15 Applications of Aqueous Equilibria

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Stalactites are formed when carbonate minerals dissolve in ground water acidified by carbon dioxide and then solidify when the water evaporates.

Much important chemistry, including almost all the chemistry of the natural world, occurs in aqueous solution. We have already introduced one very significant class of aqueous equilibria, acid–base reactions. In this chapter we consider more applications of acid–base chemistry and introduce two additional types of aqueous equilibria, those involving the solubility of salts and those involving the formation of complex ions.

The interplay of acid–base, solubility, and complex ion equilibria is often important in natural processes, such as the weathering of minerals, the uptake of nutrients by plants, and tooth decay. For example, limestone ($CaCO_3$) will dissolve in water made acidic by dissolved carbon dioxide:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$H^+(aq) + CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq)$$

This two-step process and its reverse account for the formation of limestone caves and the stalactites and stalagmites found therein. In the forward direction of the process, the acidic water (containing carbon dioxide) dissolves the underground limestone deposits, thereby forming a cavern. The reverse process occurs as the water drips from the ceiling of the cave, and the carbon dioxide is lost to the air. This causes solid calcium carbonate to form, producing stalactites on the ceiling and stalagmites where the drops hit the cave floor.

Before we consider the other types of aqueous equilibria, we will deal with acid–base equilibria in more detail.

Acid–Base Equilibria

15.1 Solutions of Acids or Bases Containing a Common Ion

In Chapter 14 we were concerned with calculating the equilibrium concentrations of species (particularly H^+ ions) in solutions containing an acid or a base. In this section we discuss solutions that contain not only the weak acid HA but also its salt NaA. Although this appears to be a new type of problem, we will see that this case can be handled rather easily using the procedures developed in Chapter 14.

Suppose we have a solution containing the weak acid hydrofluoric acid (HF, $K_a = 7.2 \times 10^{-4}$) and its salt sodium fluoride (NaF). Recall that when a salt dissolves in water, it breaks up completely into its ions—it is a strong electrolyte:

$$NaF(s) \xrightarrow{H_2O(l)} Na^+(aq) + F^-(aq)$$

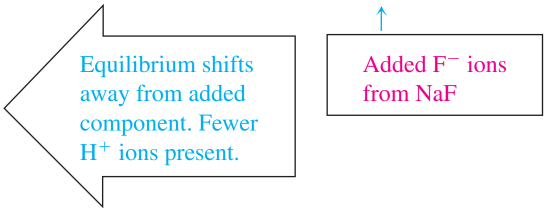
Since hydrofluoric acid is a weak acid and only slightly dissociated, the major species in the solution are HF, Na^+, F^-, and H_2O. The **common ion** in this solution is F^-, since it is produced by both hydrofluoric acid and sodium fluoride. What effect does the presence of the dissolved sodium fluoride have on the dissociation equilibrium of hydrofluoric acid?

To answer this question, we compare the extent of dissociation of hydrofluoric acid in two different solutions, the first containing 1.0 *M* HF and the second containing 1.0 *M* HF and 1.0 *M* NaF. By Le Châtelier's principle, we would expect the dissociation equilibrium for HF

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

in the second solution to be *driven to the left by the presence of F^- ions from the NaF.* Thus the extent of dissociation of HF will be *less* in the presence of dissolved NaF:

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



The common ion effect is an application of Le Châtelier's principle.

The shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium reaction is called the **common ion effect.** This effect makes a solution of NaF and HF less acidic than a solution of HF alone.

The common ion effect is quite general. For example, solid NH_4Cl added to a 1.0 *M* NH_3 solution produces additional ammonium ions:

$$\mathrm{NH_4Cl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$

and this causes the position of the ammonia–water equilibrium to shift to the left:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

This reduces the equilibrium concentration of OH^- ions.

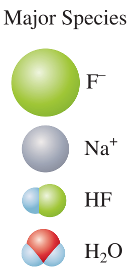
The common ion effect is also important in solutions of polyprotic acids. The production of protons by the first dissociation step greatly inhibits the succeeding dissociation steps, which, of course, also produce protons, the common ion in this case. We will see later in this chapter that the common ion effect is also important in dealing with the solubility of salts.

Equilibrium Calculations

The procedures for finding the pH of a solution containing a weak acid or base plus a common ion are very similar to the procedures, which we covered in Chapter 14, for solutions containing the acids or bases alone. For example, in the case of a weak acid, the only important difference is that the initial concentration of the anion A^- is not zero in a solution that also contains the salt NaA. Sample Exercise 15.1 illustrates a typical example using the same general approach we developed in Chapter 14.

Sample Exercise 15.1 Acidic Solutions Containing Common Ions

In Section 14.5 we found that the equilibrium concentration of H^+ in a 1.0 *M* HF solution is 2.7×10^{-2} *M*, and the percent dissociation of HF is 2.7%. Calculate $[H^+]$ and the percent dissociation of HF in a solution containing 1.0 *M* HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 *M* NaF.



Solution

As the aqueous solutions we consider become more complex, it is more important than ever to be systematic and to *focus on the chemistry* occurring in the solution before thinking about mathematical procedures. The way to do this is *always* to write the major species first and consider the chemical properties of each one.

In a solution containing 1.0 M HF and 1.0 M NaF, the major species are

$$HF, \quad F^-, \quad Na^+, \quad \text{and} \quad H_2O$$

We know that Na^+ ions have neither acidic nor basic properties and that water is a very weak acid (or base). Therefore, the important species are HF and F^-, which participate in the acid dissociation equilibrium that controls $[H^+]$ in this solution. That is, the position of the equilibrium

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

will determine $[H^+]$ in the solution. The equilibrium expression is

$$K_a = \frac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4}$$

The important concentrations are shown in the following table.

Initial Concentration (mol/L)		**Equilibrium Concentration (mol/L)**
$[HF]_0 = 1.0$ (from dissolved HF)		$[HF] = 1.0 - x$
$[F^-]_0 = 1.0$ (from dissolved NaF)	$\xrightarrow[\text{dissociates}]{x \text{ mol/L HF}}$	$[F^-] = 1.0 + x$
$[H^+]_0 = 0$ (neglect contribution from H_2O)		$[H^+] = x$

Note that $[F^-]_0 = 1.0\ M$ because of the dissolved sodium fluoride and that at equilibrium $[F^-] > 1.0\ M$ because when the acid dissociates it produces F^- as well as H^+. Then

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(1.0 + x)}{1.0 - x} \approx \frac{(x)(1.0)}{1.0}$$

(since x is expected to be small).

Solving for x gives

$$x = \frac{1.0}{1.0}(7.2 \times 10^{-4}) = 7.2 \times 10^{-4}$$

Noting that x is small compared to 1.0, we conclude that this result is acceptable. Thus

$$[H^+] = x = 7.2 \times 10^{-4}\ M \qquad \text{(The pH is 3.14.)}$$

The percent dissociation of HF in this solution is

$$\frac{[H^+]}{[HF]_0} \times 100 = \frac{7.2 \times 10^{-4}\ M}{1.0\ M} \times 100 = 0.072\%$$

Compare these values for $[H^+]$ and percent dissociation of HF with those for a 1.0 M HF solution, where $[H^+] = 2.7 \times 10^{-2}\ M$ and the percent dissociation is 2.7%. The large difference shows clearly that the presence of the F^- ions from the dissolved NaF greatly inhibits the dissociation of HF. The position of the acid dissociation equilibrium has been shifted to the left by the presence of F^- ions from NaF.

See Exercises 15.25 and 15.26.

15.2 Buffered Solutions

The most important buffering system in the blood involves HCO_3^- and H_2CO_3.

The most important application of acid–base solutions containing a common ion is for buffering. A **buffered solution** is one that *resists a change in its pH* when either hydroxide ions or protons are added. The most important practical example of a buffered solution is our blood, which can absorb the acids and bases produced in biologic reactions without changing its pH. A constant pH for blood is vital because cells can survive only in a very narrow pH range.

A buffered solution may contain a *weak* acid and its salt (for example, HF and NaF) or a *weak* base and its salt (for example, NH_3 and NH_4Cl). By choosing the appropriate components, a solution can be buffered at virtually any pH.

In treating buffered solutions in this chapter, we will start by considering the equilibrium calculations. We will then use these results to show how buffering works. That is, we will answer the question: How does a buffered solution resist changes in pH when an acid or a base is added?

The systematic approach developed in Chapter 14 for weak acids and bases applies to buffered solutions.

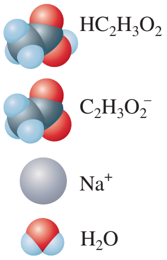
As you do the calculations associated with buffered solutions, keep in mind that these are merely solutions containing weak acids or bases, and the procedures required are the same ones we have already developed. Be sure to use the systematic approach introduced in Chapter 14.

Sample Exercise 15.2 The pH of a Buffered Solution I

Notice as you do this problem that it is exactly like examples you have seen in Chapter 14.

A buffered solution contains 0.50 *M* acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) and 0.50 *M* sodium acetate ($NaC_2H_3O_2$). Calculate the pH of this solution.

Major Species



Solution

The major species in the solution are

$HC_2H_3O_2$,	Na^+,	$C_2H_3O_2^-$,	and	H_2O
↑	↑	↑		↑
Weak acid	Neither acid nor base	Base (conjugate base of $HC_2H_3O_2$)		Very weak acid or base

Examination of the solution components leads to the conclusion that the acetic acid dissociation equilibrium, which involves both $HC_2H_3O_2$ and $C_2H_3O_2^-$, will control the pH of the solution:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

The concentrations are as follows:

A digital pH meter shows the pH of the buffered solution to be 4.740.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HC_2H_3O_2]_0 = 0.50$ $[C_2H_3O_2^-]_0 = 0.50$ $[H^+]_0 \approx 0$	x mol/L of $HC_2H_3O_2$ $\xrightarrow{}$ dissociates to reach equilibrium	$[HC_2H_3O_2] = 0.50 - x$ $[C_2H_3O_2^-] = 0.50 + x$ $[H^+] = x$

The corresponding ICE table is

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial:	0.50		≈ 0		0.50
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.50 - x$		x		$0.50 + x$

Then

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(0.50 + x)}{0.50 - x} \approx \frac{(x)(0.50)}{0.50}$$

and $$x \approx 1.8 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

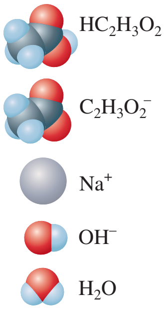
$$[H^+] = x = 1.8 \times 10^{-5}\ M \qquad \text{and} \qquad \text{pH} = 4.74$$

See Exercises 15.33 and 15.34.

Sample Exercise 15.3 pH Changes in Buffered Solutions

Calculate the change in pH that occurs when 0.010 mol solid NaOH is added to 1.0 L of the buffered solution described in Sample Exercise 15.2. Compare this pH change with that which occurs when 0.010 mol solid NaOH is added to 1.0 L of water.

Major Species



Solution

Since the added solid NaOH will completely dissociate, the major species in solution *before any reaction occurs* are $HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, OH^-, and H_2O. Note that the solution contains a relatively large amount of the very strong base hydroxide ion, which has a great affinity for protons. The best source of protons is the acetic acid, and the reaction that will occur is

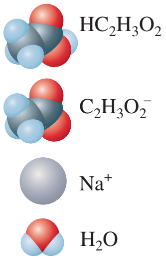
$$OH^- + HC_2H_3O_2 \longrightarrow H_2O + C_2H_3O_2^-$$

Although acetic acid is a weak acid, the hydroxide ion is such a strong base that the reaction above will *proceed essentially to completion* (until the OH^- ions are consumed).

The best approach to this problem involves two distinct steps: (1) assume that the reaction goes to completion, and carry out the stoichiometric calculations, and then (2) carry out the equilibrium calculations.

1. *The stoichiometry problem.* The stoichiometry for the reaction is shown below.

Major Species



	$HC_2H_3O_2$	$+$	OH^-	$\longrightarrow$	$C_2H_3O_2^-$	$+$	H_2O
Before reaction:	$1.0\ L \times 0.50\ M$ $= 0.50$ mol		0.010 mol		$1.0\ L \times 0.50\ M$ $= 0.50$ mol		
After reaction:	$0.50 - 0.010$ $= 0.49$ mol		$0.010 - 0.010$ $= 0$ mol		$0.50 + 0.010$ $= 0.51$ mol		

Note that 0.010 mol $HC_2H_3O_2$ has been converted to 0.010 mol $C_2H_3O_2^-$ by the added OH^-.

2. *The equilibrium problem.* After the reaction between OH^- and $HC_2H_3O_2$ is complete, the major species in solution are

$$HC_2H_3O_2, \quad Na^+, \quad C_2H_3O_2^-, \quad \text{and} \quad H_2O$$

The dominant equilibrium involves the dissociation of acetic acid.

This problem is then very similar to that in Sample Exercise 15.2. The only difference is that the addition of 0.010 mol OH^- has consumed some $HC_2H_3O_2$ and produced some $C_2H_3O_2^-$, yielding the following ICE table:

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial:	0.49		0		0.51
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.49 - x$		x		$0.51 + x$

Note that the initial concentrations are defined after the reaction with OH^- is complete but before the system adjusts to equilibrium. Following the usual procedure gives

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(0.51 + x)}{0.49 - x} \approx \frac{(x)(0.51)}{0.49}$$

and $$x \approx 1.7 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[H^+] = x = 1.7 \times 10^{-5} \qquad \text{and} \qquad pH = 4.76$$

The change in pH produced by the addition of 0.01 mol OH^- to this buffered solution is then

$$\underset{\substack{\uparrow \\ \text{New solution}}}{4.76} \quad - \quad \underset{\substack{\uparrow \\ \text{Original solution}}}{4.74} \quad = +0.02$$

The pH increased by 0.02 pH units.

Now compare this with what happens when 0.01 mol solid NaOH is added to 1.0 L water to give 0.01 *M* NaOH. In this case $[OH^-] = 0.01\ M$ and

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$pH = 12.00$$

Thus the change in pH is

$$\underset{\substack{\uparrow \\ \text{New solution}}}{12.00} \quad - \quad \underset{\substack{\uparrow \\ \text{Pure water}}}{7.00} \quad = +5.00$$

The increase is 5.00 pH units. Note how well the buffered solution resists a change in pH as compared with pure water.

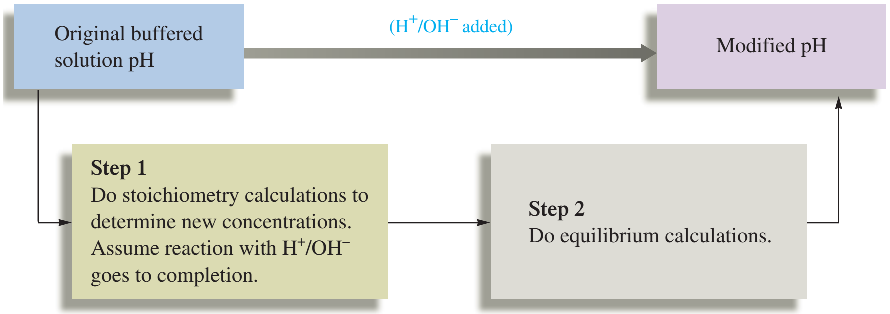
See Exercises 15.35 and 15.36.

(top) Pure water at pH 7.000. (bottom) When 0.01 mol NaOH is added to 1.0 L of pure water, the pH jumps to 12.000.

Sample Exercises 15.2 and 15.3 represent typical buffer problems that involve all the concepts that you need to know to handle buffered solutions containing weak acids. Pay special attention to the following points:

1. Buffered solutions are simply solutions of weak acids or bases containing a common ion. The pH calculations on buffered solutions require exactly the same procedures introduced in Chapter 14. *This is not a new type of problem.*

2. When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first. After the stoichiometric calculations are completed, then consider the equilibrium calculations. This procedure can be presented as follows:



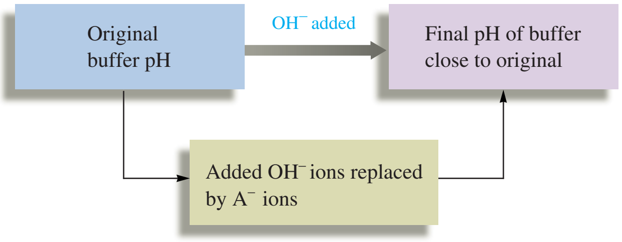
Buffering: How Does It Work?

Visualization: Buffers

Sample Exercises 15.2 and 15.3 demonstrate the ability of a buffered solution to absorb hydroxide ions without a significant change in pH. *But how does a buffer work?* Suppose a buffered solution contains relatively large quantities of a weak acid HA and its conjugate base A^-. When hydroxide ions are added to the solution, since the weak acid represents the best source of protons, the following reaction occurs:

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

The net result is that OH^- ions are not allowed to accumulate but are replaced by A^- ions.



The stability of the pH under these conditions can be understood by examining the equilibrium expression for the dissociation of HA:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or, rearranging,

$$[H^+] = K_a\frac{[HA]}{[A^-]}$$

In a buffered solution the pH is governed by the ratio $[HA]/[A^-]$.

In other words, the *equilibrium concentration of H^+, and thus the pH, is determined by the ratio $[HA]/[A^-]$.* When OH^- ions are added, HA is converted to A^-, and the ratio $[HA]/[A^-]$ decreases. However, *if the amounts of HA and A^- originally present are very large compared with the amount of OH^- added,* the change in the $[HA]/[A^-]$ ratio will be small.

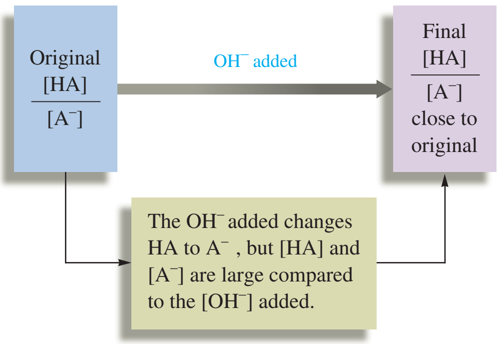
In Sample Exercises 15.2 and 15.3,

$$\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = \frac{0.50}{0.50} = 1.0 \qquad \text{Initially}$$

$$\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = \frac{0.49}{0.51} = 0.96 \qquad \text{After adding 0.01 mol/L OH}^-$$

The change in the ratio $[\mathrm{HA}]/[\mathrm{A}^-]$ is very small. Thus the $[\mathrm{H}^+]$ and the pH remain essentially constant.

The essence of buffering, then, is that [HA] and $[\mathrm{A}^-]$ are large compared with the amount of OH^- added. Thus, when the OH^- is added, the concentrations of HA and A^- change, but only by small amounts. Under these conditions, the $[\mathrm{HA}]/[\mathrm{A}^-]$ ratio and thus the $[\mathrm{H}^+]$ remain virtually constant.



Visualization: Adding an Acid to a Buffer

Similar reasoning applies when protons are added to a buffered solution of a weak acid and a salt of its conjugate base. Because the A^- ion has a high affinity for H^+, the added H^+ ions react with A^- to form the weak acid:

$$\mathrm{H}^+ + \mathrm{A}^- \longrightarrow \mathrm{HA}$$

and free H^+ ions do not accumulate. In this case there will be a net change of A^- to HA. However, if $[\mathrm{A}^-]$ and [HA] are large compared with the $[\mathrm{H}^+]$ added, little change in the pH will occur.

The form of the acid dissociation equilibrium expression

$$[\mathrm{H}^+] = K_a\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} \tag{15.1}$$

is often useful for calculating $[\mathrm{H}^+]$ in a buffered solution, since [HA] and $[\mathrm{A}^-]$ are known. For example, to calculate $[\mathrm{H}^+]$ in a buffered solution containing 0.10 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.30 M NaF, we simply substitute into Equation (15.1):

$$[\mathrm{H}^+] = (\underset{K_a\nearrow}{7.2 \times 10^{-4}})\frac{\overset{\overset{[\mathrm{HF}]}{\searrow}}{0.10}}{\underset{\nwarrow[\mathrm{F}^-]}{0.30}} = 2.4 \times 10^{-4}\ M$$

Another useful form of Equation (15.1) can be obtained by taking the negative log of both sides:

$$-\log[\mathrm{H}^+] = -\log(K_a) - \log\left(\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}\right)$$

That is,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} - \log\left(\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}\right)$$

or, where inverting the log term reverses the sign:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{base}]}{[\mathrm{acid}]}\right) \qquad (15.2)$$

This log form of the expression for K_a is called the **Henderson–Hasselbalch equation** and is useful for calculating the pH of solutions when the ratio $[\mathrm{HA}]/[\mathrm{A}^-]$ is known.

For a particular buffering system (conjugate acid–base pair), all solutions that have the same ratio $[\mathrm{A}^-]/[\mathrm{HA}]$ *will have the same pH.* For example, a buffered solution containing 5.0 *M* $HC_2H_3O_2$ and 3.0 *M* $NaC_2H_3O_2$ will have the same pH as one containing 0.050 *M* $HC_2H_3O_2$ and 0.030 *M* $NaC_2H_3O_2$. This can be shown as follows:

System	$[\mathrm{A}^-]/[\mathrm{HA}]$
5.0 *M* $HC_2H_3O_2$ and 3.0 *M* $NaC_2H_3O_2$	$\frac{3.0\,M}{5.0\,M} = 0.60$
0.050 *M* $HC_2H_3O_2$ and 0.030 *M* $NaC_2H_3O_2$	$\frac{0.030\,M}{0.050\,M} = 0.60$

Therefore,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{C_2H_3O_2}^-]}{[\mathrm{HC_2H_3O_2}]}\right) = 4.74 + \log(0.60) = 4.74 - 0.22 = 4.52$$

Note that in using this equation we have assumed that the equilibrium concentrations of A^- and HA are equal to the initial concentrations. That is, we are assuming the validity of the approximations

$$[\mathrm{A}^-] = [\mathrm{A}^-]_0 + x \approx [\mathrm{A}^-]_0 \quad \text{and} \quad [\mathrm{HA}] = [\mathrm{HA}]_0 - x \approx [\mathrm{HA}]_0$$

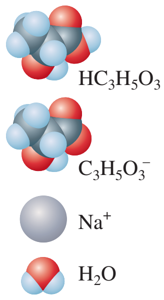
where x is the amount of acid that dissociates. Since the initial concentrations of HA and A^- are relatively large in a buffered solution, this assumption is generally acceptable.

Sample Exercise 15.4

The pH of a Buffered Solution II

Calculate the pH of a solution containing 0.75 *M* lactic acid ($K_\mathrm{a} = 1.4 \times 10^{-4}$) and 0.25 *M* sodium lactate. Lactic acid ($HC_3H_5O_3$) is a common constituent of biologic systems. For example, it is found in milk and is present in human muscle tissue during exertion.

Major Species



Solution

The major species in solution are

$$HC_3H_5O_3, \quad Na^+, \quad C_3H_5O_3^-, \quad \text{and} \quad H_2O$$

Since Na^+ has no acid–base properties and H_2O is a weak acid or base, the pH will be controlled by the lactic acid dissociation equilibrium:

$$HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$

$$K_\mathrm{a} = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = 1.4 \times 10^{-4}$$

Since $[HC_3H_5O_3]_0$ and $[C_3H_5O_3^-]_0$ are relatively large,

$$[HC_3H_5O_3] \approx [HC_3H_5O_3]_0 = 0.75\ M$$

and

$$[C_3H_5O_3^-] \approx [C_3H_5O_3^-]_0 = 0.25\ M$$

Thus, using the rearranged K_a expression, we have

$$[H^+] = K_a\frac{[HC_3H_5O_3]}{[C_3H_5O_3^-]} = (1.4 \times 10^{-4})\frac{(0.75\ M)}{(0.25\ M)} = 4.2 \times 10^{-4}\ M$$

and

$$pH = -\log(4.2 \times 10^{-4}) = 3.38$$

Alternatively, we could use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[C_3H_5O_3^-]}{[HC_3H_5O_3]}\right) = 3.85 + \log\left(\frac{0.25\ M}{0.75\ M}\right) = 3.38$$

See Exercises 15.37 and 15.38.

Buffered solutions also can be formed from a weak base and the corresponding conjugate acid. In these solutions, the weak base B reacts with any H^+ added:

$$B + H^+ \longrightarrow BH^+$$

and the conjugate acid BH^+ reacts with any added OH^-:

$$BH^+ + OH^- \longrightarrow B + H_2O$$

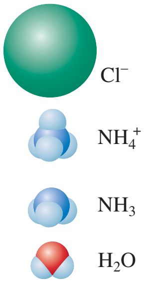
The approach needed to perform pH calculations for these systems is virtually identical to that used above. This makes sense because, as is true of all buffered solutions, a weak acid (BH^+) and a weak base (B) are present. A typical case is illustrated in Sample Exercise 15.5.

Sample Exercise 15.5

The pH of a Buffered Solution III

A buffered solution contains 0.25 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.40 M NH_4Cl. Calculate the pH of this solution.

Major Species



Solution

The major species in solution are

$$NH_3,\quad \underbrace{NH_4^+,\quad Cl^-,}_{\text{From the dissolved } NH_4Cl}\quad \text{and}\quad H_2O$$

Since Cl^- is such a weak base and water is a weak acid or base, the important equilibrium is

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

and

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The appropriate ICE table is:

	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	0.25		—		0.40		≈0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.25 - x$		—		$0.40 + x$		x

Then

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.40 + x)(x)}{0.25 - x} \approx \frac{(0.40)(x)}{0.25}$$

and $$x \approx 1.1 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$\begin{aligned}[OH^-] &= x = 1.1 \times 10^{-5}\\ pOH &= 4.95\\ pH &= 14.00 - 4.95 = 9.05\end{aligned}$$

This case is typical of a buffered solution in that the initial and equilibrium concentrations of buffering materials are essentially the same.

Alternative Solution

There is another way of looking at this problem. Since the solution contains relatively large quantities of *both* NH_4^+ and NH_3, we can use the equilibrium

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

to calculate $[OH^-]$ and then calculate $[H^+]$ from K_w as we have just done. Or we can use the dissociation equilibrium for NH_4^+, that is,

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

to calculate $[H^+]$ directly. *Either choice will give the same answer,* since the same equilibrium concentrations of NH_3 and NH_4^+ must satisfy both equilibria.

We can obtain the K_a value for NH_4^+ from the given K_b value for NH_3, since $K_a \times K_b = K_w$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Then, using the Henderson–Hasselbalch equation, we have

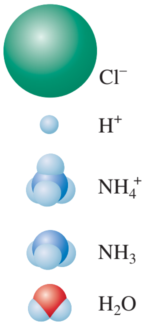
$$\begin{aligned}pH &= pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)\\ &= 9.25 + \log\left(\frac{0.25\ M}{0.40\ M}\right) = 9.25 - 0.20 = 9.05\end{aligned}$$

See Exercises 15.37 and 15.38.

Sample Exercise 15.6 Adding Strong Acid to a Buffered Solution I

Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0 L of the buffered solution from Sample Exercise 15.5.

Major Species



Solution

Before any reaction occurs, the solution contains the following major species:

$$NH_3, \quad NH_4^+, \quad Cl^-, \quad H^+, \quad \text{and} \quad H_2O$$

What reaction can occur? We know that H^+ will not react with Cl^- to form HCl. In contrast to Cl^-, the NH_3 molecule has a great affinity for protons (this is demonstrated by the fact that NH_4^+ is such a weak acid [$K_a = 5.6 \times 10^{-10}$]). Thus NH_3 will react with H^+ to form NH_4^+:

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

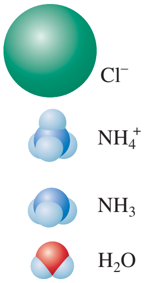
Since this reaction can be assumed to go essentially to completion to form the very weak acid NH_4^+, we will do the stoichiometry calculations before we consider the equilibrium calculations. That is, we will let the reaction run to completion and then consider the equilibrium.

