

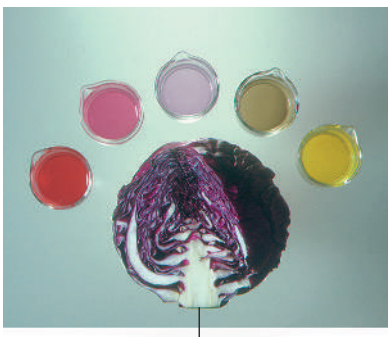


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Figure 14.6 Red cabbage juice, a natural acid-base indicator. The picture shows (*left to right*) its colors at pH 1, 4, 7, 10, and 13.

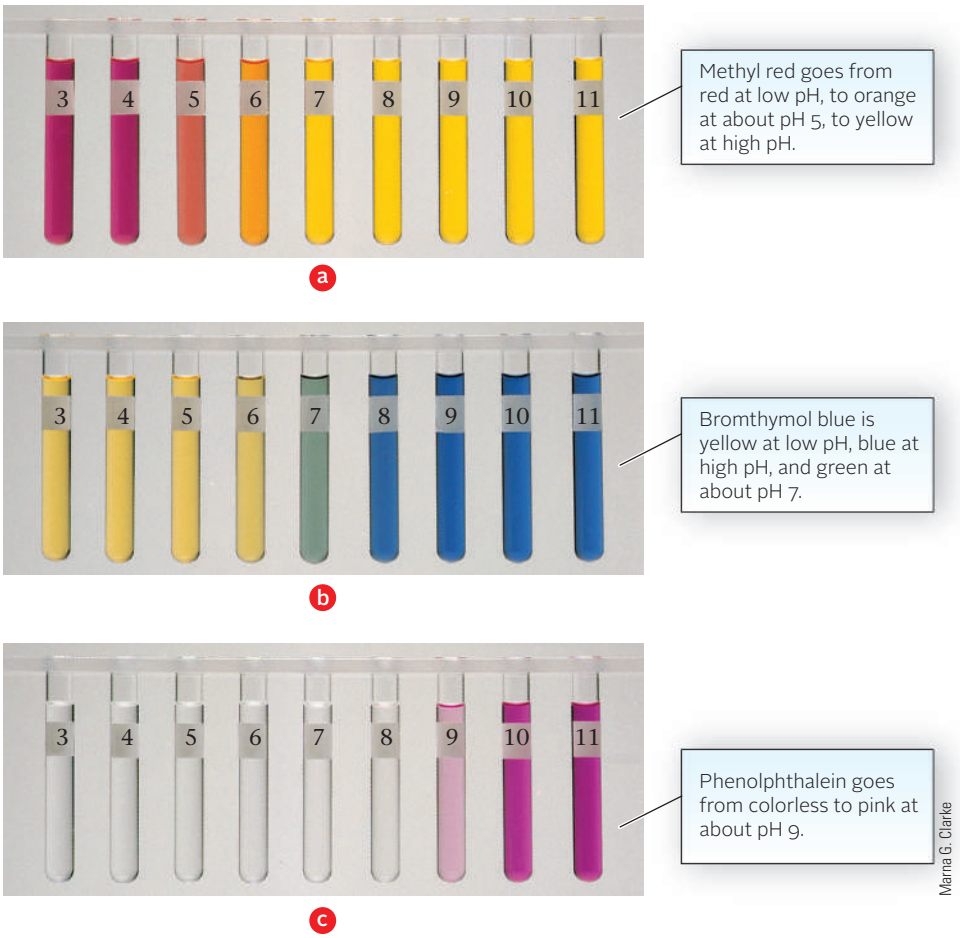

Figure 14.7 **Acid-base indicators.**

2. If $\frac{[HIn]}{[In^-]} \leq 0.1$
   the principal species is In^-; you see the "base" color, that of the In^- ion.

For litmus, HIn is red; In^- is blue.

3. If $\frac{[HIn]}{[In^-]} \approx 1$
   the color observed is intermediate between those of the two species, HIn and In^-.

The expression for the ionization of the indicator molecule, HIn,

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

can be rearranged to give

$$\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a} \qquad (14.3)$$

From this expression, it follows that the ratio $[HIn]/[In^-]$ and hence the color of an indicator depends on two factors.

1. ***[H⁺] or the pH of the solution.*** At high $[H^+]$ (low pH), you see the color of the HIn molecule; at low $[H^+]$ (high pH), the color of the In^- ion dominates.
2. ***K_a of the indicator.*** Because K_a varies from one indicator to another, different indicators change colors at different pHs. A color change occurs when

$$[H^+] \approx K_a \qquad pH \approx pK_a$$

Because only a drop or two of indicator is used, it does not affect the pH of the solution.

Table 14.2 Colors and End Points of Indicators

	Color [HIn]	Color [In^-]	K_a	pH at End Point
Methyl red	Red	Yellow	1×10^{-5}	5
Bromthymol blue	Yellow	Blue	1×10^{-7}	7
Phenolphthalein	Colorless	Pink	1×10^{-9}	9

Table 14.2 shows the characteristics of three indicators: methyl red, bromthymol blue, and phenolphthalein. These indicators change colors at pH 5, 7, and 9, respectively.

What is the color of phenolphthalein at pH 11? pH 7?

In practice it is usually possible to detect an indicator color change over a range of about two pH units. Consider, for example, what happens with bromthymol blue as the pH increases:

- below pH 6 (e.g., . . . 3, 4, 5) the color is pure yellow.
- between pH 6 and 7, the indicator starts to take on a greenish tinge; we might describe its color as yellow-green.
- at pH 7, the color is a 50–50 mixture of yellow and blue so it looks green.
- between pH 7 and 8, a blue color becomes visible.
- above pH 8 (or 9, 10, 11, . . .) the color is pure blue.

EXAMPLE 14.6

Consider bromthymol blue ($K_a = 1 \times 10^{-7}$). At pH 6.5,

(a) calculate the ratio $[In^-]/[HIn]$.

(b) what is the color of the indicator at this point?

ANALYSIS

Information given:	K_a for bromthymol blue (1×10^{-7}) pH (6.5)
Information implied:	color of bromthymol blue at different pH values
Asked for:	(a) $[In^-]/[HIn]$ (b) color of bromthymol blue at pH 6.5

STRATEGY

(a) Convert pH to $[H^+]$ and substitute into Equation 14.1 to find $[In^-]/[HIn]$.

(b) Find the color of bromthymol blue at pH 6.5 by using the information in the above discussion of the colors for bromthymol blue at different pH values.

SOLUTION

(a) $[In^-]/[HIn]$

$$6.5 = -\log_{10}[H^+] \longrightarrow [H^+] = 3 \times 10^{-7}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_a}{[H^+]} = \frac{1 \times 10^{-7}}{3 \times 10^{-7}} = \frac{1}{3}$$

(b) bromthymol blue color

At pH 7, bromthymol blue is green.

Below pH 6, bromthymol blue is yellow.

Since 6.5 is halfway between 6 and 7, bromthymol blue at pH 6.5 is yellow-green.

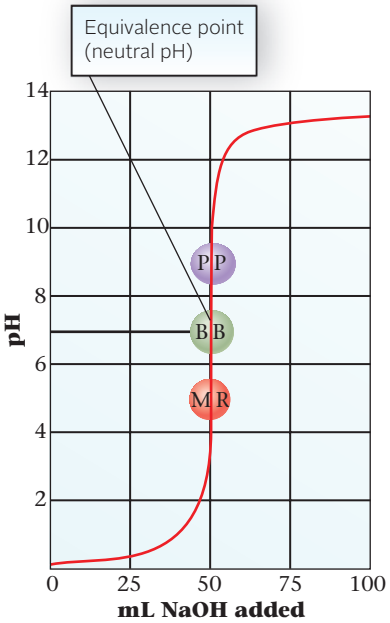

Figure 14.8 A strong acid–strong base titration. The curve represents the titration of 50.00 mL of 1.000 *M* HCl with 1.000 *M* NaOH. The solution at the equivalence point is neutral (pH = 7). The pH rises so rapidly near the equivalence point that any of the three indicators, methyl red (MR, end point pH = 5), bromthymol blue (BB, end point pH = 7), or phenolphthalein (PP, end point pH = 9) can be used.

14-3 Acid-Base Titrations

The discussion of **acid-base titrations** in Chapter 4 focused on stoichiometry. Here, the emphasis is on the equilibrium principles that apply to the acid-base reactions involved. It is convenient to distinguish between titrations involving

- a strong acid (e.g., HCl) and a strong base (e.g., NaOH, $Ba(OH)_2$).
- a weak acid (e.g., $HC_2H_3O_2$) and a strong base (e.g., NaOH).
- a strong acid (e.g., HCl) and a weak base (e.g., NH_3).

