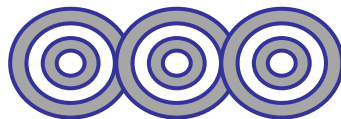




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Chapter 17

Additional Aspects of Aqueous Equilibria

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The various aqueous solutions encountered in nature typically contain many solutes. For example, the aqueous solutions in hot springs and oceans.

The idea in this chapter is to consider not only solutions in which there is a single solute but also those containing a mixture of solutes.

In this chapter we take a step toward understanding such complex solutions by looking first at further applications of acid-base equilibria.

17.1

The Common Ion Effect

In chapter 16 we examined the equilibrium concentrations of ions in solutions containing a weak acid or a weak base. We now consider solutions that contain a weak acid and a soluble salt of that acid.

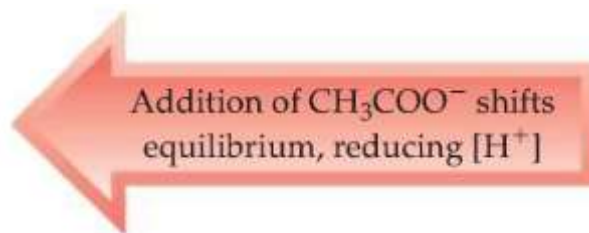
Sodium acetate is a soluble ionic compound and is therefore a strong electrolyte. Consequently, it dissociates completely in aqueous solution to form Na^+ and CH_3COO^- ions:



In contrast, CH_3COOH is a weak electrolyte that ionizes as follows:



According to Le Chatelier's principle, the CH_3COO^- from CH_3COONa causes this equilibrium to shift to the left, thereby decreasing the equilibrium concentration of $\text{H}^+(aq)$.

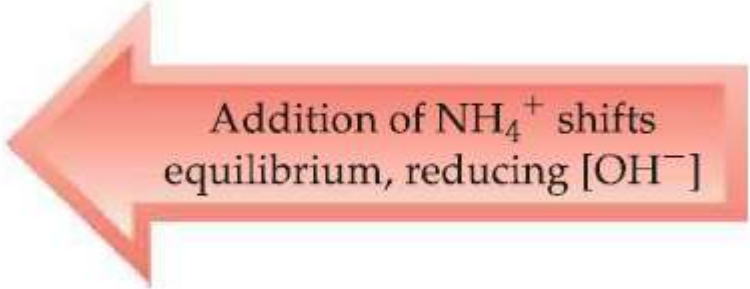
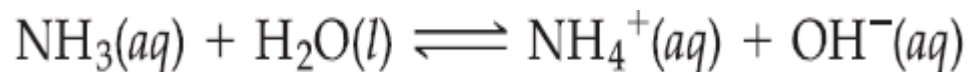


In other words, the presence of the added acetate ion causes the acetic acid to ionize less than it normally would.

Whenever a weak electrolyte and a strong electrolyte contain a common ion, the weak electrolyte ionizes less than it would if it were alone in solution. We call this observation the **common-ion effect**.

The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.

The ionization of a weak base is also decreased by the addition of a common ion. For example, the addition of NH_4^+ (as from the strong electrolyte NH_4Cl) causes the base-dissociation equilibrium of NH_3 to shift to the left, decreasing the equilibrium concentration of OH^- and lowering the pH:



Addition of NH_4^+ shifts equilibrium, reducing $[\text{OH}^-]$

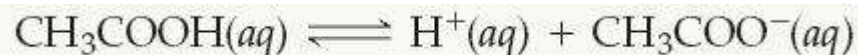
Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

Solution

First, because CH_3COOH is a weak electrolyte and CH_3COONa is a strong electrolyte, the major species in the solution are CH_3COOH (a weak acid), Na^+ (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and CH_3COO^- (which is the conjugate base of CH_3COOH).

Second, $[\text{H}^+]$ and, therefore, the pH are controlled by the dissociation equilibrium of CH_3COOH : (We have written the equilibrium using $\text{H}^+(\text{aq})$ rather than $\text{H}_3\text{O}^+(\text{aq})$ but both representations of the hydrated hydrogen ion are equally valid).



Third, we tabulate the initial and equilibrium concentrations (as we did in solving other equilibrium problems):

| | $\text{CH}_3\text{COOH}(\text{aq})$ | \rightleftharpoons | $\text{H}^+(\text{aq})$ | + | $\text{CH}_3\text{COO}^-(\text{aq})$ |
|-------------|-------------------------------------|----------------------|-------------------------|---|--------------------------------------|
| Initial | 0.30 M | | 0 | | 0.30 M |
| Change | $-x$ M | | $+x$ M | | $+x$ M |
| Equilibrium | $(0.30 - x)$ M | | x M | | $(0.30 + x)$ M |

The equilibrium concentration of CH_3COO^- (the common ion) is the initial concentration that is due to CH_3COONa (0.30 M) plus the change in concentration (x) that is due to the ionization of CH_3COOH .

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Now we can use the equilibrium-constant expression:

(The dissociation constant for CH_3COOH at 25 °C is from Appendix D; addition of CH_3COONa does not change the value of this constant). Substituting the equilibrium-constant concentrations from our table into the equilibrium expression gives

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x}$$

Because K_a is small, we assume that x is small compared to the original concentrations of CH_3COOH and CH_3COO^- (0.30 M each). Thus, we can ignore the very small x relative to 0.30 M , giving

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$
$$x = 1.8 \times 10^{-5} M = [\text{H}^+]$$

The resulting value of x is indeed small relative to 0.30, justifying the approximation made in simplifying the problem.

The resulting value of x is indeed small relative to 0.30, justifying the approximation made in simplifying the problem.