The stoichiometry calculations for this process are shown below.

Remember: Think about the chemistry first. Ask yourself if a reaction will occur among the major species.

	NH_3	+	H^+	$\longrightarrow$	NH_4^+
Before reaction:	(1.0 L)(0.25 M) = 0.25 mol		0.10 mol ↑ Limiting reactant		(1.0 L)(0.40 M) = 0.40 mol
After reaction:	0.25 − 0.10 = 0.15 mol		0		0.40 + 0.10 = 0.50 mol

Major Species



After the reaction goes to completion, the solution contains the major species

$$NH_3,\quad NH_4^+,\quad Cl^-,\quad \text{and}\quad H_2O$$

and

$$[NH_3]_0 = \frac{0.15\text{ mol}}{1.0\text{ L}} = 0.15\ M$$

$$[NH_4^+]_0 = \frac{0.50\text{ mol}}{1.0\text{ L}} = 0.50\ M$$

We can use the Henderson–Hasselbalch equation, where

$$[\text{Base}] = [NH_3] \approx [NH_3]_0 = 0.15\ M$$
$$[\text{Acid}] = [NH_4^+] \approx [NH_4^+]_0 = 0.50\ M$$

Then

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) \\ &= 9.25 + \log\left(\frac{0.15\ M}{0.50\ M}\right) = 9.25 - 0.52 = 8.73 \end{aligned}$$

Note that the addition of HCl only slightly decreases the pH, as we would expect in a buffered solution.

See Exercise 15.39.

Summary of the Most Important Characteristics of Buffered Solutions

- **Buffered solutions contain relatively large concentrations of a weak acid and the corresponding weak base. They can involve a weak acid HA and the conjugate base A^- or a weak base B and the conjugate acid BH^+.**
- **When H^+ is added to a buffered solution, it reacts essentially to completion with the weak base present:**

$$H^+ + A^- \longrightarrow HA \quad \text{or} \quad H^+ + B \longrightarrow BH^+$$

- **When OH^- is added to a buffered solution, it reacts essentially to completion with the weak acid present:**

$$OH^- + HA \longrightarrow A^- + H_2O \quad \text{or} \quad OH^- + BH^+ \longrightarrow B + H_2O$$

- The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and weak base. As long as this ratio remains virtually constant, the pH will remain virtually constant. This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with the amounts of H^+ or OH^- added.

15.3 Buffering Capacity

A buffer with a large capacity contains large concentrations of the buffering components.

The **buffering capacity** of a buffered solution represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH. A buffer with a large capacity contains large concentrations of buffering components and so can absorb a relatively large amount of protons or hydroxide ions and show little pH change. *The pH of a buffered solution is determined by the ratio* $[A^-]/[HA]$. *The capacity of a buffered solution is determined by the magnitudes of* $[HA]$ *and* $[A^-]$.

Sample Exercise 15.7 Adding Strong Acid to a Buffered Solution II

Calculate the change in pH that occurs when 0.010 mol gaseous HCl is added to 1.0 L of each of the following solutions:

Solution A: $5.00\ M\ HC_2H_3O_2$ and $5.00\ M\ NaC_2H_3O_2$
Solution B: $0.050\ M\ HC_2H_3O_2$ and $0.050\ M\ NaC_2H_3O_2$

For acetic acid, $K_a = 1.8 \times 10^{-5}$.

Solution

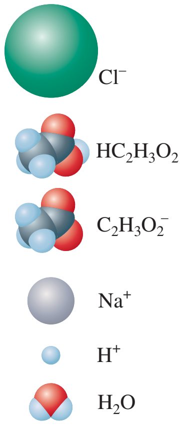
For both solutions the initial pH can be determined from the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

In each case, $[C_2H_3O_2^-] = [HC_2H_3O_2]$. Therefore, the initial pH for both A and B is

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Major Species



After the addition of HCl to each of these solutions, the major species *before any reaction occurs* are

$$HC_2H_3O_2,\quad Na^+,\quad C_2H_3O_2^-,\quad \underbrace{H^+,\quad Cl^-,}_{\text{From the added HCl}}\quad \text{and}\quad H_2O$$

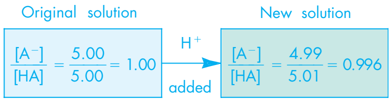
Will any reactions occur among these species? Note that we have a relatively large quantity of H^+, which will readily react with any effective base. We know that Cl^- will not react with H^+ to form HCl in water. However, $C_2H_3O_2^-$ will react with H^+ to form the weak acid $HC_2H_3O_2$:

$$H^+(aq) + C_2H_3O_2^-(aq) \longrightarrow HC_2H_3O_2(aq)$$

Because $HC_2H_3O_2$ is a weak acid, we assume that this reaction runs to completion; the 0.010 mol of added H^+ will convert 0.010 mol $C_2H_3O_2^-$ to 0.010 mol $HC_2H_3O_2$.

For solution A (since the solution volume is 1.0 L, the number of moles equals the molarity), the following calculations apply:

	H^+	$+$	$C_2H_3O_2^-$	$\longrightarrow$	$HC_2H_3O_2$
Before reaction:	$0.010\ M$		$5.00\ M$		$5.00\ M$
After reaction:	0		$4.99\ M$		$5.01\ M$



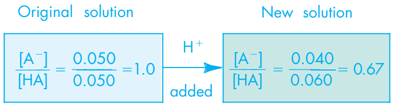
The new pH can be obtained by substituting the new concentrations into the Henderson–Hasselbalch equation:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right) \\ &= 4.74 + \log\left(\frac{4.99}{5.01}\right) = 4.74 - 0.0017 = 4.74 \end{aligned}$$

There is virtually no change in pH for solution A when 0.010 mol gaseous HCl is added.

For solution B, the following calculations apply:

	H^+	+	$C_2H_3O_2^-$	$\longrightarrow$	$HC_2H_3O_2$
Before reaction:	0.010 *M*		0.050 *M*		0.050 *M*
After reaction:	0		0.040 *M*		0.060 *M*



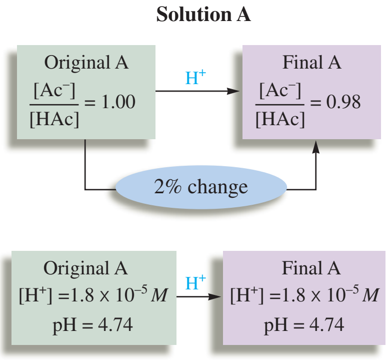
The new pH is

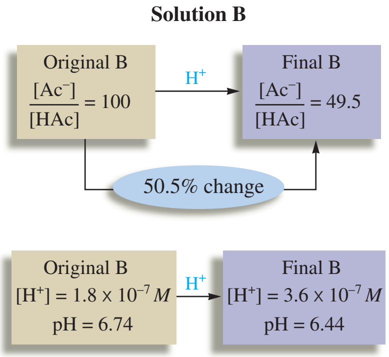
$$\begin{aligned} pH &= 4.74 + \log\left(\frac{0.040}{0.060}\right) \\ &= 4.74 - 0.18 = 4.56 \end{aligned}$$

Although the pH change for solution B is small, a change did occur, which is in contrast to solution A.

These results show that solution A, which contains much larger quantities of buffering components, has a much higher buffering capacity than solution B.

See Exercises 15.39 and 15.40.





We have seen that the pH of a buffered solution depends on the ratio of the concentrations of buffering components. When this ratio is least affected by added protons or hydroxide ions, the solution is the most resistant to a change in pH. To find the ratio that gives optimal buffering, let's suppose we have a buffered solution containing a large concentration of acetate ion and only a small concentration of acetic acid. Addition of protons to form acetic acid will produce a relatively large *percent* change in the concentration of acetic acid and so will produce a relatively large change in the ratio $[C_2H_3O_2^-]/[HC_2H_3O_2]$ (see Table 15.1). Similarly, if hydroxide ions are added to remove some acetic acid, the percent change in the concentration of acetic acid is again large. The same effects are seen if the initial concentration of acetic acid is large and that of acetate ion is small.

TABLE 15.1 Change in $[C_2H_3O_2^-]/[HC_2H_3O_2^-]$ for Two Solutions When 0.01 mol H^+ Is Added to 1.0 L of Each

Solution	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{orig}$	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{new}$	Change	Percent Change
A	$\frac{1.00\ M}{1.00\ M} = 1.00$	$\frac{0.99\ M}{1.01\ M} = 0.98$	1.00 → 0.98	2.00%
B	$\frac{1.00\ M}{0.01\ M} = 100$	$\frac{0.99\ M}{0.02\ M} = 49.5$	100 → 49.5	50.5%

Because large changes in the ratio $[A^-]/[HA]$ will produce large changes in pH, we want to avoid this situation for the most effective buffering. This type of reasoning leads us to the general conclusion that optimal buffering occurs when [HA] is equal to $[A^-]$. It is for this condition that the ratio $[A^-]/[HA]$ is most resistant to change when H^+ or OH^- is added to the buffered solution. This means that when choosing the buffering components for a specific application, we want $[A^-]/[HA]$ to equal 1. It follows that since

$$\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) = \text{p}K_a + \log(1) = \text{p}K_a$$

the *p*K_a *of the weak acid to be used in the buffer should be as close as possible to the desired pH.* For example, suppose we need a buffered solution with a pH of 4.00. The most effective buffering will occur when [HA] is equal to $[A^-]$. From the Henderson–Hasselbalch equation,

$$\underset{\substack{\uparrow \\ \text{4.00 is} \\ \text{wanted}}}{\text{pH}} = \text{p}K_a + \log\left(\underset{\substack{\uparrow \\ \text{Ratio = 1 for most effective buffer}}}{\frac{[A^-]}{[HA]}}\right)$$

That is, $4.00 = \text{p}K_a + \log(1) = \text{p}K_a + 0$ and $\text{p}K_a = 4.00$

Thus the best choice of a weak acid is one that has $\text{p}K_a = 4.00$ or $K_a = 1.0 \times 10^{-4}$.

Sample Exercise 15.8

Preparing a Buffer

A chemist needs a solution buffered at pH 4.30 and can choose from the following acids (and their sodium salts):

a. chloroacetic acid ($K_a = 1.35 \times 10^{-3}$)
b. propanoic acid ($K_a = 1.3 \times 10^{-5}$)
c. benzoic acid ($K_a = 6.4 \times 10^{-5}$)
d. hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)

Calculate the ratio $[HA]/[A^-]$ required for each system to yield a pH of 4.30. Which system will work best?

Solution

A pH of 4.30 corresponds to

$$[H^+] = 10^{-4.30} = \text{antilog}(-4.30) = 5.0 \times 10^{-5}\,M$$

Since K_a values rather than pK_a values are given for the various acids, we use Equation (15.1)

$$[H^+] = K_a\frac{[HA]}{[A^-]}$$

rather than the Henderson–Hasselbalch equation. We substitute the required $[H^+]$ and K_a for each acid into Equation (15.1) to calculate the ratio $[HA]/[A^-]$ needed in each case.

Acid	$[H^+] = K_a\frac{[HA]}{[A^-]}$	$\frac{[HA]}{[A^-]}$
a. Chloroacetic	$5.0 \times 10^{-5} = 1.35 \times 10^{-3}\left(\frac{[HA]}{[A^-]}\right)$	3.7×10^{-2}
b. Propanoic	$5.0 \times 10^{-5} = 1.3 \times 10^{-5}\left(\frac{[HA]}{[A^-]}\right)$	3.8
c. Benzoic	$5.0 \times 10^{-5} = 6.4 \times 10^{-5}\left(\frac{[HA]}{[A^-]}\right)$	0.78
d. Hypochlorous	$5.0 \times 10^{-5} = 3.5 \times 10^{-8}\left(\frac{[HA]}{[A^-]}\right)$	1.4×10^3

Since $[HA]/[A^-]$ for benzoic acid is closest to 1, the system of benzoic acid and its sodium salt will be the best choice among those given for buffering a solution at pH 4.3. This example demonstrates the principle that the optimal buffering system has a pK_a value close to the desired pH. The pK_a for benzoic acid is 4.19.

See Exercises 15.45 and 15.46.

15.4 Titrations and pH Curves

As we saw in Chapter 4, a titration is commonly used to determine the amount of acid or base in a solution. This process involves a solution of known concentration (the titrant) delivered from a buret into the unknown solution until the substance being analyzed is just consumed. The stoichiometric (equivalence) point is often signaled by the color change of an indicator. In this section we will discuss the pH changes that occur during an acid–base titration. We will use this information later to show how an appropriate indicator can be chosen for a particular titration.

The progress of an acid–base titration is often monitored by plotting the pH of the solution being analyzed as a function of the amount of titrant added. Such a plot is called a **pH curve** or **titration curve.**

A setup used to do the pH titration of an acid or a base.

Strong Acid–Strong Base Titrations

The net ionic reaction for a strong acid–strong base titration is

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

To compute $[H^+]$ at a given point in the titration, we must determine the amount of H^+ that remains at that point and divide by the total volume of the solution. Before we proceed, we need to consider a new unit, which is especially convenient for titrations. Since titrations usually involve small quantities (burets are typically graduated in milliliters), the mole is inconveniently large. Therefore, we will use the **millimole** (abbreviated **mmol**), which, as the prefix indicates, is a thousandth of a mole:

$$1 \text{ mmol} = \frac{1 \text{ mol}}{1000} = 10^{-3} \text{ mol}$$

So far we have defined molarity only in terms of moles per liter. We can now define it in terms of *millimoles per milliliter,* as shown below:

$1 \text{ millimole} = 1 \times 10^{-3} \text{ mol}$
$1 \text{ mL} = 1 \times 10^{-3} \text{ L}$

$$\frac{\text{mmol}}{\text{mL}} = \frac{\text{mol}}{\text{L}} = M$$

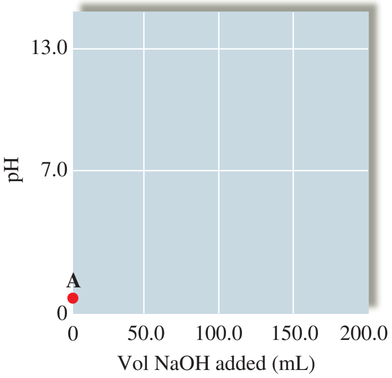
$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{\dfrac{\text{mol solute}}{1000}}{\dfrac{\text{L solution}}{1000}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

A 1.0 M solution thus contains 1.0 mole of solute per liter of solution or, *equivalently,* 1.0 millimole of solute per milliliter of solution. Just as we obtain the number of moles of solute from the product of the volume in liters and the molarity, we obtain the number of millimoles of solute from the product of the volume in milliliters and the molarity:

$$\text{Number of mmol} = \text{volume (in mL)} \times \text{molarity}$$

CASE STUDY: *Strong Acid–Strong Base Titration*

We will illustrate the calculations involved in a strong acid–strong base titration by considering the titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH. We will calculate the pH of the solution at selected points during the course of the titration, where specific volumes of 0.100 M NaOH have been added.



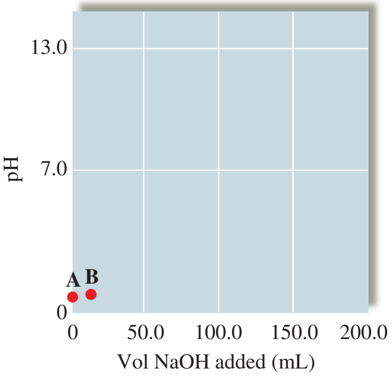
A. No NaOH has been added.

Since HNO_3 is a strong acid (is completely dissociated), the solution contains the major species

$$H^+, \quad NO_3^-, \quad \text{and} \quad H_2O$$

and the pH is determined by the H^+ from the nitric acid. Since 0.200 M HNO_3 contains 0.200 M H^+,

$$[H^+] = 0.200\,M \quad \text{and} \quad \text{pH} = 0.699$$



B. 10.0 mL of 0.100 M NaOH has been added.

In the mixed solution *before any reaction occurs,* the major species are

$$H^+, \quad NO_3^-, \quad Na^+, \quad OH^-, \quad \text{and} \quad H_2O$$

Note that large quantities of both H^+ and OH^- are present. The 1.00 mmol (10.0 mL × 0.100 M) of added OH^- will react with 1.00 mmol H^+ to form water:

	H^+	+	OH^-	$\longrightarrow$	H_2O
Before reaction:	$50.0 \text{ mL} \times 0.200\,M$ $= 10.0 \text{ mmol}$		$10.0 \text{ mL} \times 0.100\,M$ $= 1.00 \text{ mmol}$		
After reaction:	$10.0 - 1.00$ $= 9.0 \text{ mmol}$		$1.00 - 1.00$ $= 0$		

After the reaction, the solution contains

$$H^+, \quad NO_3^-, \quad Na^+, \quad \text{and} \quad H_2O \text{ (the } OH^- \text{ ions have been consumed)}$$

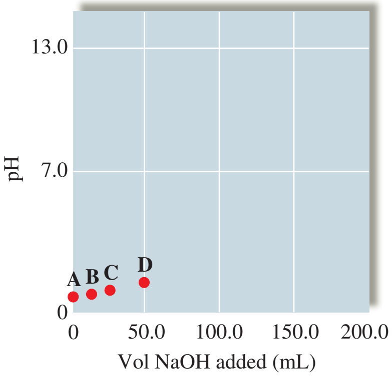
and the pH will be determined by the H^+ remaining:

The final solution volume is the sum of the original volume of HNO_3 and the volume of added NaOH.

$$[H^+] = \frac{\text{mmol } H^+ \text{ left}}{\text{volume of solution (mL)}} = \frac{9.0 \text{ mmol}}{(\underset{\substack{\nearrow \\ \text{Original volume of} \\ HNO_3 \text{ solution}}}{50.0} + \underset{\substack{\nwarrow \\ \text{Volume of} \\ \text{NaOH added}}}{10.0}) \text{ mL}} = 0.15\,M$$

$$\text{pH} = -\log(0.15) = 0.82$$

C. 20.0 mL (total) of 0.100 *M* NaOH has been added.
We consider this point from the perspective that a total of 20.0 mL NaOH has been added to the *original* solution, rather than that 10.0 mL has been added to the solution from point B. It is best to go back to the original solution each time so that a mistake made at an earlier point does not show up in each succeeding calculation. As before, the added OH^- will react with H^+ to form water:



	H^+	+	OH^-	$\longrightarrow$	H_2O
Before reaction:	50.0 mL × 0.200 *M* = 10.0 mmol		20.0 mL × 0.100 *M* = 2.00 mmol		
After reaction:	10.0 − 2.00 = 8.00 mmol		2.00 − 2.00 = 0 mmol		

After the reaction

$$[H^+] = \frac{\overset{(H^+\ \text{remaining})}{8.00\ \text{mmol}}}{(50.0 + 20.0)\ \text{mL}} = 0.11\ M$$

$$\text{pH} = 0.942$$

D. 50.0 mL (total) of 0.100 *M* NaOH has been added.
Proceeding exactly as for points B and C, the pH is found to be 1.301.

Equivalence (stoichiometric) point: The point in the titration where an amount of base has been added to exactly react with all the acid originally present.

E. 100.0 mL (total) of 0.100 *M* NaOH has been added.
At this point the amount of NaOH that has been added is

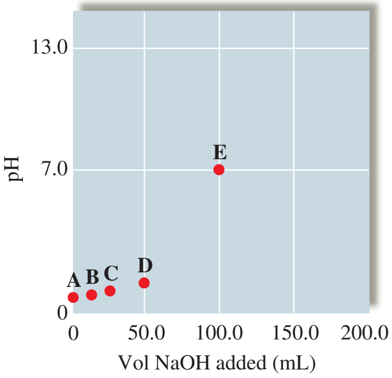
$$100.0\ \text{mL} \times 0.100\ M = 10.0\ \text{mmol}$$

The original amount of nitric acid was

$$50.0\ \text{mL} \times 0.200\ M = 10.0\ \text{mmol}$$

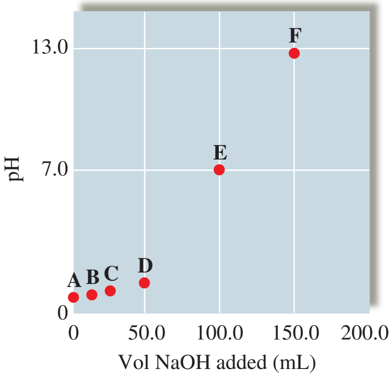
Enough OH^- has been added to react exactly with the H^+ from the nitric acid. This is the **stoichiometric point,** or **equivalence point,** of the titration. At this point the major species in solution are

$$Na^+, \quad NO_3^-, \quad \text{and} \quad H_2O$$



Since Na^+ has no acid or base properties and NO_3^- is the anion of the strong acid HNO_3 and is therefore a very weak base, neither NO_3^- nor Na^+ affects the pH, and the solution is neutral (the pH is 7.00).

F. 150.0 mL (total) of 0.100 *M* NaOH has been added.
The stoichiometric calculations for the titration reaction are as follows:



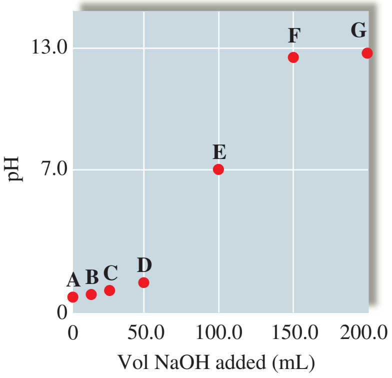
	H^+	+	OH^-	$\longrightarrow$	H_2O
Before reaction:	50.0 mL × 0.200 *M* = 10.0 mmol		150.0 mL × 0.100 *M* = 15.0 mmol		
After reaction:	10.0 − 10.0 = 0 mmol		15.0 − 10.0 = 5.0 mmol ↑ Excess OH^- added		

Now OH^- is *in excess* and will determine the pH:

$$[OH^-] = \frac{\text{mmol OH}^- \text{ in excess}}{\text{volume (mL)}} = \frac{5.0 \text{ mmol}}{(50.0 + 150.0) \text{ mL}} = \frac{5.0 \text{ mmol}}{200.0 \text{ mL}} = 0.025\ M$$

Since $[H^+][OH^-] = 1.0 \times 10^{-14}$,

$$[H^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-2}} = 4.0 \times 10^{-13}\ M \qquad \text{and} \qquad \text{pH} = 12.40$$



G. 200.0 mL (total) of 0.100 *M* NaOH has been added.
Proceeding as for point F, the pH is found to be 12.60.

The results of these calculations are summarized by the pH curve shown in Fig. 15.1. Note that the pH changes very gradually until the titration is close to the equivalence point, where a dramatic change occurs. This behavior is due to the fact that early in the titration there is a relatively large amount of H^+ in the solution, and the addition of a given amount of OH^- thus produces a small change in pH. However, near the equivalence point $[H^+]$ is relatively small, and the addition of a small amount of OH^- produces a large change.

The pH curve in Fig. 15.1, typical of the titration of a strong acid with a strong base, has the following characteristics:

> Before the equivalence point, $[H^+]$ (and hence the pH) can be calculated by dividing the number of millimoles of H^+ remaining by the total volume of the solution in millimeters.
>
> At the equivalence point, the pH is 7.00.
>
> After the equivalence point, $[OH^-]$ can be calculated by dividing the number of millimoles of excess OH^- by the total volume of the solution. Then $[H^+]$ is obtained from K_w.

The titration of a strong base with a strong acid requires reasoning very similar to that used above, except, of course, that OH^- is in excess before the equivalence point and H^+ is in excess after the equivalence point. The pH curve for the titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl is shown in Fig. 15.2.

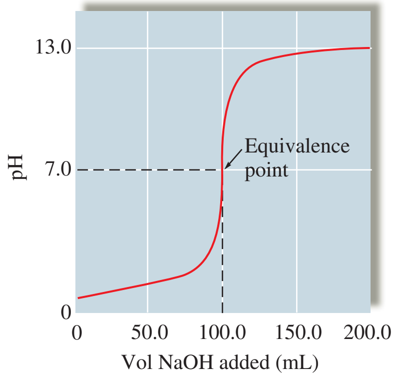


FIGURE 15.1
The pH curve for the titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH. Note that the equivalence point occurs at 100.0 mL of NaOH added, the point where exactly enough OH^- has been added to react with all the H^+ originally present. The pH of 7 at the equivalence point is characteristic of a strong acid–strong base titration.

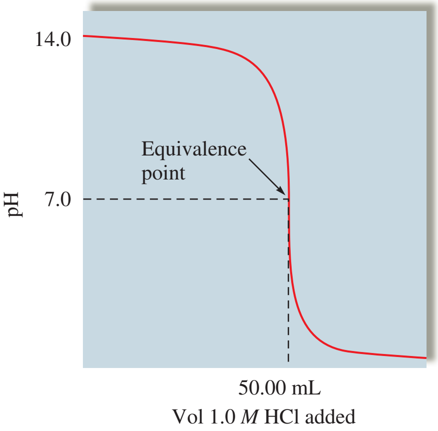
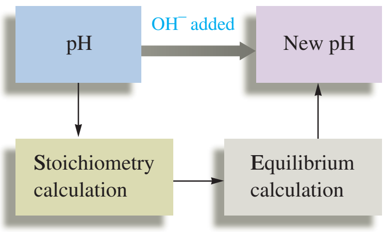


FIGURE 15.2
The pH curve for the titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl. The equivalence point occurs at 50.00 mL of HCl added, since at this point 5.0 mmol H^+ has been added to react with the original 5.0 mmol OH^-.

Titrations of Weak Acids with Strong Bases

We have seen that since strong acids and strong bases are completely dissociated, the calculations to obtain the pH curves for titrations involving the two are quite straightforward. However, when the acid being titrated is a weak acid, there is a major difference: To calculate $[H^+]$ after a certain amount of strong base has been added, we must deal with the weak acid dissociation equilibrium. We have dealt with this same situation earlier in this chapter when we treated buffered solutions. Calculation of the pH curve for a titration of a weak acid with a strong base really amounts to a series of buffer problems. In performing these calculations it is very important to remember that even though the acid is weak, it *reacts essentially to completion* with hydroxide ion, a very strong base.



Calculating the pH curve for a weak acid–strong base titration involves a two-step procedure.

1. ***A stoichiometry problem.*** **The reaction of hydroxide ion with the weak acid is assumed to run to completion, and the concentrations of the acid *remaining* and the conjugate base *formed* are determined.**
2. ***An equilibrium problem.*** **The position of the weak acid equilibrium is determined, and the pH is calculated.**

Treat the stoichiometry and equilibrium problems separately.

It is *essential* to do these steps *separately*. Note that the procedures necessary to do these calculations have all been used before.

CASE STUDY: *Weak Acid–Strong Base Titration*

As an illustration, we will consider the titration of 50.0 mL of 0.10 *M* acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) with 0.10 *M* NaOH. As before, we will calculate the pH at various points representing volumes of added NaOH.

A. No NaOH has been added.

This is a typical weak acid calculation of the type introduced in Chapter 14. The pH is 2.87. (Check this yourself.)

B. 10.0 mL of 0.10 *M* NaOH has been added.

The major species in the mixed solution *before any reaction takes place* are

$$HC_2H_3O_2,\quad OH^-,\quad Na^+,\quad \text{and}\quad H_2O$$

The strong base OH^- will react with the strongest proton donor, which in this case is $HC_2H_3O_2$.

The Stoichiometry Problem

You are again doing exactly the same type of calculation already considered in Chapter 14.