Strong Acid–Strong Base

As pointed out in Chapter 13, strong acids ionize completely in water to form H_3O^+ ions; strong bases dissolve in water to form OH^- ions. The neutralization reaction that takes place when *any* strong acid reacts with *any* strong base can be represented by a net ionic equation of the Brønsted-Lowry type:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O$$

or, more simply, substituting H^+ ions for H_3O^+ ions, as

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The equation just written is the reverse of that for the ionization of water, so the equilibrium constant can be calculated by using the reciprocal rule (Chapter 12).

$$K = 1/K_w = 1/(1.0 \times 10^{-14}) = 1.0 \times 10^{14}$$

The enormous value of K means that for all practical purposes this reaction goes to completion, consuming the limiting reactant, H^+ or OH^-.

Consider now what happens when HCl, a typical strong acid, is titrated with NaOH. Figure 14.8 shows how the pH changes during the titration. Two features of this curve are of particular importance:

1. At the equivalence point, when all the HCl has been neutralized by NaOH, a solution of NaCl, a neutral salt, is present. The pH at the equivalence point is 7.
2. Near the equivalence point, the pH rises very rapidly. Indeed, the pH may increase by as much as six units (from 4 to 10) when half a drop, ≈ 0.02 mL, of NaOH is added (Example 14.7).

EXAMPLE 14.7

When 50.00 mL of 1.000 *M* HCl is titrated with 0.7450 *M* NaOH (Figure 14.9), the pH increases.

a How many milliliters of NaOH are required to reach the equivalence point and a pH of 7.00?

ANALYSIS

Information given:	HCl: V (50.00 mL); M (1.000) NaOH: M (0.7450)
Information implied:	acid-base reaction
Asked for:	volume of NaOH required to reach the equivalence point

STRATEGY

1. Recall the stoichiometry of acid-base reactions discussed in Chapter 4 and write the reaction.
2. Find mol HCl.
3. Follow the plan below to find the mol of NaOH and the volume of NaOH needed.

$$\text{mol HCl} \xrightarrow[\text{ratio}]{\text{atomic}} \text{mol } H^+ \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{mol } OH^- \xrightarrow[\text{ratio}]{\text{atomic}} \text{mol NaOH} \xrightarrow{M} V \text{ NaOH}$$

continued

SOLUTION

1. Reaction	$H^+(aq) + OH^-(aq) \longrightarrow H_2O$
2. mol HCl	mol HCl $= V \times M = (0.05000\ \text{L})(1.000\ \text{mol/L}) = 0.05000$
3. mol NaOH	$0.05000\ \text{mol HCl} \times \frac{1\ \text{mol H}^+}{1\ \text{mol HCl}} \times \frac{1\ \text{mol OH}^-}{1\ \text{mol H}^+} \times \frac{1\ \text{mol NaOH}}{1\ \text{mol OH}^-}$ $= 0.05000\ \text{mol NaOH}$
Volume of NaOH	$V = \frac{0.05000\ \text{mol}}{0.7450\ \text{mol/L}} = 0.06711\ L$

b Find the pH when the volume of NaOH added is 0.02 mL less than the volume required to reach the equivalence point.

ANALYSIS

Information given:	HCl: V (0.05000 L); M (1.000) from part (a): mol H^+ (0.05000); V NaOH (67.11 mL) volume NaOH in the titration (67.11 − 0.02 = 67.09 mL)
Asked for:	pH of the solution after NaOH is added

STRATEGY

1. Find mol OH^-.

2. Fill in the following stoichiometric table.

	H^+	OH^-
Mol before reaction		
Change		
Mol after reaction		
Volume		

This table almost looks like the equilibrium table in Chapter 12.

3. Find [excess reactant]

$$[\text{excess reactant}] = \frac{\text{mol excess reactant}}{(\text{volume } H^+) + (\text{volume } OH^-)}$$

4. Find pH

SOLUTION

1. mol OH^-: $(0.06709\ \text{L})(0.7450\ \text{mol/L}) = 0.04998\ \text{mol}$

2. Table

	H^+	OH^-
Mol before reaction	0.05000	0.04998
Change	−0.04998	−0.04998
Mol after reaction	2×10^{-5}	0
Volume	50.00 mL	67.09 mL

3. [Excess reactant] = $[H^+]$: $[H^+] = \frac{2 \times 10^{-5}}{(0.05000 + 0.06709)\ \text{L}} = 2 \times 10^{-4}\ M$

4. pH: $\text{pH} = -\log_{10}(2 \times 10^{-4}) = 3.7$

continued

c Find the pH when the volume of NaOH added is 0.02 mL more than the volume required to reach the equivalence point.

ANALYSIS

Information given:	HCl: V (0.05000 L); M (1.000) from part (a): mol H^+ (0.05000); V NaOH (67.11 mL) volume NaOH in the titration (67.11 + 0.02 = 67.13 mL)
Asked for:	pH of the solution after NaOH is added

STRATEGY

1. Find mol OH^-.
2. Fill in a stoichiometric table as in part (b).
3. Find [excess reactant] as in part (b).
4. Find pH.

SOLUTION

1. mol OH^-: (0.06713 L)(0.7450 mol/L) = 0.05001 mol
2. Table

	H^+	OH^-
Mol before reaction	0.05000	0.05001
Change	−0.05000	−0.05000
Mol after reaction	0	1×10^{-5}
Volume	50.00 mL	67.13 mL

3. [Excess reactant] = $[OH^-]$: $[OH^-] = \dfrac{1 \times 10^{-5}}{0.05000 + 0.06713\ \text{L}} = 9 \times 10^{-5}\ M$; $[H^+] = 1 \times 10^{-10}\ M$
4. pH: $\text{pH} = -\log_{10}(1 \times 10^{-10}) = 10.0$

END POINT

Note that half a drop before the end point (pH = 7) is reached, the pH is 3.8. When half a drop is added after the end point is reached, the end point changes from 7 to 10. This is predicted by Figure 14.8.

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Figure 14.9 Titrating a solution of HCl with NaOH using phenolphthalein as the indicator.

From Figure 14.8 and Example 14.7, we conclude that any indicator that changes color between pH 4 and 10 should be satisfactory for a strong acid–strong base titration. Bromthymol blue (BB: end point pH = 7) would work very well, but so would methyl red (MR: end point pH = 5) or phenolphthalein (PP: end point pH = 9).

Weak Acid–Strong Base

A typical weak acid–strong base titration is that of acetic acid with sodium hydroxide. The net ionic equation for the reaction is

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$$

Notice that this reaction is the reverse of the reaction of the weak base $C_2H_3O_2^-$ (the acetate ion) with water (Chapter 13). It follows from the reciprocal rule that for this reaction,

$$K = \frac{1}{(K_b\ C_2H_3O_2^-)} = \frac{1}{(5.6 \times 10^{-10})} = 1.8 \times 10^9$$

Here again, K is a very large number; the reaction of acetic acid with a strong base goes essentially to completion.

For an effective titration, the reaction must go to completion, which requires $K > 10^4$ (approximately).

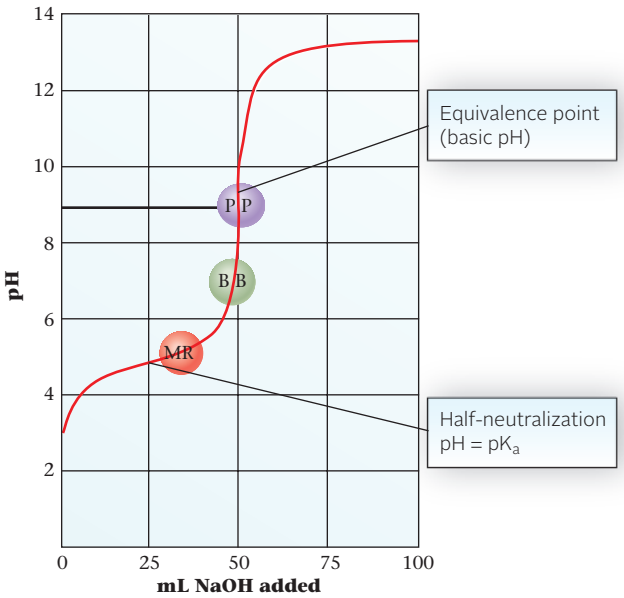


Figure 14.10 A weak acid–strong base titration. The curve represents the titration of 50.00 mL of 1.000 *M* acetic acid, $HC_2H_3O_2$, with 1.000 *M* NaOH. The solution at the equivalence point is basic (pH = 9.22). Phenolphthalein is a suitable indicator. Methyl red would change color much too early, when only about 33 mL of NaOH had been added. Bromthymol blue would change color slightly too quickly.

