

## Chapter 14

# Acid-Base Equilibria



**Figure 14.1** Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

### Chapter Outline

- 14.1 Brønsted-Lowry Acids and Bases
- 14.2 pH and pOH
- 14.3 Relative Strengths of Acids and Bases
- 14.4 Hydrolysis of Salt Solutions
- 14.5 Polyprotic Acids
- 14.6 Buffers
- 14.7 Acid-Base Titrations

## Introduction

In our bodies, in our homes, and in our industrial society, acids and bases play key roles. Proteins, enzymes, blood, genetic material, and other components of living matter contain both acids and bases. We seem to like the sour taste of acids; we add them to soft drinks, salad dressings, and spices. Many foods, including citrus fruits and some vegetables, contain acids. Cleaners in our homes contain acids or bases. Acids and bases play important roles in the chemical industry. Currently, approximately 36 million metric tons of sulfuric acid are produced annually in the United States alone. Huge quantities of ammonia (8 million tons), urea (10 million tons), and phosphoric acid (10 million tons) are also produced annually.

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

## 14.1 Brønsted-Lowry Acids and Bases

By the end of this section, you will be able to:

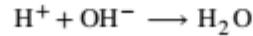
- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO<sub>2</sub>), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Carl Axel Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

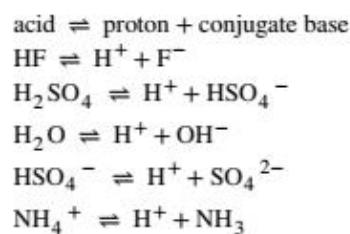
In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H<sub>3</sub>O<sup>+</sup>) and a base as a compound that dissolves in water to yield hydroxide ions (OH<sup>-</sup>). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H<sup>+</sup>. A proton is what remains when a normal hydrogen atom, <sup>1</sup>H, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

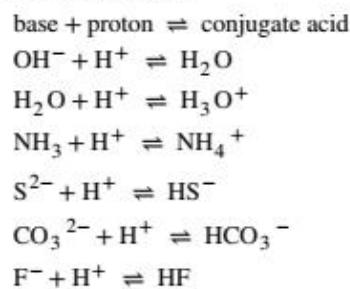
Acids may be compounds such as HCl or H<sub>2</sub>SO<sub>4</sub>, organic acids like acetic acid (CH<sub>3</sub>COOH) or ascorbic acid (vitamin C), or H<sub>2</sub>O. Anions (such as HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HS<sup>-</sup>, and HCO<sub>3</sub><sup>-</sup>) and cations (such as H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>3</sub>NH<sub>2</sub>), anions (such as OH<sup>-</sup>, HS<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>), or cations (such as [Al(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup>). The most familiar bases are ionic compounds such as NaOH and Ca(OH)<sub>2</sub>, which contain the hydroxide ion, OH<sup>-</sup>. The hydroxide ion in these compounds accepts a proton from acids to form water:



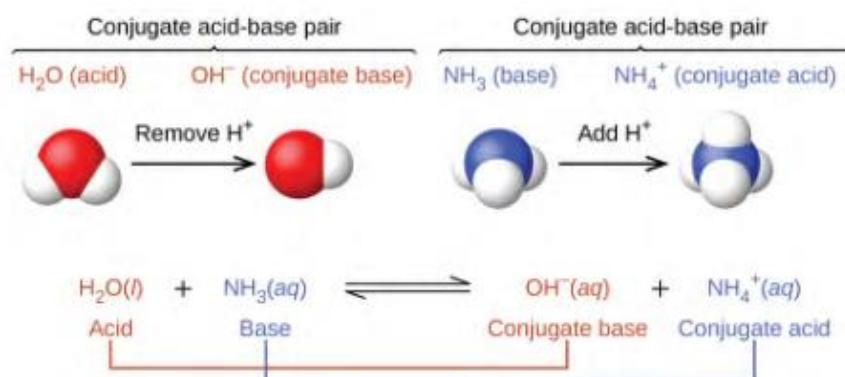
We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):



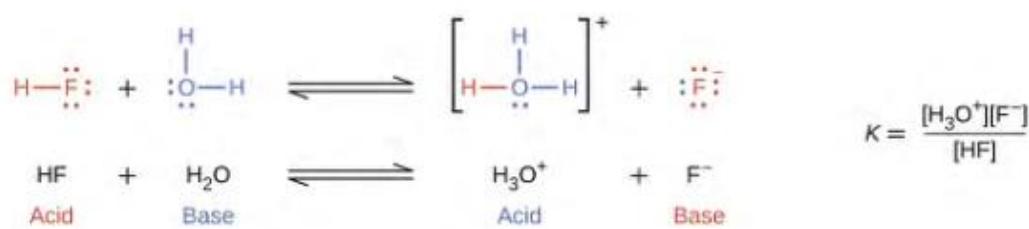
We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):



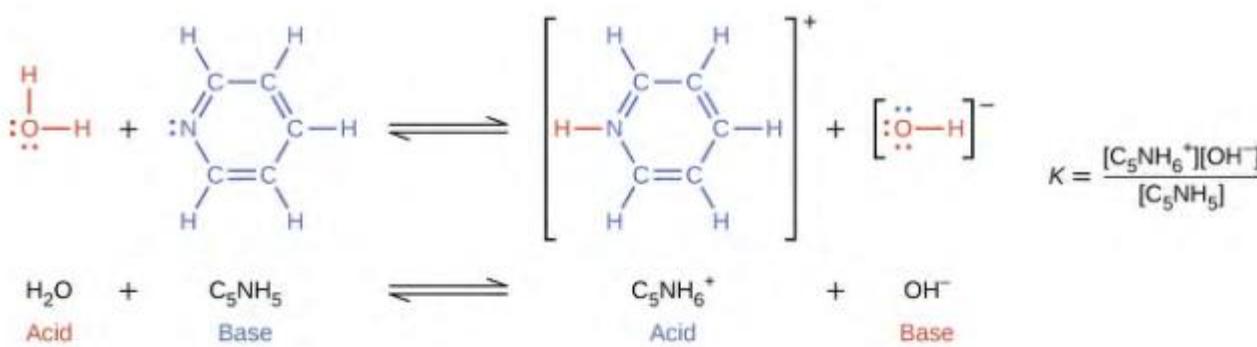
In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water,  $\text{OH}^-$ , and the conjugate acid of ammonia,  $\text{NH}_4^+$ :



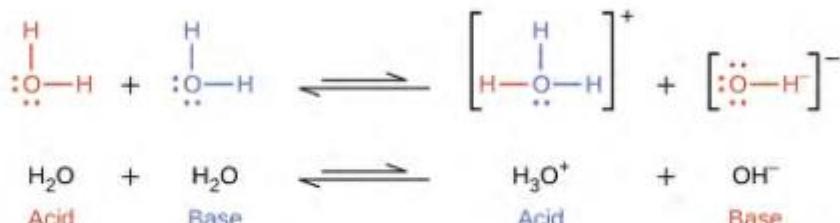
The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



When we add a base to water, a **base ionization** reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding ammonia to water yields hydroxide ions and ammonium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

Pure water undergoes autoionization to a very slight extent. Only about two out of every  $10^9$  molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water ( $K_w$ )**:



The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C,  $K_w$  has a value of  $1.0 \times 10^{-14}$ . The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for  $K_w$  is about  $5.1 \times 10^{-13}$ , roughly 100-times larger than the value at 25 °C.

### Example 14.1

## **Ion Concentrations in Pure Water**

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

### Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water,  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal  $1.0 \times 10^{-7} M$ .

### Check Your Learning

The ion product of water at  $80^\circ\text{C}$  is  $2.4 \times 10^{-13}$ . What are the concentrations of hydronium and hydroxide ions in pure water at  $80^\circ\text{C}$ ?

**Answer:**  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 4.9 \times 10^{-7} M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. **Example 14.2** demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

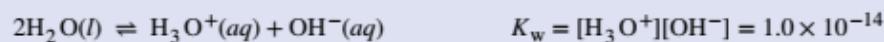
### Example 14.2

#### The Inverse Proportionality of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of  $2.0 \times 10^{-6} M$ . What is the concentration of hydroxide ion at  $25^\circ\text{C}$ ?

### Solution

We know the value of the ion-product constant for water at  $25^\circ\text{C}$ :



Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the  $K_w$  expression yields that  $[\text{OH}^-]$  is directly proportional to the inverse of  $[\text{H}_3\text{O}^+]$ :

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to  $5.0 \times 10^{-9} M$  as the hydrogen ion concentration increases to  $2.0 \times 10^{-6} M$ . This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the  $[\text{OH}^-]$  is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

### Check Your Learning

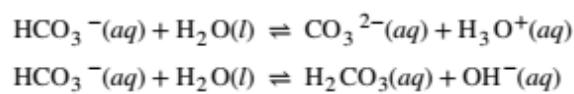
What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of  $0.001 M$  at  $25^\circ\text{C}$ ?

**Answer:**  $[\text{H}_3\text{O}^+] = 1 \times 10^{-11} M$

### Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term

for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:



### Example 14.3

#### Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of  $\text{HSO}_3^-$

- (a) as an acid with  $\text{OH}^-$
- (b) as a base with  $\text{HI}$

#### Solution

- (a)  $\text{HSO}_3^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{SO}_3^{2-}(aq) + \text{H}_2\text{O}(l)$
- (b)  $\text{HSO}_3^-(aq) + \text{HI}(aq) \rightleftharpoons \text{H}_2\text{SO}_3(aq) + \text{I}^-(aq)$

#### Check Your Learning

Write separate equations representing the reaction of  $\text{H}_2\text{PO}_4^-$

- (a) as a base with  $\text{HBr}$
- (b) as an acid with  $\text{OH}^-$

**Answer:** (a)  $\text{H}_2\text{PO}_4^-(aq) + \text{HBr}(aq) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{Br}^-(aq)$ ; (b)  
 $\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l)$

## 14.2 pH and pOH

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water ( $K_w$ ). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\text{p}X = -\log X$$

The **pH** of a solution is therefore defined as shown here, where  $[H_3O^+]$  is the molar concentration of hydronium ion in the solution:

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

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$pOH = -\log[OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the  $K_w$  expression:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ -\log K_w &= -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-] \\ pK_w &= pH + pOH \end{aligned}$$

At 25 °C, the value of  $K_w$  is  $1.0 \times 10^{-14}$ , and so:

$$14.00 = pH + pOH$$

As was shown in [Example 14.1](#), the hydronium ion molarity in pure water (or any neutral solution) is  $1.0 \times 10^{-7} M$  at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\begin{aligned} pH &= -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00 \\ pOH &= -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00 \end{aligned}$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than  $1.0 \times 10^{-7} M$  and hydroxide ion molarities less than  $1.0 \times 10^{-7} M$  (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than  $1.0 \times 10^{-7} M$  and hydroxide ion molarities greater than  $1.0 \times 10^{-7} M$  (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant  $K_w$  is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the “Check Your Learning” exercise accompanying [Example 14.1](#) showed the hydronium molarity of pure water at 80 °C is  $4.9 \times 10^{-7} M$ , which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[H_3O^+] = -\log(4.9 \times 10^{-7}) = 6.31 \\ pOH &= -\log[OH^-] = -\log(4.9 \times 10^{-7}) = 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit  $pH = pOH = 6.31$ , acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) ([Table 14.1](#)).

**Summary of Relations for Acidic, Basic and Neutral Solutions**

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$\text{pH} < 7$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$\text{pH} = 7$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$\text{pH} > 7$

**Table 14.1**

**Figure 14.2** shows the relationships between  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

$[\text{H}_3\text{O}^+]$ (M)	$[\text{OH}^-]$ (M)	pH	pOH	Sample Solution
$10^1$	$10^{-15}$	-1	15	
$10^0$ or 1	$10^{-14}$	0	14	1 M HCl      acidic
$10^{-1}$	$10^{-13}$	1	13	gastric juice
$10^{-2}$	$10^{-12}$	2	12	lime juice
$10^{-3}$	$10^{-11}$	3	11	1 M $\text{CH}_3\text{CO}_2\text{H}$ (vinegar)
$10^{-4}$	$10^{-10}$	4	10	stomach acid
$10^{-5}$	$10^{-9}$	5	9	wine
$10^{-6}$	$10^{-8}$	6	8	orange juice
$10^{-7}$	$10^{-7}$	7	7	coffee
$10^{-8}$	$10^{-6}$	8	6	rain water
$10^{-9}$	$10^{-5}$	9	5	pure water      neutral
$10^{-10}$	$10^{-4}$	10	4	blood
$10^{-11}$	$10^{-3}$	11	3	ocean water
$10^{-12}$	$10^{-2}$	12	2	baking soda
$10^{-13}$	$10^{-1}$	13	1	Milk of Magnesia
$10^{-14}$	$10^0$ or 1	14	0	household ammonia, $\text{NH}_3$
$10^{-15}$	$10^1$	15	-1	bleach
				1 M NaOH      basic

**Figure 14.2** The pH and pOH scales represent concentrations of  $[\text{H}_3\text{O}^+]$  and  $\text{OH}^-$ , respectively. The pH and pOH values of some common substances at standard temperature ( $25^\circ\text{C}$ ) are shown in this chart.

#### Example 14.4

##### Calculation of pH from $[\text{H}_3\text{O}^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of  $1.2 \times 10^{-3}\text{ M}$ ?

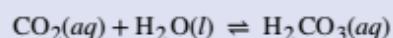
##### Solution

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92\end{aligned}$$

(The use of logarithms is explained in **Appendix B**. Recall that, as we have done here, when taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

### Check Your Learning

Water exposed to air contains carbonic acid,  $\text{H}_2\text{CO}_3$ , due to the reaction between carbon dioxide and water:



Air-saturated water has a hydronium ion concentration caused by the dissolved  $\text{CO}_2$  of  $2.0 \times 10^{-6} M$ , about 20-times larger than that of pure water. Calculate the pH of the solution at  $25^\circ\text{C}$ .

**Answer:** 5.70

### Example 14.5

#### Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

#### Solution

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

$$\log[\text{H}_3\text{O}^+] = -7.3$$

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} M$$

(On a calculator take the antilog, or the “inverse” log, of  $-7.3$ , or calculate  $10^{-7.3}$ .)

### Check Your Learning

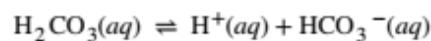
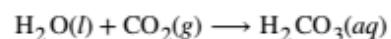
Calculate the hydronium ion concentration of a solution with a pH of  $-1.07$ .