	OH^-	+	$HC_2H_3O_2$	$\longrightarrow$	$C_2H_3O_2^-$	+	H_2O
Before reaction:	10 mL × 0.10 *M* = 1.0 mmol		50.0 mL × 0.10 *M* = 5.0 mmol		0 mmol		
After reaction:	1.0 − 1.0 = 0 mmol ↑ Limiting reactant		5.0 − 1.0 = 4.0 mmol		1.0 mmol ↑ Formed by the reaction		

The Equilibrium Problem

We examine the major components left in the solution *after the reaction takes place* to decide on the dominant equilibrium. The major species are

$$HC_2H_3O_2,\quad C_2H_3O_2^-,\quad Na^+,\quad \text{and}\quad H_2O$$

Since $HC_2H_3O_2$ is a much stronger acid than H_2O, and since $C_2H_3O_2^-$ is the conjugate base of $HC_2H_3O_2$, the pH will be determined by the position of the acetic acid dissociation equilibrium:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

where

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

We follow the usual steps to complete the equilibrium calculations:

The initial concentrations are defined after the reaction with OH^- has gone to completion but before any dissociation of $HC_2H_3O_2$ occurs.

Initial Concentration		**Equilibrium Concentration**
$[HC_2H_3O_2]_0 = \frac{4.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{4.0}{60.0}$		$[HC_2H_3O_2] = \frac{4.0}{60.0} - x$
$[C_2H_3O_2^-]_0 = \frac{1.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{1.0}{60.0}$	$\xrightarrow[\text{dissociates}]{x \text{ mmol/mL } HC_2H_3O_2}$	$[C_2H_3O_2^-] = \frac{1.0}{60.0} + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

The appropriate ICE table is

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:	$\frac{4.0}{60.0}$		≈ 0		$\frac{1.0}{60.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{4.0}{60.0} - x$		x		$\frac{1.0}{60.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x\left(\frac{1.0}{60.0} + x\right)}{\frac{4.0}{60.0} - x} \approx \frac{x\left(\frac{1.0}{60.0}\right)}{\frac{4.0}{60.0}} = \left(\frac{1.0}{4.0}\right)x$$

Note that the approximations made are well within the 5% rule.

$$x = \left(\frac{4.0}{1.0}\right)(1.8 \times 10^{-5}) = 7.2 \times 10^{-5} = [H^+] \quad \text{and} \quad \text{pH} = 4.14$$

C. 25.0 mL (total) of 0.10 *M* NaOH has been added.

The procedure here is very similar to that used at point B and will only be summarized briefly. The stoichiometry problem is summarized as follows:

	OH^-	+	$HC_2H_3O_2$	$\longrightarrow$	$C_2H_3O_2^-$	+	H_2O
Before reaction:	25.0 mL × 0.10 *M* = 2.5 mmol		50.0 mL × 0.10 *M* = 5.0 mmol		0 mmol		
After reaction:	2.5 − 2.5 = 0		5.0 − 2.5 = 2.5 mmol		2.5 mmol		

After the reaction, the major species in solution are

$$HC_2H_3O_2, \quad C_2H_3O_2^-, \quad Na^+, \quad \text{and} \quad H_2O$$

The equilibrium that will control the pH is

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

and the pertinent concentrations are as follows:

Initial Concentration		Equilibrium Concentration
$[HC_2H_3O_2]_0 = \dfrac{2.5\text{ mmol}}{(50.0 + 25.0)\text{ mL}}$	$\xrightarrow[\text{dissociates}]{x\text{ mmol/mL } HC_2H_3O_2}$	$[HC_2H_3O_2] = \dfrac{2.5}{75.0} - x$
$[C_2H_3O_2^-]_0 = \dfrac{2.5\text{ mmol}}{(50.0 + 25.0)\text{ mL}}$		$[C_2H_3O_2^-] = \dfrac{2.5}{75.0} + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

The corresponding ICE table is

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial:	$\dfrac{2.5}{75.0}$		≈ 0		$\dfrac{2.5}{75.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\dfrac{2.5}{75.0} - x$		x		$\dfrac{2.5}{75.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x\left(\dfrac{2.5}{75.0} + x\right)}{\dfrac{2.5}{75.0} - x} \approx \frac{x\left(\dfrac{2.5}{75.0}\right)}{\dfrac{2.5}{75.0}}$$

$$x = 1.8 \times 10^{-5} = [H^+] \quad \text{and} \quad \text{pH} = 4.74$$

This is a special point in the titration because it is *halfway to the equivalence point.* The original solution, 50.0 mL of 0.10 M $HC_2H_3O_2$, contained 5.0 mmol $HC_2H_3O_2$. Thus 5.0 mmol OH^- is required to reach the equivalence point. That is, 50 mL NaOH is required, since

$$(50.0\text{ mL})(0.10\ M) = 5.0\text{ mmol}$$

After 25.0 mL NaOH has been added, half the original $HC_2H_3O_2$ has been converted to $C_2H_3O_2^-$. At this point in the titration $[HC_2H_3O_2]_0$ is equal to $[C_2H_3O_2^-]_0$. We can neglect the effect of dissociation; that is,

At this point, half the acid has been used up, so

$$[HC_2H_3O_2] = [C_2H_3O_2^-]$$

$$[HC_2H_3O_2] = [HC_2H_3O_2]_0 - x \approx [HC_2H_3O_2]_0$$

$$[C_2H_3O_2^-] = [C_2H_3O_2^-]_0 + x \approx [C_2H_3O_2^-]_0$$

The expression for K_a at the halfway point is

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{[H^+][C_2H_3O_2^-]_0}{[HC_2H_3O_2]_0} = [H^+]$$

Equal at the halfway point

Then, *at the halfway point* in the titration,

$$[H^+] = K_a \quad \text{and} \quad pH = pK_a$$

D. 40.0 mL (total) of 0.10 *M* NaOH has been added.

The procedures required here are the same as those used for points B and C. The pH is 5.35. (Check this yourself.)

E. 50.0 mL (total) of 0.10 *M* NaOH has been added.

This is the equivalence point of the titration; 5.0 mmol OH^- has been added, which will just react with the 5.0 mmol $HC_2H_3O_2$ originally present. At this point the solution contains the major species

$$Na^+, \quad C_2H_3O_2^-, \quad \text{and} \quad H_2O$$

Note that the solution contains $C_2H_3O_2^-$, which is a base. Remember that a base wants to combine with a proton, and the only source of protons in this solution is water. Thus the reaction will be

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

This is a *weak base* reaction characterized by K_b:

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The relevant concentrations are as follows:

Initial Concentration (before any $C_2H_3O_2^-$ reacts with H_2O)		Equilibrium Concentration
$[C_2H_3O_2^-]_0 = \frac{5.0 \text{ mmol}}{(50.0 + 50.0) \text{ mL}} = 0.050\ M$	$\xrightarrow[\text{with } H_2O]{x \text{ mmol/mL } C_2H_3O_2^- \text{ reacts}}$	$[C_2H_3O_2^-] = 0.050 - x$
$[OH^-]_0 \approx 0$		$[OH^-] = x$
$[HC_2H_3O_2]_0 = 0$		$[HC_2H_3O_2] = x$

The corresponding ICE table is

	$C_2H_3O_2^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HC_2H_3O_2(aq)$	+	$OH^-(aq)$
Initial:	0.050		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Therefore,

$$5.6 \times 10^{-10} = K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{(x)(x)}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x \approx 5.3 \times 10^{-6}$$

The approximation is valid (by the 5% rule), so

$$[OH^-] = 5.3 \times 10^{-6}\ M$$

and

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$[H^+] = 1.9 \times 10^{-9}\ M$$

$$pH = 8.72$$

The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.

This is another important result: *The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.* This is so because the anion of the acid, which remains in solution at the equivalence point, is a base. In contrast, for the titration of a strong acid with a strong base, the pH at the equivalence point is 7.0, because the anion remaining in this case is *not* an effective base.

F. 60.0 mL (total) of 0.10 *M* NaOH has been added.
At this point, excess OH^- has been added. The stoichiometric calculations are as follows:

	OH^-	+	$HC_2H_3O_2$	$\longrightarrow$	$C_2H_3O_2^-$	+	H_2O
Before reaction:	$60.0\text{ mL} \times 0.10\ M = 6.0\text{ mmol}$		$50.0\text{ mL} \times 0.10\ M = 5.0\text{ mmol}$		0 mmol		
After reaction:	$6.0 - 5.0 = 1.0$ mmol in excess		$5.0 - 5.0 = 0$		5.0 mmol		

After the reaction is complete, the solution contains the major species

$$Na^+,\quad C_2H_3O_2^-,\quad OH^-,\quad \text{and}\quad H_2O$$

There are two bases in this solution, OH^- and $C_2H_3O_2^-$. However, $C_2H_3O_2^-$ is a weak base compared with OH^-. Therefore, the amount of OH^- produced by reaction of $C_2H_3O_2^-$ with H_2O will be small compared with the excess OH^- already in solution. You can verify this conclusion by looking at point E, where only $5.3 \times 10^{-6}\ M$ OH^- was produced by $C_2H_3O_2^-$. The amount in this case will be even smaller, since the excess OH^- will push the K_b equilibrium to the left.

Thus the pH is determined by the excess OH^-:

$$[OH^-] = \frac{\text{mmol of } OH^- \text{ in excess}}{\text{volume (in mL)}} = \frac{1.0\text{ mmol}}{(50.0 + 60.0)\text{ mL}}$$
$$= 9.1 \times 10^{-3}\ M$$

and

$$[H^+] = \frac{1.0 \times 10^{-14}}{9.1 \times 10^{-3}} = 1.1 \times 10^{-12}\ M$$
$$\text{pH} = 11.96$$

G. 75.0 mL (total) of 0.10 *M* NaOH has been added.
The procedure needed here is very similar to that for point F. The pH is 12.30. (Check this yourself.)

The pH curve for this titration is shown in Fig. 15.3. It is important to note the differences between this curve and that in Fig. 15.1. For example, the shapes of the plots are

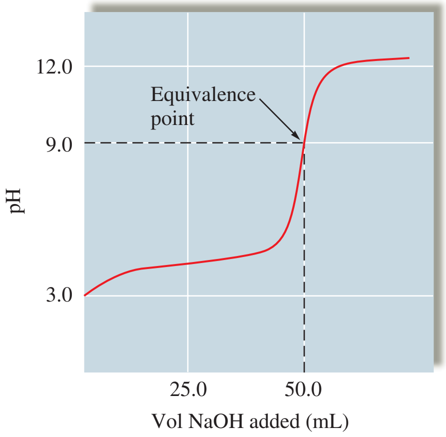
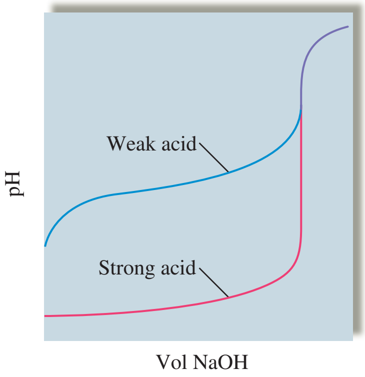


FIGURE 15.3
The pH curve for the titration of 50.0 mL of 0.100 *M* $HC_2H_3O_2$ with 0.100 *M* NaOH. Note that the equivalence point occurs at 50.0 mL of NaOH added, where the amount of added OH^- exactly equals the original amount of acid. The pH at the equivalence point is greater than 7.0 because the $C_2H_3O_2^-$ ion present at this point is a base and reacts with water to produce OH^-.



quite different before the equivalence point, although they are very similar after that point. (The shapes of the strong and weak acid curves are the same after the equivalence points because excess OH^- controls the pH in this region in both cases.) Near the beginning of the titration of the weak acid, the pH increases more rapidly than it does in the strong acid case. It levels off near the halfway point and then increases rapidly again. The leveling off near the halfway point is caused by buffering effects. Earlier in this chapter we saw that optimal buffering occurs when [HA] is equal to $[A^-]$. This is exactly the case at the halfway point of the titration. As we can see from the curve, the pH changes least rapidly in this region of the titration.

The other notable difference between the curves for strong and weak acids is the value of the pH at the equivalence point. For the titration of a strong acid, the equivalence point occurs at pH 7. For the titration of a weak acid, the pH at the equivalence point is greater than 7 because of the basicity of the conjugate base of the weak acid.

The equivalence point is defined by the stoichiometry, not by the pH.

It is important to understand that the equivalence point in an acid–base titration is *defined by the stoichiometry, not by the pH.* The equivalence point occurs when enough titrant has been added to react exactly with all the acid or base being titrated.

Sample Exercise 15.9 Titration of a Weak Acid

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a very weak acid ($K_a = 6.2 \times 10^{-10}$) when dissolved in water. If a 50.0-mL sample of 0.100 *M* HCN is titrated with 0.100 *M* NaOH, calculate the pH of the solution

a. after 8.00 mL of 0.100 *M* NaOH has been added.
b. at the halfway point of the titration.
c. at the equivalence point of the titration.

Solution

a. *The stoichiometry problem.* After 8.00 mL of 0.100 *M* NaOH has been added, the following calculations apply:

	HCN	+	OH^-	$\longrightarrow$	CN^-	+	H_2O
Before reaction:	50.0 mL × 0.100 *M* = 5.00 mmol		8.00 mL × 0.100 *M* = 0.800 mmol		0 mmol		
After reaction:	5.00 − 0.800 = 4.20 mmol		0.800 − 0.800 = 0		0.800 mmol		

The equilibrium problem. Since the solution contains the major species

$$HCN,\quad CN^-,\quad Na^+,\quad \text{and}\quad H_2O$$

the position of the acid dissociation equilibrium

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

will determine the pH.

Initial Concentration		Equilibrium Concentration
$[HCN]_0 = \dfrac{4.2\text{ mmol}}{(50.0 + 8.0)\text{ mL}}$		$[HCN] = \dfrac{4.2}{58.0} - x$
$[CN^-]_0 = \dfrac{0.800\text{ mmol}}{(50.0 + 8.0)\text{ mL}}$	$\xrightarrow[\text{dissociates}]{x\text{ mmol/mL HCN}}$	$[CN^-] = \dfrac{0.80}{58.0} + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

The corresponding ICE table is

	$HCN(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CN^-(aq)$
Initial:	$\frac{4.2}{58.0}$		≈ 0		$\frac{0.80}{58.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{4.2}{58.0} - x$		x		$\frac{0.80}{58.0} + x$

Substituting the equilibrium concentrations into the expression for K_a gives

The approximations made here are well within the 5% rule.

$$6.2 \times 10^{-10} = K_a = \frac{[H^+][CN^-]}{[HCN]} = \frac{x\left(\frac{0.80}{58.0} + x\right)}{\frac{4.2}{58.0} - x} \approx \frac{x\left(\frac{0.80}{58.0}\right)}{\left(\frac{4.2}{58.0}\right)} = x\left(\frac{0.80}{4.2}\right)$$

$$x = 3.3 \times 10^{-9}\ M = [H^+] \quad \text{and} \quad \text{pH} = 8.49$$

b. *At the halfway point of the titration.* The amount of HCN originally present can be obtained from the original volume and molarity:

$$50.0\ \text{mL} \times 0.100\ M = 5.00\ \text{mmol}$$

Thus the halfway point will occur when 2.50 mmol OH^- has been added:

$$\text{Volume of NaOH (in mL)} \times 0.100\ M = 2.50\ \text{mmol}\ OH^-$$

or

$$\text{Volume of NaOH} = 25.0\ \text{mL}$$

As was pointed out previously, at the halfway point [HCN] is equal to $[CN^-]$ and pH is equal to pK_a. Thus, after 25.0 mL of 0.100 M NaOH has been added,

$$\text{pH} = \text{p}K_a = -\log(6.2 \times 10^{-10}) = 9.21$$

c. *At the equivalence point.* The equivalence point will occur when a total of 5.00 mmol OH^- has been added. Since the NaOH solution is 0.100 M, the equivalence point occurs when 50.0 mL NaOH has been added. This amount will form 5.00 mmol CN^-. The major species in solution at the equivalence point are

$$CN^-, \quad Na^+, \quad \text{and} \quad H_2O$$

Thus the reaction that will control the pH involves the basic cyanide ion extracting a proton from water:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

and

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]}$$

Initial Concentration		**Equilibrium Concentration**
$[CN^-]_0 = \frac{5.00\ \text{mmol}}{(50.0 + 50.0)\ \text{mL}}$ $= 5.00 \times 10^{-2}\ M$	$\xrightarrow[\text{with } H_2O]{x \text{ mmol/mL of } CN^- \text{ reacts}}$	$[CN^-] = (5.00 \times 10^{-2}) - x$
$[HCN]_0 = 0$		$[HCN] = x$
$[OH^-]_0 \approx 0$		$[OH^-] = x$

The corresponding ICE table is

	$CN^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HCN(aq)$	+	$OH^-(aq)$
Initial:	0.050		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Substituting the equilibrium concentrations into the expression for K_b and solving in the usual way gives

$$[OH^-] = x = 8.9 \times 10^{-4}$$

Then, from K_w, we have

$$[H^+] = 1.1 \times 10^{-11} \quad \text{and} \quad pH = 10.96$$

See Exercises 15.55, 15.57, and 15.58.

The amount of acid present, not its strength, determines the equivalence point.

Two important conclusions can be drawn from a comparison of the titration of 50.0 mL of 0.1 *M* acetic acid covered earlier in this section and that of 50.0 mL of 0.1 *M* hydrocyanic acid analyzed in Sample Exercise 15.9. First, the same amount of 0.1 *M* NaOH is required to reach the equivalence point in both cases. The fact that HCN is a much weaker acid than $HC_2H_3O_2$ has no bearing on the amount of base required. It is the *amount* of acid, not its strength, that determines the equivalence point. Second, the pH value at the equivalence point *is* affected by the acid strength. For the titration of acetic acid, the pH at the equivalence point is 8.72; for the titration of hydrocyanic acid, the pH at the equivalence point is 10.96. This difference occurs because the CN^- ion is a much stronger base than the $C_2H_3O_2^-$ ion. Also, the pH at the halfway point of the titration is much higher for HCN than for $HC_2H_3O_2$, again because of the greater base strength of the CN^- ion (or equivalently, the smaller acid strength of HCN).

The strength of a weak acid has a significant effect on the shape of its pH curve. Figure 15.4 shows pH curves for 50-mL samples of 0.10 *M* solutions of various acids titrated with 0.10 *M* NaOH. Note that the equivalence point occurs in each case when the same volume of 0.10 *M* NaOH has been added but that the shapes of the curves are dramatically different. The weaker the acid, the greater the pH value at the equivalence point. In particular, note that the vertical region that surrounds the equivalence point becomes shorter as the acid being titrated becomes weaker. We will see in the next section that the choice of an indicator is more limited for such a titration.

Besides being used to analyze for the amount of acid or base in a solution, titrations can be used to determine the values of equilibrium constants, as shown in Sample Exercise 15.10.

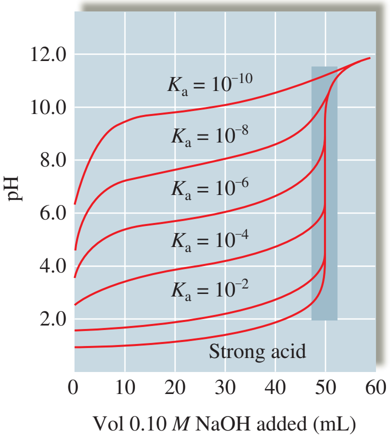


FIGURE 15.4
The pH curves for the titrations of 50.0-mL samples of 0.10 *M* acids with various K_a values with 0.10 *M* NaOH.

Calculation of K_a

Sample Exercise 15.10

Calculating K_a

A chemist has synthesized a monoprotic weak acid and wants to determine its K_a value. To do so, the chemist dissolves 2.00 mmol of the solid acid in 100.0 mL water and titrates the resulting solution with 0.0500 *M* NaOH. After 20.0 mL NaOH has been added, the pH is 6.00. What is the K_a value for the acid?

Solution

The stoichiometry problem. We represent the monoprotic acid as HA. The stoichiometry for the titration reaction is shown below.

2.00 mmol HA
↓ add OH^-
1.00 mmol HA
1.00 mmol A^-

	HA	+	OH^-	$\longrightarrow$	A^-	+	H_2O
Before reaction:	2.00 mmol		$20.0\text{ mL} \times 0.0500\ M$ $= 1.00\text{ mmol}$		0 mmol		
After reaction:	$2.00 - 1.00$ $= 1.00\text{ mmol}$		$1.00 - 1.00 = 0$		1.00 mmol		

The equilibrium problem. After the reaction the solution contains the major species

$$HA, \quad A^-, \quad Na^+, \quad \text{and} \quad H_2O$$

The pH will be determined by the equilibrium

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

for which

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Initial Concentration		Equilibrium Concentration
$[HA]_0 = \dfrac{1.00\text{ mmol}}{(100.0 + 20.0)\text{ mL}}$ $= 8.33 \times 10^{-3}\ M$	$\xrightarrow[\text{dissociates}]{x\text{ mmol/mL HA}}$	$[HA] = 8.33 \times 10^{-3} - x$
$[A^-] = \dfrac{1.00\text{ mmol}}{(100.0 + 20.0)\text{ mL}}$ $= 8.33 \times 10^{-3}\ M$		$[A^-] = 8.33 \times 10^{-3} + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

The corresponding ICE table is

	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$A^-(aq)$
Initial:	8.33×10^{-3}		≈ 0		8.33×10^{-3}
Change:	$-x$		$+x$		$+x$
Equilibrium:	$8.33 \times 10^{-3} - x$		x		$8.33 \times 10^{-3} + x$

Note that x is known here because the pH at this point is known to be 6.00. Thus

$$x = [H^+] = \text{antilog}(-\text{pH}) = 1.0 \times 10^{-6}\ M$$

Substituting the equilibrium concentrations into the expression for K_a allows calculation of the K_a value:

$$\begin{aligned} K_a = \frac{[H^+][A^-]}{[HA]} &= \frac{x(8.33 \times 10^{-3} + x)}{(8.33 \times 10^{-3}) - x} \\ &= \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3} + 1.0 \times 10^{-6})}{(8.33 \times 10^{-3}) - (1.0 \times 10^{-6})} \\ &\approx \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3})}{8.33 \times 10^{-3}} = 1.0 \times 10^{-6} \end{aligned}$$

There is an easier way to think about this problem. The original solution contained 2.00 mmol of HA, and since 20.0 mL of added 0.0500 *M* NaOH contains 1.0 mmol OH^-, this is the halfway point in the titration (where [HA] is equal to $[A^-]$). Thus

$$[H^+] = K_a = 1.0 \times 10^{-6}$$

See Exercise 15.63.

Titrations of Weak Bases with Strong Acids

Titrations of weak bases with strong acids can be treated using the procedures we introduced previously. As always, you should *think first about the major species in solution* and decide whether a reaction occurs that runs essentially to completion. If such a reaction does occur, let it run to completion and do the stoichiometric calculations. Finally, choose the dominant equilibrium and calculate the pH.

CASE STUDY: *Weak Base–Strong Acid Titration*

The calculations involved for the titration of a weak base with a strong acid will be illustrated by the titration of 100.0 mL of 0.050 *M* NH_3 with 0.10 *M* HCl.

Before the addition of any HCl.

1. Major species:

$$NH_3 \quad \text{and} \quad H_2O$$

   NH_3 is a base and will seek a source of protons. In this case H_2O is the only available source.

2. No reactions occur that go to completion, since NH_3 cannot readily take a proton from H_2O. This is evidenced by the small K_b value for NH_3.

3. The equilibrium that controls the pH involves the reaction of ammonia with water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

   Use K_b to calculate $[OH^-]$. Although NH_3 is a weak base (compared with OH^-), it produces much more OH^- in this reaction than is produced from the autoionization of H_2O.

Before the equivalence point.

1. Major species (before any reaction occurs):

$$NH_3,\ \underbrace{H^+,\ Cl^-,}_{\text{From added HCl}}\ \text{and}\ H_2O$$

2. The NH_3 will react with H^+ from the added HCl:

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

   This reaction proceeds essentially to completion because the NH_3 readily reacts with a free proton. This case is much different from the previous case, where H_2O was the only source of protons. The stoichiometric calculations are then carried out using the known volume of 0.10 *M* HCl added.

3. After the reaction of NH_3 with H^+ is run to completion, the solution contains the following major species:

$$NH_3,\ \underset{\substack{\uparrow \\ \text{Formed in} \\ \text{titration reaction}}}{NH_4^+},\ Cl^-,\ \text{and}\ H_2O$$

Note that the solution contains NH_3 and NH_4^+, and the equilibria involving these species will determine $[H^+]$. You can use either the dissociation reaction of NH_4^+

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

or the reaction of NH_3 with H_2O

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

At the equivalence point.

1. By definition, the equivalence point occurs when all the original NH_3 is converted to NH_4^+. Thus the major species in solution are

$$NH_4^+, \quad Cl^-, \quad \text{and} \quad H_2O$$

2. No reactions occur that go to completion.
3. The dominant equilibrium (the one that controls the $[H^+]$) will be the dissociation of the weak acid NH_4^+, for which

$$K_a = \frac{K_w}{K_b(\text{for } NH_3)}$$

Beyond the equivalence point.

1. Excess HCl has been added, and the major species are

$$H^+, \quad NH_4^+, \quad Cl^-, \quad \text{and} \quad H_2O$$

2. No reaction occurs that goes to completion.
3. Although NH_4^+ will dissociate, it is such a weak acid that $[H^+]$ will be determined simply by the excess H^+:

$$[H^+] = \frac{\text{mmol } H^+ \text{ in excess}}{\text{mL solution}}$$

The results of these calculations are shown in Table 15.2. The pH curve is shown in Fig. 15.5.

TABLE 15.2 Summary of Results for the Titration of 100.0 mL 0.050 *M* NH_3 with 0.10 *M* HCl

Volume of 0.10 M HCl Added (mL)	$[NH_3]_0$	$[NH_4^+]_0$	$[H^+]$	pH
0	0.05 *M*	0	1.1×10^{-11} *M*	10.96
10.0	$\frac{4.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	$\frac{1.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	1.4×10^{-10} *M*	9.85
25.0*	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	5.6×10^{-10} *M*	9.25
50.0†	0	$\frac{5.0 \text{ mmol}}{(100 + 50) \text{ mL}}$	4.3×10^{-6} *M*	5.36
60.0‡	0	$\frac{5.0 \text{ mmol}}{(100 + 60) \text{ mL}}$	$\frac{1.0 \text{ mmol}}{160 \text{ mL}}$ $= 6.2 \times 10^{-3}$ *M*	2.21

*Halfway point

†Equivalence point

‡$[H^+]$ determined by the 1.0 mmol of excess H^+

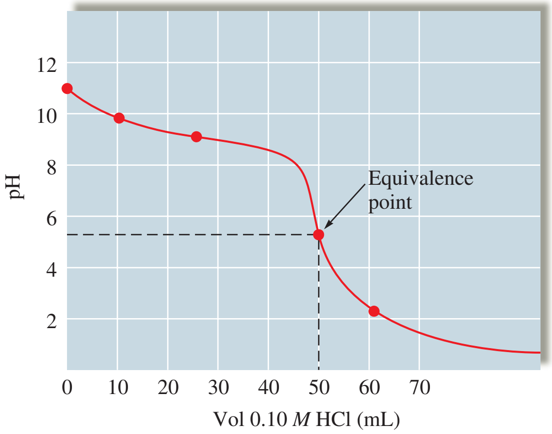


FIGURE 15.5
The pH curve for the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl. Note the pH at the equivalence point is less than 7, since the solution contains the weak acid NH_4^+.