Figure 14.10 shows how the pH changes as fifty milliliters of one molar acetic acid is titrated with one molar sodium hydroxide. Notice that

- the pH starts off above 2; we are dealing with a weak acid, $HC_2H_3O_2$.
- there is a region, centered at the *halfway point* of the titration, where pH changes very slowly. The solution contains equal amounts of unreacted $HC_2H_3O_2$ and its conjugate base, $C_2H_3O_2^-$, formed by reaction with NaOH. As pointed out earlier, such a system acts as a buffer. Figure 14.11 shows how $[H^+] = K_a$ at half-neutralization.
- at the equivalence point, there is a solution of sodium acetate, $NaC_2H_3O_2$. The acetate ion is a weak base, so the pH at the equivalence point must be greater than 7.

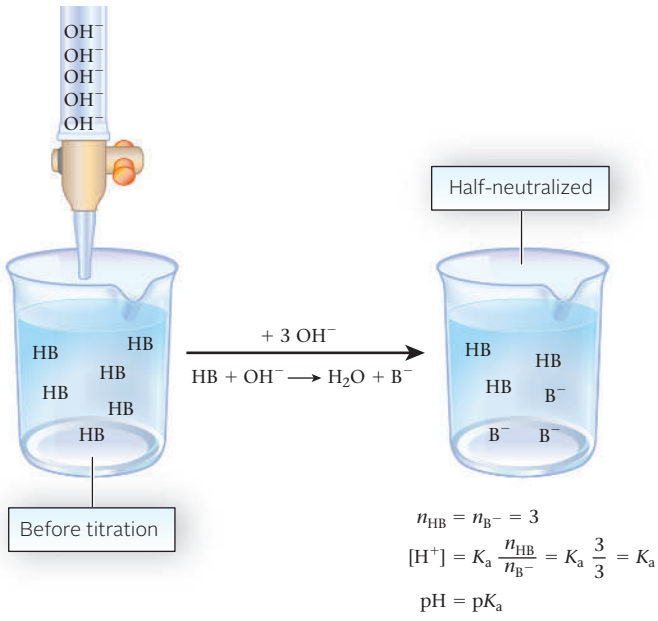


Figure 14.11 Schematic showing that $[H^+] = K_a$ at half-neutralization.

EXAMPLE 14.8

50.00 mL of 1.000 *M* acetic acid, $HC_2H_3O_2$, is titrated with 0.8000 *M* NaOH.

a Find the pH of the solution before any base is added.

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): *V* (0.05000 L), *M* (1.000) NaOH: *M* (0.8000)
Information implied:	K_a for HAc
Asked for:	pH before titration starts (no base added)

STRATEGY

1. This is simply determining the pH of a weak acid. Recall Example 13.7.
2. Let $x = [H^+] = [Ac^-]$ at equilibrium. HAc at equilibrium = $[HAc]_o - x$. Make the assumption that $x = [H^+] << [HAc]_o$.
3. Substitute into Equation 13.5, solve for x, and check the assumption.
4. Find pH.

SOLUTION

2. $x = [H^+]$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{1.000 - x} = \frac{x^2}{1.000} \longrightarrow x = 4.2 \times 10^{-3}\ M$$

3. Check assumption

$$\% \text{ ionization} = \frac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\% < 5\%$$

The assumption is valid.

4. pH

$$pH = -\log_{10}(4.2 \times 10^{-3}) = 2.38$$

b Find the pH of the solution when half the acetic acid has been neutralized.

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): *V* (0.05000 L), *M* (1.000) NaOH: *M* (0.8000)
Information implied:	K_a for HAc
Asked for:	pH at half-neutralization.

SOLUTION

1. $[H^+]$

At half-neutralization $[H^+] = K_a$; $[H^+] = 1.8 \times 10^{-5}$

2. pH

$$pH = -\log_{10}(1.8 \times 10^{-5}) = 4.74$$

c Find the pH of the solution at the equivalence point.

ANALYSIS

Information given:	$HC_2H_3O_2$ (HAc): *V* (0.05000 L), *M* (1.000); from part (a): mol HAc (0.05000 mol) NaOH: *M* (0.8000)
Information implied:	K_a for HAc and K_b for Ac^-
Asked for:	pH at the equivalence point

STRATEGY

1. Write the reaction for the titration.
2. Find the volume of NaOH required to reach the equivalence point.

   For the titration: mol HAc = mol OH^-

continued

3. At the equivalence point, all the acetic acid has been converted to acetate ions and mol Ac^- = mol HAc at the start. Find $[Ac^-]$.

$$[Ac^-] = \frac{\text{mol } Ac^-}{V_{HAc} + V_{OH^-}}$$

4. Find $[OH^-]$ by substituting into Equation 13.8.

5. Find $[H^+]$ and pH.

SOLUTION

1. Reaction

$$HAc(aq) + OH^-(aq) \longrightarrow Ac^-(aq) + H_2O$$

2. Volume NaOH required

$$\text{mol HAc} = 0.05000 \text{ mol} = \text{mol } OH^- = \text{mol NaOH}$$

$$\text{volume} = \frac{0.05000 \text{ mol}}{0.800 \text{ mol/L}} = 0.0625 \text{ L}$$

3. $[Ac^-]$

$$\text{mol } Ac^- = \text{mol HAc} = 0.05000 \text{ mol}$$

$$[Ac^-] = \frac{0.05000 \text{ mol}}{(0.05000 + 0.06250) \text{ L}} = 0.4444\ M$$

4. $[OH^-]$

$$K_b = \frac{[OH^-][HAc^-]}{[Ac^-]} \longrightarrow 5.6 \times 10^{-10} = \frac{(x)(x)}{0.4444}$$

$$x = [OH^-] = 1.6 \times 10^{-5}\ M$$

5. $[H^+]$; pH

$$[H^+] = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-5}} = 6.2 \times 10^{-10}; \text{ pH} = 9.20$$

From Figure 14.10 and Example 14.8, it should be clear that the indicator used in this titration must change color at about pH 9. Phenolphthalein (end point pH = 9) is satisfactory. Methyl red (end point pH = 5) is not suitable. If we used methyl red, we would stop the titration much too early, when reaction is only about 65% complete. This situation is typical of *weak acid-strong base titrations.* ◂ For such a titration, we choose an indicator that *changes color above pH 7.*

ⓘ If either the acid or base is weak, pH changes relatively slowly near the end point.

Strong Acid–Weak Base

The reaction between solutions of hydrochloric acid and ammonia can be represented by the Brønsted-Lowry equation:

$$H_3O^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) + H_2O$$

Again, we simplify the equation by replacing H_3O^+ with H^+:

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

To find the equilibrium constant, note that this equation is the reverse of that for the acid dissociation of the NH_4^+ ion. Hence

$$K = \frac{1}{K_a NH_4^+} = \frac{1}{5.6 \times 10^{-10}} = 1.8 \times 10^9$$

Because K is so large, the reaction goes virtually to completion.

Figure 14.12 shows how pH changes when fifty milliliters of one molar NH_3 is titrated with one molar HCl. In many ways, this curve is the inverse of that shown in Figure 14.10 for the weak acid–strong base case. In particular,

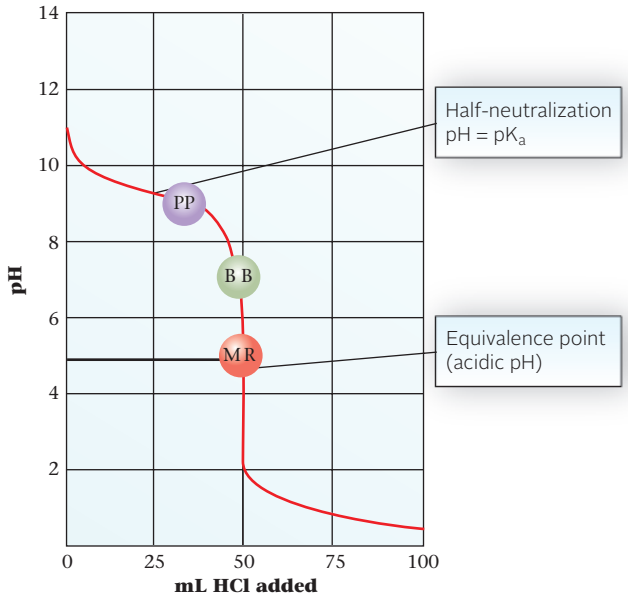


Figure 14.12 A strong acid–weak base titration. The curve represents the titration of 50.00 mL of 1.000 *M* ammonia, a weak base, with 1.000 *M* HCl. The solution at the equivalence point is acidic because of the NH_4^+ ion. Methyl red is a suitable indicator; phenolphthalein would change color much too early.

- the original pH is that of 1.000 *M* NH_3, a weak base ($K_b = 1.8 \times 10^{-5}$). As you would expect, it lies between 7 and 14:

$$[OH^-]^2 \approx K_b \times [NH_3]_o = (1.8 \times 10^{-5})(1.000)$$
$$[OH^-] = 4.2 \times 10^{-3}\ M;\ \text{pOH} = 2.38$$
$$\text{pH} = 14.00 - 2.38 = 11.62$$

- addition of 25 mL of HCl gives a buffer containing equal amounts of NH_3 and NH_4^+ ($K_a = 5.6 \times 10^{-10}$). Hence

$$\text{pH} = \text{p}K_a \text{ of } NH_4^+ = 9.25$$

- at the equivalence point, there is a 0.5000 *M* solution of NH_4^+, a weak acid. As you would expect, the pH is on the acid side.