**Answer:**  $12 M$

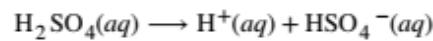
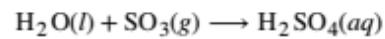
### How Sciences Interconnect

#### Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved  $\text{CO}_2$  which forms carbonic acid:



Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:



Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone ([Figure 14.3](#)). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this [website](http://openstaxcollege.org/l/16EPA) (<http://openstaxcollege.org/l/16EPA>) hosted by the US Environmental Protection Agency.



(a)



(b)

**Figure 14.3** (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

### Example 14.6

### Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

#### Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding  $[\text{OH}^-] = 0.0125\text{ M}$ :

$$\begin{aligned}\text{pOH} &= -\log[\text{OH}^-] = -\log 0.0125 \\ &= -(-1.903) = 1.903\end{aligned}$$

The pH can be found from the pOH:

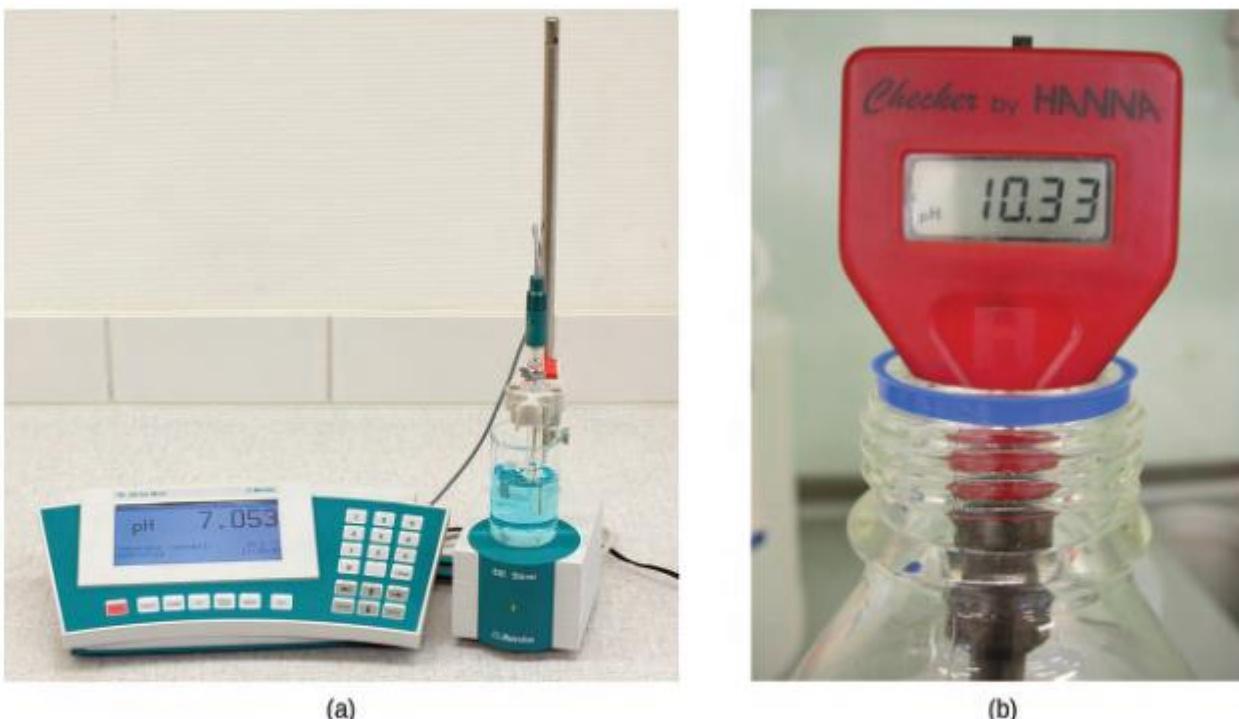
$$\begin{aligned}\text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10\end{aligned}$$

#### Check Your Learning

The hydronium ion concentration of vinegar is approximately  $4 \times 10^{-3}\text{ M}$ . What are the corresponding values of pOH and pH?

**Answer:** pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (**Figure 14.4**).



**Figure 14.4** (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of  $\pm 0.002$  pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy ( $\pm 0.2$  pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators ([Figure 14.5](#)).



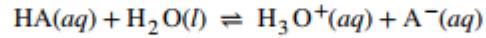
**Figure 14.5** (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = 1), CH<sub>3</sub>CO<sub>2</sub>H (pH = 3), and NH<sub>4</sub>Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (pH = 9), NH<sub>3</sub> (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

## 14.3 Relative Strengths of Acids and Bases

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

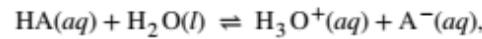


Water is the base that reacts with the acid HA, A<sup>-</sup> is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H<sub>3</sub>O<sup>+</sup> and A<sup>-</sup> when the acid ionizes in water; [Figure 14.6](#) lists several strong acids. A weak acid gives small amounts of H<sub>3</sub>O<sup>+</sup> and A<sup>-</sup>.

6 Strong Acids		6 Strong Bases	
HClO <sub>4</sub>	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	Ca(OH) <sub>2</sub>	calcium hydroxide
HNO <sub>3</sub>	nitric acid	Sr(OH) <sub>2</sub>	strontium hydroxide
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid	Ba(OH) <sub>2</sub>	barium hydroxide

**Figure 14.6** Some of the common strong acids and bases are listed here.

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant**,  $K_a$ . For the reaction of an acid HA:

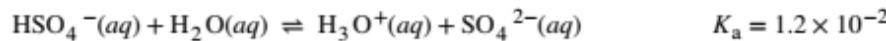
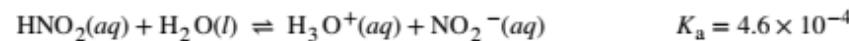
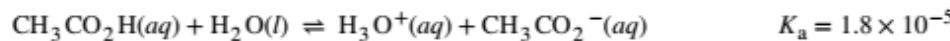


we write the equation for the ionization constant as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include  $[\text{H}_2\text{O}]$  in the equation. The larger the  $K_a$  of an acid, the larger the concentration of  $\text{H}_3\text{O}^+$  and  $\text{A}^-$  relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase. (A table of ionization constants of weak acids appears in **Appendix H**, with a partial listing in **Table 14.2**.)

The following data on acid-ionization constants indicate the order of acid strength  $\text{CH}_3\text{CO}_2\text{H} < \text{HNO}_2 < \text{HSO}_4^-$ :



Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

### Example 14.7

#### Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-M solution of nitrous acid (a weak acid), with a pH of 2.09.

### Solution

The percent ionization for an acid is:

$$\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HNO}_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:  $\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$ . Since  $10^{-\text{pH}} = [\text{H}_3\text{O}^+]$ , we find that  $10^{-2.09} = 8.1 \times 10^{-3} \text{ M}$ , so that percent ionization is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

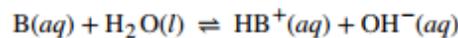
Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

### Check Your Learning

Calculate the percent ionization of a 0.10-M solution of acetic acid with a pH of 2.89.

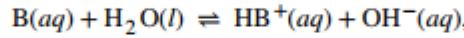
**Answer:** 1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:



Water is the acid that reacts with the base,  $\text{HB}^+$  is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of  $\text{OH}^-$  and  $\text{HB}^+$  when it reacts with water; [Figure 14.6](#) lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

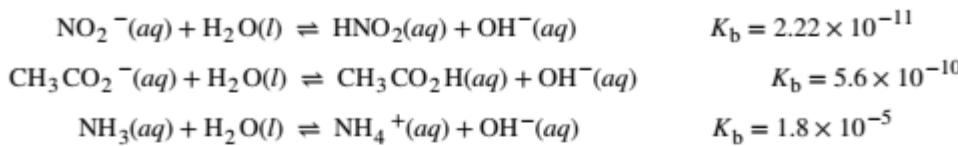
As we did with acids, we can measure the relative strengths of bases by measuring their **base-ionization constant ( $K_b$ )** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:



we write the equation for the ionization constant as:

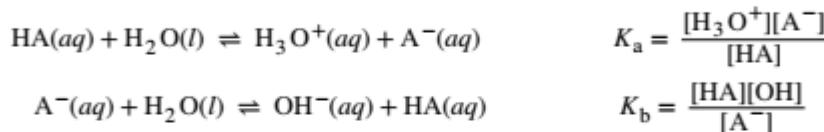
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where the concentrations are those at equilibrium. Again, we do not include  $[H_2O]$  in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

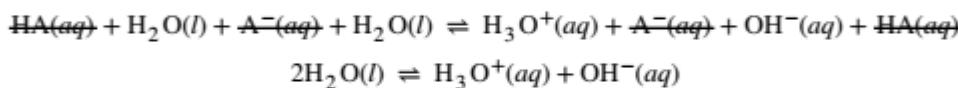


A table of ionization constants of weak bases appears in **Appendix I** (with a partial list in **Table 14.3**). As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair,  $HA - A^-$ :



Adding these two chemical equations yields the equation for the autoionization for water:



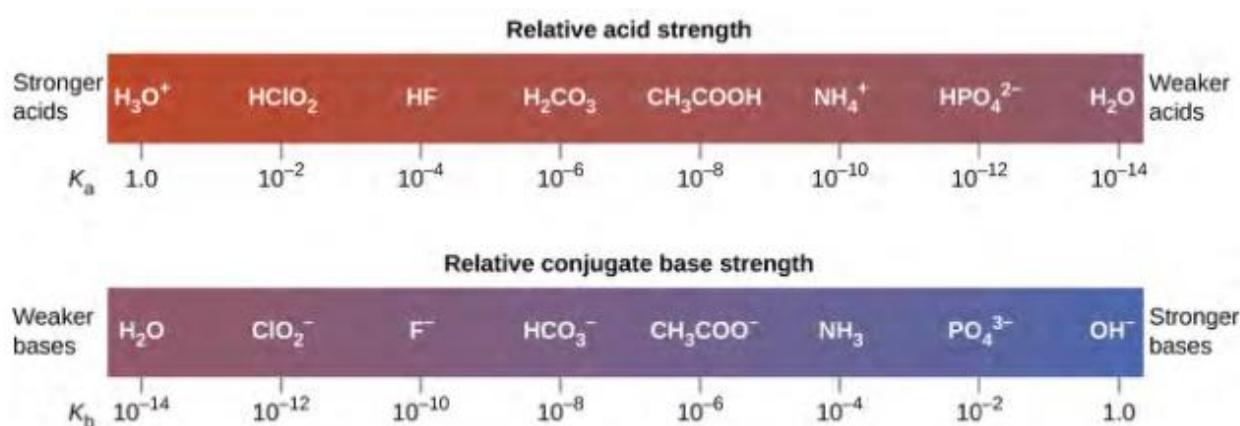
As shown in the previous chapter on equilibrium, the  $K$  expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations'  $K$  expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

For example, the acid ionization constant of acetic acid ( $CH_3COOH$ ) is  $1.8 \times 10^{-5}$ , and the base ionization constant of its conjugate base, acetate ion ( $CH_3COO^-$ ), is  $5.6 \times 10^{-10}$ . The product of these two constants is indeed equal to  $K_w$ :

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

The extent to which an acid,  $HA$ , donates protons to water molecules depends on the strength of the conjugate base,  $A^-$ , of the acid. If  $A^-$  is a strong base, any protons that are donated to water molecules are recaptured by  $A^-$ . Thus there is relatively little  $A^-$  and  $H_3O^+$  in solution, and the acid,  $HA$ , is weak. If  $A^-$  is a weak base, water binds the protons more strongly, and the solution contains primarily  $A^-$  and  $H_3O^+$ —the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (**Figure 14.7**).



**Figure 14.7** This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

**Figure 14.8** lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

Acid		Base	
perchloric acid	$\text{HClO}_4$	$\text{ClO}_4^-$	perchlorate ion
sulfuric acid	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	hydrogen sulfate ion
hydrogen iodide	$\text{HI}$	$\text{I}^-$	iodide ion
hydrogen bromide	$\text{HBr}$	$\text{Br}^-$	bromide ion
hydrogen chloride	$\text{HCl}$	$\text{Cl}^-$	chloride ion
nitric acid	$\text{HNO}_3$	$\text{NO}_3^-$	nitrate ion
hydronium ion	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	water
hydrogen sulfate ion	$\text{HSO}_4^-$	$\text{SO}_4^{2-}$	sulfate ion
phosphoric acid	$\text{H}_3\text{PO}_4$	$\text{H}_2\text{PO}_4^-$	dihydrogen phosphate ion
hydrogen fluoride	$\text{HF}$	$\text{F}^-$	fluoride ion
nitrous acid	$\text{HNO}_2$	$\text{NO}_2^-$	nitrite ion
acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_3\text{CO}_2^-$	acetate ion
carbonic acid	$\text{H}_2\text{CO}_3$	$\text{HCO}_3^-$	hydrogen carbonate ion
hydrogen sulfide	$\text{H}_2\text{S}$	$\text{HS}^-$	hydrogen sulfide ion
ammonium ion	$\text{NH}_4^+$	$\text{HN}_3$	ammonia
hydrogen cyanide	$\text{HCN}$	$\text{CN}^-$	cyanide ion
hydrogen carbonate ion	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	carbonate ion
water	$\text{H}_2\text{O}$	$\text{OH}^-$	hydroxide ion
hydrogen sulfide ion	$\text{HS}^-$	$\text{S}^{2-}$	sulfide ion
ethanol	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{O}^-$	ethoxide ion
ammonia	$\text{NH}_3$	$\text{NH}_2^-$	amide ion
hydrogen	$\text{H}_2$	$\text{H}^-$	hydride ion
methane	$\text{CH}_4$	$\text{CH}_3^-$	methide ion

**Figure 14.8** The chart shows the relative strengths of conjugate acid-base pairs.

The first six acids in **Figure 14.8** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in **Figure 14.8** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in **Figure 14.8** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in **Figure 14.8**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

**Example 14.8****The Product  $K_a \times K_b = K_w$** 

Use the  $K_b$  for the nitrite ion,  $\text{NO}_2^-$ , to calculate the  $K_a$  for its conjugate acid.

**Solution**

$K_b$  for  $\text{NO}_2^-$  is given in this section as  $2.22 \times 10^{-11}$ . The conjugate acid of  $\text{NO}_2^-$  is  $\text{HNO}_2$ ;  $K_a$  for  $\text{HNO}_2$  can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for  $K_a$ , we get:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.22 \times 10^{-11}} = 4.5 \times 10^{-4}$$

This answer can be verified by finding the  $K_a$  for  $\text{HNO}_2$  in [Appendix H](#).

