

The differences between the various acid–base concepts are not concerned with which is right, but which is most convenient to use in a particular situation.

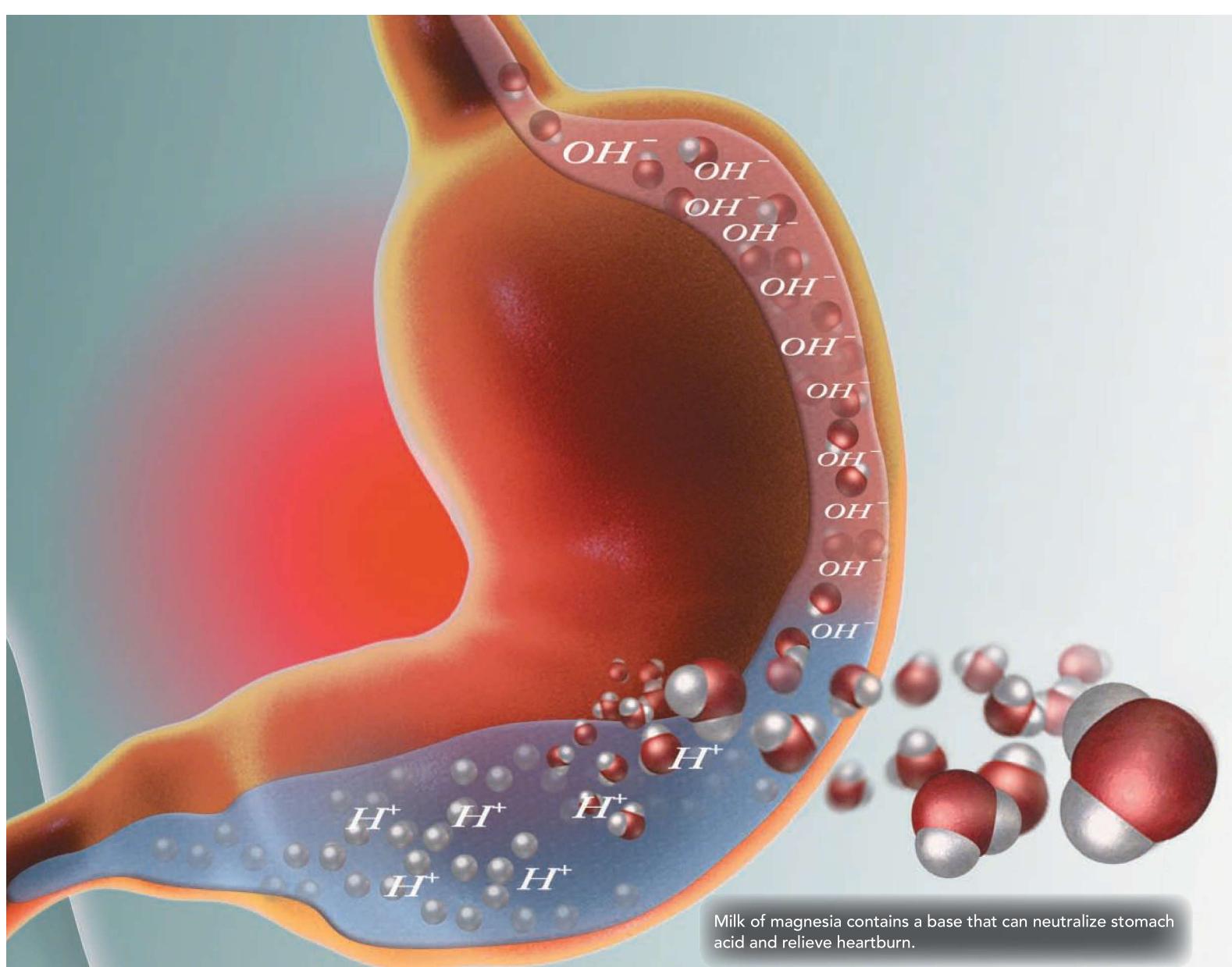
—JAMES E. HUHEEY (1935—)

CHAPTER

17

Acids and Bases

In this chapter, we apply the equilibrium concepts learned in the previous chapter to acid–base phenomena. Acids are common in many foods, such as limes, lemons, and vinegar, and in a number of consumer products, such as toilet cleaners and batteries. Bases are less common in foods but are key ingredients in consumer products such as drain openers and antacids. We will examine three different models for acid–base behavior, all of which define that behavior differently. In spite of their differences, the three models coexist, each being useful at explaining a particular range of acid–base phenomena. We also examine how to calculate the acidity or basicity of solutions and define a useful scale, called the pH scale, to quantify acidity and basicity. These types of calculations often involve solving the kind of equilibrium problems that we explored in Chapter 16.