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

Finally, we calculate the pH from the equilibrium concentration of $\text{H}^+(\text{aq})$:

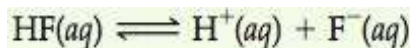
Comment: In Section 16.6 we calculated that a 0.30 M solution of CH_3COOH has a pH of 2.64, corresponding to $[\text{H}^+] = 2.3 \times 10^{-3} M$. Thus, the addition of CH_3COONa has substantially decreased $[\text{H}^+]$ as we would expect from Le Châtelier's principle.

Sample Exercise 17.2 Calculating Ion Concentrations When a Common Ion is Involved

Calculate the fluoride ion concentration and pH of a solution that is 0.20 M in HF and 0.10 M in HCl.

Solution

Because HF is a weak acid and HCl is a strong acid, the major species in solution are HF, H⁺, and Cl⁻. The Cl⁻, which is the conjugate base of a strong acid, is merely a spectator ion in any acid–base chemistry. The problem asks for [F⁻], which is formed by ionization of HF. Thus, the important equilibrium is



| | | | | | |
|-------------|-----------------|----------------------|------------------|---|------------------|
| | $\text{HF}(aq)$ | \rightleftharpoons | $\text{H}^+(aq)$ | + | $\text{F}^-(aq)$ |
| Initial | 0.20 M | | 0.10 M | | 0 |
| Change | -x M | | +x M | | +x M |
| Equilibrium | (0.20 - x) M | | (0.10 + x) M | | x M |

The common ion in this problem is the hydrogen (or hydronium) ion. Now we can tabulate the initial and equilibrium concentrations of each species involved in this equilibrium:

The equilibrium constant for the ionization of HF, from Appendix D, is 6.8×10^{-4} . Substituting the equilibrium-constant concentrations into the equilibrium expression gives

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.10 + x)(x)}{0.20 - x}$$

$$\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}$$

$$x = \frac{0.20}{0.10} (6.8 \times 10^{-4}) = 1.4 \times 10^{-3} \text{ M} = [\text{F}^-]$$

If we assume that x is small relative to 0.10 or 0.20 M , this expression simplifies to

This F^- concentration is substantially smaller than it would be in a 0.20 M solution of HF with no added HCl.

The common ion, H^+ , suppresses the ionization of HF. The concentration of $H^+(aq)$ is

Thus,

$$[H^+] = (0.10 + x) M \simeq 0.10 M$$
$$pH = 1.00$$

Comment: Notice that for all practical purposes, $[H^+]$ is due entirely to the HCl; the HF makes a negligible contribution by comparison.

17.2

Buffered Solutions

Buffers are solutions of a weak conjugate acid-base pair.

They are particularly resistant to pH changes, even when strong acid or base is added.

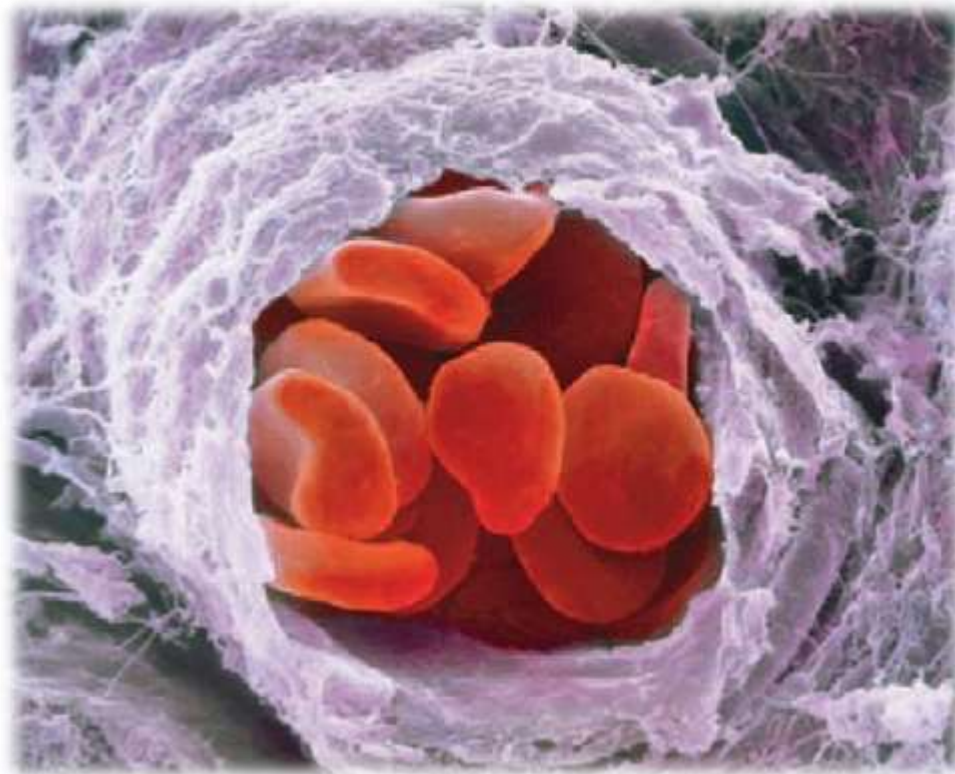
Solutions, which contain a weak conjugate acid-base pair, can resist drastic changes in pH upon the addition of small amounts of strong acid or base. These solutions are called **buffered solutions** (or merely buffers).



Much of the chemical behavior of seawater is determined by its pH, buffered at about 8.1 to 8.3 near the surface. Buffered solutions find many important applications in the laboratory and in medicine.