**Check Your Learning**

We can determine the relative acid strengths of  $\text{NH}_4^+$  and HCN by comparing their ionization constants.

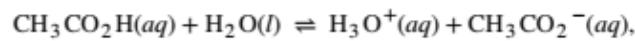
The ionization constant of HCN is given in [Appendix H](#) as  $4 \times 10^{-10}$ . The ionization constant of  $\text{NH}_4^+$  is not listed, but the ionization constant of its conjugate base,  $\text{NH}_3$ , is listed as  $1.8 \times 10^{-5}$ . Determine the ionization constant of  $\text{NH}_4^+$ , and decide which is the stronger acid, HCN or  $\text{NH}_4^+$ .

**Answer:**  $\text{NH}_4^+$  is the slightly stronger acid ( $K_a$  for  $\text{NH}_4^+ = 5.6 \times 10^{-10}$ ).

**The Ionization of Weak Acids and Weak Bases**

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:



giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment ([Figure 14.9](#)). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$



**Figure 14.9** pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and  $[H_3O^+] = 0.1\text{ M}$ . A 0.1-M solution of  $\text{CH}_3\text{CO}_2\text{H}$  (beaker on right) has a pH of 3 ( $[H_3O^+] = 0.001\text{ M}$ ) because the weak acid  $\text{CH}_3\text{CO}_2\text{H}$  is only partially ionized. In this solution,  $[H_3O^+] < [CH_3\text{CO}_2\text{H}]$ . (credit: modification of work by Sahar Atwa)

Ionization Constants of Some Weak Acids

Ionization Reaction	$K_a$ at 25 °C
$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	$1.2 \times 10^{-2}$
$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	$7.2 \times 10^{-4}$
$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	$4.5 \times 10^{-4}$
$\text{HNCO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NCO}^-$	$3.46 \times 10^{-4}$
$\text{HCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_2^-$	$1.8 \times 10^{-4}$
$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^-$	$1.8 \times 10^{-5}$
$\text{HClO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}^-$	$3.5 \times 10^{-8}$
$\text{HBrO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^-$	$2 \times 10^{-9}$

Table 14.2

Ionization Constants of Some Weak Acids

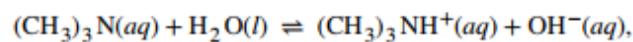
Ionization Reaction	$K_a$ at 25 °C
$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	$4 \times 10^{-10}$

**Table 14.2**

**Table 14.2** gives the ionization constants for several weak acids; additional ionization constants can be found in **Appendix H**.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine,  $(\text{CH}_3)_3\text{N}$ , in water reacts according to the equation:



giving an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (**Figure 14.10**). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base,  $K_b$ , is called the ionization constant of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$



**Figure 14.10** pH paper indicates that a 0.1-*M* solution of  $\text{NH}_3$  (left) is weakly basic. The solution has a  $\text{pOH}$  of 3 ( $[\text{OH}^-] = 0.001 \text{ M}$ ) because the weak base  $\text{NH}_3$  only partially reacts with water. A 0.1-*M* solution of  $\text{NaOH}$  (right) has a  $\text{pOH}$  of 1 because  $\text{NaOH}$  is a strong base. (credit: modification of work by Sahar Atwa)

The ionization constants of several weak bases are given in **Table 14.3** and in **Appendix I**.

Ionization Constants of Some Weak Bases

Ionization Reaction	$K_b$ at 25 °C
$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	$7.4 \times 10^{-4}$
$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	$4.4 \times 10^{-4}$
$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	$7.4 \times 10^{-5}$
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	$4.6 \times 10^{-10}$

Table 14.3

**Example 14.9****Determination of  $K_a$  from Equilibrium Concentrations**

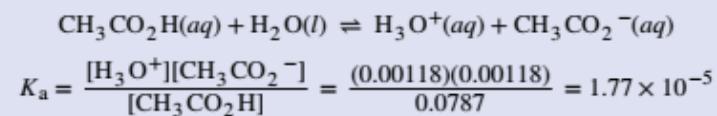
Acetic acid is the principal ingredient in vinegar (Figure 14.11); that's why it tastes sour. At equilibrium, a solution contains  $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787\text{ M}$  and  $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118\text{ M}$ . What is the value of  $K_a$  for acetic acid?



Figure 14.11 Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

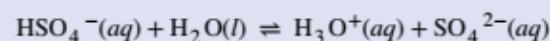
**Solution**

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:



### Check Your Learning

What is the equilibrium constant for the ionization of the  $\text{HSO}_4^-$  ion, the weak acid used in some household cleansers:



In one mixture of  $\text{NaHSO}_4$  and  $\text{Na}_2\text{SO}_4$  at equilibrium,  $[\text{H}_3\text{O}^+] = 0.027\text{ M}$ ;  $[\text{HSO}_4^-] = 0.29\text{ M}$ ; and  $[\text{SO}_4^{2-}] = 0.13\text{ M}$ .

**Answer:**  $K_a$  for  $\text{HSO}_4^- = 1.2 \times 10^{-2}$

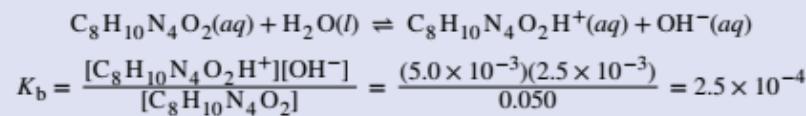
### Example 14.10

#### Determination of $K_b$ from Equilibrium Concentrations

Caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  is a weak base. What is the value of  $K_b$  for caffeine if a solution at equilibrium has  $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2] = 0.050\text{ M}$ ,  $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+] = 5.0 \times 10^{-3}\text{ M}$ , and  $[\text{OH}^-] = 2.5 \times 10^{-3}\text{ M}$ ?

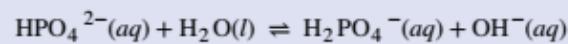
### Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:



### Check Your Learning

What is the equilibrium constant for the ionization of the  $\text{HPO}_4^{2-}$  ion, a weak base:



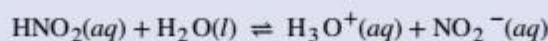
In a solution containing a mixture of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  at equilibrium,  $[\text{OH}^-] = 1.3 \times 10^{-6}\text{ M}$ ;  $[\text{H}_2\text{PO}_4^-] = 0.042\text{ M}$ ; and  $[\text{HPO}_4^{2-}] = 0.341\text{ M}$ .

**Answer:**  $K_b$  for  $\text{HPO}_4^{2-} = 1.6 \times 10^{-7}$

### Example 14.11

### Determination of $K_a$ or $K_b$ from pH

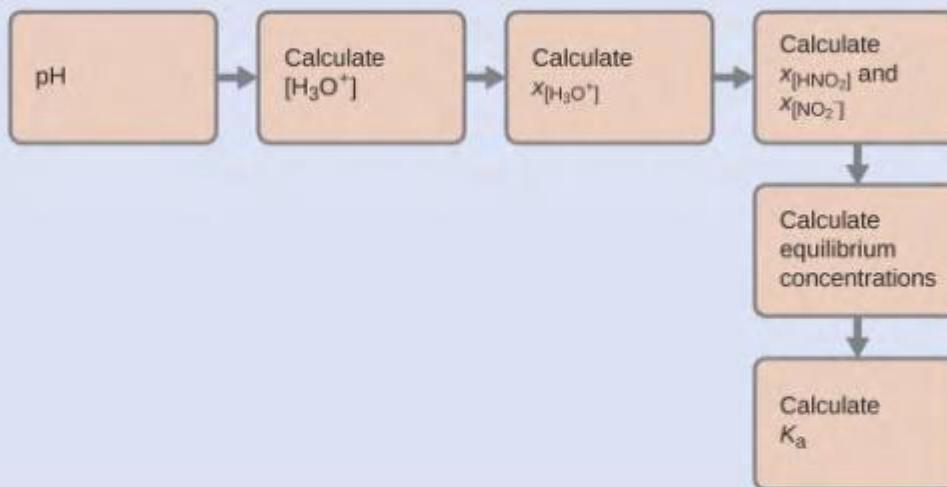
The pH of a 0.0516-M solution of nitrous acid,  $\text{HNO}_2$ , is 2.34. What is its  $K_a$ ?



#### Solution

We determine an equilibrium constant starting with the initial concentrations of  $\text{HNO}_2$ ,  $\text{H}_3\text{O}^+$ , and  $\text{NO}_2^-$  as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which  $x$  is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	$\text{HNO}_2$	$+$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$+$	$\text{NO}_2^-$
Initial concentration (M)	0.0516				~0		0
Change (M)	$-x$		+		$x$		$x$
Equilibrium concentration (M)	$[\text{HNO}_2]_i + (-x) = 0.0516 + (-x)$				$[\text{H}_3\text{O}]^+ + x[\text{NO}_2^-] + x \sim 0 + x$		0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate  $[\text{H}_3\text{O}^+]$ , the equilibrium concentration of  $\text{H}_3\text{O}^+$ , from the pH:

$$[\text{H}_3\text{O}^+] = 10^{-2.34} = 0.0046 \text{ M}$$

The change in concentration of  $\text{H}_3\text{O}^+$ ,  $x_{[\text{H}_3\text{O}^+]}$ , is the difference between the equilibrium concentration of  $\text{H}_3\text{O}^+$ , which we determined from the pH, and the initial concentration,  $[\text{H}_3\text{O}^+]_i$ . The initial concentration of  $\text{H}_3\text{O}^+$  is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero ( $\sim 0$ ).

The change in concentration of  $\text{NO}_2^-$  is equal to the change in concentration of  $[\text{H}_3\text{O}^+]$ . For each 1 mol of  $\text{H}_3\text{O}^+$  that forms, 1 mol of  $\text{NO}_2^-$  forms. The equilibrium concentration of  $\text{HNO}_2$  is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	$\text{HNO}_2$	$+\text{H}_2\text{O} \rightleftharpoons$	$\text{H}_3\text{O}^+$	$+\text{NO}_2^-$
Initial concentration ( $M$ )	0.0516		~0	0
Change ( $M$ )	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration ( $M$ )	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

#### Check Your Learning.

The pH of a solution of household ammonia, a 0.950- $M$  solution of  $\text{NH}_3$ , is 11.612. What is  $K_b$  for  $\text{NH}_3$ .

**Answer:**  $K_b = 1.8 \times 10^{-5}$

### Example 14.12

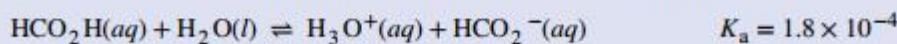
#### Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid,  $\text{HCO}_2\text{H}$ , is the irritant that causes the body's reaction to ant stings (Figure 14.12).



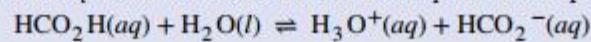
**Figure 14.12** The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534- $M$  solution of formic acid?



#### Solution

**Step 1.** Determine  $x$  and equilibrium concentrations. The equilibrium expression is:



The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO <sub>2</sub> H	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>
Initial concentration (M)	0.534		~0		0
Change (M)	-x		x		x
Equilibrium concentration (M)	0.534 + (-x)		0 + x = x		0 + x = x

**Step 2.** Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and  $K_a$  is very small, we assume that  $x \ll 0.534$ , which permits us to simplify the denominator term as  $(0.534 - x) = 0.534$ . This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} \text{ (1.8\% of 0.534)}$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[\text{H}_3\text{O}^+] = \sim 0 + x = 0 + 9.8 \times 10^{-3} M$$

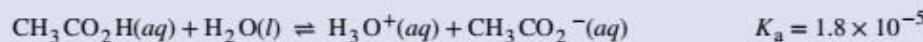
$$= 9.8 \times 10^{-3} M$$

The pH of the solution can be found by taking the negative log of the  $[\text{H}_3\text{O}^+]$ , so:

$$-\log(9.8 \times 10^{-3}) = 2.01$$

### Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-M solution of acetic acid, CH<sub>3</sub>CO<sub>2</sub>H?



(Hint: Determine  $[\text{CH}_3\text{CO}_2^-]$  at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized  $\times 100$ , or  $\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]_{\text{initial}}} \times 100$ .

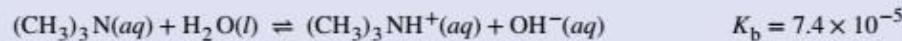
**Answer:** percent ionization = 1.3%

The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

### Example 14.13

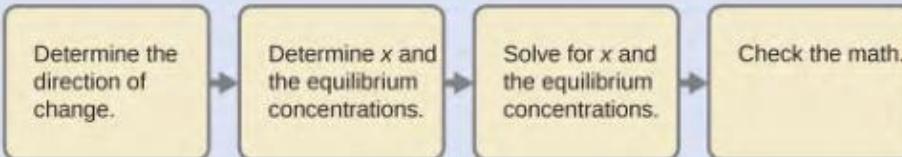
#### Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-M solution of trimethylamine, a weak base:



#### Solution

This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in [Example 14.12](#). The reactants and products will be different and the numbers will be different, but the logic will be the same:



**Step 1.** Determine  $x$  and equilibrium concentrations. The table shows the changes and concentrations:

$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$				
Initial concentration (M)	0.25		0	$\sim 0$
Change (M)	$-x$		$x$	$x$
Equilibrium concentration (M)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

**Step 2.** Solve for  $x$  and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 7.4 \times 10^{-5}$$

If we assume that  $x$  is small relative to 0.25, then we can replace  $(0.25 - x)$  in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.3 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation,  $x$  is equal to the equilibrium concentration of hydroxide ion in the solution (see earlier tabulation):

$$[\text{OH}^-] = \sim 0 + x = x = 4.3 \times 10^{-3} M$$

$$= 4.3 \times 10^{-3} M$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.37$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.63$$

**Step 3.** *Check the work.* A check of our arithmetic shows that  $K_b = 7.4 \times 10^{-5}$ .

### Check Your Learning

(a) Show that the calculation in Step 2 of this example gives an  $x$  of  $4.3 \times 10^{-3}$  and the calculation in Step 3 shows  $K_b = 7.4 \times 10^{-5}$ .