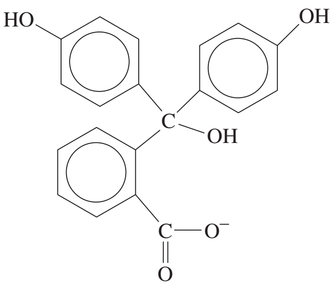
15.5 Acid–Base Indicators

There are two common methods for determining the equivalence point of an acid–base titration:

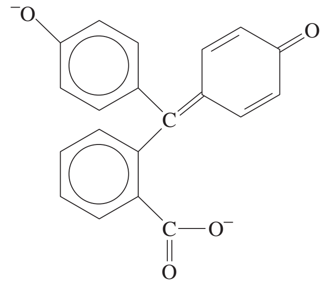
1. Use a pH meter (see Fig. 14.9) to monitor the pH and then plot the titration curve. The center of the vertical region of the pH curve indicates the equivalence point (for example, see Figs. 15.1 through 15.5).
2. Use an **acid–base indicator,** which marks the end point of a titration by changing color. Although the *equivalence point of a titration, defined by the stoichiometry, is not necessarily the same as the end point* (where the indicator changes color), careful selection of the indicator will ensure that the error is negligible.

The most common acid–base indicators are complex molecules that are themselves weak acids (represented by HIn). They exhibit one color when the proton is attached to the molecule and a different color when the proton is absent. For example, **phenolphthalein,** a commonly used indicator, is colorless in its HIn form and pink in its In^-, or basic, form. The actual structures of the two forms of phenolphthalein are shown in Fig. 15.6.

To see how molecules such as phenolphthalein function as indicators, consider the following equilibrium for some hypothetical indicator HIn, a weak acid with $K_a = 1.0 \times 10^{-8}$.



(Colorless acid form, HIn)



(Pink base form, In^-)

FIGURE 15.6
The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (In^-), the color changes to pink.

The indicator phenolphthalein is colorless in acidic solution and pink in basic solution.

$$\underset{\text{Red}}{\mathrm{HIn}(aq)} \rightleftharpoons \mathrm{H^+}(aq) + \underset{\text{Blue}}{\mathrm{In^-}(aq)}$$

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

By rearranging, we get

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

Suppose we add a few drops of this indicator to an acidic solution whose pH is 1.0 ($[\mathrm{H^+}] = 1.0 \times 10^{-1}$). Then

$$\frac{K_a}{[\mathrm{H^+}]} = \frac{1.0 \times 10^{-8}}{1.0 \times 10^{-1}} = 10^{-7} = \frac{1}{10{,}000{,}000} = \frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}$$

The *end point* is defined by the change in color of the indicator. The *equivalence point* is defined by the reaction stoichiometry.

This ratio shows that the predominant form of the indicator is HIn, resulting in a red solution. As $\mathrm{OH^-}$ is added to this solution in a titration, $[\mathrm{H^+}]$ decreases and the equilibrium shifts to the right, changing HIn to $\mathrm{In^-}$. At some point in a titration, enough of the $\mathrm{In^-}$ form will be present in the solution so that a purple tint will be noticeable. That is, a color change from red to reddish purple will occur.

How much $\mathrm{In^-}$ must be present for the human eye to detect that the color is different from the original one? For most indicators, about a tenth of the initial form must be converted to the other form before a new color is apparent. We will assume, then, that in the titration of an acid with a base, the color change will occur at a pH where

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{1}{10}$$

Sample Exercise 15.11

Indicator Color Change

Bromthymol blue, an indicator with a K_a value of 1.0×10^{-7}, is yellow in its HIn form and blue in its $\mathrm{In^-}$ form. Suppose we put a few drops of this indicator in a strongly acidic solution. If the solution is then titrated with NaOH, at what pH will the indicator color change first be visible?

Methyl orange indicator is yellow in basic solution and red in acidic solution.

(a) (b) (c)

FIGURE 15.7
(a) Yellow acid form of bromthymol blue; (b) a greenish tint is seen when the solution contains 1 part blue and 10 parts yellow; (c) blue basic form.

Solution

For bromthymol blue,

$$K_a = 1.0 \times 10^{-7} = \frac{[H^+][In^-]}{[HIn]}$$

We assume that the color change is visible when

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

That is, we assume that we can see the first hint of a greenish tint (yellow plus a little blue) when the solution contains 1 part blue and 10 parts yellow (see Fig. 15.7). Thus

$$K_a = 1.0 \times 10^{-7} = \frac{[H^+](1)}{10}$$

$$[H^+] = 1.0 \times 10^{-6} \quad \text{or} \quad \text{pH} = 6.00$$

The color change is first visible at pH 6.00.

See Exercises 15.65 through 15.68.

The Henderson–Hasselbalch equation is very useful in determining the pH at which an indicator changes color. For example, application of Equation (15.2) to the K_a expression for the general indicator HIn yields

$$\text{pH} = \text{p}K_a + \log\left(\frac{[In^-]}{[HIn]}\right)$$

where K_a is the dissociation constant for the acid form of the indicator (HIn). Since we assume that the color change is visible when

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

we have the following equation for determining the pH at which the color change occurs:

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

For bromthymol blue ($K_a = 1 \times 10^{-7}$, or $\text{p}K_a = 7$), the pH at the color change is

$$\text{pH} = 7 - 1 = 6$$

as we calculated in Sample Exercise 15.11.

When a basic solution is titrated, the indicator HIn will initially exist as In^- in solution, but as acid is added, more HIn will be formed. In this case the color change will be visible when there is a mixture of 10 parts In^- and 1 part HIn. That is, a color change from blue to blue-green will occur (see Fig. 15.7) due to the presence of some of the yellow HIn molecules. This color change will be first visible when

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

Note that this is the reciprocal of the ratio for the titration of an acid. Substituting this ratio into the Henderson–Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log(\tfrac{10}{1}) = \text{p}K_a + 1$$

For bromthymol blue ($\text{p}K_a = 7$), we have a color change at

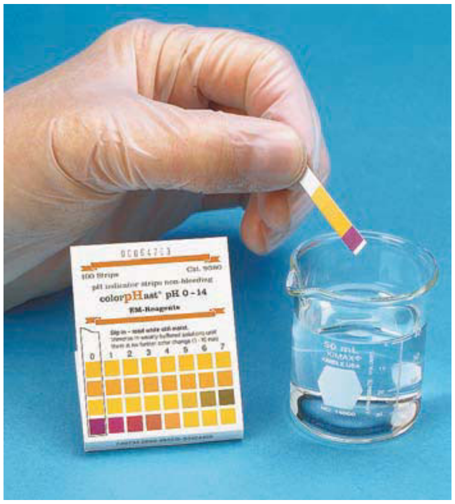
$$\text{pH} = 7 + 1 = 8$$

In summary, when bromthymol blue is used for the titration of an acid, the starting form will be HIn (yellow), and the color change occurs at a pH of about 6. When bromthymol blue is used for the titration of a base, the starting form is In^- (blue), and the color change occurs at a pH of about 8. Thus the useful pH range for bromthymol blue is

$$\text{p}K_a(\text{bromthymol blue}) \pm 1 = 7 \pm 1$$

or from 6 to 8. This is a general result. For a typical acid–base indicator with dissociation constant K_a, the color transition occurs over a range of pH values given by $\text{p}K_a \pm 1$. The useful pH ranges for several common indicators are shown in Fig. 15.8.

When we choose an indicator for a titration, we want the indicator end point (where the color changes) and the titration equivalence point to be as close as possible. Choosing an indicator is easier if there is a large change in pH near the equivalence point of the titration. The dramatic change in pH near the equivalence point in a strong acid–strong base titration (Figs. 15.1 and 15.2) produces a sharp end point; that is, the complete color change (from the acid-to-base or base-to-acid colors) usually occurs over one drop of added titrant.



Universal indicator paper can be used to estimate the pH of a solution.

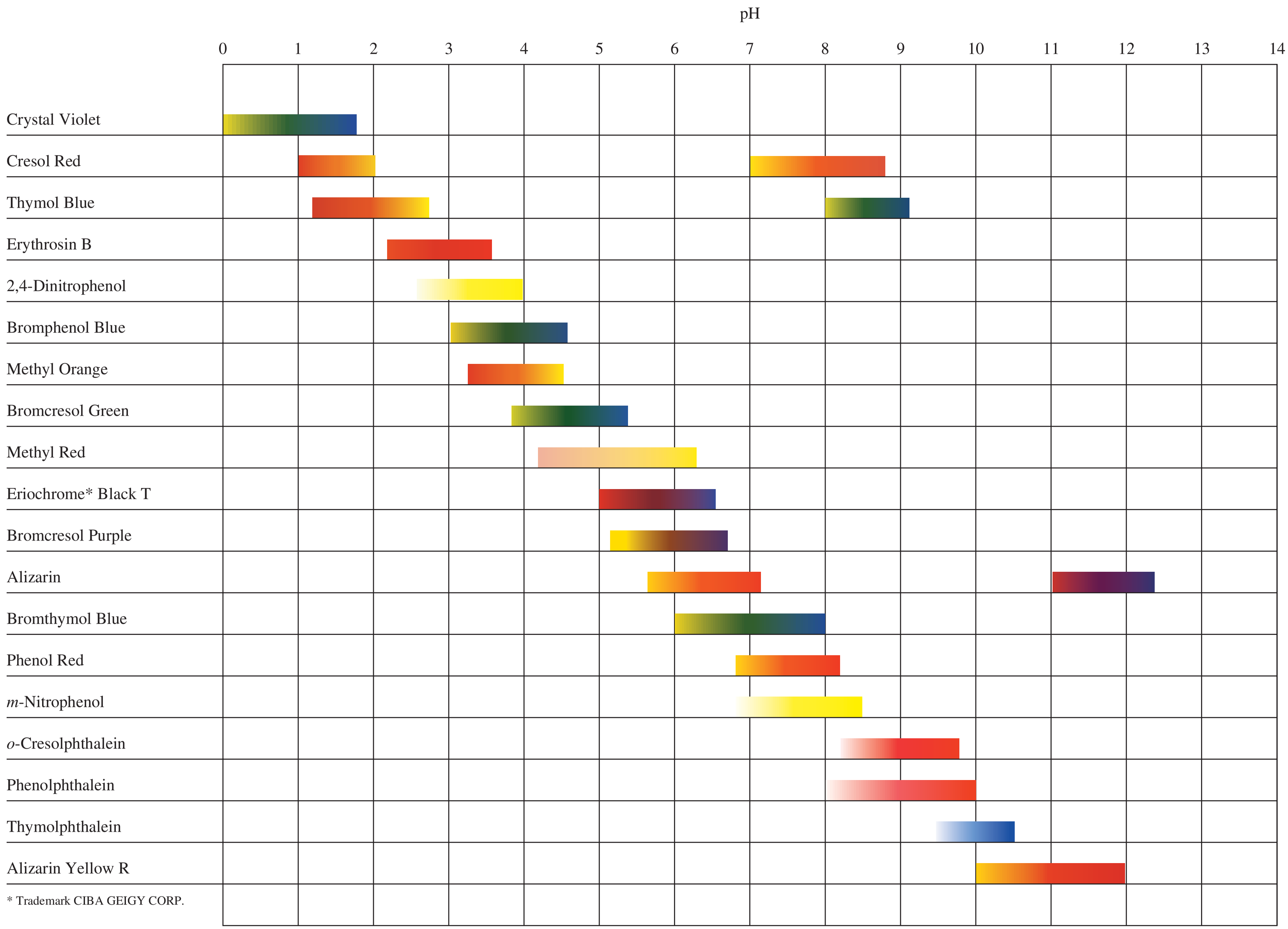
What indicator should we use for the titration of 100.00 mL of 0.100 *M* HCl with 0.100 *M* NaOH? We know that the equivalence point occurs at pH 7.00. In the initially acidic solution, the indicator will be predominantly in the HIn form. As OH^- ions are added, the pH increases rather slowly at first (see Fig. 15.1) and then rises rapidly at the equivalence point. This sharp change causes the indicator dissociation equilibrium

$$\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$$

to shift suddenly to the right, producing enough In^- ions to give a color change. Since we are titrating an acid, the indicator is predominantly in the acid form initially. Therefore, the first observable color change will occur at a pH where

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

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



The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.

FIGURE 15.8
The useful pH ranges for several common indicators. Note that most indicators have a useful range of about two pH units, as predicted by the expression $pK_a \pm 1$.

If we want an indicator that changes color at pH 7, we can use this relationship to find the pK_a value for a suitable indicator:

$$\mathrm{pH} = 7 = \mathrm{p}K_a - 1 \quad \text{or} \quad \mathrm{p}K_a = 7 + 1 = 8$$

Thus an indicator with a pK_a value of 8 ($K_a = 1 \times 10^{-8}$) changes color at about pH 7 and is ideal for marking the end point for a strong acid–strong base titration.

How crucial is it for a strong acid–strong base titration that the indicator change color exactly at pH 7? We can answer this question by examining the pH change near the equivalence point of the titration of 100 mL of 0.10 *M* HCl and 0.10 *M* NaOH. The data for a few points at or near the equivalence point are shown in Table 15.3. Note that in going from 99.99 to 100.01 mL of added NaOH solution (about half of a drop), the pH changes from 5.3 to 8.7—a very dramatic change. This behavior leads to the following general conclusions about indicators for a strong acid–strong base titration:

TABLE 15.3 Selected pH Values Near the Equivalence Point in the Titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH

NaOH Added (mL)	pH
99.99	5.3
100.00	7.0
100.01	8.7

> Indicator color changes will be sharp, occurring with the addition of a single drop of titrant.
>
> There is a wide choice of suitable indicators. The results will agree within one drop of titrant, using indicators with end points as far apart as pH 5 and pH 9 (see Fig. 15.9).

The titration of weak acids is somewhat different. Figure 15.4 shows that the weaker the acid being titrated, the smaller the vertical area around the equivalence point. This allows much less flexibility in choosing the indicator. We must choose an indicator whose useful pH range has a midpoint as close as possible to the pH at the equivalence point. For example, we saw earlier that in the titration of 0.1 *M* $HC_2H_3O_2$ with 0.1 *M* NaOH the pH at the equivalence point is 8.7 (see Fig. 15.3). A good indicator choice would be phenolphthalein, since its useful pH range is 8 to 10. Thymol blue (changes color, pH 8–9) also would be acceptable, but methyl red would not. The choice of an indicator is illustrated graphically in Fig. 15.10.

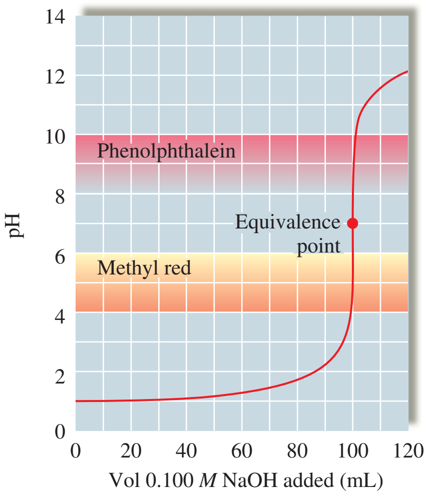


FIGURE 15.9
The pH curve for the titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH. Note that the end points of phenolphthalein and methyl red occur at virtually the same amounts of added NaOH.

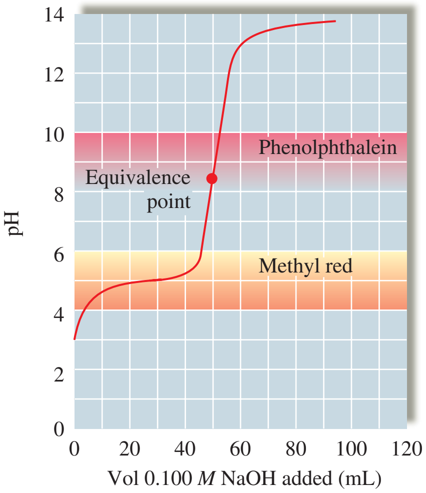


FIGURE 15.10
The pH curve for the titration of 50 mL of 0.1 *M* $HC_2H_3O_2$ with 0.1 *M* NaOH. Phenolphthalein will give an end point very close to the equivalence point of the titration. Methyl red would change color well before the equivalence point (so the end point would be very different from the equivalence point) and would not be a suitable indicator for this titration.

Solubility Equilibria

15.6 Solubility Equilibria and the Solubility Product

Solubility is a very important phenomenon. The fact that substances such as sugar and table salt dissolve in water allows us to flavor foods easily. The fact that calcium sulfate is less soluble in hot water than in cold water causes it to coat tubes in boilers, reducing thermal efficiency. Tooth decay involves solubility: When food lodges between the teeth, acids form that dissolve tooth enamel, which contains a mineral called *hydroxyapatite,* $Ca_5(PO_4)_3OH$. Tooth decay can be reduced by treating teeth with fluoride (see Chemical Impact, p. 720). Fluoride replaces the hydroxide in hydroxyapatite to produce the corresponding fluorapatite, $Ca_5(PO_4)_3F$, and calcium fluoride, CaF_2, both of which are less soluble in acids than the original enamel. Another important consequence of solubility involves the use of a suspension of barium sulfate to improve the clarity of X rays of the gastrointestinal tract. The very low solubility of barium sulfate, which contains the toxic ion Ba^{2+}, makes ingestion of the compound safe.

Adding F^- to drinking water is controversial. See Geoff Rayner-Canham, "Fluoride: Trying to Separate Fact from Fallacy," *Chem 13 News,* Sept. 2001, pp. 16–19.

In this section we consider the equilibria associated with solids dissolving to form aqueous solutions. We will assume that when a typical ionic solid dissolves in water, it dissociates completely into separate hydrated cations and anions. For example, calcium fluoride dissolves in water as follows:

For simplicity, we will ignore the effects of ion associations in these solutions.

$$CaF_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2F^-(aq)$$

When the solid salt is first added to the water, no Ca^{2+} and F^- ions are present. However, as the dissolution proceeds, the concentrations of Ca^{2+} and F^- increase, making it more and more likely that these ions will collide and re-form the solid phase. Thus two competing processes are occurring—the dissolution reaction and its reverse:

$$Ca^{2+}(aq) + 2F^-(aq) \longrightarrow CaF_2(s)$$

Ultimately, dynamic equilibrium is reached:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

At this point no more solid dissolves (the solution is said to be *saturated*).

We can write an equilibrium expression for this process according to the law of mass action:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

where $[Ca^{2+}]$ and $[F^-]$ are expressed in mol/L. The constant K_{sp} is called the **solubility product constant** or simply the **solubility product** for the equilibrium expression.

An X ray of the lower gastrointestinal tract using barium sulfate.

Since CaF_2 is a pure solid, it is not included in the equilibrium expression. The fact that the amount of excess solid present does not affect the position of the solubility equilibrium might seem strange at first; more solid means more surface area exposed to the solvent, which would seem to result in greater solubility. This is not the case, however. When the ions in solution re-form the solid, they do so on the surface of the solid. Thus doubling the surface area of the solid not only doubles the rate of dissolving, but also doubles the rate of re-formation of the solid. The amount of excess solid present therefore has no effect on the equilibrium position. Similarly, although either increasing the surface area by grinding up the solid or stirring the solution speeds up the attainment of equilibrium, neither procedure changes the amount of solid dissolved at equilibrium. Neither the amount of excess solid nor the size of the particles present will shift the *position* of the solubility equilibrium.

Pure liquids and pure solids are never included in an equilibrium expression (Section 13.4).

It is very important to distinguish between the *solubility* of a given solid and its *solubility product.* The solubility product is an *equilibrium constant* and has only *one* value

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)
Fluorides	
BaF_2	2.4×10^{-5}
MgF_2	6.4×10^{-9}
PbF_2	4×10^{-8}
SrF_2	7.9×10^{-10}
CaF_2	4.0×10^{-11}
Chlorides	
$PbCl_2$	1.6×10^{-5}
$AgCl$	1.6×10^{-10}
Hg_2Cl_2*	1.1×10^{-18}
Bromides	
$PbBr_2$	4.6×10^{-6}
$AgBr$	5.0×10^{-13}
Hg_2Br_2*	1.3×10^{-22}
Iodides	
PbI_2	1.4×10^{-8}
AgI	1.5×10^{-16}
Hg_2I_2*	4.5×10^{-29}
Sulfates	
$CaSO_4$	6.1×10^{-5}
Ag_2SO_4	1.2×10^{-5}
$SrSO_4$	3.2×10^{-7}
$PbSO_4$	1.3×10^{-8}
$BaSO_4$	1.5×10^{-9}
Chromates	
$SrCrO_4$	3.6×10^{-5}
Hg_2CrO_4*	2×10^{-9}
$BaCrO_4$	8.5×10^{-11}
Ag_2CrO_4	9.0×10^{-12}
$PbCrO_4$	2×10^{-16}
Carbonates	
$NiCO_3$	1.4×10^{-7}
$CaCO_3$	8.7×10^{-9}
$BaCO_3$	1.6×10^{-9}
$SrCO_3$	7×10^{-10}
$CuCO_3$	2.5×10^{-10}
$ZnCO_3$	2×10^{-10}
$MnCO_3$	8.8×10^{-11}
$FeCO_3$	2.1×10^{-11}
Ag_2CO_3	8.1×10^{-12}
$CdCO_3$	5.2×10^{-12}
$PbCO_3$	1.5×10^{-15}
$MgCO_3$	6.8×10^{-6}
Hg_2CO_3*	9.0×10^{-15}
Hydroxides	
$Ba(OH)_2$	5.0×10^{-3}
$Sr(OH)_2$	3.2×10^{-4}
$Ca(OH)_2$	1.3×10^{-6}
$AgOH$	2.0×10^{-8}
$Mg(OH)_2$	8.9×10^{-12}
$Mn(OH)_2$	2×10^{-13}
$Cd(OH)_2$	5.9×10^{-15}
$Pb(OH)_2$	1.2×10^{-15}
$Fe(OH)_2$	1.8×10^{-15}
$Co(OH)_2$	2.5×10^{-16}
$Ni(OH)_2$	1.6×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Cu(OH)_2$	1.6×10^{-19}
$Hg(OH)_2$	3×10^{-26}
$Sn(OH)_2$	3×10^{-27}
$Cr(OH)_3$	6.7×10^{-31}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}
$Co(OH)_3$	2.5×10^{-43}
Sulfides	
MnS	2.3×10^{-13}
FeS	3.7×10^{-19}
NiS	3×10^{-21}
CoS	5×10^{-22}
ZnS	2.5×10^{-22}
SnS	1×10^{-26}
CdS	1.0×10^{-28}
PbS	7×10^{-29}
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
HgS	1.6×10^{-54}
Phosphates	
Ag_3PO_4	1.8×10^{-18}
$Sr_3(PO_4)_2$	1×10^{-31}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$Ba_3(PO_4)_2$	6×10^{-39}
$Pb_3(PO_4)_2$	1×10^{-54}

*Contains Hg_2^{2+} ions. $K = [Hg_2^{2+}][X^-]^2$ for Hg_2X_2 salts, for example.

for a given solid at a given temperature. Solubility, on the other hand, is an *equilibrium position.* In pure water at a specific temperature a given salt has a particular solubility. On the other hand, if a common ion is present in the solution, the solubility varies according to the concentration of the common ion. However, in all cases the product of the ion concentrations must satisfy the K_{sp} expression. The K_{sp} values at 25°C for many common ionic solids are listed in Table 15.4. The units are customarily omitted.

Solving solubility equilibria problems requires many of the same procedures we have used to deal with acid–base equilibria, as illustrated in Sample Exercises 15.12 and 15.13.

Visualization: Solution Equilibrium

Visualization: Supersaturated Sodium Acetate

K_{sp} is an equilibrium constant; solubility is an equilibrium position.

Sample Exercise 15.12

Calculating K_{sp} from Solubility I

Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. Calculate its K_{sp} value.

Solution

In this experiment the solid was placed in contact with water. Thus, before any reaction occurred, the system contained solid CuBr and H_2O. The process that occurs is the dissolving of CuBr to form the separated Cu^+ and Br^- ions:

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$

where $$K_{sp} = [Cu^+][Br^-]$$

Initially, the solution contains no Cu^+ or Br^-, so the initial concentrations are

$$[Cu^+]_0 = [Br^-]_0 = 0$$

The equilibrium concentrations can be obtained from the measured solubility of CuBr, which is 2.0×10^{-4} mol/L. This means that 2.0×10^{-4} mol solid CuBr dissolves per 1.0 L of solution to come to equilibrium with the excess solid. The reaction is

$$CuBr(s) \longrightarrow Cu^+(aq) + Br^-(aq)$$

Thus

$$2.0 \times 10^{-4}\ \text{mol/L}\ CuBr(s) \longrightarrow 2.0 \times 10^{-4}\ \text{mol/L}\ Cu^+(aq) + 2.0 \times 10^{-4}\ \text{mol/L}\ Br^-(aq)$$

We can now write the equilibrium concentrations:

$$\begin{aligned}[Cu^+] &= [Cu^+]_0 + \text{change to reach equilibrium}\\ &= 0 + 2.0 \times 10^{-4}\ \text{mol/L}\end{aligned}$$

and

$$\begin{aligned}[Br^-] &= [Br^-]_0 + \text{change to reach equilibrium}\\ &= 0 + 2.0 \times 10^{-4}\ \text{mol/L}\end{aligned}$$

These equilibrium concentrations allow us to calculate the value of K_{sp} for CuBr:

$$\begin{aligned}K_{sp} &= [Cu^+][Br^-] = (2.0 \times 10^{-4}\ \text{mol/L})(2.0 \times 10^{-4}\ \text{mol/L})\\ &= 4.0 \times 10^{-8}\ \text{mol}^2/\text{L}^2 = 4.0 \times 10^{-8}\end{aligned}$$

The units for K_{sp} values are usually omitted.

See Exercise 15.77.

Sample Exercise 15.13

Calculating K_{sp} from Solubility II

Calculate the K_{sp} value for bismuth sulfide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C.

Precipitation of bismuth sulfide.

Solution

The system initially contains H_2O and solid Bi_2S_3, which dissolves as follows:

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

Therefore, $$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$$

Since no Bi^{3+} and S^{2-} ions were present in solution before the Bi_2S_3 dissolved,

$$[Bi^{3+}]_0 = [S^{2-}]_0 = 0$$

Thus the equilibrium concentrations of these ions will be determined by the amount of salt that dissolves to reach equilibrium, which in this case is 1.0×10^{-15} mol/L. Since each Bi_2S_3 unit contains $2Bi^{3+}$ and $3S^{2-}$ ions:

$$1.0 \times 10^{-15}\ \text{mol/L}\ Bi_2S_3(s) \longrightarrow 2(1.0 \times 10^{-15}\ \text{mol/L})\ Bi^{3+}(aq) + 3(1.0 \times 10^{-15}\ \text{mol/L})\ S^{2-}(aq)$$

The equilibrium concentrations are

Sulfide is a very basic anion and really exists in water as HS^-. We will not consider this complication.

$$\begin{aligned}[Bi^{3+}] &= [Bi^{3+}]_0 + \text{change} = 0 + 2.0 \times 10^{-15}\ \text{mol/L}\\ [S^{2-}] &= [S^{2-}]_0 + \text{change} = 0 + 3.0 \times 10^{-15}\ \text{mol/L}\end{aligned}$$

Then

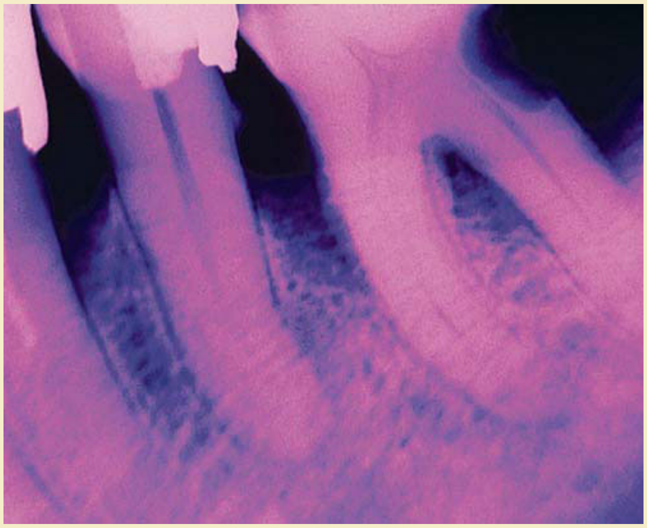
Solubilities must be expressed in mol/L in K_{sp} calculations.