As strong acid is added, the pH drops.

$$[H^+]^2 \approx (0.5000)(5.6 \times 10^{-10})$$
$$[H^+] = 1.7 \times 10^{-5}\ M$$
$$\text{pH} = 4.77$$

From Figure 14.12, it should be clear that the only suitable indicator listed is methyl red. The other two indicators would change color too early, before the equivalence point. In general, *for the titration of a weak base with a strong acid, the indicator should change color on the acid side of pH 7.*

Titration of Diprotic Acids

Recall from Chapter 13 that a diprotic acid is one with two ionizable hydrogen ions. The hydrogen ions come off the diprotic acid one at a time and each ionization has its own equilibrium constant.

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq) \quad K_{a1}$$
$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq) \quad K_{a2}$$

Because of this stepwise ionization, titration curves of diprotic acids have two equivalence points as shown in Figure 14.13. The first equivalence point in the titration curve represents the titration of the first H^+, and the second equivalence point represents the titration of the second proton.

Notice from Figure 14.13 that the volume of NaOH required to reach the second equivalence point is the same as that required to reach the first equivalence point. That is because the number of moles of H_2X yields HX^- in a 1:1 ratio.

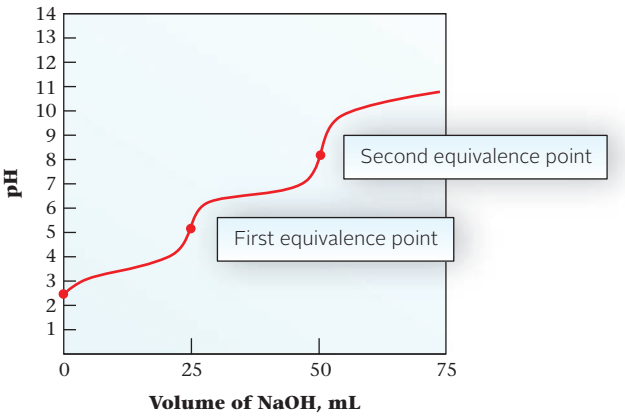


Figure 14.13 A titration curve for a diprotic acid. Two equivalence points are shown, each corresponding to the reaction of one H^+ ion.

Thus the titration to the second equivalence point requires the same number of moles to neutralize H_2X to HX^- as to neutralize HX^- to X^{2-}. This makes sense since the overall neutralization reaction for one mole of H_2X requires two moles of OH^-.

$$H_2X(aq) + 2OH^-(aq) \longrightarrow X^{2-}(aq) + 2H_2O$$

Table 14.3 Characteristics of Acid-Base Titrations

Example	Equation	K	Species at Equivalence Point	pH at Equivalence Point	Indicator*
Strong Acid–Strong Base					
		$K = 1/K_w$			
NaOH–HCl	$H^+(aq) + OH^-(aq) \longrightarrow H_2O$	1.0×10^{14}	Na^+, Cl^-	7.00	MR, BB, PP
$Ba(OH)_2$–HNO_3	$H^+(aq) + OH^-(aq) \longrightarrow H_2O$	1.0×10^{14}	Ba^{2+}, NO_3^-	7.00	MR, BB, PP
Weak Acid–Strong Base					
		$K = 1/K_b$			
$HC_2H_3O_2$–NaOH	$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$	1.8×10^9	Na^+, $C_2H_3O_2^-$	9.22†	PP
HF–KOH	$HF(aq) + OH^-(aq) \longrightarrow F^-(aq) + H_2O$	6.9×10^{10}	K^+, F^-	8.42†	PP
Strong Acid–Weak Base					
		$K = 1/K_a$			
NH_3–HCl	$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$	1.8×10^9	NH_4^+, Cl^-	4.78†	MR
ClO^-–HCl	$ClO^-(aq) + H^+(aq) \longrightarrow HClO(aq)$	3.6×10^7	HClO, Cl^-	3.93†	MR

*MR = methyl red (end point pH = 5); BB = bromthymol blue (end point pH = 7); PP = phenolphthalein (end point pH = 9).
†When 1 *M* acid is titrated with 1 *M* base.

Summary

Table 14.3 summarizes our discussion of acid-base titrations. Notice that for these three types of titrations,

- ***the equations (second column) that describe the reactions are quite different.*** Strong acids and bases are represented by H^+ and OH^- ions, respectively; weak acids and weak bases are represented by their chemical formulas.
- ***the equilibrium constants (K) for all these reactions are very large, indicating that the reactions go essentially to completion.***
- ***the pH at the equivalence point is determined by which species are present.*** When only "spectator ions" are present, as in a strong acid–strong base titration,

H^+ and OH^- ions are the reacting species in strong acids and strong bases, respectively.

the pH at the equivalence point is 7. Basic anions (F^-, $C_2H_3O_2^-$), formed during a weak acid–strong base titration, make the pH at the equivalence point greater than 7. Conversely, acidic species (NH_4^+, HClO) formed during a strong acid–weak base titration make the pH at the equivalence point less than 7.

EXAMPLE 14.9

Consider the titration of formic acid, $HCHO_2$, with barium hydroxide.

(a) Write a balanced net ionic equation for the reaction.

(b) Calculate K for the reaction.

(c) Is the solution at the equivalence point acidic, basic, or neutral?

(d) What would be an appropriate indicator for the titration?

SOLUTION

(a) Reaction

$$HCH_2O(aq) + OH^-(aq) \longrightarrow CHO_2^-(aq) + H_2O$$

(b) K

$$CHO_2^-(aq) + H_2O \rightleftharpoons HCH_2O(aq) + OH^-(aq) \quad K_b$$

$$K = 1/K_b = 1/5.3 \times 10^{-11} = 1.9 \times 10^{10}$$

(c) Acidic, basic or neutral?

basic, due to the presence of CHO_2^-

(d) Indicator

phenolphthalein

CHEMISTRY **BEYOND** THE CLASSROOM

Acid Rain

Natural rainfall has a pH of about 5.5. It is slightly acidic because of dissolved carbon dioxide, which reacts with water to form the weak acid H_2CO_3. In contrast, the average pH of rainfall in the eastern United States and southeastern Canada is about 4.4, corresponding to an H^+ ion concentration more than ten times the normal value. In an extreme case, rain with a pH of 1.5 was recorded in Wheeling, West Virginia (distilled vinegar has a pH of 2.4).

Acid rain results from the presence of two strong acids in polluted air: H_2SO_4 and HNO_3. Nitric acid comes largely from a three-step process. The first step involves the formation of NO from the elements by high-temperature combustion, as in an automobile engine. This is then oxidized to NO_2, which in turn undergoes the following reaction:

$$2NO_2(g) + H_2O \longrightarrow HNO_3(aq) + HNO_2(aq)$$

The principal source of sulfur dioxide, the precursor of sulfuric acid, is high-sulfur coal. Coal used in power plants can contain up to 4% sulfur, mostly in the form of minerals such as pyrite, FeS_2. Combustion forms sulfur dioxide:

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Sulfur dioxide formed by reactions such as this is converted to H_2SO_4 in the air by a two-step process:

$$(1)\ SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

$$(2)\ SO_3(g) + H_2O \longrightarrow H_2SO_4(aq)$$

The sulfuric acid forms as tiny droplets high in the atmosphere. These may be carried by prevailing winds as far as 1500 km. The acid rain that falls in the Adirondacks of New York (where up to 40% of the lakes are acidic) comes from sulfur dioxide produced by power plants in Ohio and Illinois.

The effects of acid rain are particularly severe in areas where the bedrock is granite or other materials incapable of neutralizing H^+ ions. As the concentration of acid builds up in a lake, aquatic life, from algae to brook trout, dies. The end product is a crystal-clear, totally sterile lake.

Acid rain adversely affects trees as well (Figure A). It appears that the damage is largely due to the leaching of

Figure A Trees damaged by acid rain in the Great Smoky Mountains.

metal cations from the soil. In particular, H^+ ions in acid rain can react with insoluble aluminum compounds in the soil, bringing Al^{3+} ions into solution. The following reaction is typical:

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O$$

Al^{3+} ions in solution can have a direct toxic effect on the roots of trees. Perhaps more important, Al^{3+} can replace Ca^{2+}, an ion that is essential to the growth of all plants.