(b) Find the concentration of hydroxide ion in a 0.0325-M solution of ammonia, a weak base with a  $K_b$  of  $1.76 \times 10^{-5}$ . Calculate the percent ionization of ammonia, the fraction ionized  $\times 100$ , or  $\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \times 100$

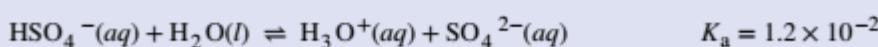
**Answer:**  $7.56 \times 10^{-4} M$ , 2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that  $x$  is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

### Example 14.14

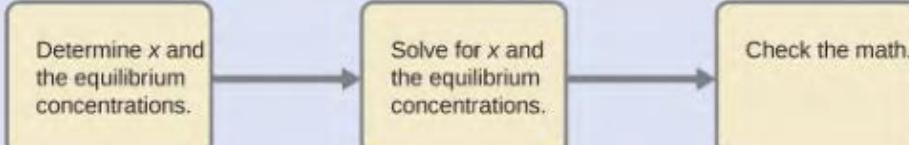
#### Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate,  $\text{NaHSO}_4$ , is used in some household cleansers because it contains the  $\text{HSO}_4^-$  ion, a weak acid. What is the pH of a 0.50-M solution of  $\text{HSO}_4^-$ ?



#### Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of  $\text{HSO}_4^-$  so that we can use  $[\text{H}_3\text{O}^+]$  to determine the pH. As in the previous examples, we can approach the solution by the following steps:



**Step 1.** Determine  $x$  and equilibrium concentrations. This table shows the changes and concentrations:

	$\text{HSO}_4^-$	$+\text{H}_2\text{O} \rightleftharpoons$	$\text{H}_3\text{O}^+$	$+\text{SO}_4^{2-}$
Initial concentration ( $M$ )	0.50		~0	0
Change ( $M$ )	$-x$		$x$	$x$
Equilibrium concentration ( $M$ )	$0.50 + (-x) = 0.50 - x$		$0 + x = x$	$0 + x = x$

**Step 2.** Solve for  $x$  and the concentrations. As we begin solving for  $x$ , we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of  $x$ .

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that  $x$  is small and approximate  $(0.50 - x)$  as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we calculate:

$$\frac{x}{[\text{HSO}_4^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15 \text{ (15%)}$$

The value of  $x$  is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find  $x$ .

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

or

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^2 + bx + c = 0,$$

$x$  is given by the equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this problem,  $a = 1$ ,  $b = 1.2 \times 10^{-3}$ , and  $c = -6.0 \times 10^{-3}$ .

Solving for  $x$  gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0 + x = 0 + 7.2 \times 10^{-2} \text{ M} \\ &= 7.2 \times 10^{-2} \text{ M} \end{aligned}$$

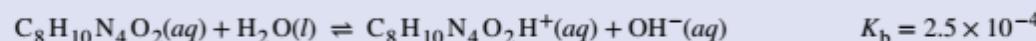
The pH of this solution is:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 7.2 \times 10^{-2} = 1.14$$

### Check Your Learning

(a) Show that the quadratic formula gives  $x = 7.2 \times 10^{-2}$ .

(b) Calculate the pH in a 0.010-M solution of caffeine, a weak base:



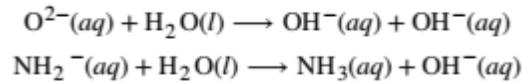
(Hint: It will be necessary to convert  $[\text{OH}^-]$  to  $[\text{H}_3\text{O}^+]$  or pOH to pH toward the end of the calculation.)

**Answer:** pH 11.16

## The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order  $\text{HCl} < \text{HBr} < \text{HI}$ , and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the **leveling effect of water**.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion,  $\text{O}^{2-}$ , and the amide ion,  $\text{NH}_2^-$ , are such strong bases that they react completely with water:

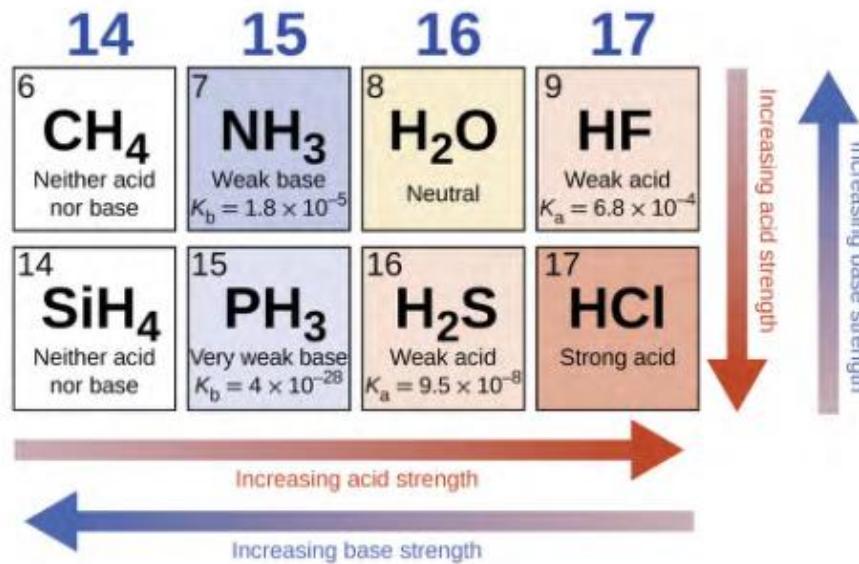


Thus,  $\text{O}^{2-}$  and  $\text{NH}_2^-$  appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

### Effect of Molecular Structure on Acid-Base Strength

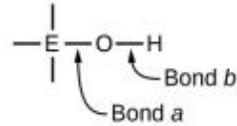
In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 7A, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 6A, the order of increasing acid strength is H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is CH<sub>4</sub> < NH<sub>3</sub> < H<sub>2</sub>O < HF; across the third row, it is SiH<sub>4</sub> < PH<sub>3</sub> < H<sub>2</sub>S < HCl (see Figure 14.13).



**Figure 14.13** As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula O<sub>n</sub>E(OH)<sub>m</sub>, and include sulfuric acid, O<sub>2</sub>S(OH)<sub>2</sub>, sulfurous acid, OS(OH)<sub>2</sub>, nitric acid, O<sub>2</sub>NOH, perchloric acid, O<sub>3</sub>ClOH, aluminum hydroxide, Al(OH)<sub>3</sub>, calcium hydroxide, Ca(OH)<sub>2</sub>, and potassium hydroxide, KOH:

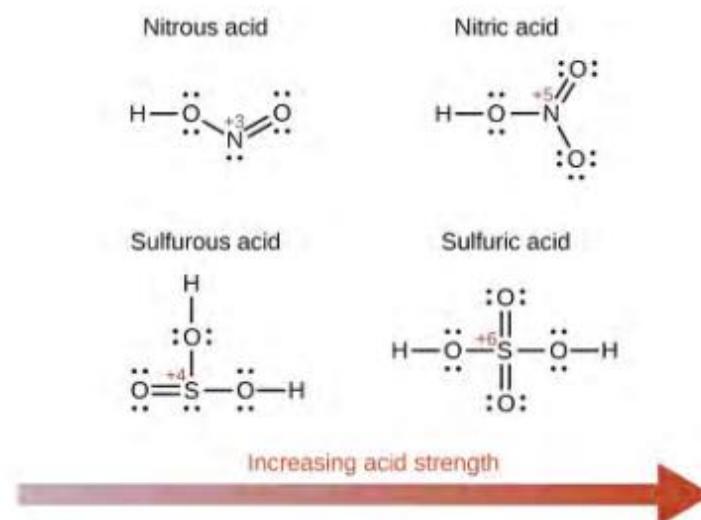


If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with Ca(OH)<sub>2</sub> and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the

solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic -OH groups that are called **oxyacids**.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, or O<sub>2</sub>S(OH)<sub>2</sub> (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H<sub>2</sub>SO<sub>3</sub>, or OS(OH)<sub>2</sub> (with a sulfur oxidation number of +4). Likewise nitric acid, HNO<sub>3</sub>, or O<sub>2</sub>NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO<sub>2</sub>, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 14.14).

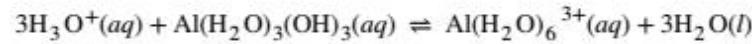


**Figure 14.14** As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphotericism of aluminum hydroxide, which commonly exists as the hydrate Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>, is converted into the soluble ion, [Al(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>4</sub>]<sup>-</sup>, by reaction with hydroxide ion:



In this reaction, a proton is transferred from one of the aluminum-bound H<sub>2</sub>O molecules to a hydroxide ion in solution. The Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub> compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> by reaction with hydronium ion:



In this case, protons are transferred from hydronium ions in solution to Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>, and the compound functions as a base.

## 14.4 Hydrolysis of Salt Solutions

By the end of this section, you will be able to:

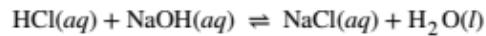
- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

### Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as  $\text{HCl}(aq)$  and  $\text{NaOH}(aq)$  will react to form a neutral solution since the conjugate partners produced are of negligible strength (see [Figure 14.8](#)):



2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated  $K$  values of the conjugates must be compared.

### Chemistry in Everyday Life

#### Stomach Antacids

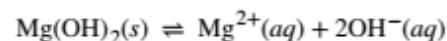
Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking

an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate,  $\text{CaCO}_3$ . The reaction,



not only neutralizes stomach acid, it also produces  $\text{CO}_2(g)$ , which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . It works according to the reaction:



The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :



This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect.

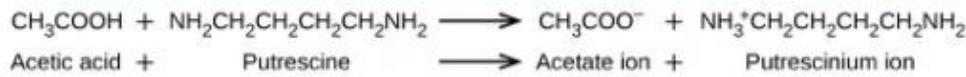
Several antacids have aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

## Chemistry in Everyday Life

### Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking.  $\text{NaHCO}_3$  is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 14.15). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.

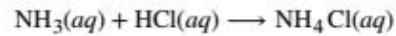


**Figure 14.15** A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

### Salts of Weak Bases and Strong Acids

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride,  $\text{NH}_4\text{Cl}$ , is a salt formed by the reaction of the weak base ammonia with the strong acid HCl:



A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:



The equilibrium equation for this reaction is simply the ionization constant,  $K_a$ , for the acid  $\text{NH}_4^+$ :

$$\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = K_a$$

We will not find a value of  $K_a$  for the ammonium ion in **Appendix H**. However, it is not difficult to determine  $K_a$  for  $\text{NH}_4^+$  from the value of the ionization constant of water,  $K_w$ , and  $K_b$ , the ionization constant of its conjugate base,  $\text{NH}_3$ , using the following relationship:

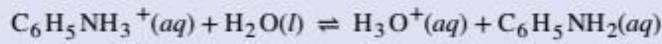
$$K_w = K_a \times K_b$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

### Example 14.15

#### The pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride,  $[\text{C}_6\text{H}_5\text{NH}_3^+]\text{Cl}$ , a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of aniline hydrochloride?



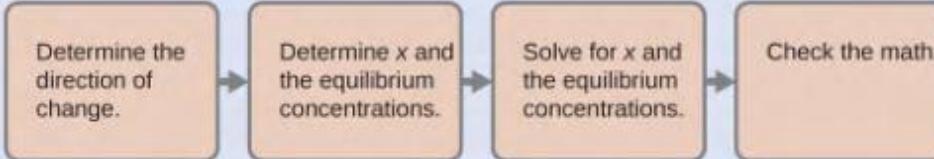
#### Solution

The new step in this example is to determine  $K_a$  for the  $\text{C}_6\text{H}_5\text{NH}_3^+$  ion. The  $\text{C}_6\text{H}_5\text{NH}_3^+$  ion is the conjugate acid of a weak base. The value of  $K_a$  for this acid is not listed in **Appendix H**, but we can determine it from the value of  $K_b$  for aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , which is given as  $4.6 \times 10^{-10}$  (**Table 14.3** and **Appendix I**):

$$K_a \text{ (for } \text{C}_6\text{H}_5\text{NH}_3^+ \text{)} \times K_b \text{ (for } \text{C}_6\text{H}_5\text{NH}_2 \text{)} = K_w = 1.0 \times 10^{-14}$$

$$K_a \text{ (for } \text{C}_6\text{H}_5\text{NH}_3^+ \text{)} = \frac{K_w}{K_b \text{ (for } \text{C}_6\text{H}_5\text{NH}_2 \text{)}} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-10}} = 2.2 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of  $\text{H}_3\text{O}^+$ , and the pH:



With these steps we find  $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$  and  $\text{pH} = 2.64$

#### Check Your Learning

- Do the calculations and show that the hydronium ion concentration for a 0.233-M solution of  $\text{C}_6\text{H}_5\text{NH}_3^+$  is  $2.3 \times 10^{-3}$  and the pH is 2.64.
- What is the hydronium ion concentration in a 0.100-M solution of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , a salt composed of the ions  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Use the data in **Table 14.3** to determine  $K_b$  for the ammonium ion. Which is the stronger acid  $\text{C}_6\text{H}_5\text{NH}_3^+$  or  $\text{NH}_4^+$ ?

**Answer:** (a)  $K_a$  (for  $\text{NH}_4^+$ ) =  $5.6 \times 10^{-10}$ ,  $[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} M$ ; (b)  $\text{C}_6\text{H}_5\text{NH}_3^+$  is the stronger acid.

## Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate,  $\text{NaCH}_3\text{CO}_2$ , is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:



A solution of this salt contains sodium ions and acetate ions. The sodium ion, as the conjugate acid of a strong base, has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:



The equilibrium equation for this reaction is the ionization constant,  $K_b$ , for the base  $\text{CH}_3\text{CO}_2^-$ . The value of  $K_b$  can be calculated from the value of the ionization constant of water,  $K_w$ , and  $K_a$ , the ionization constant of the conjugate acid of the anion using the equation:

$$K_w = K_a \times K_b$$

For the acetate ion and its conjugate acid we have:

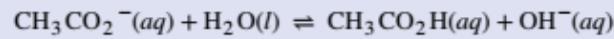
$$K_b \text{ (for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a \text{ (for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Some handbooks do not report values of  $K_b$ . They only report ionization constants for acids. If we want to determine a  $K_b$  value using one of these handbooks, we must look up the value of  $K_a$  for the conjugate acid and convert it to a  $K_b$  value.

### Example 14.16

#### Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with  $[\text{CH}_3\text{CO}_2^-] = 0.050 M$  and  $[\text{OH}^-] = 2.5 \times 10^{-6} M$  at equilibrium. The reaction is:



#### Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine  $K_b$  as follows:

$$K_b \text{ (for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a \text{ (for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now find the missing concentration:

$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[\text{CH}_3\text{CO}_2\text{H}](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving this equation we get  $[\text{CH}_3\text{CO}_2\text{H}] = 1.1 \times 10^{-5} \text{ M}$ .