Human blood is a complex aqueous mixture, it is slightly basic with a normal pH of 7.35 to 7.45. death may result if the blood pH falls below 6.8 or rises above 7.8. when the pH falls below 7.35, the condition is called acidosis; when it rises above 7.45, the condition is called alkalosis.

The major buffer system that used to control the pH of blood is the carbonic acid-bicarbonate buffer system. The important equilibria in this buffer system are:



A scanning electromicrograph of a group red blood cells

Composition and Action of Buffered Solutions

A buffer resists changes in pH because it contains both an acid to neutralize OH^- ions and a base to neutralize H^+ ions.

The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid-base conjugate pair such as



Thus, buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base.

The $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$ buffer can be prepared, for example, by adding CH_3COONa to a solution of CH_3COOH . The $\text{NH}_4^+-\text{NH}_3$ buffer can be prepared by adding NH_4Cl to a solution of NH_3 .

To understand better how a buffer works, let's consider a buffer composed of a weak acid (HX) and one of its salt (MX, where M^+ could be Na^+ , K^+ , or another cation). The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:



The corresponding acid-dissociation-constant expression is

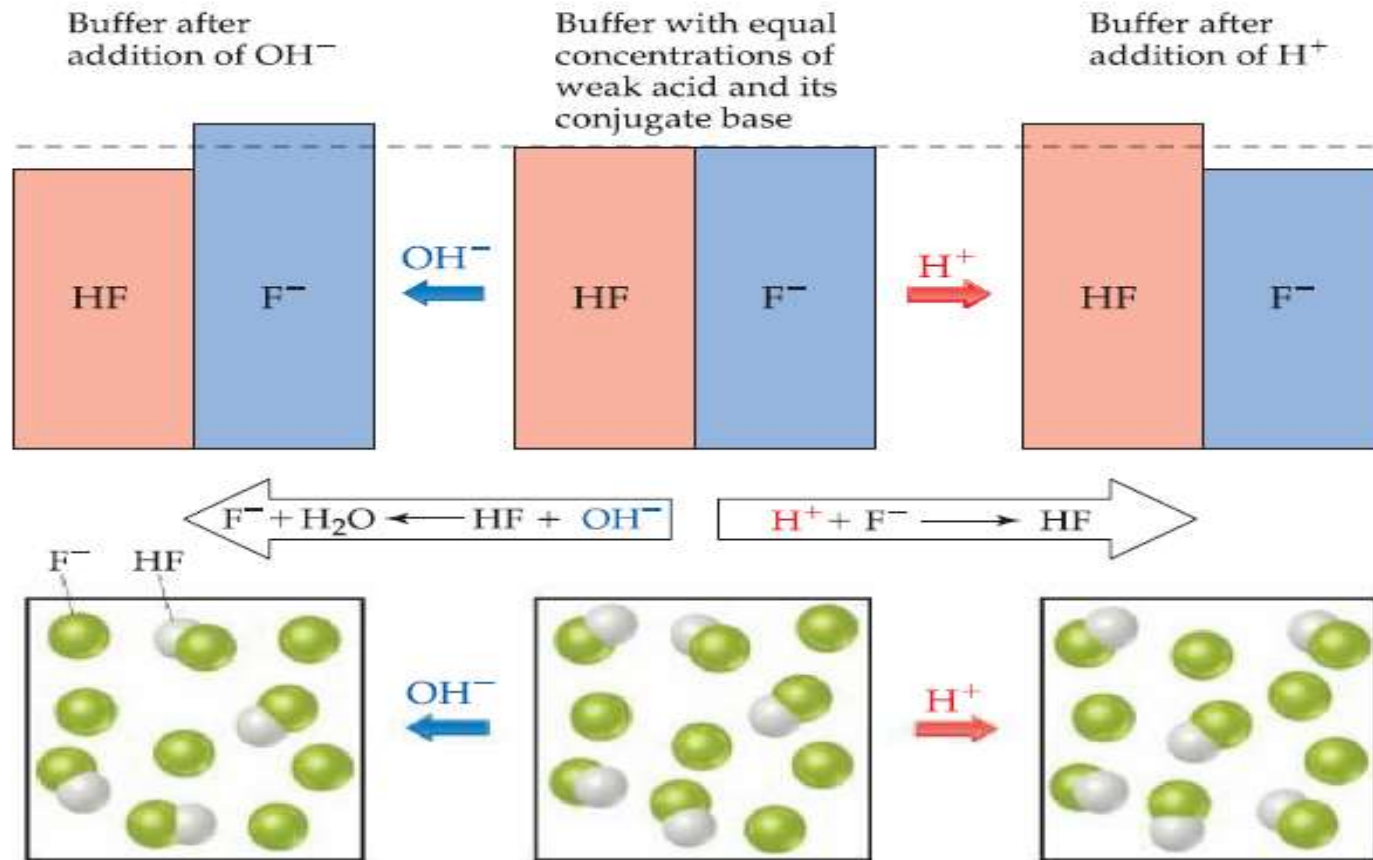
$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Solving this expression for $[H^+]$, we have

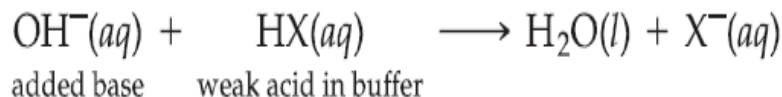
$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

We see from this expression that $[H^+]$, and thus the pH, is determined by two factors: the value of K_a for the weak-acid component of the buffer and the ratio of the concentrations of the conjugate acid-base pair, $[HX] / [X^-]$.