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3 = (2.0 \times 10^{-15})^2(3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

See Exercises 15.78 through 15.80.

CHEMICAL IMPACT

The Chemistry of Teeth



X-ray photo showing decay (dark area) on the molar (right).

If dental chemistry continues to progress at the present rate, tooth decay may soon be a thing of the past. Cavities are holes that develop in tooth enamel, which is composed of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$. Recent research has shown that there is constant dissolving and re-forming of the tooth mineral in the saliva at the tooth's surface. Demineralization (dissolving of tooth enamel) is mainly caused by weak acids in the saliva created by bacteria as they metabolize carbohydrates in food. (The solubility of $Ca_5(PO_4)_3OH$ in acidic saliva should come as no surprise to you if you understand how pH affects the solubility of a salt with basic anions.)

In the first stages of tooth decay, parts of the tooth surface become porous and spongy and develop swiss-cheese-like holes that, if untreated, eventually turn into cavities (see photo). However, recent results indicate that if the affected tooth is bathed in a solution containing appropriate amounts of Ca^{2+}, PO_4^{3-}, and F^-, it remineralizes. Because the F^- replaces OH^- in the tooth mineral ($Ca_5(PO_4)_3OH$ is changed to $Ca_5(PO_4)_3F$), the remineralized area is more resistant to future decay, since fluoride is a weaker base than hydroxide ion. In addition, it has been shown that the presence of Sr^{2+} in the remineralizing fluid significantly increases resistance to decay.

If these results hold up under further study, the work of dentists will change dramatically. Dentists will be much more involved in preventing damage to teeth than in repairing damage that has already occurred. One can picture the routine use of a remineralization rinse that will repair problem areas before they become cavities. Dental drills could join leeches as a medical anachronism.

We have seen that the experimentally determined solubility of an ionic solid can be used to calculate its K_{sp} value.* The reverse is also possible: The solubility of an ionic solid can be calculated if its K_{sp} value is known.

Sample Exercise 15.14 Calculating Solubility from K_{sp}

The K_{sp} value for copper(II) iodate, $Cu(IO_3)_2$, is 1.4×10^{-7} at 25°C. Calculate its solubility at 25°C.

Solution

The system initially contains H_2O and solid $Cu(IO_3)_2$, which dissolves according to the following equilibrium:

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

Therefore,

$$K_{sp} = [Cu^{2+}][IO_3^-]^2$$

---

*This calculation assumes that all the dissolved solid is present as separated ions. In some cases, such as $CaSO_4$, large numbers of ion pairs exist in solution, so this method yields an incorrect value for K_{sp}.

To find the solubility of $Cu(IO_3)_2$, we must find the equilibrium concentrations of the Cu^{2+} and IO_3^- ions. We do this in the usual way by specifying the initial concentrations (before any solid has dissolved) and then defining the change required to reach equilibrium. Since in this case we do not know the solubility, we will assume that x mol/L of the solid dissolves to reach equilibrium. The 1:2 stoichiometry of the salt means that

$$x \text{ mol/L } Cu(IO_3)_2(s) \longrightarrow x \text{ mol/L } Cu^{2+}(aq) + 2x \text{ mol/L } IO_3^-(aq)$$

The concentrations are as follows:

Initial Concentration (mol/L) (before any $Cu(IO_3)_2$ dissolves)		**Equilibrium Concentration (mol/L)**
$[Cu^{2+}]_0 = 0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L dissolves}}$	$[Cu^{2+}] = x$
$[IO_3^-]_0 = 0$		$[IO_3^-] = 2x$

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$1.4 \times 10^{-7} = K_{sp} = [Cu^{2+}][IO_3^-]^2 = (x)(2x)^2 = 4x^3$$

Then
$$x = \sqrt[3]{3.5 \times 10^{-8}} = 3.3 \times 10^{-3} \text{ mol/L}$$

Thus the solubility of solid $Cu(IO_3)_2$ is 3.3×10^{-3} mol/L.

See Exercises 15.81 and 15.82.

Relative Solubilities

A salt's K_{sp} value gives us information about its solubility. However, we must be careful in using K_{sp} values to predict the *relative* solubilities of a group of salts. There are two possible cases:

1. The salts being compared produce the same number of ions. For example, consider

$$\begin{array}{ll} AgI(s) & K_{sp} = 1.5 \times 10^{-16} \\ CuI(s) & K_{sp} = 5.0 \times 10^{-12} \\ CaSO_4(s) & K_{sp} = 6.1 \times 10^{-5} \end{array}$$

Each of these solids dissolves to produce two ions:

$$\text{Salt} \rightleftharpoons \text{cation} + \text{anion}$$
$$K_{sp} = [\text{cation}][\text{anion}]$$

If x is the solubility in mol/L, then at equilibrium

$$[\text{Cation}] = x$$
$$[\text{Anion}] = x$$
$$K_{sp} = [\text{cation}][\text{anion}] = x^2$$
$$x = \sqrt{K_{sp}} = \text{solubility}$$

Therefore, in this case we can compare the solubilities for these solids by comparing the K_{sp} values:

$$\underset{\substack{\text{Most soluble;}\\ \text{largest } K_{sp}}}{CaSO_4(s)} > CuI(s) > \underset{\substack{\text{Least soluble;}\\ \text{smallest } K_{sp}}}{AgI(s)}$$

TABLE 15.5 Calculated Solubilities for CuS, Ag_2S, and Bi_2S_3 at 25°C

Salt	K_{sp}	Calculated Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

2. The salts being compared produce different numbers of ions. For example, consider

$$\begin{aligned} &CuS(s) && K_{sp} = 8.5 \times 10^{-45} \\ &Ag_2S(s) && K_{sp} = 1.6 \times 10^{-49} \\ &Bi_2S_3(s) && K_{sp} = 1.1 \times 10^{-73} \end{aligned}$$

Because these salts produce different numbers of ions when they dissolve, the K_{sp} values cannot be compared *directly* to determine relative solubilities. In fact, if we calculate the solubilities (using the procedure in Sample Exercise 15.14), we obtain the results summarized in Table 15.5. The order of solubilities is

$$\underset{\text{Most soluble}}{Bi_2S_3(s)} > Ag_2S(s) > \underset{\text{Least soluble}}{CuS(s)}$$

which is opposite to the order of the K_{sp} values.

Remember that relative solubilities can be predicted by comparing K_{sp} values *only* for salts that produce the same total number of ions.

Common Ion Effect

So far we have considered ionic solids dissolved in pure water. We will now see what happens when the water contains an ion in common with the dissolving salt. For example, consider the solubility of solid silver chromate (Ag_2CrO_4, $K_{sp} = 9.0 \times 10^{-12}$) in a 0.100 M solution of $AgNO_3$. Before any Ag_2CrO_4 dissolves, the solution contains the major species Ag^+, NO_3^-, and H_2O, with solid Ag_2CrO_4 on the bottom of the container. Since NO_3^- is not found in Ag_2CrO_4, we can ignore it. The relevant initial concentrations (before any Ag_2CrO_4 dissolves) are

$$[Ag^+]_0 = 0.100\ M \text{ (from the dissolved } AgNO_3)$$
$$[CrO_4^{2-}]_0 = 0$$

A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate.

The system comes to equilibrium as the solid Ag_2CrO_4 dissolves according to the reaction

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

for which $$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 9.0 \times 10^{-12}$$

We assume that x mol/L of Ag_2CrO_4 dissolves to reach equilibrium, which means that

$$x \text{ mol/L } Ag_2CrO_4(s) \longrightarrow 2x \text{ mol/L } Ag^+(aq) + x \text{ mol/L } CrO_4^{2-}$$

Now we can specify the equilibrium concentrations in terms of x:

$$[Ag^+] = [Ag^+]_0 + \text{change} = 0.100 + 2x$$
$$[CrO_4^{2-}] = [CrO_4^{2-}]_0 + \text{change} = 0 + x = x$$

Substituting these concentrations into the expression for K_{sp} gives

$$9.0 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}] = (0.100 + 2x)^2(x)$$

The mathematics required here appear to be complicated, since the multiplication of terms on the right-hand side produces an expression that contains an x^3 term. However, as is usually the case, we can make simplifying assumptions. Since the K_{sp} value for Ag_2CrO_4 is small (the position of the equilibrium lies far to the left), x is expected to be small compared with 0.100 M. Therefore, $0.100 + 2x \approx 0.100$, which allows simplification of the expression:

$$9.0 \times 10^{-12} = (0.100 + 2x)^2(x) \approx (0.100)^2(x)$$

Then

$$x \approx \frac{9.0 \times 10^{-12}}{(0.100)^2} = 9.0 \times 10^{-10} \text{ mol/L}$$

Since x is much less than 0.100 M, the approximation is valid (by the 5% rule). Thus

$$\text{Solubility of } Ag_2CrO_4 \text{ in } 0.100\ M\ AgNO_3 = x = 9.0 \times 10^{-10} \text{ mol/L}$$

and the equilibrium concentrations are

$$[Ag^+] = 0.100 + 2x = 0.100 + 2(9.0 \times 10^{-10}) = 0.100\ M$$
$$[CrO_4^{2-}] = x = 9.0 \times 10^{-10}\ M$$

Now we compare the solubilities of Ag_2CrO_4 in pure water and in 0.100 M $AgNO_3$:

$$\text{Solubility of } Ag_2CrO_4 \text{ in pure water} = 1.3 \times 10^{-4} \text{ mol/L}$$
$$\text{Solubility of } Ag_2CrO_4 \text{ in } 0.100\ M\ AgNO_3 = 9.0 \times 10^{-10} \text{ mol/L}$$

Note that the solubility of Ag_2CrO_4 is much less in the presence of Ag^+ ions from $AgNO_3$. This is another example of the common ion effect. The solubility of a solid is lowered if the solution already contains ions common to the solid.

Sample Exercise 15.15 Solubility and Common Ions

Calculate the solubility of solid CaF_2 ($K_{sp} = 4.0 \times 10^{-11}$) in a 0.025 M NaF solution.

Solution

Before any CaF_2 dissolves, the solution contains the major species Na^+, F^-, and H_2O. The solubility equilibrium for CaF_2 is

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

and

$$K_{sp} = 4.0 \times 10^{-11} = [Ca^{2+}][F^-]^2$$

Initial Concentration (mol/L) (before any CaF_2 dissolves)		**Equilibrium Concentration (mol/L)**
$[Ca^{2+}]_0 = 0$	x mol/L CaF_2 dissolves $\longrightarrow$ to reach equilibrium	$[Ca^{2+}] = x$
$[F^-]_0 = 0.025\ M$ ↗ From 0.025 M NaF		$[F^-] = 0.025 + 2x$ ↗ ↗ From NaF From CaF_2

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$K_{sp} = 4.0 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (x)(0.025 + 2x)^2$$

Assuming that $2x$ is negligible compared with 0.025 (since K_{sp} is small) gives

$$4.0 \times 10^{-11} \approx (x)(0.025)^2$$
$$x \approx 6.4 \times 10^{-8}$$

The approximation is valid (by the 5% rule), and

$$\text{Solubility} = x = 6.4 \times 10^{-8} \text{ mol/L}$$

Thus 6.4×10^{-8} mol solid CaF_2 dissolves per liter of the 0.025 *M* NaF solution.

See Exercises 15.89 through 15.92.

pH and Solubility

The pH of a solution can greatly affect a salt's solubility. For example, magnesium hydroxide dissolves according to the equilibrium

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Addition of OH^- ions (an increase in pH) will, by the common ion effect, force the equilibrium to the left, decreasing the solubility of $Mg(OH)_2$. On the other hand, an addition of H^+ ions (a decrease in pH) increases the solubility, because OH^- ions are removed from solution by reacting with the added H^+ ions. In response to the lower concentration of OH^-, the equilibrium position moves to the right. This is why a suspension of solid $Mg(OH)_2$, known as *milk of magnesia,* dissolves as required in the stomach to combat excess acidity.

This idea also applies to salts with other types of anions. For example, the solubility of silver phosphate (Ag_3PO_4) is greater in acid than in pure water because the PO_4^{3-} ion is a strong base that reacts with H^+ to form the HPO_4^{2-} ion. The reaction

$$H^+ + PO_4^{3-} \longrightarrow HPO_4^{2-}$$

occurs in acidic solution, thus lowering the concentration of PO_4^{3-} and shifting the solubility equilibrium

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

to the right. This, in turn, increases the solubility of silver phosphate.

Silver chloride (AgCl), however, has the same solubility in acid as in pure water. Why? Since the Cl^- ion is a very weak base (that is, HCl is a very strong acid), no HCl molecules are formed. Thus the addition of H^+ to a solution containing Cl^- does not affect $[Cl^-]$ and has no effect on the solubility of a chloride salt.

The general rule is that if the anion X^- is an effective base—that is, if HX is a weak acid—the salt MX will show increased solubility in an acidic solution. Examples of common anions that are effective bases are OH^-, S^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, and CrO_4^{2-}. Salts containing these anions are much more soluble in an acidic solution than in pure water.

As mentioned at the beginning of this chapter, one practical result of the increased solubility of carbonates in acid is the formation of huge limestone caves such as Mammoth Cave in Kentucky and Carlsbad Caverns in New Mexico. Carbon dioxide dissolved in groundwater makes it acidic, increasing the solubility of calcium carbonate and eventually producing huge caverns. As the carbon dioxide escapes to the air, the pH of the dripping water goes up and the calcium carbonate precipitates, forming stalactites and stalagmites.

15.7 Precipitation and Qualitative Analysis

So far we have considered solids dissolving in solutions. Now we will consider the reverse process—the formation of a solid from solution. When solutions are mixed, various reactions can occur. We have already considered acid–base reactions in some detail. In this section we show how to predict whether a precipitate will form when two solutions are mixed. We will use the **ion product,** which is defined just like the expression for K_{sp} for a given solid except that *initial concentrations are used* instead of equilibrium concentrations. For solid CaF_2, the expression for the ion product Q is written

$$Q = [Ca^{2+}]_0[F^-]_0^2$$

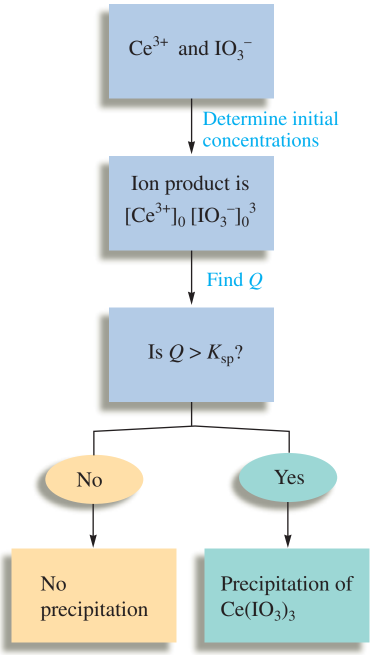
If we add a solution containing Ca^{2+} ions to a solution containing F^- ions, a precipitate may or may not form, depending on the concentrations of these ions in the resulting mixed solution. To predict whether precipitation will occur, we consider the relationship between Q and K_{sp}.

Q is used here in a very similar way to the use of the reaction quotient in Chapter 13.

If Q is greater than K_{sp}, precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy K_{sp}.

If Q is less than K_{sp}, no precipitation occurs.

Sample Exercise 15.16 Determining Precipitation Conditions



A solution is prepared by adding 750.0 mL of 4.00×10^{-3} M $Ce(NO_3)_3$ to 300.0 mL of 2.00×10^{-2} M KIO_3. Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?

Solution

First, we calculate $[Ce^{3+}]_0$ and $[IO_3^-]_0$ in the mixed solution before any reaction occurs:

$$[Ce^{3+}]_0 = \frac{(750.0\text{ mL})(4.00 \times 10^{-3}\text{ mmol/mL})}{(750.0 + 300.0)\text{ mL}} = 2.86 \times 10^{-3}\ M$$

$$[IO_3^-]_0 = \frac{(300.0\text{ mL})(2.00 \times 10^{-2}\text{ mmol/mL})}{(750.0 + 300.0)\text{ mL}} = 5.71 \times 10^{-3}\ M$$

The ion product for $Ce(IO_3)_3$ is

$$Q = [Ce^{3+}]_0[IO_3^-]_0^3 = (2.86 \times 10^{-3})(5.71 \times 10^{-3})^3 = 5.32 \times 10^{-10}$$

Since Q is greater than K_{sp}, $Ce(IO_3)_3$ will precipitate from the mixed solution.

See Exercises 15.97 and 15.98.

Sometimes we want to do more than simply predict whether precipitation will occur; we may want to calculate the equilibrium concentrations in the solution after precipitation occurs. For example, let us calculate the equilibrium concentrations of Pb^{2+} and I^- ions in a solution formed by mixing 100.0 mL of 0.0500 M $Pb(NO_3)_2$ and 200.0 mL of 0.100 M NaI. First, we must determine whether solid PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) forms when the solutions are mixed. To do so, we need to calculate $[Pb^{2+}]_0$ and $[I^-]_0$ before any reaction occurs:

For $Ce(IO_3)_3(s)$, $K_{sp} = [Ce^{3+}][IO_3^-]^3$.

$$[Pb^{2+}]_0 = \frac{\text{mmol Pb}^{2+}}{\text{mL solution}} = \frac{(100.0\text{ mL})(0.0500\text{ mmol/mL})}{300.0\text{ mL}} = 1.67 \times 10^{-2}\ M$$

$$[I^-]_0 = \frac{\text{mmol I}^-}{\text{mL solution}} = \frac{(200.0\text{ mL})(0.100\text{ mmol/mL})}{300.0\text{ mL}} = 6.67 \times 10^{-2}\ M$$

The ion product for PbI_2 is

$$Q = [Pb^{2+}]_0[I^-]_0^2 = (1.67 \times 10^{-2})(6.67 \times 10^{-2})^2 = 7.43 \times 10^{-5}$$

Since Q is greater than K_{sp}, a precipitate of PbI_2 will form.

Since the K_{sp} for PbI_2 is quite small (1.4×10^{-8}), only very small quantities of Pb^{2+} and I^- can coexist in aqueous solution. In other words, when Pb^{2+} and I^- are mixed, most of these ions will precipitate out as PbI_2. That is, the reaction

The equilibrium constant for formation of solid PbI_2 is $1/K_{sp}$, or 7×10^7, so this equilibrium lies far to the right.

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

(which is the reverse of the dissolution reaction) goes essentially to completion.

If, when two solutions are mixed, a reaction occurs that goes virtually to completion, it is essential to do the stoichiometry calculations before considering the equilibrium calculations. Therefore, in this case we let the system go completely in the direction toward which it tends. Then we will let it adjust back to equilibrium. If we let Pb^{2+} and I^- react to completion, we have the following concentrations:

	Pb^{2+}	+	$2I^-$	$\longrightarrow$	PbI_2
Before reaction:	(100.0 mL)(0.0500 *M*) = 5.00 mmol		(200.0 mL)(0.100 *M*) = 20.0 mmol		The amount of PbI_2 formed does not influence the equilibrium.
After reaction:	0 mmol		20.0 − 2(5.00) = 10.0 mmol		

In this reaction 10 mmol I^- is in excess.

Next we must allow the system to adjust to equilibrium. At equilibrium $[Pb^{2+}]$ is not actually zero because the reaction does not go quite to completion. The best way to think about this is that once the PbI_2 is formed, a very small amount redissolves to reach equilibrium. Since I^- is in excess, the PbI_2 is dissolving into a solution that contains 10.0 mmol I^- per 300.0 mL of solution, or 3.33×10^{-2} *M* I^-.

We could state this problem as follows: What is the solubility of solid PbI_2 in a 3.33×10^{-2} *M* NaI solution? The lead iodide dissolves according to the equation

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

The concentrations are as follows:

Initial Concentration (mol/L)		**Equilibrium Concentration (mol/L)**
$[Pb^{2+}]_0 = 0$ $[I^-]_0 = 3.33 \times 10^{-2}$	$\xrightarrow[\text{dissolves}]{x \text{ mol/L } PbI_2(s)}$	$[Pb^{2+}] = x$ $[I^-] = 3.33 \times 10^{-2} + 2x$

Substituting into the expression for K_{sp} gives

$$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2 = (x)(3.33 \times 10^{-2} + 2x)^2 \approx (x)(3.33 \times 10^{-2})^2$$

Then

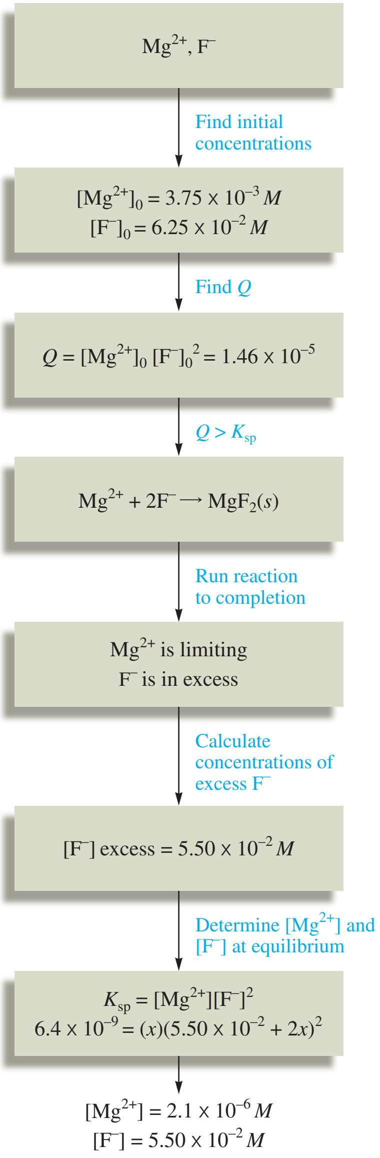
$$[Pb^{2+}] = x = 1.3 \times 10^{-5}\ M$$
$$[I^-] = 3.33 \times 10^{-2}\ M$$

Note that $3.33 \times 10^{-2} \gg 2x$, so the approximation is valid. These Pb^{2+} and I^- concentrations thus represent the equilibrium concentrations present in a solution formed by mixing 100.0 mL of 0.0500 *M* $Pb(NO_3)_2$ and 200.0 mL of 0.100 *M* NaI.

Sample Exercise 15.17

Precipitation

A solution is prepared by mixing 150.0 mL of 1.00×10^{-2} *M* $Mg(NO_3)_2$ and 250.0 mL of 1.00×10^{-1} *M* NaF. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{sp} = 6.4 \times 10^{-9}$).



Solution

The first step is to determine whether solid MgF_2 forms. To do this, we need to calculate the concentrations of Mg^{2+} and F^- in the mixed solution and find Q:

$$[Mg^{2+}]_0 = \frac{\text{mmol Mg}^{2+}}{\text{mL solution}} = \frac{(150.0\ \text{mL})(1.00 \times 10^{-2}\ M)}{400.0\ \text{mL}} = 3.75 \times 10^{-3}\ M$$

$$[F^-]_0 = \frac{\text{mmol F}^-}{\text{mL solution}} = \frac{(250.0\ \text{mL})(1.00 \times 10^{-1}\ M)}{400.0\ \text{mL}} = 6.25 \times 10^{-2}\ M$$

$$Q = [Mg^{2+}]_0[F^-]_0^2 = (3.75 \times 10^{-3})(6.25 \times 10^{-2})^2 = 1.46 \times 10^{-5}$$

Since Q is greater than K_{sp}, solid MgF_2 will form.

The next step is to run the precipitation reaction to completion:

	Mg^{2+}	+	$2F^-$	$\longrightarrow$	$MgF_2(s)$
Before reaction:	$(150.0)(1.00 \times 10^{-2})$ $= 1.50$ mmol		$(250.0)(1.00 \times 10^{-1})$ $= 25.0$ mmol		
After reaction:	$1.50 - 1.50 = 0$		$25.0 - 2(1.50)$ $= 22.0$ mmol		

Note that excess F^- remains after the precipitation reaction goes to completion. The concentration is

$$[F^-]_{\text{excess}} = \frac{22.0\ \text{mmol}}{400.0\ \text{mL}} = 5.50 \times 10^{-2}\ M$$

Although we have assumed that the Mg^{2+} is completely consumed, we know that $[Mg^{2+}]$ will not be zero at equilibrium. We can compute the equilibrium $[Mg^{2+}]$ by letting MgF_2 redissolve to satisfy the expression for K_{sp}. How much MgF_2 will dissolve in a $5.50 \times 10^{-2}\ M$ NaF solution? We proceed as usual:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

$$K_{sp} = [Mg^{2+}][F^-]^2 = 6.4 \times 10^{-9}$$

Initial Concentration (mol/L)		**Equilibrium Concentration (mol/L)**
$[Mg^{2+}]_0 = 0$ $[F^-]_0 = 5.50 \times 10^{-2}$	$\xrightarrow[\text{dissolves}]{x\ \text{mol/L}\ MgF_2(s)}$	$[Mg^{2+}] = x$ $[F^-] = 5.50 \times 10^{-2} + 2x$

$$\begin{aligned} K_{sp} &= 6.4 \times 10^{-9} = [Mg^{2+}][F^-]^2 \\ &= (x)(5.50 \times 10^{-2} + 2x)^2 \approx (x)(5.50 \times 10^{-2})^2 \\ [Mg^{2+}] &= x = 2.1 \times 10^{-6}\ M \\ [F^-] &= 5.50 \times 10^{-2}\ M \end{aligned}$$

See Exercises 15.99 and 15.100.

Selective Precipitation

The approximations made here fall within the 5% rule.

Mixtures of metal ions in aqueous solution are often separated by **selective precipitation,** that is, by using a reagent whose anion forms a precipitate with only one or a few of the metal ions in the mixture. For example, suppose we have a solution containing both Ba^{2+} and Ag^+ ions. If NaCl is added to the solution, AgCl precipitates as a white solid, but since $BaCl_2$ is soluble, the Ba^{2+} ions remain in solution.

Sample Exercise 15.18 Selective Precipitation

A solution contains 1.0×10^{-4} *M* Cu^+ and 2.0×10^{-3} *M* Pb^{2+}. If a source of I^- is added gradually to this solution, will PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) or CuI ($K_{sp} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I^- necessary to begin precipitation of each salt.

Solution

For PbI_2, the K_{sp} expression is

$$1.4 \times 10^{-8} = K_{sp} = [Pb^{2+}][I^-]^2$$

Since $[Pb^{2+}]$ in this solution is known to be 2.0×10^{-3} *M*, the greatest concentration of I^- that can be present without causing precipitation of PbI_2 can be calculated from the K_{sp} expression:

$$1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2 = (2.0 \times 10^{-3})[I^-]^2$$
$$[I^-] = 2.6 \times 10^{-3}\ M$$

Any I^- in excess of this concentration will cause solid PbI_2 to form.

Similarly, for CuI, the K_{sp} expression is

$$5.3 \times 10^{-12} = K_{sp} = [Cu^+][I^-] = (1.0 \times 10^{-4})[I^-]$$

and

$$[I^-] = 5.3 \times 10^{-8}\ M$$

A concentration of I^- in excess of 5.3×10^{-8} *M* will cause formation of solid CuI.

As I^- is added to the mixed solution, CuI will precipitate first, since the $[I^-]$ required is less. Therefore, Cu^+ would be separated from Pb^{2+} using this reagent.

See Exercises 15.101 and 15.102.

We can compare K_{sp} values to find relative solubilities because FeS and MnS produce the same number of ions in solution.