### Check Your Learning

What is the pH of a 0.083-M solution of  $\text{CN}^-$ ? Use  $4.0 \times 10^{-10}$  as  $K_a$  for HCN. Hint: We will probably need to convert pOH to pH or find  $[\text{H}_3\text{O}^+]$  using  $[\text{OH}^-]$  in the final stages of this problem.

**Answer:** 11.16

## Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, to predict the pH, we must know both the  $K_a$  of the weak acid and the  $K_b$  of the weak base. If  $K_a > K_b$ , the solution is acidic, and if  $K_b > K_a$ , the solution is basic.

### Example 14.17

#### Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a) KBr
- (b) NaHCO<sub>3</sub>
- (c) NH<sub>4</sub>Cl
- (d) Na<sub>2</sub>HPO<sub>4</sub>
- (e) NH<sub>4</sub>F

#### Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The  $\text{K}^+$  cation and the  $\text{Br}^-$  anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.

(b) The  $\text{Na}^+$  cation is a spectator, and will not affect the pH of the solution; while the  $\text{HCO}_3^-$  anion is amphiprotic, it could either behave as an acid or a base. The  $K_a$  of  $\text{HCO}_3^-$  is  $4.7 \times 10^{-11}$ , so the  $K_b$  of its conjugate base is  $\frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}$ .

Since  $K_b \gg K_a$ , the solution is basic.

(c) The  $\text{NH}_4^+$  ion is acidic and the  $\text{Cl}^-$  ion is a spectator. The solution will be acidic.

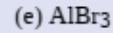
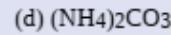
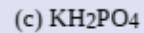
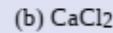
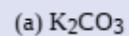
(d) The  $\text{Na}^+$  ion is a spectator, while the  $\text{HPO}_4^{2-}$  ion is amphiprotic, with a  $K_a$  of  $3.6 \times 10^{-13}$

so that the  $K_b$  of its conjugate base is  $\frac{1.0 \times 10^{-14}}{3.6 \times 10^{-13}} = 2.8 \times 10^{-2}$ . Because  $K_b \gg K_a$ , the solution is basic.

(e) The  $\text{NH}_4^+$  ion is listed as being acidic, and the  $\text{F}^-$  ion is listed as a base, so we must directly compare the  $K_a$  and the  $K_b$  of the two ions.  $K_a$  of  $\text{NH}_4^+$  is  $5.6 \times 10^{-10}$ , which seems very small, yet the  $K_b$  of  $\text{F}^-$  is  $1.4 \times 10^{-11}$ , so the solution is acidic, since  $K_a > K_b$ .

### Check Your Learning

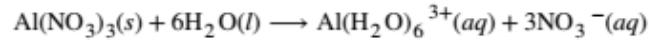
Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:



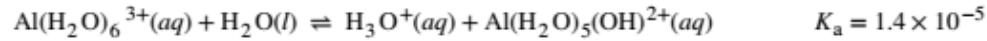
**Answer:** (a) basic; (b) neutral; (c) basic; (d) basic; (e) acidic

## The Ionization of Hydrated Metal Ions

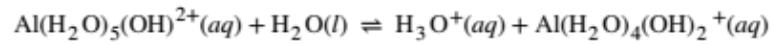
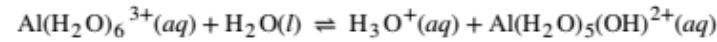
If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ , dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  cluster as well:



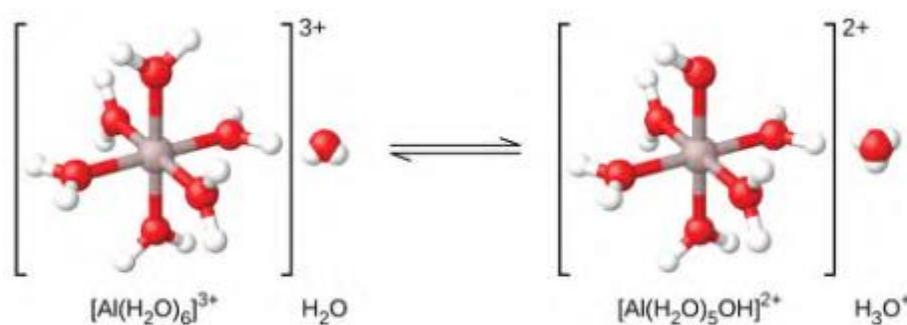
We frequently see the formula of this ion simply as “ $\text{Al}^{3+}(aq)$ ”, without explicitly noting the six water molecules that are the closest ones to the aluminum ion and just describing the ion as being solvated in water (hydrated). This is similar to the simplification of the formula of the hydronium ion,  $\text{H}_3\text{O}^+$  to  $\text{H}^+$ . However, in this case, the hydrated aluminum ion is a weak acid (**Figure 14.16**) and donates a proton to a water molecule. Thus, the hydration becomes important and we may use formulas that show the extent of hydration:



As with other polyprotic acids, the hydrated aluminum ion ionizes in stages, as shown by:

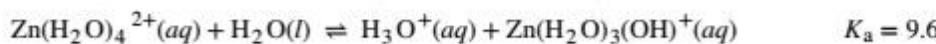
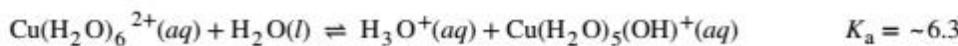
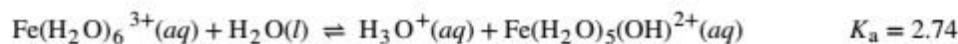


Note that some of these aluminum species are exhibiting amphiprotic behavior, since they are acting as acids when they appear on the right side of the equilibrium expressions and as bases when they appear on the left side.



**Figure 14.16** When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

However, the ionization of a cation carrying more than one charge is usually not extensive beyond the first stage. Additional examples of the first stage in the ionization of hydrated metal ions are:



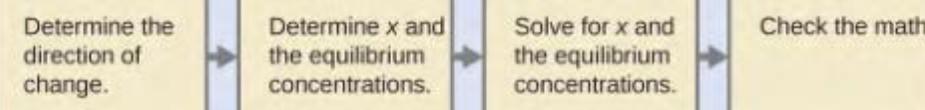
### Example 14.18

#### Hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

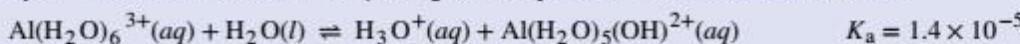
Calculate the pH of a 0.10-M solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in solution.

##### Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



**Step 1. Determine the direction of change.** The equation for the reaction and  $K_a$  are:



The reaction shifts to the right to reach equilibrium.

**Step 2. Determine x and equilibrium concentrations.** Use the table:

$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$			
Initial concentration (M)	0.10	~0	0
Change (M)	$-x$	$x$	$x$
Equilibrium constant (M)	$0.10 - x$	$x$	$x$

**Step 3. Solve for x and the equilibrium concentrations.** Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Solving this equation gives:

$$x = 1.2 \times 10^{-3} M$$

From this we find:

$$[\text{H}_3\text{O}^+] = 0 + x = 1.2 \times 10^{-3} M$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.92 \text{ (an acidic solution)}$$

**Step 4.** Check the work. The arithmetic checks; when  $1.2 \times 10^{-3} M$  is substituted for  $x$ , the result  $= K_a$ .

#### Check Your Learning

What is  $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]$  in a 0.15- $M$  solution of  $\text{Al}(\text{NO}_3)_3$  that contains enough of the strong acid  $\text{HNO}_3$  to bring  $[\text{H}_3\text{O}^+]$  to 0.10  $M$ ?

**Answer:**  $2.1 \times 10^{-5} M$

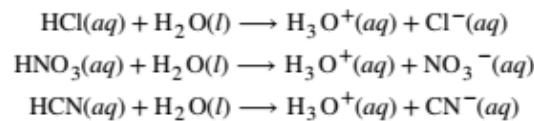
The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

## 14.5 Polyprotic Acids

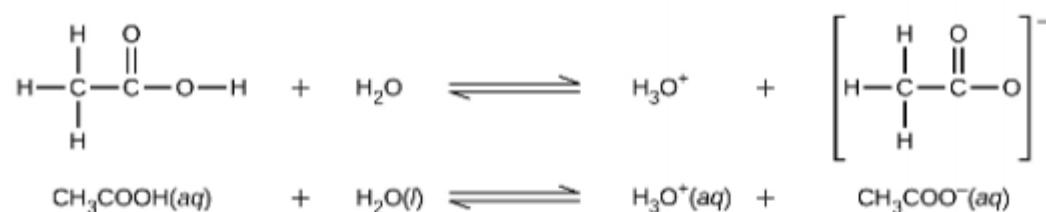
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HCN}$  that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

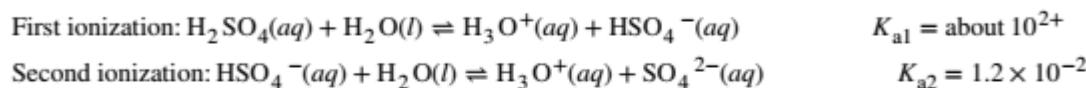


Even though it contains four hydrogen atoms, acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , is also monoprotic because only the hydrogen atom from the carboxyl group ( $\text{COOH}$ ) reacts with bases:

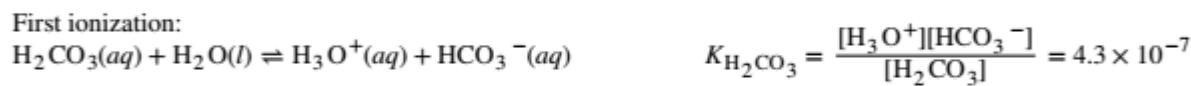


Similarly, monoprotic bases are bases that will accept a single proton.

**Diprotic acids** contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:



This **stepwise ionization** process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid,  $\text{H}_2\text{CO}_3$ , is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.



The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.



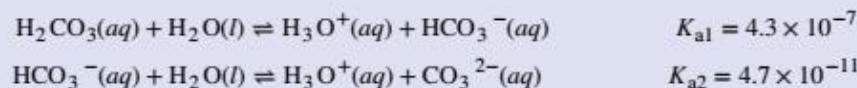
$K_{\text{H}_2\text{CO}_3}$  is larger than  $K_{\text{HCO}_3^-}$  by a factor of  $10^4$ , so  $\text{H}_2\text{CO}_3$  is the dominant producer of hydronium ion in the solution. This means that little of the  $\text{HCO}_3^-$  formed by the ionization of  $\text{H}_2\text{CO}_3$  ionizes to give hydronium ions (and carbonate ions), and the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$  are practically equal in a pure aqueous solution of  $\text{H}_2\text{CO}_3$ .

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of  $\text{H}_3\text{O}^+$  and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

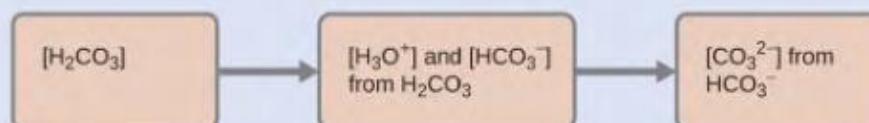
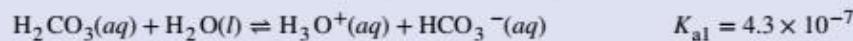
### Example 14.19

#### Ionization of a Diprotic Acid

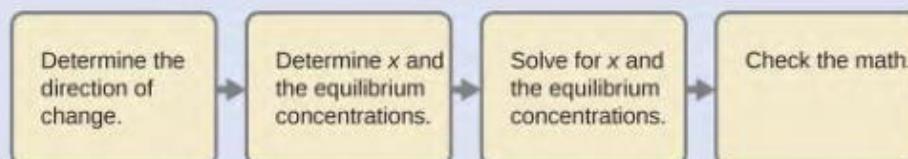
When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because  $\text{CO}_2$  reacts with water to form carbonic acid,  $\text{H}_2\text{CO}_3$ . What are  $[\text{H}_3\text{O}^+]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  in a saturated solution of  $\text{CO}_2$  with an initial  $[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$ ?

**Solution**

As indicated by the ionization constants,  $\text{H}_2\text{CO}_3$  is a much stronger acid than  $\text{HCO}_3^-$ , so  $\text{H}_2\text{CO}_3$  is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem: (1) Using the customary four steps, we determine the concentration of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$  produced by ionization of  $\text{H}_2\text{CO}_3$ . (2) Then we determine the concentration of  $\text{CO}_3^{2-}$  in a solution with the concentration of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$  determined in (1). To summarize:

**Step 1.** Determine the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$ .

As for the ionization of any other weak acid:



An abbreviated table of changes and concentrations shows:

	$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$		
Initial concentration ( $M$ )	0.033	~0	0
Change ( $M$ )	$-x$	$x$	$x$
Equilibrium constant ( $M$ )	$0.033 - x$	$x$	$x$

Substituting the equilibrium concentrations into the equilibrium gives us:

$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

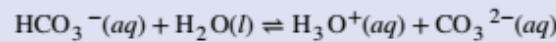
$$x = 1.2 \times 10^{-4}$$

Thus:

$$[\text{H}_2\text{CO}_3] = 0.033 M$$

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$$

**Step 2.** Determine the concentration of  $\text{CO}_3^{2-}$  in a solution at equilibrium with  $[\text{H}_3\text{O}^+]$  and  $[\text{HCO}_3^-]$  both equal to  $1.2 \times 10^{-4} \text{ M}$ .



$$K_{\text{HCO}_3^-} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(1.2 \times 10^{-4})[\text{CO}_3^{2-}]}{1.2 \times 10^{-4}}$$

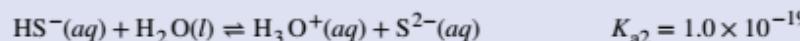
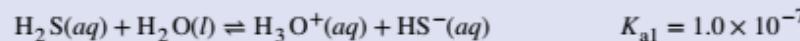
$$[\text{CO}_3^{2-}] = \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11} \text{ M}$$

To summarize: In part 1 of this example, we found that the  $\text{H}_2\text{CO}_3$  in a  $0.033\text{-M}$  solution ionizes slightly and at equilibrium  $[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$ ;  $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-4}$ ; and  $[\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$ . In part 2, we determined that  $[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$ .

### Check Your Learning

The concentration of  $\text{H}_2\text{S}$  in a saturated aqueous solution at room temperature is approximately  $0.1 \text{ M}$ .