Strong acids in the atmosphere can also attack building materials such as limestone or marble (calcium carbonate):

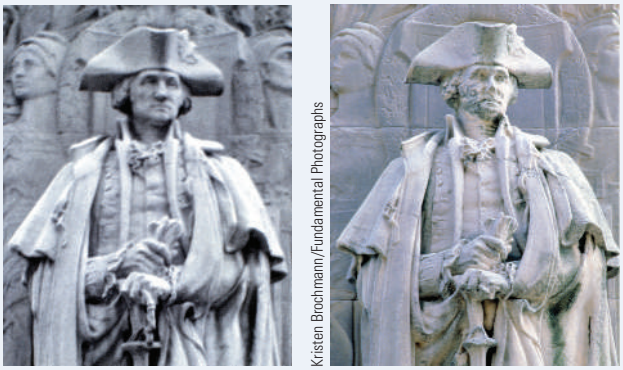
$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

The relatively soluble calcium compounds formed this way [$CaSO_4$, $Ca(NO_3)_2$] are gradually washed away (Figure B). This process is responsible for the deterioration of the Greek ruins on the Acropolis in Athens. These structures suffered more damage in the twentieth century than in the preceding 2000 years.

Sulfur dioxide emissions from power plants can be reduced by spraying a water solution of calcium hydroxide directly into the smokestack. This "scrubbing" operation brings about the reaction

$$Ca^{2+}(aq) + 2OH^-(aq) + SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CaSO_4(s) + H_2O$$

The good news is that processes such as this have reduced SO_2 emissions by 40% over the past 30 years. The bad news is that NO emissions have slowly but steadily increased.


NYC Parks Photo Archive/Fundamental Photographs

Kristen Brochmann/Fundamental Photographs

Figure B Effect of acid rain on a marble statue of George Washington in New York City. The photograph on the left was taken in the 1930s; the one on the right was taken in the 1990s.

Key Concepts

1. Calculate the pH of a buffer as originally prepared. **(Example 14.1; Problems 9–14)**
2. Choose a buffer to get a specified pH. **(Example 14.2; Problems 23–26)**
3. Determine whether a combination of a strong acid/base and its salt is a buffer. **(Example 14.3; Problems 19–22)**
4. Calculate the pH of a buffer after addition of H^+ or OH^- ions. **(Example 14.4; Problems 29–36)**
5. Determine the color of an indicator at a given pH. **(Example 14.6; Problems 39–40)**
6. Calculate the pH during an acid-base titration. **(Examples 14.7, 14.8; Problems 41–52)**
7. Choose the proper indicator for an acid-base titration. **(Example 14.9; Problems 37–38)**
8. Calculate K for an acid-base reaction. **(Example 14.9; Problems 5–8)**

Key Equations

Buffer $$[H^+] = K_a \times \frac{[HB]}{[B^-]} = K_a \times \frac{n_{HB}}{n_{B^-}}$$

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

Key Terms

acid-base titrations
buffer
buffer capacity
end point
equivalence point

Summary Problem

Consider formic acid, $HCHO_2$ ($K_a = 1.9 \times 10^{-4}$), the agent responsible for the sting in ant bites. Its conjugate base is CHO_2^- ($K_b = 5.3 \times 10^{-11}$).

(a) Write net ionic equations and calculate K for the reactions in aqueous solutions between the following:

1. $HCHO_2$ and NaOH
2. CHO_2^- and HCl
3. $HCHO_2$ and NaCN ($K_b = 1.7 \times 10^{-5}$)

(b) A buffer is prepared by dissolving 25.0 g of sodium formate, $NaCHO_2$, in 1.30 L of 0.660 M $HCHO_2$ without a volume change.

1. Calculate the pH of the buffer.
2. Calculate the pH of the buffer after 0.100 mol of HNO_3 is added.
3. Calculate the pH of the buffer after 10.00 g of KOH are added.
4. Calculate the pH of the buffer after 75.0 mL of 0.517 M HNO_3 are added.
5. What is the buffer capacity?

(c) Thirty-five milliliters of 0.739 M $HCHO_2$ is titrated with 0.431 M KOH.

1. What is the pH of the $HCHO_2$ solution before titration?
2. How many milliliters of KOH are required to reach the equivalence point?
3. What is the pH of the solution halfway to neutralization?
4. What is the pH of the solution at the equivalence point?

Answers

(a) **1.** $HCHO_2(aq) + OH^-(aq) \rightleftharpoons H_2O + CHO_2^-(aq)$ $K = 1.9 \times 10^{10}$

2. $CHO_2^-(aq) + H^+(aq) \rightleftharpoons HCHO_2(aq)$ $K = 5.3 \times 10^3$

3. $HCHO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + CHO_2^-(aq)$ $K = 3.2 \times 10^5$

(b) **1.** 3.34
2. 3.16
3. 3.63
4. 3.29
5. The buffer can theoretically absorb a maximum of 0.368 mol of H^+ and 0.858 mol of OH^-.

(c) **1.** 1.93
2. 60.0 mL
3. 3.72
4. 8.58

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

Equilibrium constants required to solve these problems can be found in the tables in Chapter 13 or in Appendix 1.

14-1 Buffers

Acid-Base Reactions

1. Write a net ionic equation for the reaction between aqueous solutions of
(a) ammonia and hydrofluoric acid.
(b) perchloric acid and rubidium hydroxide.
(c) sodium sulfite and hydriodic acid.
(d) nitric acid and calcium hydroxide.

2. Write a net ionic equation for the reaction between aqueous solutions of
(a) sodium acetate ($NaC_2H_3O_2$) and nitric acid.
(b) hydrobromic acid and strontium hydroxide.
(c) hypochlorous acid and sodium cyanide.
(d) sodium hydroxide and nitrous acid.

3. Write a balanced net ionic equation for the reaction of each of the following aqueous solutions with H^+ ions.
(a) sodium sulfite
(b) lithium hydroxide
(c) potassium benzoate ($KC_7H_5O_2$)

4. Write a balanced net ionic equation for the reaction between the following aqueous solutions and OH^- ions.
(a) $Fe(H_2O)_6^{3+}$
(b) sodium hydrogen carbonate
(c) ammonium chloride

5. Calculate K for the reactions in Question 1.
6. Calculate K for the reactions in Question 2.
7. Calculate K for the reactions in Question 3.
8. Calculate K for the reactions in Question 4.

Buffers

9. Calculate $[H^+]$ and pH in a solution in which lactic acid, $HC_3H_5O_3$, is 0.250 M and the lactate ion, $C_3H_5O_3^-$, is
(a) 0.250 M (b) 0.125 M
(c) 0.0800 M (d) 0.0500 M

10. Calculate $[OH^-]$ and pH in a solution in which the hydrogen sulfite ion, HSO_3^-, is 0.429 *M* and the sulfite ion is
(**a**) 0.0249 *M* (**b**) 0.247 *M*
(**c**) 0.504 *M* (**d**) 0.811 *M*
(**e**) 1.223 *M*

11. A buffer is prepared by dissolving 0.0250 mol of sodium nitrite, $NaNO_2$, in 250.0 mL of 0.0410 *M* nitrous acid, HNO_2. Assume no volume change after HNO_2 is dissolved. Calculate the pH of this buffer.

12. A buffer is prepared by dissolving 0.062 mol of sodium fluoride in 127 mL of 0.0399 *M* hydrofluoric acid. Assume no volume change after NaF is added. Calculate the pH of this buffer.

13. A buffer solution is prepared by adding 15.00 g of sodium acetate ($NaC_2H_3O_2$) and 12.50 g of acetic acid to enough water to make 500 mL (three significant figures) of solution.
(**a**) What is the pH of the buffer?
(**b**) The buffer is diluted by adding enough water to make 1.50 L of solution. What is the pH of the diluted buffer?

14. A buffer solution is prepared by adding 5.50 g of ammonium chloride and 0.0188 mol of ammonia to enough water to make 155 mL of solution.
(**a**) What is the pH of the buffer?
(**b**) If enough water is added to double the volume, what is the pH of the solution?

15. A solution with a pH of 9.22 is prepared by adding water to 0.413 mol of KX to make 2.00 L of solution. What is the pH of the solution after 0.368 mol of HX is added?

16. An aqueous solution of 0.057 *M* weak acid, HX, has a pH of 4.65. What is the pH of the solution if 0.018 mol of KX is dissolved in one liter of the weak acid?

17. Which of the following would form a buffer if added to 250.0 mL of 0.150 *M* SnF_2?
(**a**) 0.100 mol of HCl (**b**) 0.060 mol of HCl
(**c**) 0.040 mol of HCl (**d**) 0.040 mol of NaOH
(**e**) 0.040 mol of HF

18. Which of the following would form a buffer if added to 295 mL of 0.380 *M* HCl?
(**a**) 0.100 mol of NH_4Cl (**b**) 0.033 mol of KF
(**c**) 0.167 mol of $Sr(OH)_2$ (**d**) 0.279 mol of KNO_2
(**e**) 0.112 mol of KClO

19. Calculate the pH of a solution prepared by mixing 2.50 g of hypobromous acid (HOBr) and 0.750 g of KOH in water. (K_a HOBr $= 2.5 \times 10^{-9}$).