Milk of magnesia contains a base that can neutralize stomach acid and relieve heartburn.

- 17.1** Heartburn 731
- 17.2** The Nature of Acids and Bases 732
- 17.3** Definitions of Acids and Bases 734
- 17.4** Acid Strength and the Acid Ionization Constant (K_a) 737
- 17.5** Autoionization of Water and pH 740
- 17.6** Finding the $[H_3O^+]$ and pH of Strong and Weak Acid Solutions 745
- 17.7** Base Solutions 754

- 17.8** The Acid–Base Properties of Ions and Salts 758
 - 17.9** Polyprotic Acids 765
 - 17.10** Acid Strength and Molecular Structure 770
 - 17.11** Lewis Acids and Bases 772
 - 17.12** Acid Rain 773
- LEARNING OUTCOMES** 778

17.1 Heartburn

Heartburn is a painful burning sensation in the esophagus (the tube that joins the throat to the stomach) just below the chest. The pain is caused by hydrochloric acid (HCl), which the stomach excretes to kill microorganisms and to activate enzymes that break down food. Hydrochloric acid sometimes backs up out of the stomach and into the esophagus, a phenomenon called *acid reflux*. Recall from Section 5.7 that acids

Bases were first defined in Section 5.7.

The bicarbonate ion neutralizes stomach acid according to the reaction: $\text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$.

The concentration of stomach acid, $[\text{H}_3\text{O}^+]$, varies from about 0.01 to 0.1 M.

For a review of acid naming, see Section 3.6.

Litmus paper contains dyes that change color in the presence of acids and bases.

The formula for acetic acid can also be written as CH_3COOH .

are substances that—by one definition that we elaborate on shortly—produce H^+ ions in solution. When hydrochloric acid from the stomach comes in contact with the lining of the esophagus, the H^+ ions irritate the tissues, resulting in the burning sensation. Some of the acid can work its way into the lower throat and even the mouth, producing pain in the throat and a sour taste (characteristic of acids) in the mouth. Almost everyone experiences heartburn at some time, most commonly after a large meal when the stomach is full. Strenuous activity or lying in a horizontal position after a large meal increases the likelihood of stomach acid reflux and the resulting heartburn.

The simplest way to relieve mild heartburn is to swallow repeatedly. Saliva contains the bicarbonate ion (HCO_3^-), which acts as a base and, when swallowed, neutralizes some of the acid in the esophagus. Later in this chapter, we will see how bicarbonate acts as a base. You can also treat heartburn with antacids such as Tums, milk of magnesia, or Mylanta. These over-the-counter medications contain more base than saliva does and therefore are effective at neutralizing esophageal acid. We look at the bases in these medicines more carefully later (see *Chemistry and Medicine: What's in My Antacid?* in Section 17.7).

For some people, heartburn becomes a chronic problem. Gastroesophageal reflux disease (GERD) is the medical condition associated with chronic heartburn. In patients with GERD, the band of muscles (called the esophageal sphincter) at the bottom of the esophagus just above the stomach does not close tightly enough, allowing stomach contents to leak back into the esophagus on a regular basis. Medical researchers have developed a wireless sensor to help diagnose and evaluate treatment of GERD. Using a tube that goes down through the throat, a physician attaches the sensor to tissues in the patient's esophagus. The sensor reads pH—a measure of acidity that we discuss in Section 17.5—and transmits the readings to a recorder worn on the patient's body. The patient goes about his or her normal activities for the next few days while the recorder monitors esophageal pH. The physician then reads the record of esophageal pH to make a diagnosis or evaluate treatment.

In this chapter, we examine acid and base behavior. Acids and bases are not only important to our health (as we have just seen), but are also found in many household products, foods, medicines, and of course in nearly every chemistry laboratory. Acid-base chemistry is central to much of biochemistry and molecular biology. The building blocks of proteins, for example, are acids (called amino acids), and the molecules that carry the genetic code in DNA are bases.