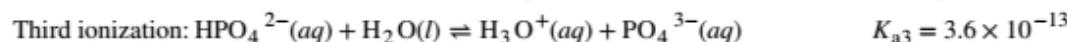
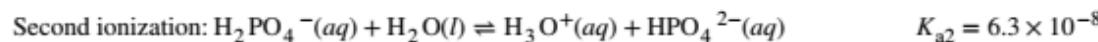
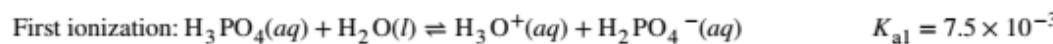
Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{HS}^-]$ , and  $[\text{S}^{2-}]$  in the solution:



$$\text{Answer: } [\text{H}_2\text{S}] = 0.1 \text{ M}; [\text{H}_3\text{O}^+] = [\text{HS}^-] = 0.0001 \text{ M}; [\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$$

We note that the concentration of the sulfide ion is the same as  $K_{\text{a2}}$ . This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

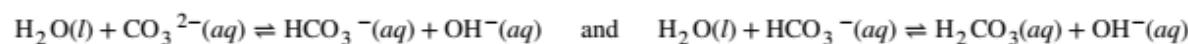
A **triprotic acid** is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:



As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about  $10^5$  to  $10^6$ .

This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of  $\text{H}_3\text{PO}_4$  complicated. However, because the successive ionization constants differ by a factor of  $10^5$  to  $10^6$ , the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a **diprotic base**, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:



## 14.6 Buffers

By the end of this section, you will be able to:

- Describe the composition and function of acid-base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

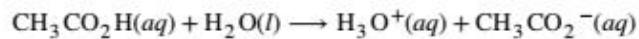
A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (**Figure 14.17**). A solution of acetic acid and sodium acetate ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ ) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ( $\text{NH}_3(aq) + \text{NH}_4\text{Cl}(aq)$ ).



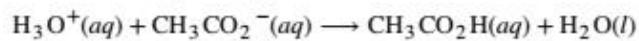
**Figure 14.17** (a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

### How Buffers Work

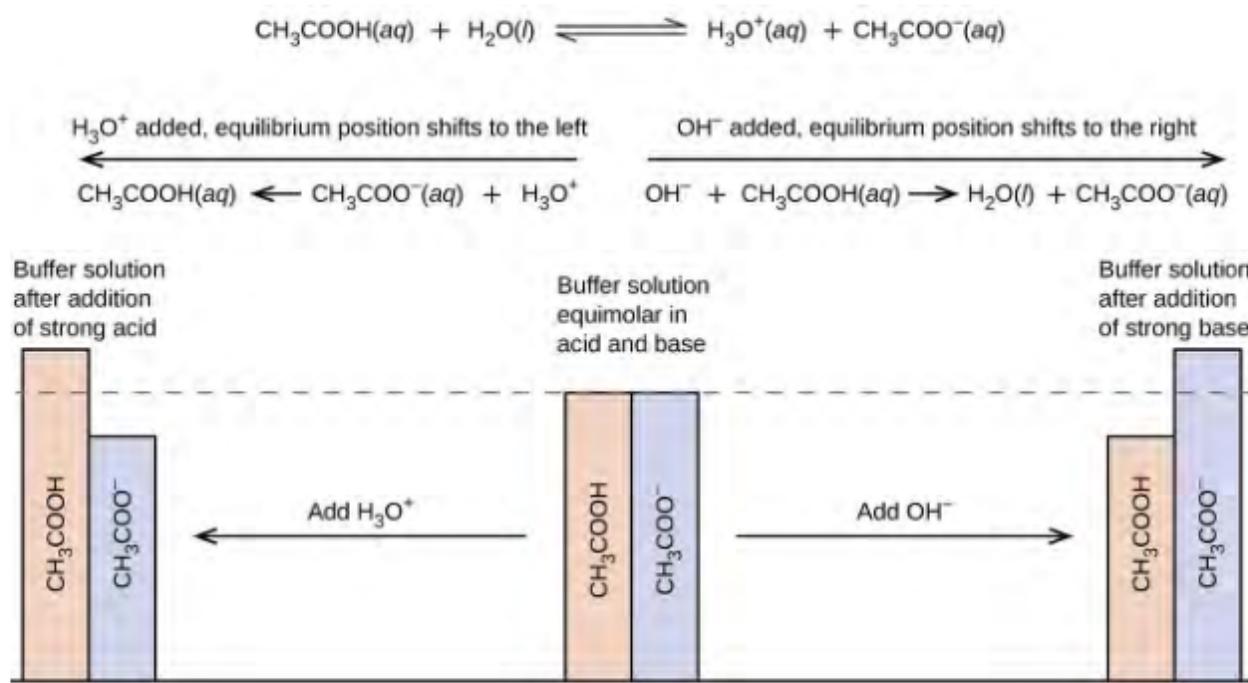
A mixture of acetic acid and sodium acetate is acidic because the  $K_a$  of acetic acid is greater than the  $K_b$  of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:



The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

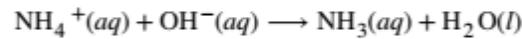


Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (**Figure 14.18**).

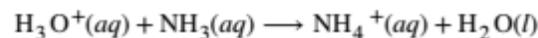


**Figure 14.18** This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the  $K_b$  for ammonia is greater than the  $K_a$  for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:



If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:



The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

### Example 14.20

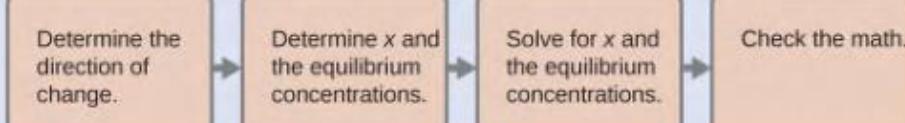
#### pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

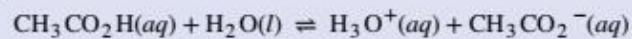
- (a) Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.

#### Solution

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



**Step 1.** *Determine the direction of change.* The equilibrium in a mixture of  $\text{H}_3\text{O}^+$ ,  $\text{CH}_3\text{CO}_2^-$ , and  $\text{CH}_3\text{CO}_2\text{H}$  is:



The equilibrium constant for  $\text{CH}_3\text{CO}_2\text{H}$  is not given, so we look it up in **Appendix H**:  $K_a = 1.8 \times 10^{-5}$ . With  $[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2^-] = 0.10 \text{ M}$  and  $[\text{H}_3\text{O}^+] = \sim 0 \text{ M}$ , the reaction shifts to the right to form  $\text{H}_3\text{O}^+$ .

**Step 2.** *Determine x and equilibrium concentrations.* A table of changes and concentrations follows:

	$[\text{CH}_3\text{CO}_2\text{H}] + [\text{H}_2\text{O}] \rightleftharpoons \text{H}_3\text{O}^+ + [\text{CH}_3\text{CO}_2^-]$		
Initial concentration (M)	0.10	$\sim 0$	0.10
Change (M)	$-x$	$x$	$x$
Equilibrium constant (M)	$0.10 - x$	$x$	$0.10 + x$

**Step 3.** *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5} \text{ M}$$

and

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5} \text{ M}$$

Thus:

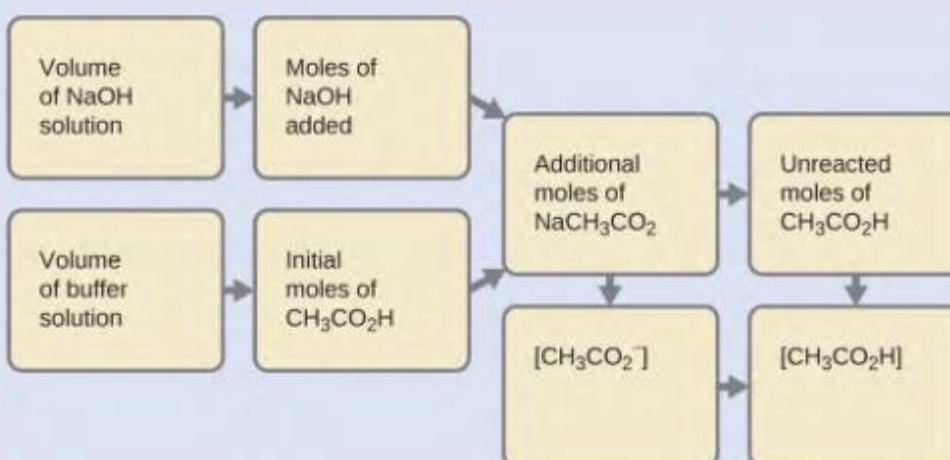
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

**Step 4.** *Check the work.* If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient,  $Q = K_a$ .

(b) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



**Step 1.** Determine the moles of NaOH. One milliliter (0.0010 L) of 0.10 M NaOH contains:

$$0.0010 \text{ L} \times \left( \frac{0.10 \text{ mol NaOH}}{1 \text{ L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

**Step 2.** Determine the moles of  $\text{CH}_3\text{CO}_2\text{H}$ . Before reaction, 0.100 L of the buffer solution contains:

$$0.100 \text{ L} \times \left( \frac{0.100 \text{ mol } \text{CH}_3\text{CO}_2\text{H}}{1 \text{ L}} \right) = 1.00 \times 10^{-2} \text{ mol } \text{CH}_3\text{CO}_2\text{H}$$

**Step 3.** Solve for the amount of  $\text{NaCH}_3\text{CO}_2$  produced. The  $1.0 \times 10^{-4}$  mol of NaOH neutralizes  $1.0 \times 10^{-4}$  mol of  $\text{CH}_3\text{CO}_2\text{H}$ , leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } \text{CH}_3\text{CO}_2\text{H}$$

and producing  $1.0 \times 10^{-4}$  mol of  $\text{NaCH}_3\text{CO}_2$ . This makes a total of:

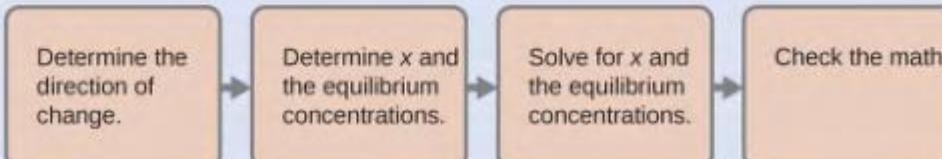
$$(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2} \text{ mol } \text{NaCH}_3\text{CO}_2$$

**Step 4.** Find the molarity of the products. After reaction,  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{NaCH}_3\text{CO}_2$  are contained in 101 mL of the intermediate solution, so:

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M}$$

$$[\text{NaCH}_3\text{CO}_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M}$$

Now we calculate the pH after the intermediate solution, which is 0.098 M in  $\text{CH}_3\text{CO}_2\text{H}$  and 0.100 M in  $\text{NaCH}_3\text{CO}_2$ , comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution (Figure 14.17).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a  $1.8 \times 10^{-5}$ -M solution of HCl). The volume of the final solution is 101 mL.

### Solution

This  $1.8 \times 10^{-5}$ -M solution of HCl has the same hydronium ion concentration as the 0.10-M solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left( \frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 M NaOH contains  $1.0 \times 10^{-4}$  mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5} \text{ M}$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5} \text{ M NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4} \text{ M}$$

The pOH of this solution is:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

### Check Your Learning

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a  $1.8 \times 10^{-5}$  M HCl solution from 4.74 to 3.00.

**Answer:** Initial pH of  $1.8 \times 10^{-5}$  M HCl;  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of  $\text{H}_3\text{O}^+$  in 100 mL  $1.8 \times 10^{-5}$  M HCl;  $1.8 \times 10^{-5}$  moles/L  $\times 0.100 \text{ L} = 1.8 \times 10^{-6}$

Moles of  $\text{H}_3\text{O}^+$  added by addition of 1.0 mL of 0.10 M HCl:  $0.10 \text{ moles/L} \times 0.0010 \text{ L} = 1.0 \times 10^{-4}$  moles; final pH after addition of 1.0 mL of 0.10 M HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} \text{ mol} + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

If we add an acid or a base to a buffer that is a mixture of a weak base and its salt, the calculations of the changes in pH are analogous to those for a buffer mixture of a weak acid and its salt.

### Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 14.19). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward

any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



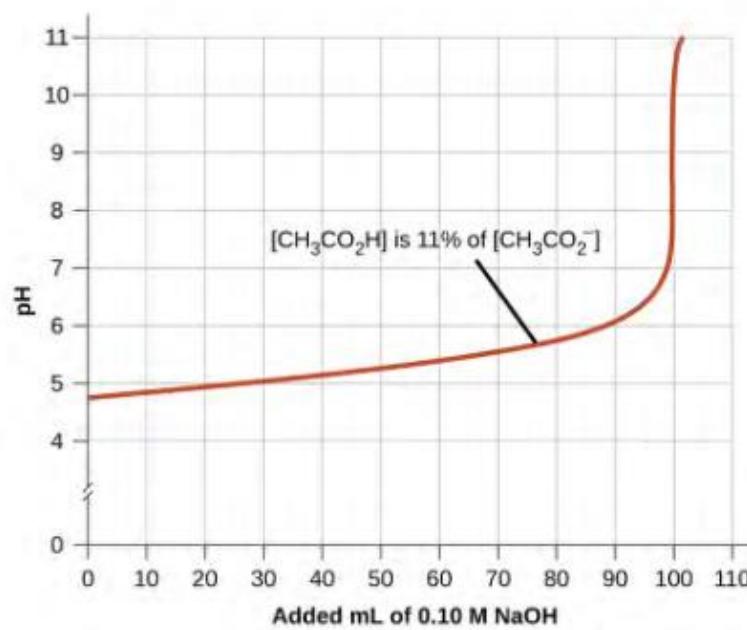
**Figure 14.19** The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

### Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

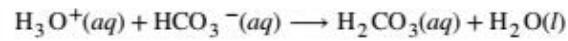
1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. **Figure 14.20** shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.



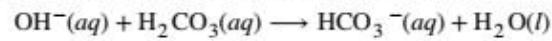
**Figure 14.20** The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially,  $[CH_3CO_2H] = 0.10\text{ M}$  and  $[CH_3CO_2^-] = 0.10\text{ M}$ .

- Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid,  $H_2CO_3$ , and the bicarbonate ion,  $HCO_3^-$ . When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:



When an excess of the hydroxide ion is present, it is removed by the reaction:



The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

### The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

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

Rearranging to solve for  $[H_3O^+]$ , we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]},$$

which can be written as

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

where  $\text{p}K_a$  is the negative of the common logarithm of the ionization constant of the weak acid ( $\text{p}K_a = -\log K_a$ ). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the “x is small” assumption must be valid to use this equation.