Buffer action

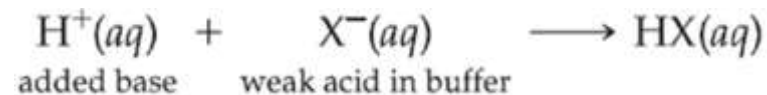


If OH^- ions are added to the buffered solution, they react with the acid component of the buffer to produce water and X^- :



This reaction causes $[\text{HX}]$ to decrease and $[\text{X}^-]$ to increase. As long as the amounts of HX and X^- in the buffer are large compared to the amount of OH^- added, however, the ratio $[\text{HX}] / [\text{X}^-]$ does not change much, and thus the change in pH is small.

If H^+ ions are added, they react with the base component of the buffer:

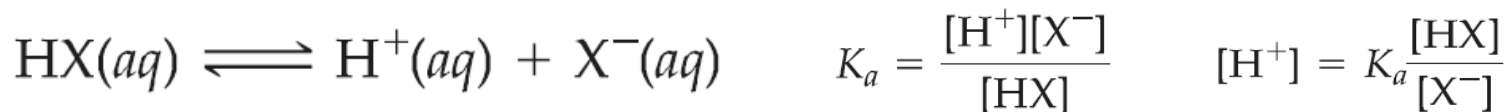


This reaction can also be represented using H_3O^+ :



Using either equation, we see that the reaction causes $[\text{X}^-]$ to decrease and $[\text{HX}]$ to increase. As long as the change in the ratio $[\text{HX}] / [\text{X}^-]$ is small, the change in pH will be small.

Calculating the pH of a Buffer



Taking -log of both sides of equation, we have

$$-\log[\text{H}^+] = -\log\left(K_a \frac{[\text{HX}]}{[\text{X}^-]}\right) = -\log K_a - \log \frac{[\text{HX}]}{[\text{X}^-]}$$

Because $-\log[\text{H}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$, we have

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HX}]}{[\text{X}^-]} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

In general,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Where [acid] and [base] refer to the equilibrium concentrations of the conjugate acid-base pair. Note that when [base] = [acid], $\text{pH} = \text{p}K_a$.

Last Equation is known as the **Henderson-Hasselbalch equation**.

Biologists, biochemists, and others who work frequently with buffers often use this equation to calculate the pH of buffers.

In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize. Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in the Henderson-Hasselbalch equation.

Sample Exercise 17.3 Calculating the pH of a Buffer

What is the pH of a buffer that is 0.12 *M* in lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, or $\text{HC}_3\text{H}_5\text{O}_3$] and 0.10 *M* in sodium lactate [$\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ or $\text{NaC}_3\text{H}_5\text{O}_3$]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

Solution

The initial and equilibrium concentrations of the species involved in this equilibrium are

| | $\text{HC}_3\text{H}_5\text{O}_3(aq)$ | \rightleftharpoons | $\text{H}^+(aq)$ | + | $\text{C}_3\text{H}_5\text{O}_3^-(aq)$ |
|-------------|---------------------------------------|----------------------|------------------|---|--|
| Initial | 0.12 <i>M</i> | | 0 | | 0.10 <i>M</i> |
| Change | $-x$ <i>M</i> | | $+x$ <i>M</i> | | $+x$ <i>M</i> |
| Equilibrium | $(0.12 - x)$ <i>M</i> | | x <i>M</i> | | $(0.10 + x)$ <i>M</i> |

The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

Because K_a is small and a common ion is present, we expect x to be small relative to either 0.12 or 0.10 *M*. Thus, our equation can be simplified to give

Solving for x gives a value that justifies our approximation:

Alternatively, we could have used the Henderson–Hasselbalch equation to calculate pH directly:

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right) \\ &= 3.85 + (-0.08) = 3.77\end{aligned}$$

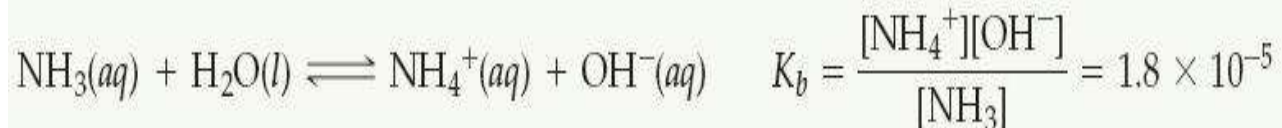
Sample Exercise 17.4 Preparing a Buffer

How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

Solution

The key to this exercise is to use this K_b expression to calculate $[\text{NH}_4^+]$.

We obtain $[\text{OH}^-]$ from the given pH:
and so



Because K_b is small and the common ion NH_4^+ is present, the equilibrium concentration of NH_3 will essentially equal its initial concentration:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00$$

$$[\text{OH}^-] = 1.0 \times 10^{-5} M$$

We now use the expression for K_b to calculate $[\text{NH}_4^+]$:

$$[\text{NH}_3] = 0.10 M$$

$$[\text{NH}_4^+] = K_b \frac{[\text{NH}_3]}{[\text{OH}^-]} = (1.8 \times 10^{-5}) \frac{(0.10 M)}{(1.0 \times 10^{-5} M)} = 0.18 M$$

Thus, for the solution to have $\text{pH} = 9.00$, $[\text{NH}_4^+]$ must equal 0.18 M . The number of moles of NH_4Cl needed to produce this concentration is given by the product of the volume of the solution and its molarity:

$$(2.0 \text{ L})(0.18 \text{ mol NH}_4\text{Cl/L}) = 0.36 \text{ mol NH}_4\text{Cl}$$

Buffer Capacity and pH Range

Buffer capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base from which the buffer is made.

The pH of the buffer depends on the K_a for the acid and on the relative concentrations of the acid and base that comprise the buffer.