20. Calculate the pH of a solution prepared by mixing 20.00 mL of aniline, $C_6H_5NH_2$ ($d = 1.022$ g/mL), with 35.0 mL of 1.67 *M* HCl. K_b for aniline is 4.3×10^{-10}. (Assume volumes are additive.)

21. Calculate the pH of a solution prepared by mixing 49.0 mL of butyric acid, $HC_4H_7O_2$, with 6.15 g of KOH in water. The following data about butyric acid may be helpful:

$$\text{density} = 0.9595 \text{ g/mL}; K_a = 1.54 \times 10^{-5}$$

22. Calculate the pH of a solution prepared by mixing 100.0 mL of 1.20 *M* ethanolamine, $C_2H_5ONH_2$, with 50.0 mL of 1.0 *M* HCl. K_a for $C_2H_5ONH_3^+$ is 3.6×10^{-10}.

23. Consider the weak acids in Table 13.2. Which acid-base pair would be best for a buffer at a pH of
(**a**) 3.0 (**b**) 6.5 (**c**) 12.0

24. Follow the instructions of Question 23 for a pH of
(**a**) 4.5 (**b**) 9.2 (**c**) 11.0

25. A sodium hydrogen carbonate-sodium carbonate buffer is to be prepared with a pH of 9.40.
(**a**) What must the $[HCO_3^-]/[CO_3^{2-}]$ ratio be?
(**b**) How many moles of sodium hydrogen carbonate must be added to a liter of 0.225 *M* Na_2CO_3 to give this pH?
(**c**) How many grams of sodium carbonate must be added to 475 mL of 0.336 *M* $NaHCO_3$ to give this pH? (Assume no volume change.)
(**d**) What volume of 0.200 *M* $NaHCO_3$ must be added to 735 mL of a 0.139 *M* solution of Na_2CO_3 to give this pH? (Assume that volumes are additive.)

26. You want to make a buffer with a pH of 10.00 from NH_4^+/NH_3.
(**a**) What must the $[NH_4^+]/[NH_3]$ ratio be?
(**b**) How many moles of NH_4Cl must be added to 465 mL of an aqueous solution of 1.24 *M* NH_3 to give this pH?
(**c**) How many milliliters of 0.236 *M* NH_3 must be added to 2.08 g of NH_4Cl to give this pH?
(**d**) What volume of 0.499 *M* NH_3 must be added to 395 mL of 0.109 *M* NH_4Cl to give this pH?

27. The buffer capacity indicates how much OH^- or H^+ ions a buffer can react with. What is the buffer capacity of the buffers in Problem 9?

28. The buffer capacity indicates how much OH^- or H^+ ions a buffer can react with. What is the buffer capacity of the buffers in Problem 10?

29. A buffer is made up of 0.300 L each of 0.500 *M* KH_2PO_4 and 0.317 *M* K_2HPO_4. Assuming that volumes are additive, calculate
(**a**) the pH of the buffer.
(**b**) the pH of the buffer after the addition of 0.0500 mol of HCl to 0.600 L of buffer.
(**c**) the pH of the buffer after the addition of 0.0500 mol of NaOH to 0.600 L of buffer.

30. A buffer is made up of 239 mL of 0.187 *M* potassium hydrogen tartrate ($KHC_4H_4O_6$) and 137 mL of 0.288 *M* potassium tartrate ($K_2C_4H_4O_6$). K_a for ($H_2C_4H_4O_6$) is 4.55×10^{-5}. Assuming volumes are additive, calculate
(**a**) the pH of the buffer.
(**b**) the pH of the buffer after adding 0.0250 mol of HCl to 0.376 L of the buffer.
(**c**) the pH of the buffer after adding 0.0250 mol of KOH to 0.376 L of the buffer.

31. Enough water is added to the buffer in Question 29 to make the total volume 10.0 L. Calculate
(**a**) the pH of the buffer.
(**b**) the pH of the buffer after the addition of 0.0500 mol of HCl to 0.600 L of diluted buffer.
(**c**) the pH of the buffer after the addition of 0.0500 mol of NaOH to 0.600 L of diluted buffer.
(**d**) Compare your answers to Question 29(a)–(c) with your answers to (a)–(c) in this problem.
(**e**) Comment on the effect of dilution on the pH of a buffer and on its buffer capacity.

32. Enough water is added to the buffer in Question 30 to make the total volume 5.00 L.
(**a**) Calculate the pH of the buffer.
(**b**) Calculate the pH of the buffer after adding 0.0250 mol of HCl to 0.376 L of the buffer.

(c) Calculate the pH of the buffer after adding 0.0250 mol of KOH to 0.376 L of the buffer.

(d) Compare your answers to Question 30 (a–c) with your answers to (a–c) of this problem.

(e) Comment on the effect of dilution on the pH of a buffer and on its buffer capacity.

33. A buffer is prepared in which the ratio $[H_2PO_4^-]/[HPO_4^{2-}]$ is 3.0.

(a) What is the pH of this buffer?

(b) Enough strong acid is added to convert 15% of HPO_4^{2-} to $H_2PO_4^-$. What is the pH of the resulting solution?

(c) Enough strong base is added to make the pH 7.00. What is the ratio of $[H_2PO_4^-]$ to $[HPO_4^{2-}]$ at this point?

34. A buffer is prepared using the butyric acid/butyrate ($HC_4H_7O_2/C_4H_7O_2^-$) acid-base pair. The ratio of acid to base is 2.2 and K_a for butyric acid is 1.54×10^{-5}.

(a) What is the pH of this buffer?

(b) Enough strong base is added to convert 15% of butyric acid to the butyrate ion. What is the pH of the resulting solution?

(c) Strong acid is added to the buffer to increase its pH. What must the acid/base ratio be so that the pH increases by exactly one unit (e.g., from 2 to 3) from the answer in (a)?

35. Blood is buffered mainly by the $HCO_3^- - H_2CO_3$ buffer system. The normal pH of blood is 7.40.

(a) Calculate the $[H_2CO_3]/[HCO_3^-]$ ratio.

(b) What does the pH become if 15% of the HCO_3^- ions are converted to H_2CO_3?

(c) What does the pH become if 15% of the H_2CO_3 molecules are converted to HCO_3^- ions?

36. There is a buffer system in blood ($H_2PO_4^- - HPO_4^{2-}$) that helps keep the blood pH at 7.40. (K_a $H_2PO_4^- = 6.2 \times 10^{-8}$).

(a) Calculate the $[H_2PO_4^-]/[HPO_4^{2-}]$ ratio at the normal pH of blood.

(b) What percentage of the HPO_4^{2-} ions are converted to $H_2PO_4^-$ when the pH is 7.00?

(c) What percentage of the $H_2PO_4^-$ ions are converted to HPO_4^{2-} when the pH is 8.00?

14-2 Acid-Base Indicators

37. Given three acid-base indicators—methyl orange (end point at pH 4), bromthymol blue (end point at pH 7), and phenolphthalein (end point at pH 9)—which would you select for the following acid-base titrations?

(a) perchloric acid with an aqueous solution of ammonia

(b) nitrous acid with lithium hydroxide

(c) hydrobromic acid with strontium hydroxide

(d) sodium fluoride with nitric acid

38. Given the acid-base indicators in Question 37, select a suitable indicator for the following titrations.

(a) sodium formate ($NaCHO_2$) with HNO_3

(b) hypochlorous acid with barium hydroxide

(c) nitric acid with HI

(d) hydrochloric acid with ammonia

39. Metacresol purple is an indicator that changes from yellow to purple at pH 8.2.

(a) What is K_a for this indicator?

(b) What is its pH range?

(c) What is the color of a solution with pH 9.0 and a few drops of metacresol purple?

40. Thymolphthalein is an indicator that changes from colorless to blue at pH 9.5.

(a) What is its K_a?

(b) What is its pH range?

(c) What is the color of a solution with a pH of 10.0 and a few drops of thymolphthalein?

14-3 Acid-Base Titrations

41. When 25.00 mL of HNO_3 are titrated with $Sr(OH)_2$, 58.4 mL of a 0.218 *M* solution are required.

(a) What is the pH of HNO_3 before titration?

(b) What is the pH at the equivalence point?

(c) Calculate $[NO_3^-]$ and $[Sr^{2+}]$ at the equivalence point. (Assume that volumes are additive.)

42. A solution of KOH has a pH of 13.29. It requires 27.66 mL of 0.2500 *M* HCl to reach the equivalence point.

(a) What is the volume of the KOH solution?

(b) What is the pH at the equivalence point?

(c) What is $[K^+]$ and $[Cl^-]$ at the equivalence point? Assume volumes are additive.

43. A solution consisting of 25.00 g NH_4Cl in 178 mL of water is titrated with 0.114 *M* KOH.

(a) How many milliliters of KOH are required to reach the equivalence point?