17.2 The Nature of Acids and Bases

Acids have the following general properties: a sour taste, the ability to dissolve many metals, the ability to turn blue litmus paper red, and the ability to neutralize bases. Table 17.1 lists some common acids.

TABLE 17.1 ■ Some Common Acids

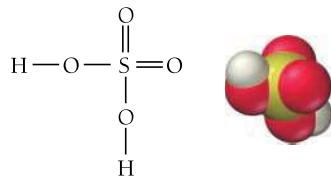
Name	Occurrence/Uses
Hydrochloric acid (HCl)	Metal cleaning; food preparation; ore refining; primary component of stomach acid
Sulfuric acid (H_2SO_4)	Fertilizer and explosives manufacturing; dye and glue production; in automobile batteries; electroplating of copper
Nitric acid (HNO_3)	Fertilizer and explosives manufacturing; dye and glue production
Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)	Plastic and rubber manufacturing; food preservation; active component of vinegar
Citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$)	In citrus fruits such as lemons and limes; used to adjust pH in foods and beverages
Carbonic acid (H_2CO_3)	In carbonated beverages due to the reaction of carbon dioxide with water
Hydrofluoric acid (HF)	Metal cleaning; glass frosting and etching
Phosphoric acid (H_3PO_4)	Fertilizer manufacturing; biological buffering; beverage preservation

You can find hydrochloric acid in most chemistry laboratories. In industry, it is used to clean metals, to prepare and process some foods, and to refine metal ores. As we discussed in Section 17.1, hydrochloric acid is also the main component of stomach acid.



Hydrochloric acid

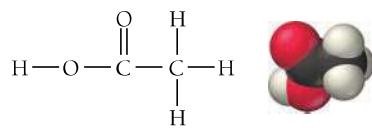
Sulfuric acid and nitric acid are also common in the laboratory. They play major roles in the manufacture of fertilizers, explosives, dyes, and glues. Sulfuric acid, produced in larger quantities than any other industrial chemical, is used in most automobile batteries.



Sulfuric acid



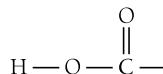
Nitric acid



Acetic acid

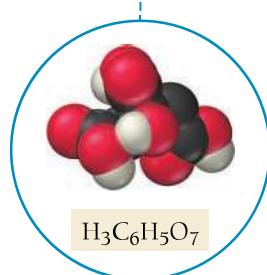
You can probably find acetic acid in your home—it is the active component of vinegar. It is also produced in improperly stored wines. The word *vinegar* originates from the French words *vin aigre*, which means “sour wine.” Wine experts consider the presence of vinegar in wines a serious fault, since it makes the wine taste like salad dressing.

Acetic acid is a **carboxylic acid**, an acid that contains the following grouping of atoms:



Carboxylic acid group

Carboxylic acids are often found in substances derived from living organisms. Other examples of carboxylic acids are citric acid, found in lemons and limes, and malic acid, found in apples, grapes, and wine.



Citric acid



Malic acid



▲ Acetic acid makes vinegar taste sour.

▲ Citrus fruits, apples, and grapes all contain acids.



▲ Many common household products and remedies contain bases.

Coffee is acidic overall, but bases present in coffee—such as caffeine—and other compounds impart a bitter flavor.

TABLE 17.2 ■ Common Bases

Name	Occurrence / Uses
Sodium hydroxide (NaOH)	Petroleum processing; soap and plastic manufacturing
Potassium hydroxide (KOH)	Cotton processing; electroplating; soap production; batteries
Sodium bicarbonate (NaHCO ₃)	Sold as baking soda; antacid; source of CO ₂
Sodium carbonate (Na ₂ CO ₃)	Glass and soap manufacturing; general cleanser; water softener
Ammonia (NH ₃)	Detergent; fertilizer and explosives manufacturing; synthetic fiber production

Bases have the following general properties: a bitter taste, a slippery feel, the ability to turn red litmus paper blue, and the ability to neutralize acids. Because of their bitterness, bases are less common in foods than are acids. Our aversion to the taste of bases is probably an evolutionary adaptation to warn us against **alkaloids**, organic bases found in plants that are often poisonous. (For example, the active component of hemlock—the poisonous plant that killed the Greek philosopher Socrates—is the alkaloid coniine.) Nonetheless, some foods, such as coffee and chocolate (especially dark chocolate), contain bitter flavors. Many people enjoy the bitterness, but only after acquiring the taste over time.