According to the Equation below, $[H^+]$ for a 1-L solution that is 1 M in CH_3COOH and 1 M in CH_3COONa will be the same as for a 1-L solution that is 0.1 M in CH_3COOH and 1.0 M in CH_3COONa . The first solution has a greater buffering capacity, however, because it contains more CH_3COOH and CH_3COO^- .

The greater the amounts of the conjugate acid-base pair, the more resistant is the ratio of their concentrations, and hence the pH, is to change.

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

The **pH range** of any buffer is the pH range over which the buffer system works or acts effectively.

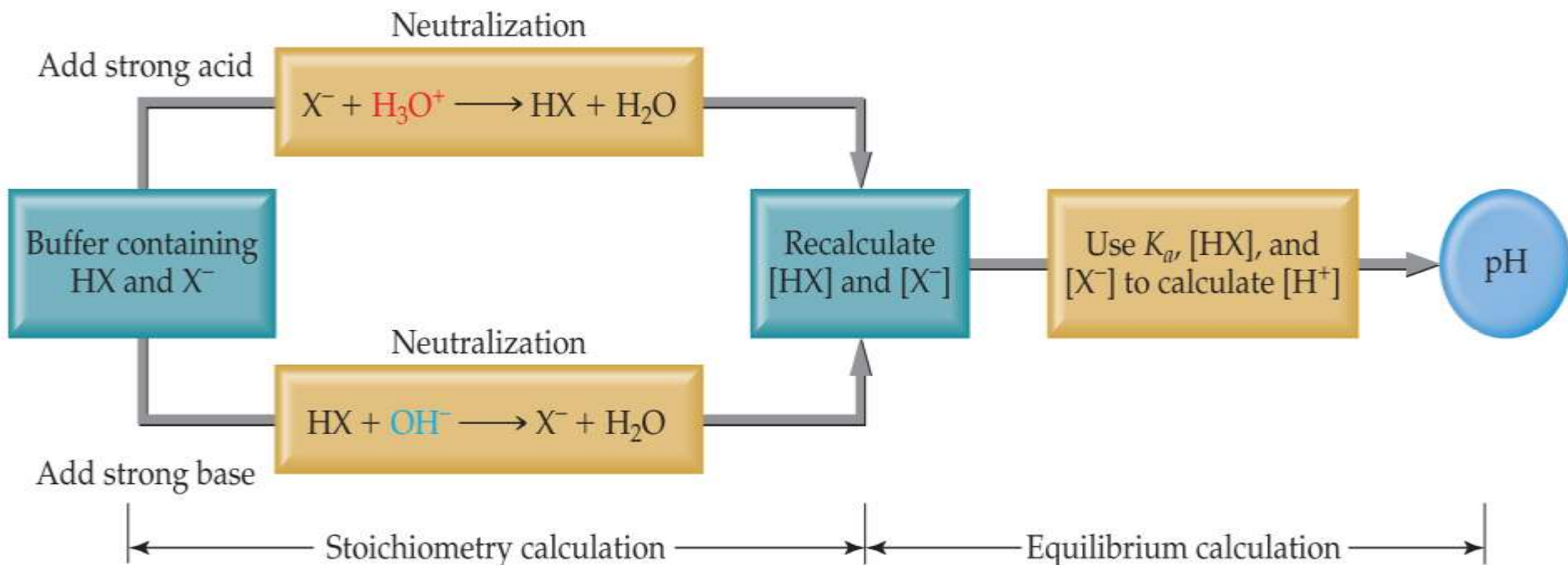
Buffers most effectively resist a change in pH in either direction when the concentrations of weak acid and conjugate base are about the same.

From Equation below, when the concentrations of weak acid and conjugate base are equal, $\text{pH} = \text{pK}_a$. This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a pK_a close to the desired pH.

In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor. Because $\log 10 = 1$, buffers usually have a usable range within ± 1 pH unit of pK_a (that is, a range of $\text{pH} = \text{pK}_a \pm 1$).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Addition of Strong Acids or Bases to Buffers



When a strong acid is added to the buffer, the added H^+ is consumed by X^- to produce HX ; thus, $[\text{HX}]$ increases and $[\text{X}^-]$ decreases.

When a strong base is added to the buffer, the added OH^- is consumed by HX to produce X^- ; thus, $[\text{HX}]$ decreases and $[\text{X}^-]$ increases.

Sample Exercise 17.5 Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol CH_3COOH and 0.300 mol CH_3COONa to enough water to make 1.00 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). **(a)** Calculate the pH of this solution after 0.020 mol of NaOH is added. **(b)** For comparison, calculate the pH that would result if 0.020 mol of NaOH were added to 1.00 L of pure water (neglect any volume changes).

Solution

0.280 M
 CH_3COOH
0.320 M
 CH_3COONa
pH = 4.80

Buffer
0.300 M
 CH_3COOH
0.300 M
 CH_3COONa
pH 4.74

add 0.020 mol H^+

0.320 M
 CH_3COOH
0.280 M
 CH_3COONa
pH = 4.68

Stoichiometry Calculation: The OH^- provided by NaOH reacts with CH_3COOH , the weak acid component of the buffer. Prior to this neutralization reaction, there are 0.300 mol each of CH_3COOH and CH_3COO^- . Neutralizing the 0.020 mol OH^- requires 0.020 mol of CH_3COOH . Consequently, the amount of CH_3COOH *decreases* by 0.020 mol, and the amount of the product of the neutralization, CH_3COO^- , *increases* by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with OH^- :

$$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CH}_3\text{COO}^-(aq)$$

| | | | | |
|------------------------|-----------|-----------|---|-----------|
| Buffer before addition | 0.300 mol | 0 | — | 0.300 mol |
| Addition | — | 0.020 mol | — | — |
| Buffer after addition | 0.280 mol | 0 | — | 0.320 mol |

Equilibrium Calculation: We now turn our attention to the equilibrium that will determine the pH of the buffer, namely the ionization of acetic acid.