(b) Calculate $[Cl^-]$, $[K^+]$, $[NH_3]$, and $[OH^-]$ at the equivalence point. (Assume that volumes are additive.)

(c) What is the pH at the equivalence point?

44. A 50.0-mL sample of $NaHSO_3$ is titrated with 22.94 mL of 0.238 *M* KOH.

(a) Write a balanced net ionic equation for the reaction.

(b) What is $[HSO_3^-]$ before the titration?

(c) Find $[HSO_3^-]$, $[SO_3^{2-}]$, $[OH^-]$, $[K^+]$, and $[Na^+]$ at the equivalence point.

(d) What is the pH at the equivalence point?

45. A 20.00-mL sample of 0.220 *M* triethylamine, $(CH_3CH_2)_3N$, is titrated with 0.544 *M* HCl. ($K_b(CH_3CH_2)_3N = 5.2 \times 10^{-4}$)

(a) Write a balanced net ionic equation for the titration.

(b) How many milliliters of HCl are required to reach the equivalence point?

(c) Calculate $[(CH_3CH_2)_3N]$, $[(CH_3CH_2)_3NH^+]$, $[H^+]$, and $[Cl^-]$ at the equivalence point. (Assume that volumes are additive.)

(d) What is the pH at the equivalence point?

46. A 35.00-mL sample of 0.487 *M* KBrO is titrated with 0.264 *M* HNO_3. (K_b $BrO^- = 4.0 \times 10^{-6}$)

(a) Write a balanced net ionic equation for the reaction.

(b) How many milliliters of HCl are required to reach the equivalence point?

(c) What is the pH at the equivalence point?

(d) Calculate $[K^+]$, $[NO_3^-]$, $[H^+]$, $[BrO^-]$, and [HBrO] at the equivalence point. (Assume volumes are additive.)

47. A 0.4000 *M* solution of nitric acid is used to titrate 50.00 mL of 0.237 *M* barium hydroxide. (Assume that volumes are additive.)

(a) Write a balanced net ionic equation for the reaction that takes place during titration.

(b) What are the species present at the equivalence point?

(c) What volume of nitric acid is required to reach the equivalence point?
(d) What is the pH of the solution before any HNO_3 is added?
(e) What is the pH of the solution halfway to the equivalence point?
(f) What is the pH of the solution at the equivalence point?

48. A 0.2481 *M* solution of KOH is used to titrate 30.00 mL of 0.269 *M* hydrobromic acid. Assume that volumes are additive.
(a) Write a balanced net ionic equation for the reaction that takes place during the titration.
(b) What are the species present at the equivalence point?
(c) What volume of KOH is required to reach the equivalence point?
(d) What is the pH of the solution
1. before any KOH is added?
2. halfway to the equivalence point?
3. at the equivalence point?

49. Consider the titration of butyric acid (HBut) with sodium hydroxide. In an experiment, 50.00 mL of 0.350 *M* butyric acid is titrated with 0.225 *M* NaOH. K_a HBut $= 1.5 \times 10^{-5}$.
(a) Write a balanced net ionic equation for the reaction that takes place during titration.
(b) What are the species present at the equivalence point?
(c) What volume of sodium hydroxide is required to reach the equivalence point?
(d) What is the pH of the solution before any NaOH is added?
(e) What is the pH of the solution halfway to the equivalence point?
(f) What is the pH of the solution at the equivalence point?

50. Morphine, $C_{17}H_{19}O_3N$, is a weak base ($K_b = 7.4 \times 10^{-7}$). Consider its titration with hydrochloric acid. In the titration, 50.0 mL of a 0.1500 *M* solution of morphine is titrated with 0.1045 *M* HCl.
(a) Write a balanced net ionic equation for the reaction that takes place during titration.
(b) What are the species present at the equivalence point?
(c) What volume of hydrochloric acid is required to reach the equivalence point?
(d) What is the pH of the solution before any HCl is added?
(e) What is the pH of the solution halfway to the equivalence point?
(f) What is the pH of the solution at the equivalence point?

51. Consider a 10.0% (by mass) solution of hypochlorous acid. Assume the density of the solution to be 1.00 g/mL. A 30.0-mL sample of the solution is titrated with 0.419 *M* KOH. Calculate the pH of the solution
(a) before titration.
(b) halfway to the equivalence point.
(c) at the equivalence point.

52. A solution is prepared by dissolving 0.350 g of benzoic acid, $HC_7H_5O_2$, in water to make 100.0 mL of solution. A 30.00-mL sample of the solution is titrated with 0.272 *M* KOH. Calculate the pH of the solution
(a) before titration.
(b) halfway to the equivalence point.
(c) at the equivalence point.

Unclassified

53. A student is given 250.0 g of sodium lactate, $NaC_3H_5O_3$, and a bottle of lactic acid marked "73.0% by mass $HC_3H_5O_3$, $d = 1.20$ g/mL." How many milliliters of 73.0% lactic acid should the student add to the sodium lactate to produce a buffer with a pH of 4.50?

54. Ammonia gas is bubbled into 275 mL of water to make an aqueous solution of ammonia. To prepare a buffer with a pH of 9.56, 15.0 g of NH_4Cl are added. How many liters of NH_3 at 25°C and 0.981 atm should be used to prepare the buffer? Assume no volume changes and ignore the vapor pressure of water.

55. For an aqueous solution of acetic acid to be called "distilled white vinegar" it must contain 5.0% acetic acid by mass. A solution with a density of 1.05 g/mL has a pH of 2.95. Can the solution be called "distilled white vinegar"?

56. Consider an unknown base, RNH. One experiment titrates a 50.0-mL aqueous solution containing 2.500 g of the base. This titration requires 59.90 mL of 0.925 *M* HCl to reach the equivalence point. A second experiment uses a 50.0-mL solution of the unknown base identical to what was used in the first experiment. To this solution is added 29.95 mL of 0.925 *M* HCl. The pH after the HCl addition is 10.77.
(a) What is the molar mass of the unknown base?
(b) What is K_b for the unknown base?
(c) What is K_a for RNH_2^+?

57. A painful arthritic condition known as gout is caused by an excess of uric acid, HUric, in the blood. An aqueous solution contains 4.00 g of uric acid. A 0.730 *M* solution of KOH is used for titration. After 12.00 mL of KOH are added, the resulting solution has pH 4.12. The equivalence point is reached after a total of 32.62 mL of KOH are added.

$$HUric(aq) + OH^-(aq) \longrightarrow Uric^-(aq) + H_2O$$

(a) What is the molar mass of uric acid?
(b) What is its K_a?

58. Water is accidentally added to 350.00 mL of a stock solution of 6.00 *M* HCl. A 75.00-mL sample of the diluted solution is titrated to pH 7.00 with 78.8 mL of 4.85 *M* NaOH. How much water was accidentally added? (Assume that volumes are additive.)

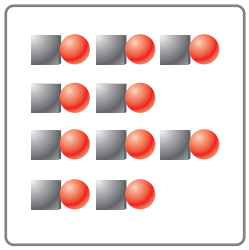
59. A solution of an unknown weak base (nonelectrolyte) at 25°C has an osmotic pressure of 1.287 atm and a pH of 8.94. (Assume that, in the equation for π [Chapter 10], $i \approx 1$.) What is K_a for its conjugate acid?

60. Consider an aqueous solution of HF. The molar heat of formation for aqueous HF is −320.1 kJ/mol.
(a) What is the pH of a 0.100 *M* solution of HF at 100°C?
(b) Compare with the pH of a 0.100 *M* solution of HF at 25°C.

Conceptual Problems

61. Each symbol in the box below represents a mole of a component in one liter of a buffer solution; ○ represents the anion (X^-), □○ = the weak acid (HX), □ = H^+, and

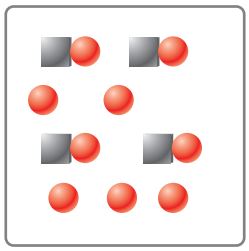
△ = OH^-. Water molecules and the few H^+ and OH^- ions from the dissociation of HX and X^- are not shown. The box contains 10 mol of a weak acid, □○, in a liter of solution. Show what happens upon



(a) the addition of 2 mol of OH^- (2 △).
(b) the addition of 5 mol of OH^- (5 △).
(c) the addition of 10 mol of OH^- (10 △).
(d) the addition of 12 mol of OH^- (12 △).

Which addition (a)–(d) represents neutralization halfway to the equivalence point?