Since metal sulfide salts differ dramatically in their solubilities, the sulfide ion is often used to separate metal ions by selective precipitation. For example, consider a solution containing a mixture of 10^{-3} *M* Fe^{2+} and 10^{-3} *M* Mn^{2+}. Since FeS ($K_{sp} = 3.7 \times 10^{-19}$) is much less soluble than MnS ($K_{sp} = 2.3 \times 10^{-13}$), careful addition of S^{2-} to the mixture will precipitate Fe^{2+} as FeS, leaving Mn^{2+} in solution.

One real advantage of the sulfide ion as a precipitating reagent is that because it is basic, its concentration can be controlled by regulating the pH of the solution. H_2S is a diprotic acid that dissociates in two steps:

$$H_2S \rightleftharpoons H^+ + HS^- \qquad K_{a_1} = 1.0 \times 10^{-7}$$
$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_{a_2} \approx 10^{-19}$$

Note from the small K_{a_2} value that S^{2-} ions have a high affinity for protons. In an acidic solution (large $[H^+]$), $[S^{2-}]$ will be relatively small, since under these conditions the dissociation equilibria will lie far to the left. On the other hand, in basic solutions $[S^{2-}]$ will be relatively large, since the very small value of $[H^+]$ will pull both equilibria to the right, producing S^{2-}.

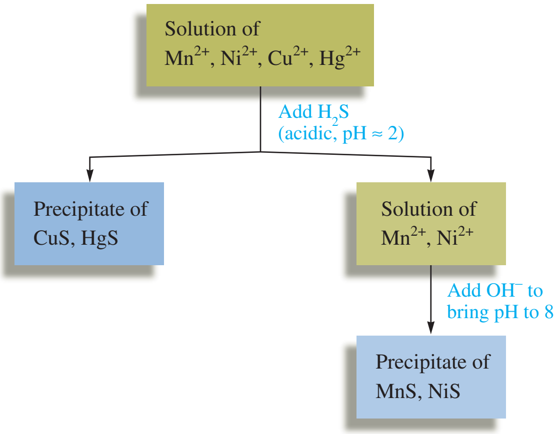


FIGURE 15.11
The separation of Cu^{2+} and Hg^{2+} from Ni^{2+} and Mn^{2+} using H_2S. At a low pH, $[S^{2-}]$ is relatively low and only the very insoluble HgS and CuS precipitate. When OH^- is added to lower $[H^+]$, the value of $[S^{2-}]$ increases, and MnS and NiS precipitate.


Flame test for potassium.


Flame test for sodium.

This means that the most insoluble sulfide salts, such as CuS ($K_{sp} = 8.5 \times 10^{-45}$) and HgS ($K_{sp} = 1.6 \times 10^{-54}$), can be precipitated from an acidic solution, leaving the more soluble ones, such as MnS ($K_{sp} = 2.3 \times 10^{-13}$) and NiS ($K_{sp} = 3 \times 10^{-21}$), still dissolved. The manganese and nickel sulfides can then be precipitated by making the solution slightly basic. This procedure is diagramed in Fig. 15.11.

Qualitative Analysis

The classic scheme for **qualitative analysis** of a mixture containing all the common cations (listed in Fig. 15.12) involves first separating them into five major groups based on solubilities. (These groups are not directly related to the groups of the periodic table.) Each group is then treated further to separate and identify the individual ions. We will be concerned here only with separation of the major groups.

Group I—Insoluble chlorides

When dilute aqueous HCl is added to a solution containing a mixture of the common cations, only Ag^+, Pb^{2+}, and $Hg_2{}^{2+}$ will precipitate out as insoluble chlorides. All other chlorides are soluble and remain in solution. The Group I precipitate is removed, leaving the other ions in solution for treatment with sulfide ion.

Group II—Sulfides insoluble in acid solution

After the insoluble chlorides are removed, the solution is still acidic, since HCl was added. If H_2S is added to this solution, only the most insoluble sulfides (those of Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, and Sn^{4+}) will precipitate, since $[S^{2-}]$ is relatively low because of the high concentration of H^+. The more soluble sulfides will remain dissolved under these conditions, and the precipitate of the insoluble salt is removed.

Group III—Sulfides insoluble in basic solution

The solution is made basic at this stage, and more H_2S is added. As we saw earlier, a basic solution produces a higher $[S^{2-}]$, which leads to precipitation of the more soluble sulfides. The cations precipitated as sulfides at this stage are Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, and Fe^{2+}. If any Cr^{3+} and Al^{3+} ions are present, they also will precipitate, but as insoluble hydroxides (remember the solution is now basic). The precipitate is separated from the solution containing the rest of the ions.

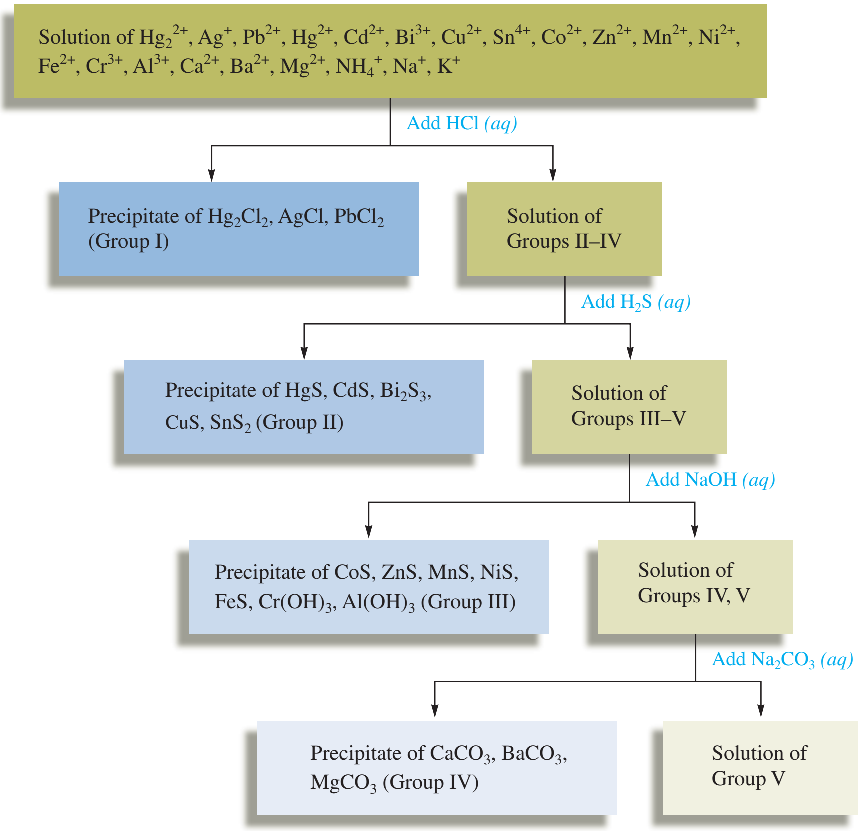
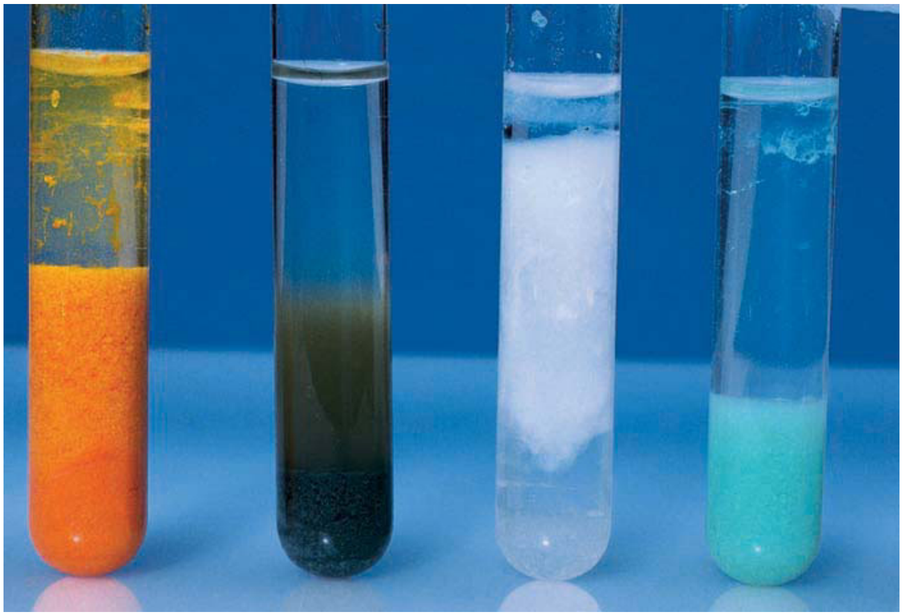


FIGURE 15.12
A schematic diagram of the classic method for separating the common cations by selective precipitation.

Group IV—Insoluble carbonates

At this point, all the cations have been precipitated except those from Groups 1A and 2A of the periodic table. The Group 2A cations form insoluble carbonates and can be precipitated by the addition of CO_3^{2-}. For example, Ba^{2+}, Ca^{2+}, and Mg^{2+} form solid carbonates and can be removed from the solution.



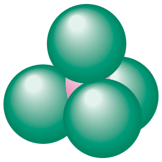
From left to right, cadmium sulfide, chromium(III) hydroxide, aluminum hydroxide, and nickel(II) hydroxide.

Group V—Alkali metal and ammonium ions
The only ions remaining in solution at this point are the Group 1A cations and the NH_4^+ ion, all of which form soluble salts with the common anions. The Group 1A cations are usually identified by the characteristic colors they produce when heated in a flame. These colors are due to the emission spectra of these ions.

The qualitative analysis scheme for cations based on the selective precipitation procedure described above is summarized in Fig. 15.12.

Complex Ion Equilibria

15.8 Equilibria Involving Complex Ions


$CoCl_4^{2-}$

A **complex ion** is a charged species consisting of a metal ion surrounded by *ligands.* A ligand is simply a Lewis base—a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. Some common ligands are H_2O, NH_3, Cl^-, and CN^-. The number of ligands attached to a metal ion is called the *coordination number.* The most common coordination numbers are 6, for example, in $Co(H_2O)_6^{2+}$ and $Ni(NH_3)_6^{2+}$; 4, for example, in $CoCl_4^{2-}$ and $Cu(NH_3)_4^{2+}$; and 2, for example, in $Ag(NH_3)_2^+$; but others are known.

The properties of complex ions will be discussed in more detail in Chapter 21. For now, we will just look at the equilibria involving these species. Metal ions add ligands one at a time in steps characterized by equilibrium constants called **formation constants** or **stability constants.** For example, when solutions containing Ag^+ ions and NH_3 molecules are mixed, the following reactions take place:

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1 = 2.1 \times 10^3$$
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

where K_1 and K_2 are the formation constants for the two steps. In a solution containing Ag^+ and NH_3, all the species NH_3, Ag^+, $Ag(NH_3)^+$, and $Ag(NH_3)_2^+$ exist at equilibrium. Calculating the concentrations of all these components can be complicated. However, usually the total concentration of the ligand is much larger than the total concentration of the metal ion, and approximations can greatly simplify the problems.

For example, consider a solution prepared by mixing 100.0 mL of 2.0 M NH_3 with 100.0 mL of 1.0×10^{-3} M $AgNO_3$. *Before any reaction occurs,* the mixed solution contains the major species Ag^+, NO_3^-, NH_3, and H_2O. What reaction or reactions will occur in this solution? From our discussions of acid–base chemistry, we know that one reaction is

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

However, we are interested in the reaction between NH_3 and Ag^+ to form complex ions, and since the position of the preceding equilibrium lies far to the left (K_b for NH_3 is 1.8×10^{-5}), we can neglect the amount of NH_3 used up in the reaction with water. Therefore, before any complex ion formation, the concentrations in the mixed solution are

$$[Ag^+]_0 = \frac{(100.0 \text{ mL})(1.0 \times 10^{-3}\ M)}{\underset{\nwarrow \text{ Total volume}}{(200.0 \text{ mL})}} = 5.0 \times 10^{-4}\ M$$

$$[NH_3]_0 = \frac{(100.0 \text{ mL})(2.0\ M)}{(200.0 \text{ mL})} = 1.0\ M$$

A solution containing the blue $CoCl_4^{2-}$ complex ion.

As mentioned already, the Ag^+ ion reacts with NH_3 in a stepwise fashion to form $AgNH_3^+$ and then $Ag(NH_3)_2^+$:

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1 = 2.1 \times 10^3$$
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

Since both K_1 and K_2 are large, and since there is a large excess of NH_3, *both reactions can be assumed to go essentially to completion.* This is equivalent to writing the net reaction in the solution as follows:

$$Ag^+ + 2NH_3 \longrightarrow Ag(NH_3)_2^+$$

The relevant stoichiometric calculations are as follows:

	Ag^+	+	$2NH_3$	$\longrightarrow$	$Ag(NH_3)_2^+$
Before reaction:	$5.0 \times 10^{-4}\ M$		$1.0\ M$		0
After reaction:	0		$1.0 - 2(5.0 \times 10^{-4}) \approx 1.0\ M$		$5.0 \times 10^{-4}\ M$

↗ Twice as much NH_3 as Ag^+ is required

Note that in this case we have used molarities when performing the stoichiometry calculations and we have assumed this reaction to be complete, using all the original Ag^+ to form $Ag(NH_3)_2^+$. In reality, a *very small amount* of the $Ag(NH_3)_2^+$ formed will dissociate to produce small amounts of $Ag(NH_3)^+$ and Ag^+. However, since the amount of $Ag(NH_3)_2^+$ dissociating will be so small, we can safely assume that $[Ag(NH_3)_2^+]$ is $5.0 \times 10^{-4}\ M$ at equilibrium. Also, we know that since so little NH_3 has been consumed, $[NH_3]$ is $1.0\ M$ at equilibrium. We can use these concentrations to calculate $[Ag^+]$ and $[Ag(NH_3)^+]$ using the K_1 and K_2 expressions.

To calculate the equilibrium concentration of $Ag(NH_3)^+$, we use

$$K_2 = 8.2 \times 10^3 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]}$$

since $[Ag(NH_3)_2^+]$ and $[NH_3]$ are known. Rearranging and solving for $[Ag(NH_3)^+]$ give

Visualization: Nickel(II) Complexes

$$[Ag(NH_3)^+] = \frac{[Ag(NH_3)_2^+]}{K_2[NH_3]} = \frac{5.0 \times 10^{-4}}{(8.2 \times 10^3)(1.0)} = 6.1 \times 10^{-8}\ M$$

Now the equilibrium concentration of Ag^+ can be calculated using K_1:

$$K_1 = 2.1 \times 10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = \frac{6.1 \times 10^{-8}}{[Ag^+](1.0)}$$

$$[Ag^+] = \frac{6.1 \times 10^{-8}}{(2.1 \times 10^3)(1.0)} = 2.9 \times 10^{-11}\ M$$

So far we have assumed that $Ag(NH_3)_2^+$ is the dominant silver-containing species in solution. Is this a valid assumption? The calculated concentrations are

$$[Ag(NH_3)_2^+] = 5.0 \times 10^{-4}\ M$$
$$[Ag(NH_3)^+] = 6.1 \times 10^{-8}\ M$$
$$[Ag^+] = 2.9 \times 10^{-11}\ M$$

These values clearly support the conclusion that

$$[Ag(NH_3)_2^+] \gg [Ag(NH_3)^+] \gg [Ag^+]$$

Essentially all the Ag^+ ions originally present end up in $Ag(NH_3)_2^+$.

Thus the assumption that $Ag(NH_3)_2^+$ is the dominant Ag^+-containing species is valid, and the calculated concentrations are correct.

This analysis shows that although complex ion equilibria have many species present and look complicated, the calculations are actually quite straightforward, especially if the ligand is present in large excess.

Sample Exercise 15.19

Complex Ions

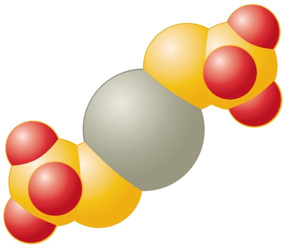
Calculate the concentrations of Ag^+, $Ag(S_2O_3)^-$, and $Ag(S_2O_3)_2^{3-}$ in a solution prepared by mixing 150.0 mL of 1.00×10^{-3} *M* $AgNO_3$ with 200.0 mL of 5.00 *M* $Na_2S_2O_3$. The stepwise formation equilibria are

$$Ag^+ + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)^- \qquad K_1 = 7.4 \times 10^8$$
$$Ag(S_2O_3)^- + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} \qquad K_2 = 3.9 \times 10^4$$

Solution

The concentrations of the ligand and metal ion in the mixed solution *before any reaction occurs* are

$$[Ag^+]_0 = \frac{(150.0 \text{ mL})(1.00 \times 10^{-3}\ M)}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 4.29 \times 10^{-4}\ M$$
$$[S_2O_3^{2-}]_0 = \frac{(200.0 \text{ mL})(5.00\ M)}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 2.86\ M$$



$Ag\ (S_2O_3)_2^{3-}$

Since $[S_2O_3^{2-}]_0 \gg [Ag^+]_0$, and since K_1 and K_2 are large, both formation reactions can be assumed to go to completion, and the net reaction in the solution is as follows:

	Ag^+	+	$2S_2O_3^{2-}$	$\longrightarrow$	$Ag(S_2O_3)_2^{3-}$
Before reaction:	$4.29 \times 10^{-4}\ M$		$2.86\ M$		0
After reaction:	~ 0		$2.86 - 2(4.29 \times 10^{-4})$ $\approx 2.86\ M$		$4.29 \times 10^{-4}\ M$

Note that Ag^+ is limiting and that the amount of $S_2O_3^{2-}$ consumed is negligible. Also note that since all these species are in the same solution, the molarities can be used to do the stoichiometry problem.

Of course, the concentration of Ag^+ is not zero at equilibrium, and there is some $Ag(S_2O_3)^-$ in the solution. To calculate the concentrations of these species, we must use the K_1 and K_2 expressions. We can calculate the concentration of $Ag(S_2O_3)^-$ from K_2:

$$3.9 \times 10^4 = K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag(S_2O_3)^-][S_2O_3^{2-}]} = \frac{4.29 \times 10^{-4}}{[Ag(S_2O_3)^-](2.86)}$$
$$[Ag(S_2O_3)^-] = 3.8 \times 10^{-9}\ M$$

We can calculate $[Ag^+]$ from K_1:

$$7.4 \times 10^8 = K_1 = \frac{[Ag(S_2O_3)^-]}{[Ag^+][S_2O_3^{2-}]} = \frac{3.8 \times 10^{-9}}{[Ag^+](2.86)}$$
$$[Ag^+] = 1.8 \times 10^{-18}\ M$$

These results show that $[Ag(S_2O_3)_2^{3-}] \gg [Ag(S_2O_3)^-] \gg [Ag^+]$

Thus the assumption is valid that essentially all the original Ag^+ is converted to $Ag(S_2O_3)_2^{3-}$ at equilibrium.

See Exercises 15.109 and 15.110.

(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form $Ag(NH_3)_2^+(aq)$ and $Cl^-(aq)$.

Complex Ions and Solubility

Often ionic solids that are very nearly water-insoluble must be dissolved somehow in aqueous solutions. For example, when the various qualitative analysis groups are precipitated out, the precipitates must be redissolved to separate the ions within each group. Consider a solution of cations that contains Ag^+, Pb^{2+}, and Hg_2^{2+}, among others. When dilute aqueous HCl is added to this solution, the Group I ions will form the insoluble chlorides AgCl, $PbCl_2$, and Hg_2Cl_2. Once this mixed precipitate is separated from the solution, it must be redissolved to identify the cations individually. How can this be done? We know that some solids are more soluble in acidic than in neutral solutions. What about chloride salts? For example, can AgCl be dissolved by using a strong acid? The answer is no, because Cl^- ions have virtually no affinity for H^+ ions in aqueous solution. The position of the dissolution equilibrium

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

is not affected by the presence of H^+.

How can we pull the dissolution equilibrium to the right, even though Cl^- is an extremely weak base? The key is to lower the concentration of Ag^+ in solution by forming complex ions. For example, Ag^+ reacts with excess NH_3 to form the stable complex ion $Ag(NH_3)_2^+$. As a result, AgCl is quite soluble in concentrated ammonia solutions. The relevant reactions are

$$\begin{aligned} AgCl(s) &\rightleftharpoons Ag^+ + Cl^- && K_{sp} = 1.6 \times 10^{-10} \\ Ag^+ + NH_3 &\rightleftharpoons Ag(NH_3)^+ && K_1 = 2.1 \times 10^3 \\ Ag(NH_3)^+ + NH_3 &\rightleftharpoons Ag(NH_3)_2^+ && K_2 = 8.2 \times 10^3 \end{aligned}$$

The Ag^+ ion produced by dissolving solid AgCl combines with NH_3 to form $Ag(NH_3)_2^+$, which causes more AgCl to dissolve, until the point at which

$$[Ag^+][Cl^-] = K_{sp} = 1.6 \times 10^{-10}$$

Here $[Ag^+]$ refers only to the Ag^+ ion that is present as a separate species in solution. It is *not* the total silver content of the solution, which is

$$[Ag]_{\text{total dissolved}} = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$$

For reasons discussed in the previous section, virtually all the Ag^+ from the dissolved AgCl ends up in the complex ion $Ag(NH_3)_2^+$. Thus we can represent the dissolving of solid AgCl in excess NH_3 by the equation

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

When reactions are added, the equilibrium constant for the overall process is the product of the constants for the individual reactions.

Since this equation is the *sum of the three stepwise reactions* given above, the equilibrium constant for the reaction is the product of the constants for the three reactions. (Demonstrate this to yourself by multiplying together the three expressions for K_{sp}, K_1, and K_2.) The equilibrium expression is

$$\begin{aligned} K &= \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} \\ &= K_{sp} \times K_1 \times K_2 = (1.6 \times 10^{-10})(2.1 \times 10^3)(8.2 \times 10^3) = 2.8 \times 10^{-3} \end{aligned}$$

Using this expression, we will now calculate the solubility of solid AgCl in a 10.0 M NH_3 solution. If we let x be the solubility (in mol/L) of AgCl in the solution, we can then write the following expressions for the equilibrium concentrations of the pertinent species:

$$[Cl^-] = x \leftarrow$$

$$[Ag(NH_3)_2{}^+] = x \leftarrow$$

x mol/L of AgCl dissolves to produce x mol/L of Cl^- and x mol/L of $Ag(NH_3)_2{}^+$

$$[NH_3] = 10.0 - 2x \longleftarrow$$

Formation of x mol/L of $Ag(NH_3)_2{}^+$ requires $2x$ mol/L of NH_3, since each complex ion contains two NH_3 ligands

Substituting these concentrations into the equilibrium expression gives

$$K = 2.8 \times 10^{-3} = \frac{[Ag(NH_3)_2{}^+][Cl^-]}{[NH_3]^2} = \frac{(x)(x)}{(10.0 - 2x)^2} = \frac{x^2}{(10.0 - 2x)^2}$$

No approximations are necessary here. Taking the square root of both sides of the equation gives

$$\sqrt{2.8 \times 10^{-3}} = \frac{x}{10.0 - 2x}$$

$$x = 0.48 \text{ mol/L} = \text{solubility of AgCl}(s) \text{ in } 10.0\ M\ NH_3$$

Thus the solubility of AgCl in 10.0 M NH_3 is much greater than its solubility in pure water, which is

$$\sqrt{K_{sp}} = 1.3 \times 10^{-5} \text{ mol/L}$$

In this chapter we have considered two strategies for dissolving a water-insoluble ionic solid. If the *anion* of the solid is a good base, the solubility is greatly increased by acidifying the solution. In cases where the anion is not sufficiently basic, the ionic solid often can be dissolved in a solution containing a ligand that forms stable complex ions with its *cation.*

Sometimes solids are so insoluble that combinations of reactions are needed to dissolve them. For example, to dissolve the extremely insoluble HgS ($K_{sp} = 10^{-54}$), it is necessary to use a mixture of concentrated HCl and concentrated HNO_3, called *aqua regia.* The H^+ ions in the aqua regia react with the S^{2-} ions to form H_2S, and Cl^- reacts with Hg^{2+} to form various complex ions, including $HgCl_4{}^{2-}$. In addition, $NO_3{}^-$ oxidizes S^{2-} to elemental sulfur. These processes lower the concentrations of Hg^{2+} and S^{2-} and thus promote the solubility of HgS.

Since the solubility of many salts increases with temperature, simple heating is sometimes enough to make a salt sufficiently soluble. For example, earlier in this section we considered the mixed chloride precipitates of the Group I ions—$PbCl_2$, AgCl, and Hg_2Cl_2. The effect of temperature on the solubility of $PbCl_2$ is such that we can precipitate $PbCl_2$ with cold aqueous HCl and then redissolve it by heating the solution to near boiling. The silver and mercury(I) chlorides remain precipitated, since they are not significantly soluble in hot water. However, solid AgCl can be dissolved using aqueous ammonia. The solid Hg_2Cl_2 reacts with NH_3 to form a mixture of elemental mercury and $HgNH_2Cl$:

$$Hg_2Cl_2(s) + 2NH_3(aq) \longrightarrow \underset{\text{White}}{HgNH_2Cl(s)} + \underset{\text{Black}}{Hg(l)} + NH_4{}^+(aq) + Cl^-(aq)$$

The mixed precipitate appears gray. This is an oxidation–reduction reaction in which one mercury(I) ion in Hg_2Cl_2 is oxidized to Hg^{2+} in $HgNH_2Cl$ and the other mercury(I) ion is reduced to Hg, or elemental mercury.

The treatment of the Group I ions is summarized in Fig. 15.13. Note that the presence of Pb^{2+} is confirmed by adding $CrO_4{}^{2-}$, which forms bright yellow lead(II) chromate

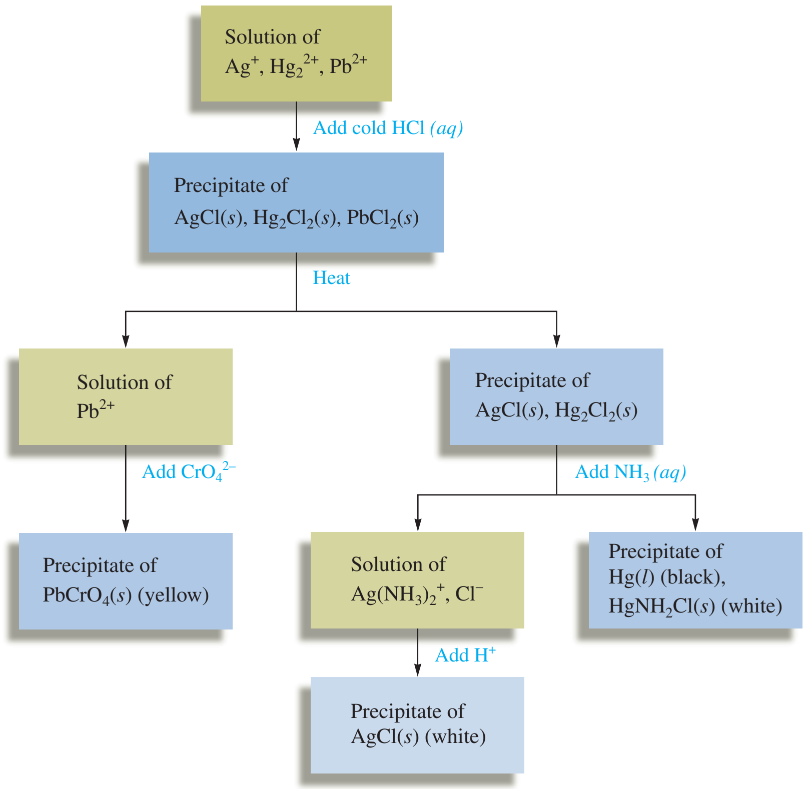


FIGURE 15.13
The separation of the Group I ions in the classic scheme of qualitative analysis.