Bases feel slippery because they react with oils on the skin to form soap-like substances. Some household cleaning solutions, such as ammonia, are basic and have the characteristic slippery feel of a base. Bases turn red litmus paper blue; in the laboratory, litmus paper is routinely used to test the basicity of solutions.

Some common bases are listed in Table 17.2. You can find sodium hydroxide and potassium hydroxide in most chemistry laboratories. They are used in petroleum and cotton processing and in soap and plastic manufacturing. Sodium hydroxide is the active ingredient in products such as Drāno that unclog drains. In many homes, you can find sodium bicarbonate in the medicine cabinet (it is an active ingredient in some antacids) as well as in the kitchen (labeled as baking soda).

ANSWER NOW!



17.1 Cc Conceptual Connection

WATCH NOW!

KEY CONCEPT VIDEO 17.3

Definitions of Acids and Bases

ACID PROPERTIES Which property is not associated with an acid?

- (a) dissolves metals
- (b) turns blue litmus red
- (c) has a bitter taste

17.3

Definitions of Acids and Bases

What are the key characteristics of the molecules and ions that exhibit acid and base behavior? In this chapter, we examine three different definitions: the Arrhenius definition, the Brønsted-Lowry definition, and the Lewis definition. Why three definitions, and which one is correct? As inorganic chemist and author James Huheey notes in the quotation that opens this chapter, no single definition is “correct.” Rather, each definition is useful in a given instance. We discuss the Lewis definition of acids and bases in Section 17.11; here we discuss the other two.

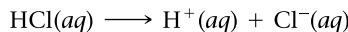
The Arrhenius Definition

In the 1880s, Swedish chemist Svante Arrhenius (1859–1927) proposed the following molecular definitions of acids and bases:

Acid: A substance that produces H⁺ ions in aqueous solution.

Base: A substance that produces OH⁻ ions in aqueous solution.

According to the **Arrhenius definition**, HCl is an acid because it produces H^+ ions in solution (Figure 17.1►):



Hydrogen chloride (HCl) is a covalent compound and does not contain ions. However, in water it *ionizes* completely to form $\text{H}^+(aq)$ ions and $\text{Cl}^-(aq)$ ions. The H^+ ions are highly reactive. In aqueous solution, the H^+ ions bond to water to form H_3O^+ :



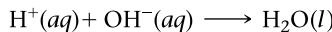
The H_3O^+ ion is the **hydronium ion**. In water, H^+ ions *always* associate with H_2O molecules to form hydronium ions and other associated species with the general formula $\text{H}(\text{H}_2\text{O})_n^+$. For example, an H^+ ion can associate with two water molecules to form $\text{H}(\text{H}_2\text{O})_2^+$, with three to form $\text{H}(\text{H}_2\text{O})_3^+$, and so on. Chemists often use $\text{H}^+(aq)$ and $\text{H}_3\text{O}^+(aq)$ interchangeably to mean the same thing—an H^+ ion that has been solvated (or dissolved) in water.

According to the Arrhenius definition, NaOH is a base because it produces OH^- ions in solution (Figure 17.2►):



NaOH is an ionic compound and therefore contains Na^+ and OH^- ions. When NaOH is added to water, it *dissociates* (breaks apart) into its component ions.

Under the Arrhenius definition, acids and bases combine to form water, neutralizing each other in the process:



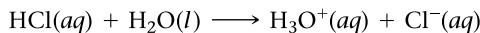
The Brønsted–Lowry Definition

A second, more widely applicable definition of acids and bases, the **Brønsted–Lowry definition**, was introduced in 1923. This definition focuses on the *transfer of H^+ ions* in an acid–base reaction. Since an H^+ ion is a proton—a hydrogen atom without its electron—this definition focuses on the idea of a proton donor and a proton acceptor:

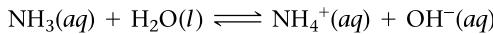
Acid: proton (H^+ ion) *donor*

Base: proton (H^+ ion) *acceptor*

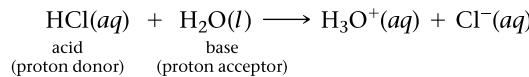
According to this definition, HCl is an acid because, in solution, it donates a proton to water:



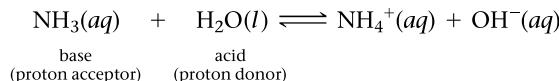
This definition clearly describes what happens to the H^+ ion from an acid—it associates with a water molecule to form H_3O^+ (a hydronium ion). The Brønsted–Lowry definition also applies nicely to bases (such as NH_3) that do not inherently contain OH^- ions but still produce OH^- ions in solution. According to the Brønsted–Lowry definition, NH_3 is a base because it accepts a proton from water:



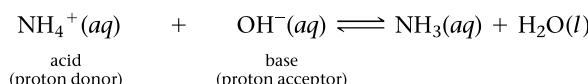
According to the Brønsted–Lowry definition, acids (proton donors) and bases (proton acceptors) always occur together in an acid–base reaction. In the reaction between HCl and H_2O , HCl is the proton donor (acid) and H_2O is the proton acceptor (base):



In the reaction between NH_3 and H_2O , H_2O is the proton donor (acid) and NH_3 is the proton acceptor (base):

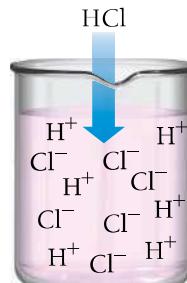


According to the Brønsted–Lowry definition, some substances—such as water in the previous two equations—can act as acids *or* bases. Substances that can act as acids or bases are **amphoteric**. Notice what happens when we reverse an equation representing a Brønsted–Lowry acid–base reaction:



Arrhenius Acid

An Arrhenius acid produces H^+ ions in solution.



▲ FIGURE 17.1 Arrhenius Acid

Arrhenius Base

An Arrhenius base produces OH^- ions in solution.



NaOH(aq) → Na⁺(aq) + OH⁻(aq)

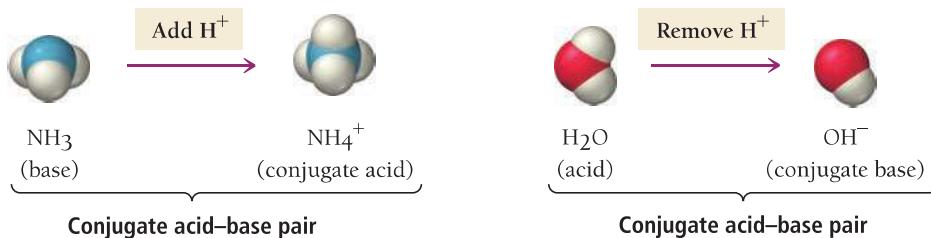
▲ FIGURE 17.2 Arrhenius Base

All Arrhenius acids and bases are acids and bases under the Brønsted–Lowry definition. However, some Brønsted–Lowry acids and bases cannot be classified as Arrhenius acids and bases.

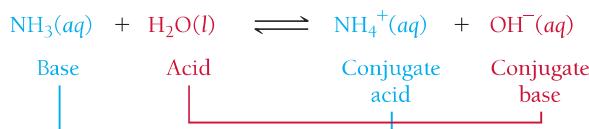
► FIGURE 17.3 Conjugate Acid–Base Pairs

Conjugate Acid–Base Pairs

A conjugate acid–base pair consists of two substances related to each other by the transfer of a proton.



In this reaction, NH_4^+ is the proton donor (acid) and OH^- is the proton acceptor (base). The substance that was the base (NH_3) has become the acid (NH_4^+) and vice versa. NH_4^+ and NH_3 are often referred to as a **conjugate acid–base pair**, two substances related to each other by the transfer of a proton (Figure 17.3▲). A **conjugate acid** is any base to which a proton has been added, and a **conjugate base** is any acid from which a proton has been removed. Going back to the original forward reaction, we can identify the conjugate acid–base pairs:



Summarizing the Brønsted–Lowry Definition of Acids and Bases:

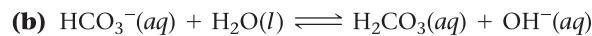
- A base accepts a proton and becomes a conjugate acid.
- An acid donates a proton and becomes a conjugate base.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.1

EXAMPLE 17.1 Identifying Brønsted–Lowry Acids and Bases and Their Conjugates

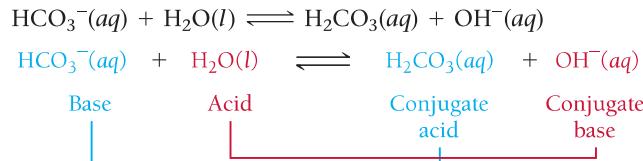
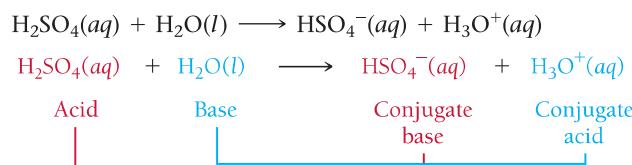
In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.