### Portrait of a Chemist

#### Lawrence Joseph Henderson and Karl Albert Hasselbalch

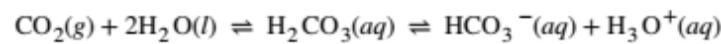
Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

### How Sciences Interconnect

#### Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:



The concentration of carbonic acid,  $\text{H}_2\text{CO}_3$  is approximately  $0.0012\text{ M}$ , and the concentration of the hydrogen carbonate ion,  $\text{HCO}_3^-$ , is around  $0.024\text{ M}$ . Using the Henderson-Hasselbalch equation and the  $\text{p}K_a$  of carbonic acid at body temperature, we can calculate the pH of blood:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log \frac{0.024}{0.0012} = 7.4$$

The fact that the  $\text{H}_2\text{CO}_3$  concentration is significantly lower than that of the  $\text{HCO}_3^-$  ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream

are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the  $\text{HCO}_3^-$  ion, producing  $\text{H}_2\text{CO}_3$ . An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes  $\text{CO}_2$  from the blood through the lungs driving the equilibrium reaction such that  $[\text{H}_3\text{O}^+]$  is lowered. If the blood is too alkaline, a lower breath rate increases  $\text{CO}_2$  concentration in the blood, driving the equilibrium reaction the other way, increasing  $[\text{H}^+]$  and restoring an appropriate pH.

## 14.7 Acid-Base Titrations

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

### Titration Curve

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

#### Example 14.21

##### Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M of a strong base NaOH the titration curve is shown in [Figure 14.21](#). Calculate the pH at these volumes of added base solution:

- (a) 0.00 mL

- (b) 12.50 mL  
 (c) 25.00 mL  
 (d) 37.50 mL

### Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of  $\text{H}_3\text{O}^+$  is  $[\text{H}_3\text{O}^+]_0 = 0.100 \text{ M}$ . When the base solution is added, it also dissociates completely, providing  $\text{OH}^-$  ions.

The  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic ( $\text{pH} < 7$ ), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic.

The total initial amount of the hydronium ions is:

$$n(\text{H}^+) = [\text{H}_3\text{O}^+]_0 \times 0.02500 \text{ L} = 0.002500 \text{ mol}$$

Once  $X \text{ mL}$  of the  $0.100\text{-M}$  base solution is added, the number of moles of the  $\text{OH}^-$  ions introduced is:

$$n(\text{OH}^-)_0 = 0.100 \text{ M} \times X \text{ mL} \times \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

The total volume becomes:  $V = (25.00 \text{ mL} + X \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)$

The number of moles of  $\text{H}_3\text{O}^+$  becomes:

$$n(\text{H}^+) = n(\text{H}^+) - n(\text{OH}^-)_0 = 0.002500 \text{ mol} - 0.100 \text{ M} \times X \text{ mL} \times \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

The concentration of  $\text{H}_3\text{O}^+$  is:

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} - 0.100 \text{ M} \times X \text{ mL} \times \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)}{(25.00 \text{ mL} + X \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)} \\ &= \frac{0.002500 \text{ mol} \times \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) - 0.100 \text{ M} \times X \text{ mL}}{25.00 \text{ mL} + X \text{ mL}} \end{aligned}$$

$$\text{pH} = -\log([\text{H}_3\text{O}^+])$$

The preceding calculations work if  $n(\text{H}^+) - n(\text{OH}^-)_0 > 0$  and so  $n(\text{H}^+) > 0$ . When  $n(\text{H}^+) = n(\text{OH}^-)_0$ , the  $\text{H}_3\text{O}^+$  ions from the acid and the  $\text{OH}^-$  ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no  $\text{OH}^-$  particles to neutralize them. Therefore, in this case:

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{OH}^-], \quad [\text{H}_3\text{O}^+] = K_w = 1.0 \times 10^{-14}; \quad [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \\ \text{pH} &= -\log(1.0 \times 10^{-7}) = 7.00 \end{aligned}$$

Finally, when  $n(\text{OH}^-)_0 > n(\text{H}^+)_0$ , there are not enough  $\text{H}_3\text{O}^+$  ions to neutralize all the  $\text{OH}^-$  ions, and instead of  $n(\text{H}^+) = n(\text{H}^+) - n(\text{OH}^-)_0$ , we calculate:  $n(\text{OH}^-) = n(\text{OH}^-)_0 - n(\text{H}^+)_0$

In this case:

$$\begin{aligned} [\text{OH}^-] &= \frac{n(\text{OH}^-)}{V} = \frac{0.100 \text{ M} \times X \text{ mL} \times \left(\frac{1\text{L}}{1000 \text{ mL}}\right) - 0.002500 \text{ mol}}{(25.00 \text{ mL} + X \text{ mL}) \left(\frac{1\text{L}}{1000 \text{ mL}}\right)} \\ &= \frac{0.100 \text{ M} \times X \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + X \text{ mL}} \end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-])$$

Let us now consider the four specific cases presented in this problem:

(a)  $X = 0 \text{ mL}$

$$[\text{H}_3\text{O}^+] = \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL}} = 0.1 \text{ M}$$

$$\text{pH} = -\log(0.100) = 1.000$$

(b)  $X = 12.50 \text{ mL}$

$$[\text{H}_3\text{O}^+] = \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100 \text{ M} \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333 \text{ M}$$

$$\text{pH} = -\log(0.0333) = 1.477$$

(c)  $X = 25.00 \text{ mL}$

Since the volumes and concentrations of the acid and base solutions are the same:  $n(\text{H}^+)_0 = n(\text{OH}^-)_0$ , and  $\text{pH} = 7.000$ , as described earlier.

(d)  $X = 37.50 \text{ mL}$

In this case:

$$n(\text{OH}^-)_0 > n(\text{H}^+_0)$$

$$[\text{OH}^-] = \frac{n(\text{OH}^-)}{V} = \frac{0.100 \text{ M} \times 37.50 \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + 37.50 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-]) = 14 + \log(0.0200) = 12.30$$

#### Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 M  $\text{HNO}_3(aq)$  and 0.200 M  $\text{NaOH}$  (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

**Answer:** 0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

In the example, we calculated pH at four points during a titration. **Table 14.4** shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

**pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base**

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl <sup>[1]</sup>	pH Values 0.100 M $\text{CH}_3\text{CO}_2\text{H}$ <sup>[2]</sup>
0.0	0.0	1.00	2.87

**Table 14.4**

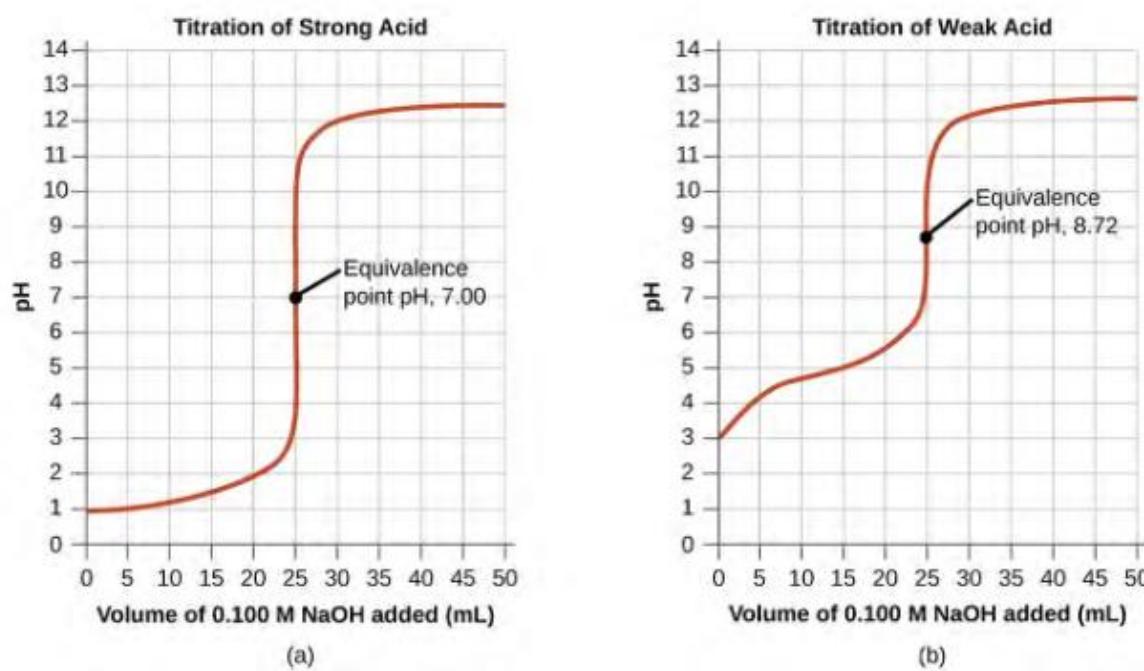
1. Titration of 25.00 mL of 0.100 M HCl (0.00250 mol of HCl) with 0.100 M NaOH.
2. Titration of 25.00 mL of 0.100 M  $\text{CH}_3\text{CO}_2\text{H}$  (0.00250 mol of  $\text{CH}_3\text{CO}_2\text{H}$ ) with 0.100 M NaOH.

**pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base**

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl <sup>[3]</sup>	pH Values 0.100 M CH <sub>3</sub> CO <sub>2</sub> H <sup>[4]</sup>
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

**Table 14.4**

The simplest acid-base reactions are those of a strong acid with a strong base. **Table 14.4** shows data for the titration of a 25.0-mL sample of 0.100 M hydrochloric acid with 0.100 M sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in **Figure 14.21**, in a form that is called a **titration curve**. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (**Table 14.4** and **Figure 14.21**).

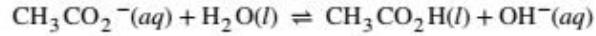


**Figure 14.21** (a) The titration curve for the titration of 25.00 mL of 0.100 M CH<sub>3</sub>CO<sub>2</sub>H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 M acetic acid (a weak acid) with 0.100 M sodium hydroxide and compare the titration curve with that of the strong acid.

**Table 14.4** gives the pH values during the titration, **Figure 14.21** shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

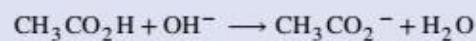


After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

### Example 14.22

#### Titration of a Weak Acid with a Strong Base

The titration curve shown in **Figure 14.23** is for the titration of 25.00 mL of 0.100 M CH<sub>3</sub>CO<sub>2</sub>H with 0.100 M NaOH. The reaction can be represented as:



(a) What is the initial pH before any amount of the NaOH solution has been added?  $K_a = 1.8 \times 10^{-5}$  for  $\text{CH}_3\text{CO}_2\text{H}$ .

(b) Find the pH after 25.00 mL of the NaOH solution have been added.

(c) Find the pH after 12.50 mL of the NaOH solution has been added.

(d) Find the pH after 37.50 mL of the NaOH solution has been added.

### Solution

(a) Assuming that the dissociated amount is small compared to 0.100 M, we find that:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{CO}_2\text{H}]_0}, \quad \text{and}$$

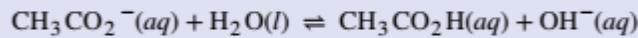
$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{CH}_3\text{CO}_2\text{H}]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$\text{pH} = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and  $\text{CH}_3\text{CO}_2\text{H}$  are equal because the amounts of the solutions and their concentrations are the same. All of the  $\text{CH}_3\text{CO}_2\text{H}$  has been converted to  $\text{CH}_3\text{CO}_2^-$ . The concentration of the  $\text{CH}_3\text{CO}_2^-$  ion is:

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ M} \text{CH}_3\text{CO}_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for  $\text{CH}_3\text{CO}_2^-$ :



so we must determine  $K_b$  for the base by using the ion product constant for water:

$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]}$$

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}, \text{ so } \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = \frac{[\text{H}^+]}{K_a}.$$

Since  $K_w = [\text{H}^+][\text{OH}^-]$ :

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

Let us denote the concentration of each of the products of this reaction,  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{OH}^-$ , as  $x$ . Using the assumption that  $x$  is small compared to 0.0500 M,  $K_b = \frac{x^2}{0.0500 \text{ M}}$ , and then:

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

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (a), 25.00 mL of the NaOH solution was added, and so practically all the  $\text{CH}_3\text{CO}_2\text{H}$  was converted into  $\text{CH}_3\text{CO}_2^-$ . In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the  $\text{CH}_3\text{CO}_2\text{H}$  is converted into  $\text{CH}_3\text{CO}_2^-$ . The total initial number of moles of  $\text{CH}_3\text{CO}_2\text{H}$  is

$0.02500\text{L} \times 0.100\text{ M} = 0.00250\text{ mol}$ , and so after adding the NaOH, the numbers of moles of  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2^-$  are both approximately equal to  $\frac{0.00250\text{ mol}}{2} = 0.00125\text{ mol}$ , and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_a) + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

(as the concentrations of  $\text{CH}_3\text{CO}_2^-$  and  $\text{CH}_3\text{CO}_2\text{H}$  are the same)

Thus:

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

(the pH = the  $pK_a$  at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is  $0.03750\text{ L} \times 0.100\text{ M} = 0.003750\text{ mol}$  NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

$$[\text{OH}^-] = \frac{(0.003750\text{ mol} - 0.00250\text{ mol})}{0.06250\text{ L}} = 2.00 \times 10^{-2}\text{ M}$$

So:

$$\text{pOH} = -\log(2.00 \times 10^{-2}) = 1.70, \text{ and pH} = 14.00 - 1.70 = 12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

### Check Your Learning

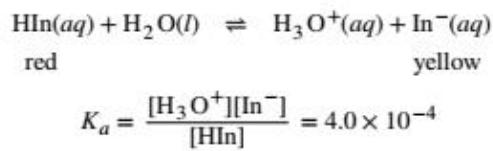
Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 M  $\text{HCOOH}(aq)$  (formic acid) and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

**Answer:** 0.00 mL: 2.37; 15.0 mL: 3.92; 25.0 mL: 8.29; 30.0 mL: 12.097

## Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than  $5.0 \times 10^{-9}\text{ M}$  ( $\text{pH} < 8.3$ ). In more basic solutions where the hydronium ion concentration is less than  $5.0 \times 10^{-9}\text{ M}$  ( $\text{pH} > 8.3$ ), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:



The anion of methyl orange,  $\text{In}^-$ , is yellow, and the nonionized form,  $\text{HIn}$ , is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species  $\text{In}^-$  and  $\text{HIn}$ . If most of the indicator (typically about 60–90% or more) is present as  $\text{In}^-$ , then we see the color of the  $\text{In}^-$  ion, which would be yellow for methyl orange. If most is present as  $\text{HIn}$ , then we see the color of the  $\text{HIn}$  molecule: red for methyl orange. For methyl orange, we can rearrange the equation for  $K_a$  and write:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{\text{[substance with yellow color]}}{\text{[substance with red color]}} = \frac{K_a}{[\text{H}_3\text{O}^+]}$$

This shows us how the ratio of  $\frac{[\text{In}^-]}{[\text{HIn}]}$  varies with the concentration of hydronium ion.