($PbCrO_4$). Also note that H^+ added to a solution containing $Ag(NH_3)_2^+$ reacts with the NH_3 to form NH_4^+, destroying the $Ag(NH_3)_2^+$ complex. Silver chloride then re-forms:

$$2H^+(aq) + Ag(NH_3)_2^+(aq) + Cl^-(aq) \longrightarrow 2NH_4^+(aq) + AgCl(s)$$

Note that the qualitative analysis of cations by selective precipitation involves all the types of reactions we have discussed and represents an excellent application of the principles of chemical equilibrium.

Key Terms

Section 15.1
common ion
common ion effect

Section 15.2
buffered solution
Henderson–Hasselbalch equation

Section 15.3
buffering capacity

Section 15.4
pH curve (titration curve)
millimole (mmol)
equivalence point (stoichiometric point)

For Review

Buffered solutions

- Contains a weak acid (HA) and its salt (NaA) or a weak base (B) and its salt (BHCl)
- Resists a change in its pH when H^+ or OH^- is added
- For a buffered solution containing HA and A^-
  - The Henderson–Hasselbalch equation is useful:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

  - The capacity of the buffered solution depends on the amounts of HA and A^- present

Section 15.5

acid–base indicator
phenolphthalein

Section 15.6

solubility product constant (solubility product)

Section 15.7

ion product
selective precipitation
qualitative analysis

Section 15.8

complex ion
formation (stability) constants

  - The most efficient buffering occurs when the $\frac{[A^-]}{[HA]}$ ratio is close to 1
  - Buffering works because the amounts of HA (which reacts with added OH^-) and A^- (which reacts with added H^+) are large enough that the $\frac{[A^-]}{[HA]}$ ratio does not change significantly when strong acids or bases are added

Acid–base titrations

- The progress of a titration is represented by plotting the pH of the solution versus the volume of added titrant; the resulting graph is called a pH curve or titration curve
- Strong acid–strong base titrations show a sharp change in pH near the equivalence point
- The shape of the pH curve for a strong base–strong acid titration is quite different before the equivalence point from the shape of the pH curve for a strong base–weak acid titration
  - The strong base–weak acid pH curve shows the effects of buffering before the equivalence point
  - For a strong base–weak acid titration, the pH is greater than 7 at the equivalence point because of the basic properties of A^-
- Indicators are sometimes used to mark the equivalence point of an acid–base titration
  - The end point is where the indicator changes color
  - The goal is to have the end point and the equivalence point be as close as possible

Solids dissolving in water

- For a slightly soluble salt, an equilibrium is set up between the excess solid (MX) and the ions in solution

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

- The corresponding constant is called K_{sp}:

$$K_{sp} = [M^+][X^-]$$

  - The solubility of MX(s) is decreased by the presence from another source of either M^+ or X^-; this is called the common ion effect
- Predicting whether precipitation will occur when two solutions are mixed involves calculating Q for the initial concentrations
  - If $Q > K_{sp}$, precipitation occurs
  - If $Q \le K_{sp}$, no precipitation occurs

REVIEW QUESTIONS

1. What is meant by the presence of a common ion? How does the presence of a common ion affect an equilibrium such as

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

What is an acid–base solution called that contains a common ion?

2. Define a buffer solution. What makes up a buffer solution? How do buffers absorb added H^+ or OH^- with little pH change?

Is it necessary that the concentrations of the weak acid and the weak base in a buffered solution be equal? Explain. What is the pH of a buffer when the weak acid and conjugate base concentrations are equal?

A buffer generally contains a weak acid and its weak conjugate base, or a weak base and its weak conjugate acid, in water. You can solve for the pH by setting up the equilibrium problem using the K_a reaction of the weak acid or the

K_b reaction of the conjugate base. Both reactions give the same answer for the pH of the solution. Explain.

A third method that can be used to solve for the pH of a buffer solution is the Henderson–Hasselbalch equation. What is the Henderson–Hasselbalch equation? What assumptions are made when using this equation?

3. One of the most challenging parts of solving acid–base problems is writing out the correct reaction. When a strong acid or a strong base is added to solutions, they are great at what they do and we always react them first. If a strong acid is added to a buffer, what reacts with the H^+ from the strong acid and what are the products? If a strong base is added to a buffer, what reacts with the OH^- from the strong base and what are the products? Problems involving the reaction of a strong acid or strong base are assumed to be stoichiometry problems and not equilibrium problems. What is assumed when a strong acid or strong base reacts to make it a stoichiometry problem?

   A good buffer generally contains relatively equal concentrations of weak acid and conjugate base. If you wanted to buffer a solution at pH = 4.00 or pH = 10.00, how would you decide which weak acid–conjugate base or weak base–conjugate acid pair to use? The second characteristic of a good buffer is good buffering capacity. What is the *capacity* of a buffer? How do the following buffers differ in capacity? How do they differ in pH?

   0.01 *M* acetic acid/0.01 *M* sodium acetate

   0.1 *M* acetic acid/0.1 *M* sodium acetate

   1.0 *M* acetic acid/1.0 *M* sodium acetate

4. Draw the general titration curve for a strong acid titrated by a strong base. At the various points in the titration, list the major species present before any reaction takes place and the major species present after any reaction takes place. What reaction takes place in a strong acid–strong base titration? How do you calculate the pH at the various points along the curve? What is the pH at the equivalence point for a strong acid–strong base titration? Why? Answer the same questions for a strong base–strong acid titration. Compare and contrast a strong acid–strong base titration versus a strong base–strong acid titration.

5. Sketch the titration curve for a weak acid titrated by a strong base. When performing calculations concerning weak acid–strong base titrations, the general two-step procedure is to solve a stoichiometry problem first, then to solve an equilibrium problem to determine the pH. What reaction takes place in the stoichiometry part of the problem? What is assumed about this reaction?

   At the various points in your titration curve, list the major species present after the strong base (NaOH, for example) reacts to completion with the weak acid, HA. What equilibrium problem would you solve at the various points in your titration curve to calculate the pH? Why is pH > 7.0 at the equivalence point of a weak acid–strong base titration? Does the pH at the halfway point to equivalence have to be less than 7.0? What does the pH at the halfway point equal? Compare and contrast the titration curves for a strong acid–strong base titration and a weak acid–strong base titration.

6. Sketch the titration curve for a weak base titrated by a strong acid. Weak base–strong acid titration problems also follow a two-step procedure. What reaction takes place in the stoichiometry part of the problem? What is assumed about this reaction? At the various points in your titration curve, list the major species present after the strong acid (HNO_3, for example) reacts to completion with the weak base, B. What equilibrium problem would you solve at the various points in your titration curve to calculate the pH? Why is pH < 7.0 at the equivalence point of a weak base–strong acid titration? If pH = 6.0 at the

halfway point to equivalence, what is the K_b value for the weak base titrated? Compare and contrast the titration curves for a strong base–strong acid titration and a weak base–strong acid titration.

7. What is an acid–base indicator? Define the equivalence (stoichiometric) point and the end point of a titration. Why should you choose an indicator so that the two points coincide? Do the pH values of the two points have to be within ±0.01 pH unit of each other? Explain. Why does an indicator change from its acid color to its base color over a range of pH values? In general, when do color changes start to occur for indicators? Can the indicator thymol blue contain only a single $—CO_2H$ group and no other acidic or basic functional group? Explain.
8. To what reaction does the solubility product constant, K_{sp}, refer? Table 15.4 lists K_{sp} values for several ionic solids. For any of these ionic compounds, you should be able to calculate the solubility. What is the solubility of a salt, and what procedures do you follow to calculate the solubility of a salt? How would you calculate the K_{sp} value for a salt given the solubility?

   Under what circumstances can you compare the relative solubilities of two salts directly by comparing the values of their solubility products? When can relative solubilities not be compared based on K_{sp} values? What is a common ion and how does its presence affect the solubility? List some salts whose solubility increases as the pH becomes more acidic. What is true about the anions in these salts? List some salts whose solubility remains unaffected by the solution pH. What is true about the anions in these salts?
9. What is the difference between the ion product, Q, and the solubility product, K_{sp}? What happens when $Q > K_{sp}$? $Q < K_{sp}$? $Q = K_{sp}$? Mixtures of metal ions in aqueous solution can sometimes be separated by selective precipitation. What is selective precipitation? If a solution contained 0.10 M Mg^{2+}, 0.10 M Ca^{2+}, and 0.10 M Ba^{2+}, how could addition of NaF be used to separate the cations out of solution—that is, what would precipitate first, then second, then third? How could addition of K_3PO_4 be used to separate out the cations in a solution that 1.0 M Ag^+, 1.0 M Pb^{2+}, and 1.0 M Sr^{2+}?
10. What is a complex ion? The stepwise formation constants for the complex ion $Cu(NH_3)_4{}^{2+}$ are $K_1 \approx 1 \times 10^3$, $K_2 \approx 1 \times 10^4$, $K_3 \approx 1 \times 10^3$, and $K_4 \approx 1 \times 10^3$. Write the reactions that refer to each of these formation constants. Given that the values of the formation constants are large, what can you deduce about the equilibrium concentration of $Cu(NH_3)_4{}^{2+}$ versus the equilibrium concentration of Cu^{2+}? When 5 M ammonia is added to a solution containing $Cu(OH)_2(s)$, the precipitate will eventually dissolve in solution. Why? If 5 M HNO_3 is then added, the $Cu(OH)_2$ precipitate re-forms. Why? In general, what effect does the ability of a cation to form a complex ion have on the solubility of salts containing that cation?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. What are the major species in solution after $NaHSO_4$ is dissolved in water? What happens to the pH of the solution as more $NaHSO_4$ is added? Why? Would the results vary if baking soda ($NaHCO_3$) were used instead?

2. A friend asks the following: "Consider a buffered solution made up of the weak acid HA and its salt NaA. If a strong base like NaOH is added, the HA reacts with the OH^- to form A^-. Thus the amount of acid (HA) is decreased, and the amount of base (A^-) is increased. Analogously, adding HCl to the buffered solution forms more of the acid (HA) by reacting with the base (A^-). Thus how can we claim that a buffered solution resists changes in the pH of the solution?" How would you explain buffering to this friend?

3. Mixing together solutions of acetic acid and sodium hydroxide can make a buffered solution. Explain. How does the amount of each solution added change the effectiveness of the buffer? Would a buffer solution made by mixing HCl and NaOH be effective? Explain.

4. Sketch two pH curves, one for the titration of a weak acid with a strong base and one for a strong acid with a strong base. How are they similar? How are they different? Account for the similarities and the differences.

5. Sketch a pH curve for the titration of a weak acid (HA) with a strong base (NaOH). List the major species and explain how you would go about calculating the pH of the solution at various points, including the halfway point and the equivalence point.

6. Devise as many ways as you can to experimentally determine the K_{sp} value of a solid. Explain why each of these would work.

7. You are browsing through the *Handbook of Hypothetical Chemistry* when you come across a solid that is reported to have a K_{sp} value of zero in water at 25°C. What does this mean?

8. A friend tells you: "The constant K_{sp} of a salt is called the solubility product constant and is calculated from the concentrations of ions in the solution. Thus, if salt A dissolves to a greater extent than salt B, salt A must have a higher K_{sp} than salt B." Do you agree with your friend? Explain.

9. Explain the following phenomenon: You have a test tube with about 20 mL of silver nitrate solution. Upon adding a few drops of sodium chromate solution, you notice a red solid forming in a relatively clear solution. Upon adding a few drops of a sodium chloride solution to the same test tube, you notice a white solid and a pale yellow solution. Use the K_{sp} values in the book to support your explanation, and include the balanced reactions.

10. What happens to the K_{sp} value of a solid as the temperature of the solution changes? Consider both increasing and decreasing temperatures, and explain your answer.

11. Which is more likely to dissolve in an acidic solution, silver sulfide or silver chloride? Why?

12. You have two salts, AgX and AgY, with very similar K_{sp} values. You know that the K_a value for HX is much greater than the K_a value for HY. Which salt is more soluble in an acidic solution? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

13. The common ion effect for weak acids is to significantly decrease the dissociation of the acid in water. The common ion effect for ionic solids (salts) is to significantly decrease the solubility of the ionic compound in water. Explain both of these common ion effects.

14. Consider a buffer solution where [weak acid] > [conjugate base]. How is the pH of the solution related to the pK_a value of the weak acid? If [conjugate base] > [weak acid], how is pH related to pK_a?

15. A best buffer has about equal quantities of weak acid and conjugate base present as well as having a large concentration of each species present. Explain.

16. Consider the following four titrations.
  i. 100.0 mL of 0.10 M HCl titrated by 0.10 M NaOH
  ii. 100.0 mL of 0.10 M NaOH titrated by 0.10 M HCl
  iii. 100.0 mL of 0.10 M CH_3NH_2 titrated by 0.10 M HCl
  iv. 100.0 mL of 0.10 M HF titrated by 0.10 M NaOH

Rank the titrations in order of:
  a. increasing volume of titrant added to reach the equivalence point.
  b. increasing pH initially before any titrant has been added.
  c. increasing pH at the halfway point in equivalence.
  d. increasing pH at the equivalence point.

How would the rankings change if C_5H_5N replaced CH_3NH_2 and if HOC_6H_5 replaced HF?

17. Figure 15.4 shows the pH curves for the titrations of six different acids by NaOH. Make a similar plot for the titration of three different bases by 0.10 M HCl. Assume 50.0 mL of 0.20 M of the bases and assume the three bases are a strong base (KOH), a weak base with $K_b = 1 \times 10^{-5}$, and another weak base with $K_b = 1 \times 10^{-10}$.

18. Acid–base indicators mark the end point of titrations by "magically" turning a different color. Explain the "magic" behind acid–base indicators.

19. The salts in Table 15.4, with the possible exception of the hydroxide salts, have one of the following mathematical relationships between the K_{sp} value and the molar solubility, s.
  i. $K_{sp} = s^2$
  ii. $K_{sp} = 4s^3$
  iii. $K_{sp} = 27s^4$
  iv. $K_{sp} = 108s^5$

For each mathematical relationship, give an example of a salt in Table 15.4 that exhibits that relationship.

20. List some ways one can increase the solubility of a salt in water.

Exercises

In this section similar exercises are paired.

Buffers

21. A certain buffer is made by dissolving $NaHCO_3$ and Na_2CO_3 in some water. Write equations to show how this buffer neutralizes added H^+ and OH^-.

22. A buffer is prepared by dissolving $HONH_2$ and $HONH_3NO_3$ in some water. Write equations to show how this buffer neutralizes added H^+ and OH^-.

23. Calculate the pH of each of the following solutions.
  a. 0.100 M propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$)
  b. 0.100 M sodium propanoate ($NaC_3H_5O_2$)
  c. pure H_2O
  d. a mixture containing 0.100 M $HC_3H_5O_2$ and 0.100 M $NaC_3H_5O_2$

24. Calculate the pH of each of the following solutions.
  a. 0.100 M $HONH_2$ ($K_b = 1.1 \times 10^{-8}$)
  b. 0.100 M $HONH_3Cl$
  c. pure H_2O
  d. a mixture containing 0.100 M $HONH_2$ and 0.100 M $HONH_3Cl$

25. Compare the percent dissociation of the acid in Exercise 23a with the percent dissociation of the acid in Exercise 23d. Explain the large difference in percent dissociation of the acid.

26. Compare the percent ionization of the base in Exercise 24a with the percent ionization of the base in Exercise 24d. Explain any differences.

27. Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 23.

28. Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 24.

29. Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the four solutions in Exercise 23.

30. Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the solutions in Exercise 24.

31. Which of the solutions in Exercise 23 shows the least change in pH upon the addition of acid or base? Explain.

32. Which of the solutions in Exercise 24 is a buffered solution?

33. Calculate the pH of a solution that is 1.00 *M* HNO_2 and 1.00 *M* $NaNO_2$.

34. Calculate the pH of a solution that is 0.60 *M* HF and 1.00 *M* KF.

35. Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 33, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 33.

36. Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 34, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 34.

37. Calculate the pH of a buffer solution prepared by dissolving 21.46 g of benzoic acid ($HC_7H_5O_2$) and 37.68 g of sodium benzoate in 200.0 mL of solution.

38. A buffered solution is made by adding 50.0 g NH_4Cl to 1.00 L of a 0.75 *M* solution of NH_3. Calculate the pH of the final solution. (Assume no volume change.)

39. Calculate the pH after 0.010 mol gaseous HCl is added to 250.0 mL of each of the following buffered solutions.
a. 0.050 *M* NH_3/0.15 *M* NH_4Cl
b. 0.50 *M* NH_3/1.50 *M* NH_4Cl
Do the two original buffered solutions differ in their pH or their capacity? What advantage is there in having a buffer with a greater capacity?

40. An aqueous solution contains dissolved $C_6H_5NH_3Cl$ and $C_6H_5NH_2$. The concentration of $C_6H_5NH_2$ is 0.50 *M* and pH is 4.20.
a. Calculate the concentration of $C_6H_5NH_3^+$ in this buffer solution.
b. Calculate the pH after 4.0 g of NaOH(*s*) is added to 1.0 L of this solution. (Neglect any volume change.)

41. Calculate the mass of sodium acetate that must be added to 500.0 mL of 0.200 *M* acetic acid to form a pH = 5.00 buffer solution.

42. What volumes of 0.50 *M* HNO_2 and 0.50 *M* $NaNO_2$ must be mixed to prepare 1.00 L of a solution buffered at pH = 3.55?

43. Consider a solution that contains both C_5H_5N and $C_5H_5NHNO_3$. Calculate the ratio $[C_5H_5N]/[C_5H_5NH^+]$ if the solution has the following pH values.
a. pH = 4.50 **c.** pH = 5.23
b. pH = 5.00 **d.** pH = 5.50

44. a. Carbonate buffers are important in regulating the pH of blood at 7.40. What is the concentration ratio of CO_2 (usually written H_2CO_3) to HCO_3^- in blood at pH = 7.40?

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \quad K_a = 4.3 \times 10^{-7}$$

b. Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of $H_2PO_4^-$ to HPO_4^{2-} in intracellular fluid at pH = 7.15?

$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \quad K_a = 6.2 \times 10^{-8}$$

c. Why is a buffer composed of H_3PO_4 and $H_2PO_4^-$ ineffective in buffering the pH of intracellular fluid?

$$H_3PO_4(aq) \rightleftharpoons H_2PO_4^-(aq) + H^+(aq) \quad K_a = 7.5 \times 10^{-3}$$

45. Consider the acids in Table 14.2. Which acid would be the best choice for preparing a pH = 7.00 buffer? Explain how to make 1.0 L of this buffer.

46. Consider the bases in Table 14.3. Which base would be the best choice for preparing a pH = 5.00 buffer? Explain how to make 1.0 L of this buffer.

47. Which of the following mixtures would result in buffered solutions when 1.0 L of each of the two solutions are mixed?
a. 0.1 *M* KOH and 0.1 *M* CH_3NH_3Cl
b. 0.1 *M* KOH and 0.2 *M* CH_3NH_2
c. 0.2 *M* KOH and 0.1 *M* CH_3NH_3Cl
d. 0.1 *M* KOH and 0.2 *M* CH_3NH_3Cl

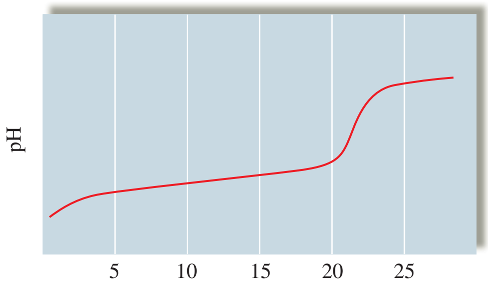
48. Which of the following mixtures would result in a buffered solution when 1.0 L of each of the two solutions are mixed?
a. 0.2 *M* HNO_3 and 0.4 *M* $NaNO_3$
b. 0.2 *M* HNO_3 and 0.4 *M* HF
c. 0.2 *M* HNO_3 and 0.4 *M* NaF
d. 0.2 *M* HNO_3 and 0.4 *M* NaOH

49. How many moles of NaOH must be added to 1.0 L of 2.0 *M* $HC_2H_3O_2$ to produce a solution buffered at each pH?
a. pH = pK_a **b.** pH = 4.00 **c.** pH = 5.00

50. Calculate the number of moles of HCl(*g*) that must be added to 1.0 L of 1.0 *M* $NaC_2H_3O_2$ to produce a solution buffered at each pH.
a. pH = pK_a **b.** pH = 4.20 **c.** pH = 5.00

Acid–Base Titrations

51. Consider the titration of a generic weak acid HA with a strong base that gives the following titration curve:



On the curve, indicate the points that correspond to the following:

a. the stoichiometric (equivalence) point
b. the region with maximum buffering
c. $pH = pK_a$
d. pH depends only on [HA]
e. pH depends only on $[A^-]$
f. pH depends only on the amount of excess strong base added

52. Sketch the titration curve for the titration of a generic weak base B with a strong acid. The titration reaction is

$$B + H^+ \rightleftharpoons BH^+$$

On this curve, indicate the points that correspond to the following:

a. the stoichiometric (equivalence) point
b. the region with maximum buffering
c. $pH = pK_a$
d. pH depends only on [B]
e. pH depends only on $[BH^+]$
f. pH depends only on the amount of excess strong acid added

53. Consider the titration of 40.0 mL of 0.200 *M* $HClO_4$ by 0.100 *M* KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.

a. 0.0 mL **d.** 80.0 mL
b. 10.0 mL **e.** 100.0 mL
c. 40.0 mL

54. Consider the titration of 80.0 mL of 0.100 *M* $Ba(OH)_2$ by 0.400 *M* HCl. Calculate the pH of the resulting solution after the following volumes of HCl have been added.

a. 0.0 mL **d.** 40.0 mL
b. 20.0 mL **e.** 80.0 mL
c. 30.0 mL

55. Consider the titration of 100.0 mL of 0.200 *M* acetic acid ($K_a = 1.8 \times 10^{-5}$) by 0.100 *M* KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.

a. 0.0 mL **d.** 150.0 mL
b. 50.0 mL **e.** 200.0 mL
c. 100.0 mL **f.** 250.0 mL

56. Consider the titration of 100.0 mL of 0.100 *M* H_2NNH_2 ($K_b = 3.0 \times 10^{-6}$) by 0.200 *M* HNO_3. Calculate the pH of the resulting solution after the following volumes of HNO_3 have been added.

a. 0.0 mL **d.** 40.0 mL
b. 20.0 mL **e.** 50.0 mL
c. 25.0 mL **f.** 100.0 mL

57. A 25.0-mL sample of 0.100 *M* lactic acid ($HC_3H_5O_3$, $pK_a = 3.86$) is titrated with 0.100 *M* NaOH solution. Calculate the pH after the addition of 0.0 mL, 4.0 mL, 8.0 mL, 12.5 mL, 20.0 mL, 24.0 mL, 24.5 mL, 24.9 mL, 25.0 mL, 25.1 mL, 26.0 mL, 28.0 mL, and 30.0 mL of the NaOH. Plot the results of your calculations as pH versus milliliters of NaOH added.

58. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 *M* propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$) with 0.100 *M* NaOH.

59. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 *M* NH_3 ($K_b = 1.8 \times 10^{-5}$) with 0.100 *M* HCl.

60. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 *M* pyridine with 0.100 *M* hydrochloric acid (K_b for pyridine is 1.7×10^{-9}). Do not do the points at 24.9 and 25.1 mL.

61. Calculate the pH at the halfway point and at the equivalence point for each of the following titrations.

a. 100.0 mL of 0.10 *M* $HC_7H_5O_2$ ($K_a = 6.4 \times 10^{-5}$) titrated by 0.10 *M* NaOH
b. 100.0 mL of 0.10 *M* $C_2H_5NH_2$ ($K_b = 5.6 \times 10^{-4}$) titrated by 0.20 *M* HNO_3
c. 100.0 mL of 0.50 *M* HCl titrated by 0.25 *M* NaOH

62. In the titration of 50.0 mL of 1.0 *M* methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$), with 0.50 *M* HCl, calculate the pH under the following conditions.

a. after 50.0 mL of 0.50 *M* HCl has been added
b. at the stoichiometric point

63. You have 75.0 mL of 0.10 *M* HA. After adding 30.0 mL of 0.10 *M* NaOH, the pH is 5.50. What is the K_a value of HA?

64. A sample of an ionic compound NaA, where A^- is the anion of a weak acid, was dissolved in enough water to make 100.0 mL of solution and was then titrated with 0.100 *M* HCl. After 500.0 mL of HCl was added, the pH was measured and found to be 5.00. The experimenter found that 1.00 L of 0.100 *M* HCl was required to reach the stoichiometric point of the titration.

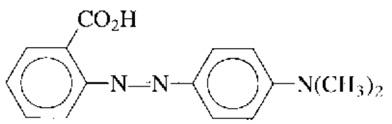
a. What is the K_b value for A^-?
b. Calculate the pH of the solution at the stoichiometric point of the titration.

Indicators

65. Two drops of indicator HIn ($K_a = 1.0 \times 10^{-9}$), where HIn is yellow and In^- is blue, are placed in 100.0 mL of 0.10 *M* HCl.

a. What color is the solution initially?
b. The solution is titrated with 0.10 *M* NaOH. At what pH will the color change (yellow to greenish yellow) occur?
c. What color will the solution be after 200.0 mL of NaOH has been added?

66. Methyl red has the following structure:



$K_a = 5.0 \times 10^{-6}$

It undergoes a color change from red to yellow as a solution gets more basic. Calculate an approximate pH range for which methyl red is useful. What is the color change and the pH at the color change when a weak acid is titrated with a strong base using methyl red as an indicator? What is the color change and the pH at the color change when a weak base is titrated with a strong acid using methyl red as an indicator? For which of these two types of titrations is methyl red a possible indicator?

67. Potassium hydrogen phthalate, known as KHP (molar mass = 204.22 g/mol), can be obtained in high purity and is used to determine the concentration of solutions of strong bases by the reaction

$$HP^-(aq) + OH^-(aq) \longrightarrow H_2O(l) + P^{2-}(aq)$$

If a typical titration experiment begins with approximately 0.5 g of KHP and has a final volume of about 100 mL, what is an appropriate indicator to use? The pK_a for HP^- is 5.51.

68. A certain indicator HIn has a pK_a of 3.00 and a color change becomes visible when 7.00% of the indicator has been converted to In^-. At what pH is this color change visible?

69. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 53 and 55?

70. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 54 and 56?

71. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 57 and 59?

72. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 58 and 60?

73. Estimate the pH of a solution in which bromcresol green is blue and thymol blue is yellow. (See Fig. 15.8.)

74. A solution has a pH of 7.0. What would be the color of the solution if each of the following indicators were added? (See Fig. 15.8.)
a. thymol blue
b. bromthymol blue
c. methyl red
d. crystal violet

Solubility Equilibria

75. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
a. $AgC_2H_3O_2$ **b.** $Al(OH)_3$ **c.** $Ca_3(PO_4)_2$

76. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
a. Ag_2CO_3 **b.** $Ce(IO_3)_3$ **c.** BaF_2

77. Use the following data to calculate the K_{sp} value for each solid.
a. The solubility of CaC_2O_4 is 6.1×10^{-3} g/L.
b. The solubility of BiI_3 is 1.32×10^{-5} mol/L.

78. Use the following data to calculate the K_{sp} value for each solid.
a. The solubility of $Pb_3(PO_4)_2$ is 6.2×10^{-12} mol/L.
b. The solubility of Li_2CO_3 is 7.4×10^{-2} mol/L.

79. The concentration of Pb^{2+} in a solution saturated with $PbBr_2(s)$ is 2.14×10^{-2} *M*. Calculate K_{sp} for $PbBr_2$.

80. The concentration of Ag^+ in a solution saturated with $Ag_2C_2O_4(s)$ is 2.2×10^{-4} *M*. Calculate K_{sp} for $Ag_2C_2O_4$.

81. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
a. Ag_3PO_4, $K_{sp} = 1.8 \times 10^{-18}$
b. $CaCO_3$, $K_{sp} = 8.7 \times 10^{-9}$
c. Hg_2Cl_2, $K_{sp} = 1.1 \times 10^{-18}$ (Hg_2^{2+} is the cation in solution.)

82. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
a. PbI_2, $K_{sp} = 1.4 \times 10^{-8}$
b. $CdCO_3$, $K_{sp} = 5.2 \times 10^{-12}$
c. $Sr_3(PO_4)_2$, $K_{sp} = 1 \times 10^{-31}$

83. The solubility of the ionic compound M_2X_3, having a molar mass of 288 g/mol, is 3.60×10^{-7} g/L. Calculate the K_{sp} of the compound.

84. A solution contains 0.018 mol each of I^-, Br^-, and Cl^-. When the solution is mixed with 200. mL of 0.24 *M* $AgNO_3$, what mass of $AgCl(s)$ precipitates out, and what is the $[Ag^+]$? Assume no volume change.

$$AgI,\ K_{sp} = 1.5 \times 10^{-16}$$
$$AgBr,\ K_{sp} = 5.0 \times 10^{-13}$$
$$AgCl,\ K_{sp} = 1.6 \times 10^{-10}$$

85. Calculate the molar solubility of $Co(OH)_3$, $K_{sp} = 2.5 \times 10^{-43}$.

86. Calculate the molar solubility of $Cd(OH)_2$, $K_{sp} = 5.9 \times 10^{-11}$.

87. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
a. $CaF_2(s)$, $K_{sp} = 4.0 \times 10^{-11}$, or $BaF_2(s)$, $K_{sp} = 2.4 \times 10^{-5}$
b. $Ca_3(PO_4)_2(s)$, $K_{sp} = 1.3 \times 10^{-32}$, or $FePO_4(s)$, $K_{sp} = 1.0 \times 10^{-22}$

88. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
a. FeC_2O_4, $K_{sp} = 2.1 \times 10^{-7}$, or $Cu(IO_4)_2$, $K_{sp} = 1.4 \times 10^{-7}$
b. Ag_2CO_3, $K_{sp} = 8.1 \times 10^{-12}$, or $Mn(OH)_2$, $K_{sp} = 2 \times 10^{-13}$

89. Calculate the solubility (in moles per liter) of $Fe(OH)_3$ ($K_{sp} = 4 \times 10^{-38}$) in each of the following.
a. water
b. a solution buffered at pH = 5.0
c. a solution buffered at pH = 11.0

90. The K_{sp} for silver sulfate (Ag_2SO_4) is 1.2×10^{-5}. Calculate the solubility of silver sulfate in each of the following.
a. water **b.** 0.10 *M* $AgNO_3$ **c.** 0.20 *M* K_2SO_4

91. Calculate the solubility of solid $Ca_3(PO_4)_2$ ($K_{sp} = 1.3 \times 10^{-32}$) in a 0.20 *M* Na_3PO_4 solution.

92. The solubility of $Ce(IO_3)_3$ in a 0.20 *M* KIO_3 solution is 4.4×10^{-8} mol/L. Calculate K_{sp} for $Ce(IO_3)_3$.

93. What mass of ZnS ($K_{sp} = 2.5 \times 10^{-22}$) will dissolve in 300.0 mL of 0.050 *M* $Zn(NO_3)_2$? Ignore the basic properties of S^{2-}.

94. The concentration of Mg^{2+} in seawater is 0.052 *M*. At what pH will 99% of the Mg^{2+} be precipitated as the hydroxide salt? [K_{sp} for $Mg(OH)_2 = 8.9 \times 10^{-12}$.]

95. Which of the substances in Exercises 81 and 82 show increased solubility as the pH of the solution becomes more acidic? Write equations for the reactions that occur to increase the solubility.

96. For which salt in each of the following groups will the solubility depend on pH?
a. AgF, AgCl, AgBr
b. $Pb(OH)_2$, $PbCl_2$
c. $Sr(NO_3)_2$, $Sr(NO_2)_2$
d. $Ni(NO_3)_2$, $Ni(CN)_2$

97. Will a precipitate form when 75.0 mL of 0.020 *M* $BaCl_2$ and 125 mL of 0.040 *M* Na_2SO_4 are mixed together?

98. Will a precipitate form when 100.0 mL of 4.0×10^{-4} *M* $Mg(NO_3)_2$ is added to 100.0 mL of 2.0×10^{-4} *M* NaOH?

99. Calculate the final concentrations of $K^+(aq)$, $C_2O_4^{2-}(aq)$, $Ba^{2+}(aq)$, and $Br^-(aq)$ in a solution prepared by adding 0.100 L of 0.200 *M* $K_2C_2O_4$ to 0.150 L of 0.250 *M* $BaBr_2$. (For BaC_2O_4, $K_{sp} = 2.3 \times 10^{-8}$.)

100. A solution is prepared by mixing 50.0 mL of 0.10 M $Pb(NO_3)_2$ with 50.0 mL of 1.0 M KCl. Calculate the concentrations of Pb^{2+} and Cl^- at equilibrium. K_{sp} for $PbCl_2(s)$ is 1.6×10^{-5}.

101. A solution contains 1.0×10^{-5} M Na_3PO_4. What is the minimum concentration of $AgNO_3$ that would cause precipitation of solid Ag_3PO_4 ($K_{sp} = 1.8 \times 10^{-18}$)?

102. A solution contains 0.25 M $Ni(NO_3)_2$ and 0.25 M $Cu(NO_3)_2$. Can the metal ions be separated by slowly adding Na_2CO_3? Assume that for successful separation 99% of the metal ion must be precipitated before the other metal ion begins to precipitate, and assume no volume change on addition of Na_2CO_3.

Complex Ion Equilibria

103. Write equations for the stepwise formation of each of the following complex ions.

a. $Ni(CN)_4^{2-}$
b. $V(C_2O_4)_3^{3-}$

104. Write equations for the stepwise formation of each of the following complex ions.

a. CoF_6^{3-}
b. $Zn(NH_3)_4^{2+}$

105. Given the following data,

$$Mn^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons MnC_2O_4(aq) \qquad K_1 = 7.9 \times 10^3$$

$$MnC_2O_4(aq) + C_2O_4^{2-}(aq) \rightleftharpoons Mn(C_2O_4)_2^{2-}(aq) \qquad K_2 = 7.9 \times 10^1$$

calculate the value for the overall formation constant for $Mn(C_2O_4)_2^{2-}$:

$$K = \frac{[Mn(C_2O_4)_2^{2-}]}{[Mn^{2+}][C_2O_4^{2-}]^2}$$

106. In the presence of CN^-, Fe^{3+} forms the complex ion $Fe(CN)_6^{3-}$. The equilibrium concentrations of Fe^{3+} and $Fe(CN)_6^{3-}$ are 8.5×10^{-40} M and 1.5×10^{-3} M, respectively, in a 0.11 M KCN solution. Calculate the value for the overall formation constant of $Fe(CN)_6^{3-}$.

$$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-} \qquad K_{overall} = ?$$

107. When aqueous KI is added gradually to mercury(II) nitrate, an orange precipitate forms. Continued addition of KI causes the precipitate to dissolve. Write balanced equations to explain these observations. (*Hint:* Hg^{2+} reacts with I^- to form HgI_4^{2-}.)

108. As sodium chloride solution is added to a solution of silver nitrate, a white precipitate forms. Ammonia is added to the mixture and the precipitate dissolves. When potassium bromide solution is then added, a pale yellow precipitate appears. When a solution of sodium thiosulfate is added, the yellow precipitate dissolves. Finally, potassium iodide is added to the solution and a yellow precipitate forms. Write reactions for all the changes mentioned above. What conclusions can you draw concerning the sizes of the K_{sp} values for AgCl, AgBr, and AgI?

109. The overall formation constant for HgI_4^{2-} is 1.0×10^{30}. That is,

$$1.0 \times 10^{30} = \frac{[HgI_4^{2-}]}{[Hg^{2+}][I^-]^4}$$

What is the concentration of Hg^{2+} in 500.0 mL of a solution that was originally 0.010 M Hg^{2+} and 0.78 M I^-? The reaction is

$$Hg^{2+}(aq) + 4I^-(aq) \rightleftharpoons HgI_4^{2-}(aq)$$

110. A solution is formed by mixing 50.0 mL of 10.0 M NaX with 50.0 mL of 2.0×10^{-3} M $CuNO_3$. Assume that Cu(I) forms complex ions with X^- as follows:

$$Cu^+(aq) + X^-(aq) \rightleftharpoons CuX(aq) \qquad K_1 = 1.0 \times 10^2$$

$$CuX(aq) + X^-(aq) \rightleftharpoons CuX_2^-(aq) \qquad K_2 = 1.0 \times 10^4$$

$$CuX_2^-(aq) + X^-(aq) \rightleftharpoons CuX_3^{2-}(aq) \qquad K_3 = 1.0 \times 10^3$$

with an overall reaction

$$Cu^+(aq) + 3X^-(aq) \rightleftharpoons CuX_3^{2-}(aq) \qquad K = 1.0 \times 10^9$$

Calculate the following concentrations at equilibrium.

a. CuX_3^{2-} **b.** CuX_2^- **c.** Cu^+

111. **a.** Calculate the molar solubility of AgI in pure water. K_{sp} for AgI is 1.5×10^{-16}.

b. Calculate the molar solubility of AgI in 3.0 M NH_3. The overall formation constant for $Ag(NH_3)_2^+$ is 1.7×10^7.

c. Compare the calculated solubilities from parts a and b. Explain any differences.

112. Solutions of sodium thiosulfate are used to dissolve unexposed AgBr ($K_{sp} = 5.0 \times 10^{-13}$) in the developing process for black-and-white film. What mass of AgBr can dissolve in 1.00 L of 0.500 M $Na_2S_2O_3$? Ag^+ reacts with $S_2O_3^{2-}$ to form a complex ion:

$$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) \qquad K = 2.9 \times 10^{13}$$

113. K_f for the complex ion $Ag(NH_3)_2^+$ is 1.7×10^7. K_{sp} for AgCl is 1.6×10^{-10}. Calculate the molar solubility of AgCl in 1.0 M NH_3.

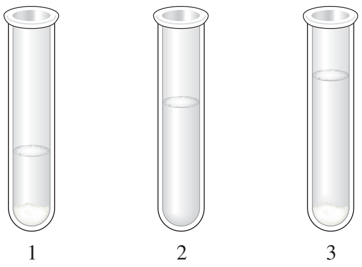
114. The copper(I) ion forms a chloride salt that has $K_{sp} = 1.2 \times 10^{-6}$. Copper(I) also forms a complex ion with Cl^-:

$$Cu^+(aq) + 2Cl^-(aq) \rightleftharpoons CuCl_2^-(aq) \qquad K = 8.7 \times 10^4$$

a. Calculate the solubility of copper(I) chloride in pure water. (Ignore $CuCl_2^-$ formation for part a.)

b. Calculate the solubility of copper(I) chloride in 0.10 M NaCl.

115. A series of chemicals were added to some $AgNO_3(aq)$. $NaCl(aq)$ was added first to the silver nitrate solution with the end result shown below in test tube 1, $NH_3(aq)$ was then added with the end result shown in test tube 2, and $HNO_3(aq)$ was added last with the end result shown in test tube 3.



Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

116. The solubility of copper(II) hydroxide in water can be increased by adding either the base NH_3 or the acid HNO_3. Explain. Would added NH_3 or HNO_3 have the same effect on the solubility of silver acetate or silver chloride? Explain.

Additional Exercises

117. Derive an equation analogous to the Henderson–Hasselbalch equation but relating pOH and pK_b of a buffered solution composed of a weak base and its conjugate acid, such as NH_3 and NH_4^+.

118. **a.** Calculate the pH of a buffered solution that is 0.100 *M* in $C_6H_5CO_2H$ (benzoic acid, $K_a = 6.4 \times 10^{-5}$) and 0.100 *M* in $C_6H_5CO_2Na$.

b. Calculate the pH after 20.0% (by moles) of the benzoic acid is converted to benzoate anion by addition of strong acid. Use the dissociation equilibrium

$$C_6H_5CO_2H(aq) \rightleftharpoons C_6H_5CO_2^-(aq) + H^+(aq)$$

to calculate the pH.

c. Do the same as in part b, but use the following equilibrium to calculate the pH:

$$C_6H_5CO_2^-(aq) + H_2O(l) \rightleftharpoons C_6H_5CO_2H(aq) + OH^-(aq)$$

d. Do your answers in parts b and c agree? Explain.

119. Consider a solution containing 0.10 *M* ethylamine ($C_2H_5NH_2$), 0.20 *M* $C_2H_5NH_3^+$, and 0.20 *M* Cl^-.

a. Calculate the pH of this solution.

b. Calculate the pH after 0.050 mol of KOH(*s*) is added to 1.00 L of this solution. (Ignore any volume changes.)

120. You make 1.00 L of a buffered solution (pH = 4.00) by mixing acetic acid and sodium acetate. You have 1.00 *M* solutions of each component of the buffered solution. What volume of each solution do you mix to make such a buffered solution?

121. You have the following reagents on hand:

Solids (pK_a of Acid Form Is Given)	Solutions
Benzoic acid (4.19)	5.0 *M* HCl
Sodium acetate (4.74)	1.0 *M* acetic acid (4.74)
Potassium fluoride (3.14)	2.6 *M* NaOH
Ammonium chloride (9.26)	1.0 *M* HOCl (7.46)

What combinations of reagents would you use to prepare buffers at the following pH values?

a. 3.0 **b.** 4.0 **c.** 5.0 **d.** 7.0 **e.** 9.0

122. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and K_b is 1.19×10^{-6} for the aqueous reaction

$$\underset{\text{TRIS}}{(HOCH_2)_3CNH_2} + H_2O \rightleftharpoons \underset{\text{TRISH}^+}{(HOCH_2)_3CNH_3^+} + OH^-$$

a. What is the optimal pH for TRIS buffers?

b. Calculate the ratio [TRIS]/[TRISH$^+$] at pH = 7.00 and at pH = 9.00.

c. A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS hydrochloride (written as TRISHCl) to a total volume of 2.0 L. What is the pH of this buffer? What is the pH after 0.50 mL of 12 *M* HCl is added to a 200.0-mL portion of the buffer?

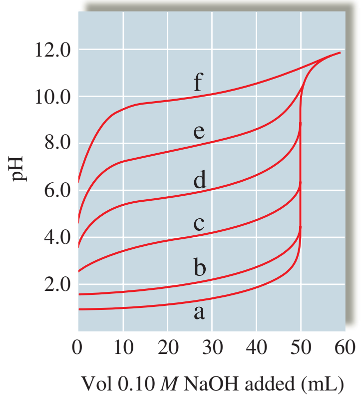
123. Calculate the value of the equilibrium constant for each of the following reactions in aqueous solution.

a. $HC_2H_3O_2 + OH^- \rightleftharpoons C_2H_3O_2^- + H_2O$

b. $C_2H_3O_2^- + H^+ \rightleftharpoons HC_2H_3O_2$

c. $HCl + NaOH \rightleftharpoons NaCl + H_2O$

124. The following plot shows the pH curves for the titrations of various acids by 0.10 *M* NaOH (all of the acids were 50.0-mL samples of 0.10 *M* concentration).



a. Which pH curve corresponds to the weakest acid?

b. Which pH curve corresponds to the strongest acid? Which point on the pH curve would you examine to see if this acid is a strong acid or a weak acid (assuming you did not know the initial concentration of the acid)?

c. Which pH curve corresponds to an acid with $K_a \approx 1 \times 10^{-6}$?

125. Calculate the volume of 1.50×10^{-2} *M* NaOH that must be added to 500.0 mL of 0.200 *M* HCl to give a solution that has pH = 2.15.

126. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 *M* HNO_3 with 0.100 *M* NaOH.

127. The active ingredient in aspirin is acetylsalicylic acid. A 2.51-g sample of acetylsalicylic acid required 27.36 mL of 0.5106 *M* NaOH for complete reaction. Addition of 13.68 mL of 0.5106 *M* HCl to the flask containing the aspirin and the sodium hydroxide produced a mixture with pH = 3.48. Find the molar mass of acetylsalicylic acid and its K_a value. State any assumptions you must make to reach your answer.

128. One method for determining the purity of aspirin (empirical formula, $C_9H_8O_4$) is to hydrolyze it with NaOH solution and then to titrate the remaining NaOH. The reaction of aspirin with NaOH is as follows:

$$\underset{\text{Aspirin}}{C_9H_8O_4(s)} + 2OH^-(aq) \xrightarrow[\text{10 min}]{\text{Boil}} \underset{\text{Salicylate ion}}{C_7H_5O_3^-(aq)} + \underset{\text{Acetate ion}}{C_2H_3O_2^-(aq)} + H_2O(l)$$

A sample of aspirin with a mass of 1.427 g was boiled in 50.00 mL of 0.500 *M* NaOH. After the solution was cooled, it took 31.92 mL of 0.289 *M* HCl to titrate the excess NaOH. Calculate the purity of the aspirin. What indicator should be used for this titration? Why?

129. A certain acetic acid solution has pH = 2.68. Calculate the volume of 0.0975 *M* KOH required to reach the equivalence point in the titration of 25.0 mL of the acetic acid solution.

130. A 0.210-g sample of an acid (molar mass = 192 g/mol) is titrated with 30.5 mL of 0.108 *M* NaOH to a phenolphthalein end point. Is the acid monoprotic, diprotic, or triprotic?

131. A student intends to titrate a solution of a weak monoprotic acid with a sodium hydroxide solution but reverses the two solutions and places the weak acid solution in the buret. After 23.75 mL of the weak acid solution has been added to 50.0 mL of the 0.100 *M* NaOH solution, the pH of the resulting solution is 10.50. Calculate the original concentration of the solution of weak acid.

132. A student titrates an unknown weak acid, HA, to a pale pink phenolphthalein end point with 25.0 mL of 0.100 *M* NaOH. The student then adds 13.0 mL of 0.100 *M* HCl. The pH of the resulting solution is 4.7. How is the value of pK_a for the unknown acid related to 4.7?

133. **a.** Using the K_{sp} value for $Cu(OH)_2$ (1.6×10^{-19}) and the overall formation constant for $Cu(NH_3)_4^{2+}$ (1.0×10^{13}), calculate the value for the equilibrium constant for the following reaction:

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$

b. Use the value of the equilibrium constant you calculated in part a to calculate the solubility (in mol/L) of $Cu(OH)_2$ in 5.0 *M* NH_3. In 5.0 *M* NH_3 the concentration of OH^- is 0.0095 *M*.

134. The solubility rules outlined in Chapter 4 say that $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are marginally soluble hydroxides. Calculate the pH of a saturated solution of each of these marginally soluble hydroxides.

135. The K_{sp} of hydroxyapatite, $Ca_5(PO_4)_3OH$, is 6.8×10^{-37}. Calculate the solubility of hydroxyapatite in pure water in moles per liter. How is the solubility of hydroxyapatite affected by adding acid? When hydroxyapatite is treated with fluoride, the mineral fluorapatite, $Ca_5(PO_4)_3F$, forms. The K_{sp} of this substance is 1×10^{-60}. Calculate the solubility of fluorapatite in water. How do these calculations provide a rationale for the fluoridation of drinking water?

136. In the chapter discussion of precipitate formation, we ran the precipitation reaction to completion and then let some of the precipitate redissolve to get back to equilibrium. To see why, redo Sample Exercise 15.17, where

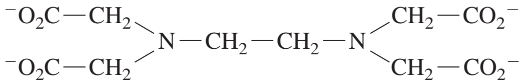
Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[Mg^{2+}]_0 = 3.75 \times 10^{-3}$ $[F^-]_0 = 6.25 \times 10^{-2}$	$\xrightarrow{x \text{ mol/}Mg^{2+}}$ reacts to form MgF_2	$[Mg^{2+}] = 3.75 \times 10^{-3} - y$ $[F^-] = 6.25 \times 10^{-2} - 2y$

137. Calculate the concentration of Pb^{2+} in each of the following.

a. a saturated solution of $Pb(OH)_2$, $K_{sp} = 1.2 \times 10^{-15}$

b. a saturated solution of $Pb(OH)_2$ buffered at pH = 13.00

c. Ethylenediaminetetraacetate ($EDTA^{4-}$) is used as a complexing agent in chemical analysis and has the following structure:



Ethylenediaminetetraacetate

Solutions of $EDTA^{4-}$ are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The complex ion virtually eliminates the heavy metal ions from reacting with biochemical systems. The reaction of $EDTA^{4-}$ with Pb^{2+} is

$$Pb^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons PbEDTA^{2-}(aq) \qquad K = 1.1 \times 10^{18}$$

Consider a solution with 0.010 mol $Pb(NO_3)_2$ added to 1.0 L of an aqueous solution buffered at pH = 13.00 and containing 0.050 *M* Na_4EDTA. Does $Pb(OH)_2$ precipitate from this solution?

Challenge Problems

138. Another way to treat data from a pH titration is to graph the absolute value of the change in pH per change in milliliters added versus milliliters added (ΔpH/ΔmL versus mL added). Make this graph using your results from Exercise 57. What advantage might this method have over the traditional method for treating titration data?

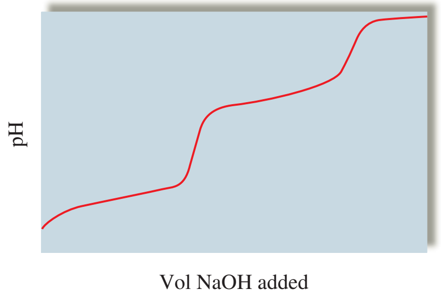
139. A buffer is made using 45.0 mL of 0.750 *M* $HC_3H_5O_2$ ($K_a = 1.3 \times 10^{-5}$) and 55.0 mL of 0.700 *M* $NaC_3H_5O_2$. What volume of 0.10 *M* NaOH must be added to change the pH of the original buffer solution by 2.5%?

140. A 0.400 *M* solution of ammonia was titrated with hydrochloric acid to the equivalence point, where the total volume was 1.50 times the original volume. At what pH does the equivalence point occur?

141. What volume of 0.0100 *M* NaOH must be added to 1.00 L of 0.0500 *M* HOCl to achieve a pH of 8.00?

142. Consider a solution formed by mixing 50.0 mL of 0.100 *M* H_2SO_4, 30.0 mL of 0.100 *M* HOCl, 25.0 mL of 0.200 *M* NaOH, 25.0 mL of 0.100 *M* $Ba(OH)_2$, and 10.0 mL of 0.150 *M* KOH. Calculate the pH of this solution.

143. When a diprotic acid, H_2A, is titrated by NaOH, the protons on the diprotic acid are generally removed one at a time, resulting in a pH curve that has the following generic shape:

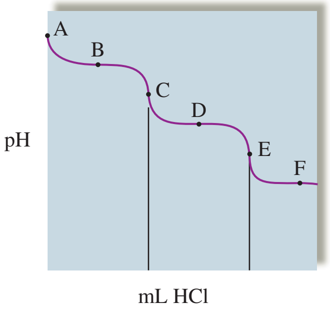


a. Notice that the plot has essentially two titration curves. If the first equivalence point occurs at 100.0 mL of NaOH added, what volume of NaOH added corresponds to the second equivalence point?

b. For the following volumes of NaOH added, list the major species present after the OH^- reacts completely.
  i. 0 mL NaOH added
  ii. between 0 and 100.0 mL NaOH added
  iii. 100.0 mL NaOH added
  iv. between 100.0 and 200.0 mL NaOH added
  v. 200.0 mL NaOH added
  vi. after 200.0 mL NaOH added

c. If the pH at 50.0 mL of NaOH added is 4.0 and the pH at 150.0 mL of NaOH added is 8.0, determine the values K_{a_1} and K_{a_2} for the diprotic acid.

144. The titration of Na_2CO_3 with HCl has the following qualitative profile:



a. Identify the major species in solution as points A–F.

b. Calculate the pH at the halfway points to equivalence, B and D. *Hint:* Refer to Exercise 143.

145. A few drops of each of the indicators shown in the accompanying table were placed in separate portions of a 1.0 *M* solution of a weak acid, HX. The results are shown in the last column of the table. What is the approximate pH of the solution containing HX? Calculate the approximate value of K_a for HX.

Indicator	Color of HIn	Color of In$^-$	pK_a of HIn	HX
Bromphenol blue	Yellow	Blue	4.0	Blue
Bromcresol purple	Yellow	Purple	6.0	Yellow
Bromcresol green	Yellow	Blue	4.8	Green
Alizarin	Yellow	Red	6.5	Yellow

146. Consider a solution made by mixing 500.0 mL of 4.0 *M* NH_3 and 500.0 mL of 0.40 *M* $AgNO_3$. Ag^+ reacts with NH_3 to form $AgNH_3^+$ and $Ag(NH_3)_2^+$:

$$Ag^+ + NH_3 \rightleftharpoons AgNH_3^+ \qquad K_1 = 2.1 \times 10^3$$

$$AgNH_3^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

Determine the concentration of all species in solution.

147. What is the maximum possible concentration of Ni^{2+} ion in water at 25°C that is saturated with 0.10 *M* H_2S and maintained at pH 3.0 with HCl?

148. You add an excess of solid MX in 250 g of water. You measure the freezing point and find it to be −0.028°C. What is the K_{sp} of the solid? Assume the density of the solution is 1.0 g/cm^3.

149. a. Calculate the molar solubility of SrF_2 in water, ignoring the basic properties of F^-. (For SrF_2, $K_{sp} = 7.9 \times 10^{-10}$.)

b. Would the measured molar solubility of SrF_2 be greater than or less than the value calculated in part a? Explain.

c. Calculate the molar solubility of SrF_2 in a solution buffered at pH = 2.00. (K_a for HF is 7.2×10^{-4}.)

150. A solution saturated with a salt of the type M_3X_2 has an osmotic pressure of 2.64×10^{-2} atm at 25°C. Calculate the K_{sp} value for the salt, assuming ideal behavior.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

151. A buffer solution is prepared by mixing 75.0 mL of 0.275 *M* fluorobenzoic acid ($C_7H_5O_2F$) with 55.0 mL of 0.472 *M* sodium fluorobenzoate. The pK_a of this weak acid is 2.90. What is the pH of the buffer solution?

152. The K_{sp} for *Q*, a slightly soluble ionic compound composed of M_2^{2+} and X^- ions, is 4.5×10^{-29}. The electron configuration of M^+ is $[Xe]6s^14f^{14}5d^{10}$. The X^- anion has 54 electrons. What is the molar solubility of *Q* in a solution of NaX prepared by dissolving 1.98 g of NaX in 150. mL of water?

153. Calculate the pH of a solution prepared by mixing 250. mL of 0.174 *m* aqueous HF (density = 1.10 g/mL) with 38.7 g of an aqueous solution that is 1.50% NaOH by mass (density = 1.02 g/mL). (K_a for HF = 7.2×10^{-4}.)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

154. A 225-mg sample of a diprotic acid is dissolved in enough water to make 250. mL of solution. The pH of this solution is 2.06. A saturated solution of calcium hydroxide ($K_{sp} = 1.3 \times 10^{-6}$) is prepared by adding excess calcium hydroxide to pure water and then removing the undissolved solid by filtration. Enough of the calcium hydroxide solution is added to the solution of the acid to reach the second equivalence point. The pH at the second equivalence point (as determined by a pH meter) is 7.96. The first dissociation constant for the acid (K_{a_1}) is 5.90×10^{-2}. Assume that the volumes of the solutions are additive, all solutions are at 25°C, and that K_{a_1} is at least 1000 times greater than K_{a_2}.

a. Calculate the molar mass of the acid.

b. Calculate the second dissociation constant for the acid (K_{a_2}).

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**

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