Using the quantities of CH_3COOH and CH_3COO^- remaining in the buffer, we can determine the pH using the Henderson–Hasselbalch equation.

$$\text{pH} = 4.74 + \log \frac{0.320 \text{ mol}/1.00 \text{ L}}{0.280 \text{ mol}/1.00 \text{ L}} = 4.80$$

Comment Notice that we could have used mole amounts in place of concentrations in the Henderson–Hasselbalch equation and gotten the same result. The volumes of the acid and base are equal and cancel. If 0.020 mol of H^+ was added to the buffer, we would proceed in a similar way to calculate the resulting pH of the buffer. In this case the pH decreases by 0.06 units, giving $\text{pH} = 4.68$, as shown in the figure in the margin.

(b) To determine the pH of a solution made by adding 0.020 mol of NaOH to 1.00 L of pure water, we can first determine pOH using Equation 16.18 and subtracting from 14.

$$\text{pH} = 14 - (-\log 0.020) = 12.30$$

Note that although the small amount of NaOH changes the pH of water significantly, the pH of the buffer changes very little.

17.3

Solubility Equilibria

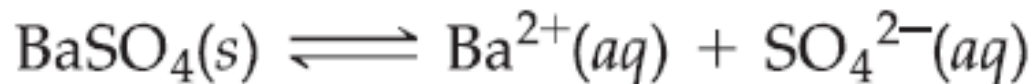
The equilibria that we have considered thus far in this chapter have involved acids and bases. Furthermore, they have been homogeneous; that is, all the species have been in the same phase.

Through the rest of this chapter we will consider the equilibria involved in the dissolution or precipitation of ionic compounds. These reactions are heterogeneous.

The Solubility Product Constant, K_{sp}

A saturated solution is one in which the solution is in contact with undissolved solute. Consider, for example, a saturated aqueous solution of BaSO_4 that is in contact with solid BaSO_4 . Because the solid is an ionic compound, it is a strong electrolyte and yields $\text{Ba}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ ions upon dissolving.

The following equilibrium is readily established between the undissolved solid and hydrated ions in solution:



Because this equilibrium equation describes the dissolution of a solid, the equilibrium constant indicates how soluble the solid is in water and is referred to as the **solubility-product constant** (or the **solubility product**). It is denoted K_{sp} , where *sp* stand for solubility product.

The equilibrium constant expression for this equilibrium is

$$K_{sp} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$

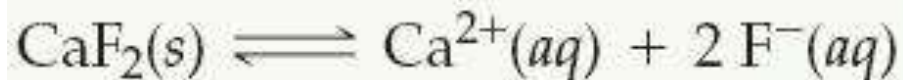
In general, the solubility product of a compound equals the product of the concentration of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation. The coefficient for each ion in the equilibrium equation also equals its subscript in the compound's chemical formula.

The value of K_{sp} for BaSO_4 is 1.1×10^{-10} , a very small number, indicating that only a very small amount of the solid will dissolve in water.

Sample Exercise 17.9 Writing Solubility-Product (K_{sp}) Expressions

Write the expression for the solubility-product constant K_{sp} for CaF_2 .

Solution



Following the italicized rule stated previously, the expression for K_{sp} is

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

In Appendix D we see that this K_{sp} has a value of 3.9×10^{-11} .

Solubility and K_{sp}

What is the difference between solubility and solubility-product constant K_{sp}

- The solubility of a substance is the quantity that dissolves to form a saturated solution. Solubility is often expressed as grams of solute that dissolve in forming a liter of saturated solution of the solute (g/L).
- The solubility-product constant is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution and is a unitless number. Thus, the magnitude of K_{sp} is a measure of how much of the solid dissolves to form a saturated solution.

Relationships between solubility and K_{sp}



K_{sp} is *not* the same as solubility.

The solubility of a substance can change considerably as the concentrations of other solutes change.

The solubility of $\text{Mg}(\text{OH})_2$, for example, depends highly on pH, and also affected by the concentrations of other ions in solution. In contrast, the solubility-product constant, K_{sp} , has only one value for a given solute at any specific temperature.

The concentrations of ions calculated from K_{sp} sometimes deviate appreciably from those found experimentally. In part, these deviations are due to electrostatic interactions between ions in solution which can lead to ion pairs.

Sample Exercise 17.10 Calculating K_{sp} from Solubility

Solid silver chromate is added to pure water at 25 °C. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved $\text{Ag}_2\text{CrO}_4(s)$ and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is $1.3 \times 10^{-4} M$. Assuming that Ag_2CrO_4 dissociates completely in water and that there are no other important equilibria involving the Ag^+ or CrO_4^{2-} ions in the solution, calculate K_{sp} for this compound.

Solution

The equilibrium equation and the expression for K_{sp} are



To calculate K_{sp} , we need the equilibrium concentrations of Ag^+ and CrO_4^{2-} . We know that at equilibrium $[\text{Ag}^+] = 1.3 \times 10^{-4} M$. All the Ag^+ and CrO_4^{2-} ions in the solution come from the Ag_2CrO_4 that dissolves. Thus, we can use $[\text{Ag}^+]$ to calculate $[\text{CrO}_4^{2-}]$.