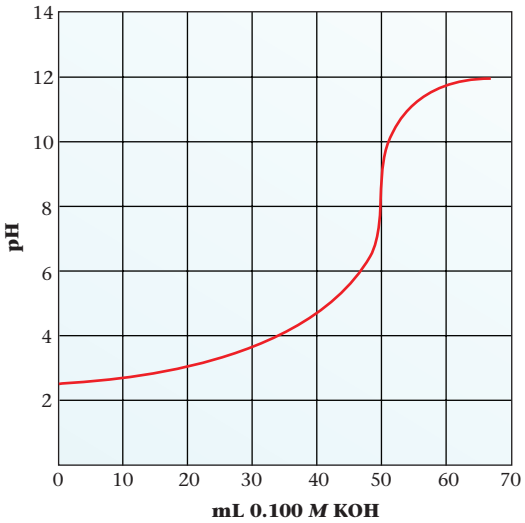
62. Use the same symbols as in Question 61 (○ = anion, △ = OH^-) for the box below.



(a) Fill in a similar box (representing one liter of the same solution) after 2 mol of H^+ (2 □) have been added. Indicate whether the resulting solution is an acid, base, or buffer.
(b) Follow the directions of part (a) for the resulting solution after 2 mol of OH^- (2 △) have been added.
(c) Follow the directions of part (a) for the resulting solution after 5 mol of OH^- (5 △) have been added.

(*Hint:* Write the equation for the reaction before you draw the results.)

63. The following is the titration curve for the titration of 50.00 mL of a 0.100 *M* acid with 0.100 *M* KOH.



(a) Is the acid strong or weak?
(b) If the acid is weak, what is its K_a?
(c) Estimate the pH at the equivalence point.

64. Consider the following five beakers:

Beaker A has 0.100 mol HA and 0.100 mol NaA in 100 mL of solution.
Beaker B has 0.100 mol HA and 0.100 mol NaA in 200 mL of solution.
Beaker C has 0.100 mol HA, 0.100 mol NaA, and 0.0500 mol HCl in 100 mL of solution.
Beaker D has 0.100 mol HA, 0.100 mol NaA, and 0.100 mol NaOH in 100 mL of solution.
Beaker E has 0.100 mol HCl and 0.100 mol NaOH in 100 mL of solution.

Answer the questions below, using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*).

(a) The pH in beaker A _____ the pH in beaker B.
(b) The pH in beaker A _____ the pH in beaker C.
(c) The pH in beaker D _____ the pH in beaker E.
(d) The pH in beaker A _____ the pH in beaker E.
(e) The pH in beaker A _____ the pH in beaker D.

65. Follow the directions of Question 64. Consider two beakers:

Beaker A has a weak acid ($K_a = 1 \times 10^{-5}$).
Beaker B has HCl.

The volume and molarity of each acid in the beakers are the same. Both acids are to be titrated with a 0.1 *M* solution of NaOH.

(a) Before titration starts (at zero time), the pH of the solution in Beaker A is _____ the pH of the solution in Beaker B.
(b) At half-neutralization (halfway to the equivalence point), the pH of the solution in Beaker A _____ the pH of the solution in Beaker B.
(c) When each solution has reached its equivalence point, the pH of the solution in Beaker A _____ the pH of the solution in Beaker B.
(d) At the equivalence point, the volume of NaOH used to titrate HCl in Beaker B _____ the volume of NaOH used to titrate the weak acid in Beaker A.

66. Which statements are true about the titration represented by the following equation?

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$$

(a) The net ionic equation could represent the titration of NaF by H_2SO_4.
(b) The reaction could be considered to be that of a strong acid with a strong base.
(c) At the equivalence point, the resulting solution can act as a buffer.
(d) Diluting the solution obtained at half-neutralization with water does not change the pH of the solution.
(e) Phenolphthalein (pH range: 9–11) would be an effective indicator in this titration.

67. Indicate whether each of the following statements is true or false. If the statement is false, restate it to make it true.

(**a**) The formate ion (CHO_2^-) concentration in 0.10 *M* $HCHO_2$ is the same as in 0.10 *M* $NaCHO_2$.

(**b**) A buffer can be destroyed by adding too much strong acid.

(**c**) A buffer can be made up by any combination of weak acid and weak base.

(**d**) Because K_a for HCO_3^- is 4.7×10^{-11}, K_b for HCO_3^- is 2.1×10^{-4}.

68. The solutions in three test tubes labeled A, B, and C all have the same pH. The test tubes are known to contain 1.0×10^{-3} *M* HCl, 6.0×10^{-3} *M* $HCHO_2$, and 4×10^{-2} *M* $C_6H_5NH_3^+$. Describe a procedure for identifying the solutions.

69. Consider the following titration curves. The solution in the buret is 0.1 *M*. The solution in the beaker has a volume of 50.0 mL. Answer the following questions.

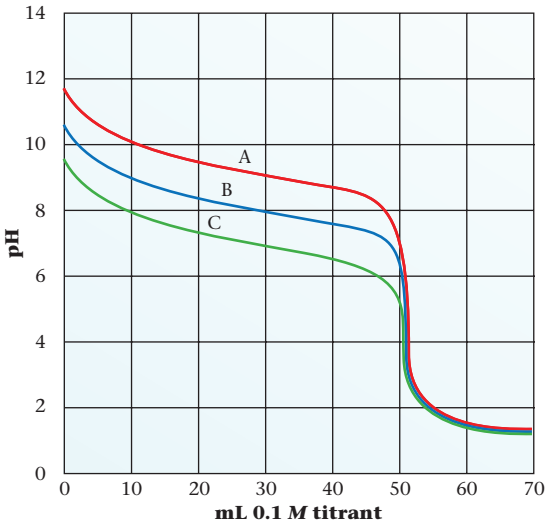
(**a**) Is the titrating agent (solution in the buret) an acid or a base?

(**b**) Which curve shows the titration of the weakest base?

(**c**) What is the K_a of the conjugate acid of the base titrated in curve B?

(**d**) What is the molarity of the solution in the beaker for curve C?

(**e**) What is the pH at the equivalence point for curve A?



Challenge Problems

70. Consider the titration of HF ($K_a = 6.7 \times 10^{-4}$) with NaOH. What is the pH when a third of the acid has been neutralized?

71. The species called *glacial acetic acid* is 98% acetic acid by mass ($d = 1.0542$ g/mL). What volume of glacial acetic acid must be added to 100.0 mL of 1.25 *M* NaOH to give a buffer with a pH of 4.20?

72. Four grams of a monoprotic weak acid are dissolved in water to make 250.0 mL of solution with a pH of 2.56. The solution is divided into two equal parts, A and B. Solution A is titrated with strong base to its equivalence point. Solution B is added to solution A after solution A is neutralized. The pH of the resulting solution is 4.26. What is the molar mass of the acid?

73. Explain why it is not possible to prepare a buffer with a pH of 6.50 by mixing NH_3 and NH_4Cl.

74. Fifty cm^3 of 1.000 *M* nitrous acid is titrated with 0.850 *M* NaOH. What is the pH of the solution

(**a**) before any NaOH is added?

(**b**) at half-neutralization?

(**c**) at the equivalence point?

(**d**) when 0.10 mL less than the volume of NaOH to reach the equivalence point is added?

(**e**) when 0.10 mL more than the volume of NaOH to reach the equivalence point is added?

(**f**) Use your data to construct a plot similar to that shown in Figure 14.10 (pH versus volume NaOH added).

75. A diprotic acid, H_2B (MM = 126 g/mol), is determined to be a hydrate, $H_2B \cdot xH_2O$. A 10.00-g sample of this hydrate is dissolved in enough water to make 150.0 mL of solution. Twenty-five milliliters of this solution requires 48.5 mL of 0.425 *M* NaOH to reach the equivalence point. What is x?

76. What is the pH of a 0.1500 *M* H_2SO_4 solution if

(**a**) the ionization of HSO_4^- is ignored?

(**b**) the ionization of HSO_4^- is taken into account? (K_a for HSO_4^- is 1.1×10^{-2}.)

77. Two students were asked to determine the K_b of an unknown base. They were given a bottle with a solution in it. The bottle was labeled "aqueous solution of a monoprotic strong acid." They were also given a pH meter, a buret, and an appropriate indicator. They reported the following data:

volume of acid required for neutralization = 21.0 mL
pH after 7.00 mL of strong acid added = 8.95

Use the students' data to determine the K_b of the unknown base.

78. How many grams of NaOH must be added to 1.00 L of a buffer made from 0.150 *M* NH_3 and 10.0 g of NH_4Cl so that the pH increases by one unit (e.g., from 5 to 6)? K_a for NH_4^+ is 5.6×10^{-10}.

79. How many grams of NaF must be added to 70.00 mL of 0.150 *M* HNO_3 to obtain a buffer with a pH of 4.68?

80. A student is asked to determine the molarity of 25.00 mL of a solution of $HClO_4$. He uses 0.731 *M* KOH. After adding 42.35 mL of KOH, he realizes that he forgot to add an indicator. His TA suggests he take the pH of the solution. The pH is 12.39.

(**a**) Did the student go beyond the equivalence point?

(**b**) What is the molarity of the strong acid?

(**c**) If he did, how many milliliters of KOH did he add in excess? If he did not, how much more (in mL) KOH should he add?