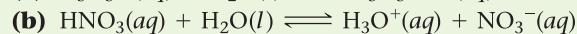
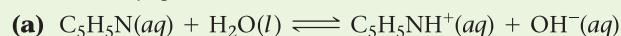
SOLUTION

(a) Because H_2SO_4 donates a proton to H_2O in this reaction, it is the acid (proton donor). After H_2SO_4 donates the proton, it becomes HSO_4^- , the conjugate base. Because H_2O accepts a proton, it is the base (proton acceptor). After H_2O accepts the proton, it becomes H_3O^+ , the conjugate acid.

(b) Because H_2O donates a proton to HCO_3^- in this reaction, it is the acid (proton donor). After H_2O donates the proton, it becomes OH^- , the conjugate base. Because HCO_3^- accepts a proton, it is the base (proton acceptor). After HCO_3^- accepts the proton, it becomes H_2CO_3 , the conjugate acid.



FOR PRACTICE 17.1 In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.



CONJUGATE ACID-BASE PAIRS

Which pair is *not* a conjugate acid-base pair?

- (a) $(CH_3)_3N$; $(CH_3)_3NH^+$
- (b) H_2SO_4 ; H_2SO_3
- (c) HNO_2 ; NO_2^-



ANSWER NOW!



17.4

Acid Strength and the Acid Ionization Constant (K_a)

The strength of an electrolyte, first discussed in Section 5.4, depends on the extent of its dissociation into its component ions in solution. A **strong electrolyte** completely dissociates into ions in solution, whereas a **weak electrolyte** only partially dissociates. We define strong and weak acids accordingly. A **strong acid** completely ionizes in solution, whereas a **weak acid** only partially ionizes. In other words, the strength of an acid depends on the equilibrium:



In the preceding equation, HA is a generic formula for an acid. If the equilibrium lies far to the right, the acid is strong—it completely ionizes. If the equilibrium lies to the left, the acid is weak—only a small percentage of the acid molecules ionize. Of course, the range of acid strength is continuous, but for most purposes, the categories of strong and weak are useful.

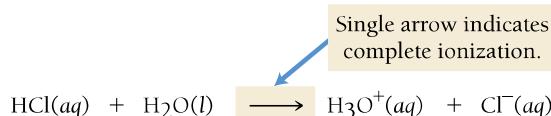
WATCH NOW!

KEY CONCEPT VIDEO 17.4

Acid Strength and the Acid Ionization Constant

Strong Acids

Hydrochloric acid (HCl) is an example of a strong acid:



An HCl solution contains virtually no intact HCl; the HCl has essentially all ionized to form $H_3O^+(aq)$ and $Cl^-(aq)$ (Figure 17.4▼). A 1.0 M HCl solution has an H_3O^+ concentration of 1.0 M. Abbreviating the concentration of H_3O^+ as $[H_3O^+]$, we say that a 1.0 M HCl solution has $[H_3O^+] = 1.0\text{ M}$.

Table 17.3 lists the six important strong acids. The first five acids in the table are **monoprotic acids**, acids containing only one ionizable proton. Sulfuric acid is an example of a **diprotic acid**, an acid containing two ionizable protons.

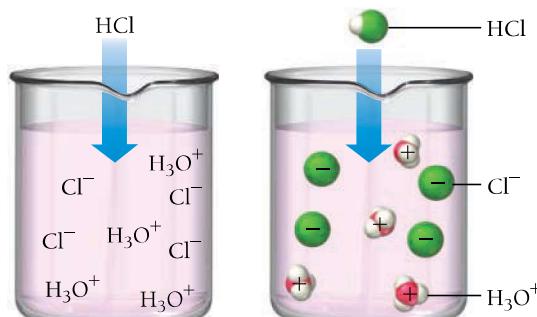
An ionizable proton is one that ionizes in solution. We discuss polyprotic acids in more detail in Section 17.9.