From the chemical formula of silver chromate, we know that there must be 2 Ag^+ ions in solution for each CrO_4^{2-} ion in solution. Consequently, the concentration of CrO_4^{2-} is half the concentration of Ag^+ :

$$[\text{CrO}_4^{2-}] = \left(\frac{1.3 \times 10^{-4} \text{ mol Ag}^+}{\text{L}} \right) \left(\frac{1 \text{ mol CrO}_4^{2-}}{2 \text{ mol Ag}^+} \right) = 6.5 \times 10^{-5} M$$

We can now calculate the value of K_{sp} .

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

Sample Exercise 17.11 Calculating Solubility from K_{sp}

The K_{sp} for CaF_2 is 3.9×10^{-11} at 25°C . Assuming that CaF_2 dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of CaF_2 in grams per liter.

Solution

Assume initially that none of the salt has dissolved, and then allow x moles/liter of CaF_2 to dissociate completely when equilibrium is achieved.

The stoichiometry of the equilibrium dictates that $2x$ moles/liter of F^- are produced for each x moles/liter of CaF_2 that dissolve. We now use the expression for K_{sp} and substitute the equilibrium concentrations to solve for the value of x :

(Remember that $\sqrt[3]{y} = y^{1/3}$ to calculate the cube root of a number, you can use the yx function on your calculator. Thus, the molar solubility of CaF_2 is 2.1×10^{-4} mol/L. The mass of CaF_2 that dissolves in water to form a liter of solution is

| | | | |
|-------------|---|---------------|----------------|
| Initial | — | 0 | 0 |
| Change | — | $+x\text{ M}$ | $+2x\text{ M}$ |
| Equilibrium | — | $x\text{ M}$ | $2x\text{ M}$ |

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4}\text{ M}$$

$$\left(\frac{2.1 \times 10^{-4}\text{ mol CaF}_2}{1\text{ L soln}}\right)\left(\frac{78.1\text{ g CaF}_2}{1\text{ mol CaF}_2}\right) = 1.6 \times 10^{-2}\text{ g CaF}_2/\text{L soln}$$

Comment: Because F^- is the anion of a weak acid, you might expect that the hydrolysis of the ion would affect the solubility of CaF_2 . The basicity of F^- is so small ($K_b = 1.5 \times 10^{-11}$), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is 0.017 g/L at 25°C , in good agreement with our calculation



Q & A



The addition of bromide ion will decrease the water solubility of which of the following salts?

- a. BaSO_4
- b. Li_2CO_3
- c. PbS
- d. AgBr

Which pair of compounds will form a buffer solution when dissolved in water in equimolar amounts?

- a. HCl and KCl
- b. HNO₃ and NaNO₃
- c. HCl and NH₄Cl
- d. NH₃ and NH₄Cl

The K_a of HCN is 4.9×10^{-10} . What is the pH of a buffer solution that is 0.100 *M* in both HCN and KCN?

- a. 4.7
- b. 7.0
- c. 9.3
- d. 14.0

The K_a of HCN is 4.9×10^{-10} . What is the pH of a buffer solution that is 0.100 M in HCN and 0.200 M in KCN?

- a. 7.0
- b. 9.0
- c. 9.3
- d. 9.6

The K_a of HCN is 4.9×10^{-10} . What is the pH of a buffer solution that is 1.00 M in HCN and 0.100 M in KCN?

- a. 7.0
- b. 8.3**
- c. 9.0
- d. 9.3

In titrating a weak base with a strong acid, the best indicator to use would be:

- a. methyl red (changes color at pH = 5)
- b. bromothymol blue (changes at pH = 7)
- c. phenolphthalein (changes at pH = 9)
- d. none of the above

In titrating a weak acid with a strong base, the best indicator to use would be:

- a. methyl red (changes color at pH = 5)
- b. bromothymol blue (changes at pH = 7)
- c. phenolphthalein (changes at pH = 9)
- d. none of the above

The K_{sp} of BaCO_3 is 5.0×10^{-9} .
What is the concentration of barium ion in a saturated aqueous solution of BaCO_3 ?

- a. $7.1 \times 10^{-5} \text{ M}$
- b. $2.5 \times 10^{-9} \text{ M}$
- c. $5.0 \times 10^{-9} \text{ M}$
- d. $1.0 \times 10^{-8} \text{ M}$

The K_{sp} of BaF_2 is 1.7×10^{-6} . What is the concentration of barium ion in a saturated aqueous solution of BaF_2 ?

- a. $1.7 \times 10^{-6} \text{ M}$
- b. $3.4 \times 10^{-6} \text{ M}$
- c. $7.6 \times 10^{-3} \text{ M}$
- d. $1.5 \times 10^{-2} \text{ M}$

The K_{sp} of BaF_2 is 1.7×10^{-6} . What is the concentration of fluoride ion in a saturated aqueous solution of BaF_2 ?

- a. $1.7 \times 10^{-6} \text{ M}$
- b. $5.7 \times 10^{-5} \text{ M}$
- c. $7.6 \times 10^{-3} \text{ M}$
- d. $1.5 \times 10^{-2} \text{ M}$

Which of the following will produce a buffer solution?

- HCl/NaCl
- HC₂H₃O₂/NH₃
- NaH₂PO₄/Na₂HPO₄
- HNO₃/Ca(OH)₂
- KNO₃/ NaOH



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In an $\text{NH}_4^+/\text{NH}_3$ buffer, what concentration changes will occur if a small amount of OH^- is added?

| | $[\text{NH}_4^+]$ | $[\text{NH}_3]$ | pH |
|----|-------------------|-----------------|----------|
| 1. | Increase | Increase | Increase |
| 2. | Decrease | Increase | Increase |
| 3. | Increase | Decrease | Increase |
| 4. | Increase | Decrease | Decrease |
| 5. | Decrease | Increase | Decrease |

Which indicator would best determine the endpoint of the titration of $\text{NaC}_2\text{H}_3\text{O}_2$ with HNO_3 ?