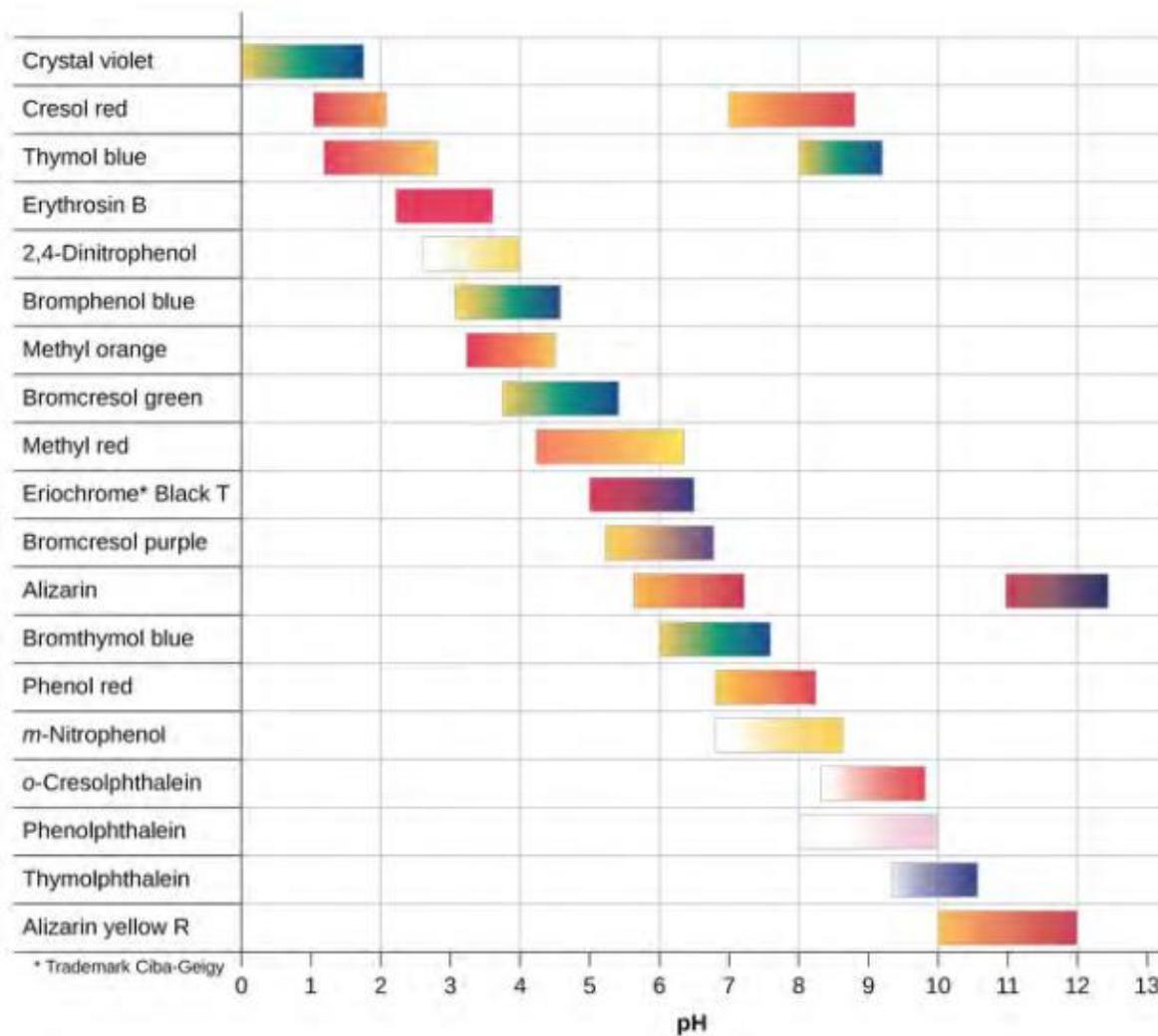
The above expression describing the indicator equilibrium can be rearranged:

$$\begin{aligned}\frac{[\text{H}_3\text{O}^+]}{K_a} &= \frac{[\text{HIn}]}{[\text{In}^-]} \\ \log\left(\frac{[\text{H}_3\text{O}^+]}{K_a}\right) &= \log\left(\frac{[\text{HIn}]}{[\text{In}^-]}\right) \\ \log([\text{H}_3\text{O}^+]) - \log(K_a) &= -\log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \\ -\text{pH} + \text{p}K_a &= -\log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \\ \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \text{ or pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)\end{aligned}$$

The last formula is the same as the Henderson-Hasselbalch equation, which can be used to describe the equilibrium of indicators.

When  $[\text{H}_3\text{O}^+]$  has the same numerical value as  $K_a$ , the ratio of  $[\text{In}^-]$  to  $[\text{HIn}]$  is equal to 1, meaning that 50% of the indicator is present in the red form ( $\text{HIn}$ ) and 50% is in the yellow ionic form ( $\text{In}^-$ ), and the solution appears orange in color. When the hydronium ion concentration increases to  $8 \times 10^{-4} M$  (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of  $4 \times 10^{-5} M$  (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the **color-change interval** of methyl orange; the pronounced color change takes place between these pH values.

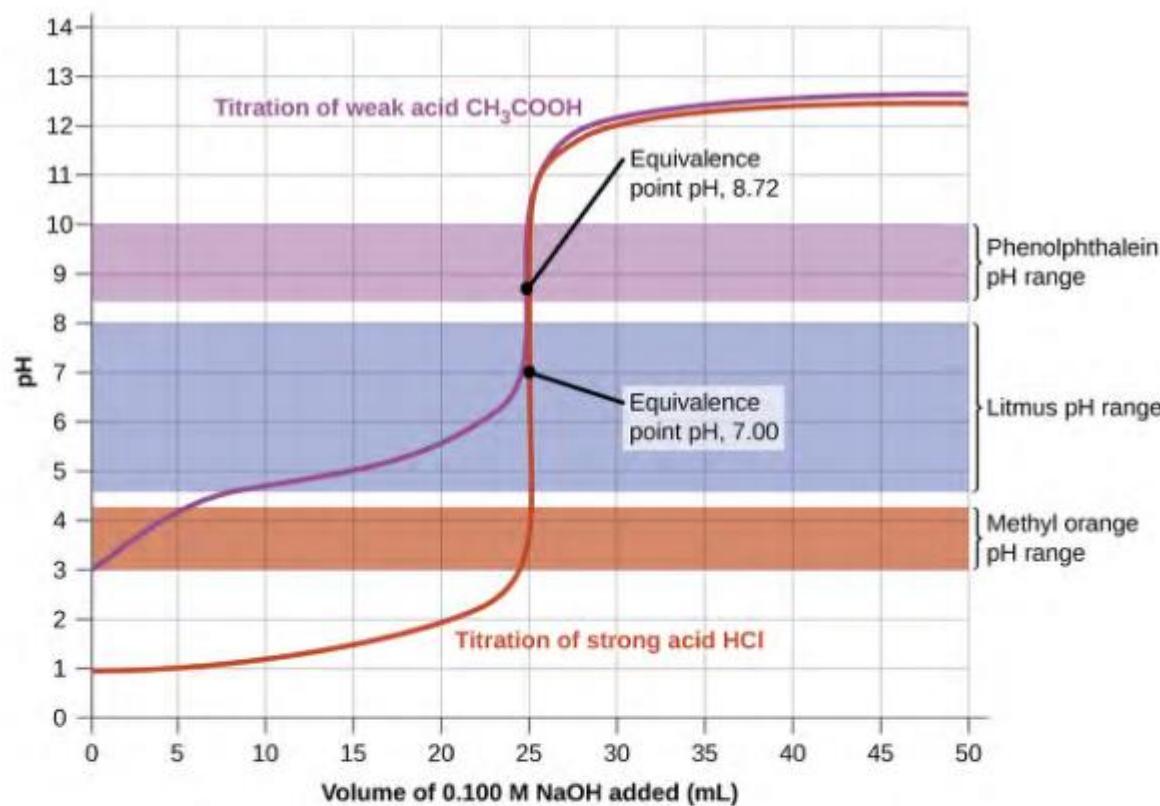
There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. **Figure 14.22** presents several indicators, their colors, and their color-change intervals.



**Figure 14.22** This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

The color change intervals of three indicators are shown in **Figure 14.23**. The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.



**Figure 14.23** The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH<sub>3</sub>CO<sub>2</sub>H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the CH<sub>3</sub>CO<sub>2</sub>H titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure 14.23 shows, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure 14.23 shows us that methyl orange would be completely useless as an indicator for the CH<sub>3</sub>CO<sub>2</sub>H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

## Key Terms

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**acid ionization** reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

**acid ionization constant ( $K_a$ )** equilibrium constant for the ionization of a weak acid

**acid-base indicator** organic acid or base whose color changes depending on the pH of the solution it is in

**acidic** describes a solution in which  $[H_3O^+] > [OH^-]$

**amphiprotic** species that may either gain or lose a proton in a reaction

**amphoteric** species that can act as either an acid or a base

**autoionization** reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

**base ionization** reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

**base ionization constant ( $K_b$ )** equilibrium constant for the ionization of a weak base

**basic** describes a solution in which  $[H_3O^+] < [OH^-]$

**Brønsted-Lowry acid** proton donor

**Brønsted-Lowry base** proton acceptor

**buffer** mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

**buffer capacity** amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

**color-change interval** range in pH over which the color change of an indicator takes place

**conjugate acid** substance formed when a base gains a proton

**conjugate base** substance formed when an acid loses a proton

**diprotic acid** acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

**diprotic base** base capable of accepting two protons. The protons are accepted in two steps

**Henderson-Hasselbalch equation** equation used to calculate the pH of buffer solutions

**ion-product constant for water ( $K_w$ )** equilibrium constant for the autoionization of water

**leveling effect of water** any acid stronger than  $H_3O^+$ , or any base stronger than  $OH^-$  will react with water to form  $H_3O^+$ , or  $OH^-$ , respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

**monoprotic acid** acid containing one ionizable hydrogen atom per molecule

**neutral** describes a solution in which  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

**oxyacid** compound containing a nonmetal and one or more hydroxyl groups

**percent ionization** ratio of the concentration of the ionized acid to the initial acid concentration, times 100

**pH** logarithmic measure of the concentration of hydronium ions in a solution

**pOH** logarithmic measure of the concentration of hydroxide ions in a solution

**stepwise ionization** process in which an acid is ionized by losing protons sequentially

**titration curve** plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

**triprotic acid** acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

## Key Equations

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- $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  (at 25 °C)

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$

- $\text{pOH} = -\log[\text{OH}^-]$

- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

- $[\text{OH}^-] = 10^{-\text{pOH}}$

- $\text{pH} + \text{pOH} = \text{p}K_w = 14.00$  at 25 °C

- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

- $K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$

- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$

- $\text{Percent ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$

- $\text{p}K_a = -\log K_a$

- $\text{p}K_b = -\log K_b$

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

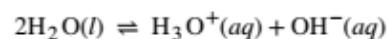
## Summary

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### 14.1 Brønsted-Lowry Acids and Bases

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an

acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion,  $\text{H}_3\text{O}^+$ , and the hydroxide ion,  $\text{OH}^-$  when it undergoes autoionization:



The ion product of water,  $K_w$  is the equilibrium constant for the autoionization reaction:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

### 14.2 pH and pOH

The concentration of hydronium ion in a solution of an acid in water is greater than  $1.0 \times 10^{-7} \text{ M}$  at  $25^\circ\text{C}$ . The concentration of hydroxide ion in a solution of a base in water is greater than  $1.0 \times 10^{-7} \text{ M}$  at  $25^\circ\text{C}$ . The concentration of  $\text{H}_3\text{O}^+$  in a solution can be expressed as the pH of the solution;  $\text{pH} = -\log \text{H}_3\text{O}^+$ . The concentration of  $\text{OH}^-$  can be expressed as the pOH of the solution:  $\text{pOH} = -\log[\text{OH}^-]$ . In pure water,  $\text{pH} = 7.00$  and  $\text{pOH} = 7.00$ .

### 14.3 Relative Strengths of Acids and Bases

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ( $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ ), and they increase down a group ( $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ ). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ( $\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$ ). The strengths of oxyacids also increase as the electronegativity of the central element increases ( $\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$ ).

### 14.4 Hydrolysis of Salt Solutions

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic.

Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative  $K_a$  and  $K_b$  of the ions involved.

### 14.5 Polyprotic Acids

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of  $K_a$  of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

### 14.6 Buffers

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

### 14.7 Acid-Base Titrations

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

## Exercises

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### 14.1 Brønsted-Lowry Acids and Bases

1. Write equations that show  $\text{NH}_3$  as both a conjugate acid and a conjugate base.
2. Write equations that show  $\text{H}_2\text{PO}_4^-$  acting both as an acid and as a base.
3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
  - (a)  $\text{H}_3\text{O}^+$
  - (b) HCl
  - (c)  $\text{NH}_3$
  - (d)  $\text{CH}_3\text{CO}_2\text{H}$
  - (e)  $\text{NH}_4^+$
  - (f)  $\text{HSO}_4^-$
4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
  - (a)  $\text{HNO}_3$
  - (b)  $\text{PH}_4^+$
  - (c)  $\text{H}_2\text{S}$
  - (d)  $\text{CH}_3\text{CH}_2\text{COOH}$
  - (e)  $\text{H}_2\text{PO}_4^-$
  - (f)  $\text{HS}^-$
5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
  - (a)  $\text{H}_2\text{O}$
  - (b)  $\text{OH}^-$
  - (c)  $\text{NH}_3$
  - (d)  $\text{CN}^-$
  - (e)  $\text{S}^{2-}$
  - (f)  $\text{H}_2\text{PO}_4^-$