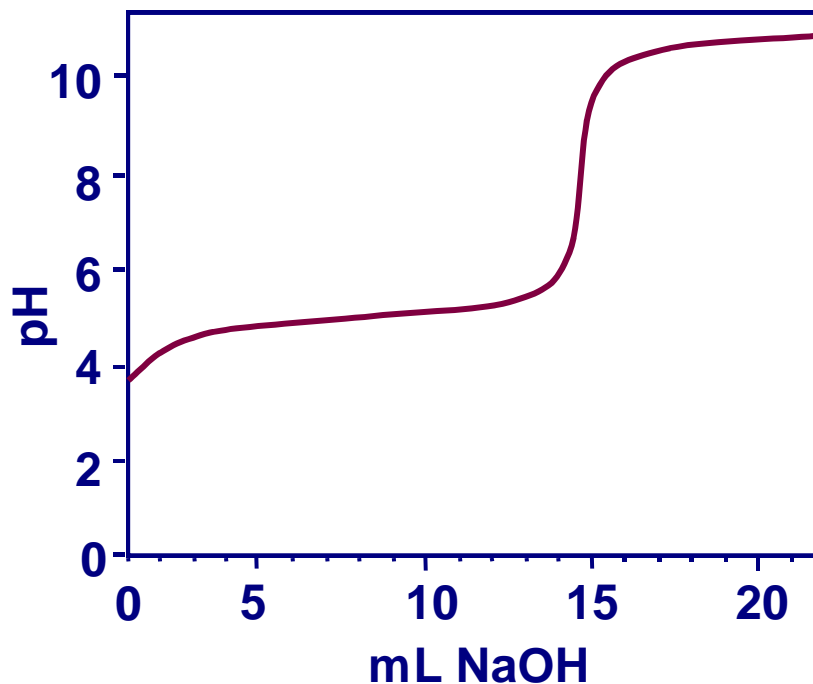
- Methyl violet
- **Methyl orange**
- Bromthymol blue
- Phenolphthalein
- Alizarin yellow R

| | pH range for color change | | | | | | | | | | |
|-------------------|---------------------------|-----|-----|--------|--------|--------|-----------|--------|--|------|-----|
| | 0 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | | | |
| Methyl violet | Yellow | | | Violet | | | | | | | |
| Thymol blue | | Red | | | Yellow | | Yellow | | | Blue | |
| Methyl orange | | | Red | | | Yellow | | | | | |
| Methyl red | | | | Red | | | Yellow | | | | |
| Bromthymol blue | | | | | Yellow | | | Blue | | | |
| Phenolphthalein | | | | | | | Colorless | | | Pink | |
| Alizarin yellow R | | | | | | | | Yellow | | | Red |

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This titration curve was obtained in the titration of an unknown acid with 0.10 M NaOH. What is the pK_a of the acid?

- ~2
- ~4
- ~5
- ~7
- ~8



Addition of _____ will increase the solubility of MgCO_3 .



- MgCl_2
- Na_2CO_3
- NaOH
- **HCl**
- KHCO_3

Which of the following conjugate acid-base pairs will not function as a buffer:



Answer: The HNO_3 will not work as buffer because it is strong acid

Predict which of the following compounds will have the greatest molar solubility in water: AgCl ($K_{sp} = 1.8 \times 10^{-10}$),
AgBr ($K_{sp} = 5.0 \times 10^{-13}$),
AgI ($K_{sp} = 8.3 \times 10^{-17}$).

Answer. AgCl > AgBr > AgI

Calculate the pH of a solution containing 0.085 M nitrous acid (HNO_2 ; $K_a = 4.5 \times 10^{-4}$) and 0.10 M potassium nitrite (KNO_2).

Answer: 3.42

Calculate the formate ion concentration and pH of a solution that is 0.050 M in formic acid (HCOOH ; $K_a = 1.8 \times 10^{-4}$) and 0.10 M in HNO_3 .

Answer: $[\text{HCOO}^-] = 9.0 \times 10^{-5}$; $\text{pH} = 1.00$

Calculate the pH of a buffer composed of 0.12 *M* benzoic acid and 0.20 *M* sodium benzoate. (Refer to Appendix D.)

Answer: 4.42

Calculate the concentration of sodium benzoate that must be present in a 0.20 *M* solution of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) to produce a pH of 4.00.

Answer: 0.13 M

Determine **(a)** the pH of the original buffer described in Sample Exercise 17.5 after the addition of 0.020 mol HCl and **(b)** the pH of the solution that would result from the addition of 0.020 mol HCl to 1.00 L of pure water.

Answers: (a) 4.68, (b) 1.70

Give the solubility-product-constant expressions and the values of the solubility-product constants (from Appendix D) for the following compounds: **(a)** barium carbonate, **(b)** silver sulfate.

Answers: (a) $K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = 5.0 \times 10^{-9}$; (b) $K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}$

A saturated solution of $\text{Mg}(\text{OH})_2$ in contact with undissolved solid is prepared at $25\text{ }^\circ\text{C}$. The pH of the solution is found to be 10.17. Assuming that $\text{Mg}(\text{OH})_2$ dissociates completely in water and that there are no other simultaneous equilibria involving the Mg^{2+} or OH^- ions in the solution, calculate K_{sp} for this compound.

Answer: 1.6×10^{-12}

The K_{sp} for LaF_3 is 2×10^{-19} . What is the solubility of LaF_3 in water in moles per liter?

Answer: 9×10^{-6} mol/L