TABLE 17.3 ■ Strong Acids

Hydrochloric acid (HCl)	Nitric acid (HNO_3)
Hydrobromic acid (HBr)	Perchloric acid ($HClO_4$)
Hydroiodic acid (HI)	Sulfuric acid (H_2SO_4) (diprotic)

A Strong Acid

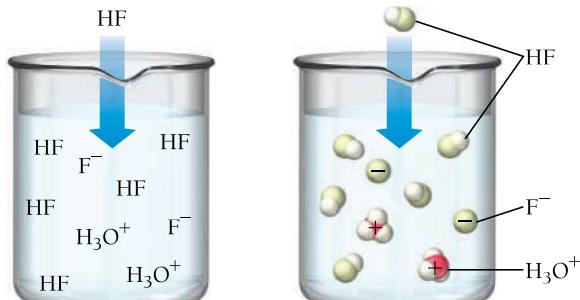
When HCl dissolves in water, it ionizes completely.



◀ FIGURE 17.4 Ionization of a Strong Acid HCl completely ionizes in water to form H_3O^+ and Cl^- . The solution contains virtually no intact HCl.

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.

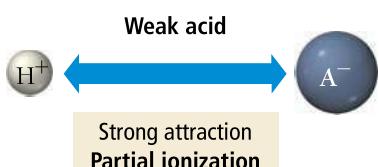
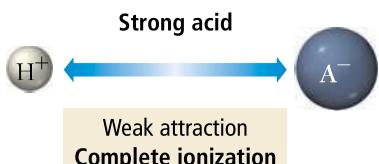


▲ FIGURE 17.5 Ionization of a Weak Acid HF partially ionizes in water to form H_3O^+ and F^- . The solution contains many intact HF molecules.

Weak Acids

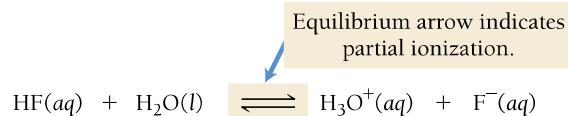
In contrast to HCl, HF is a weak acid, one that does not completely ionize in solution:

The terms **strong** and **weak** acids are often confused with the terms **concentrated** and **dilute** acids. Can you articulate the difference between these terms?



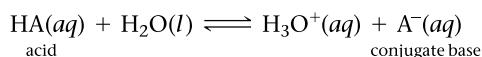
▲ FIGURE 17.6 Ionic Attraction and Acid Strength In a strong acid, the attraction between H^+ and A^- is weak, resulting in complete ionization. In a weak acid, the attraction between H^+ and A^- is strong, resulting in only partial ionization.

Alternatively, we can write the formulas for acetic acid and formic acid as CH_3COOH and HCOOH , respectively, to indicate that in these compounds the only H that ionizes is the one attached to an oxygen atom.



An HF solution contains a large number of intact (or un-ionized) HF molecules; it also contains some $\text{H}_3\text{O}^+(aq)$ and $\text{F}^-(aq)$ (Figure 17.5▲). In other words, a 1.0 M HF solution has an $[\text{H}_3\text{O}^+]$ that is much less than 1.0 M because only some of the HF molecules ionize to form H_3O^+ .

The degree to which an acid is strong or weak depends on the attraction between the anion of the acid (the conjugate base) and the hydrogen ion, relative to the attractions of these ions to water. Recall that HA is a generic formula for an acid. The degree to which the following reaction proceeds in the forward direction depends on the strength of the attraction between H^+ and A^- :



If the attraction between H^+ and A^- is *weak*, then the reaction favors the forward direction and the acid is *strong*. If the attraction between H^+ and A^- is *strong*, then the reaction favors the reverse direction and the acid is *weak*, as shown in Figure 17.6.

For example, in HCl, on one hand, the conjugate base (Cl^-) has a relatively weak attraction to H^+ —the reverse reaction does not occur to any significant extent. In HF, on the other hand, the conjugate base (F^-) has a greater attraction to H^+ —the reverse reaction occurs to a significant degree. *In general, the stronger the acid, the weaker the conjugate base and vice versa.* If the forward reaction (that of the acid) has a high tendency to occur, then the reverse reaction (that of the conjugate base) has a low tendency to occur. Table 17.4 lists some common weak acids.

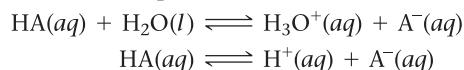
Notice that two of the weak acids in Table 17.4 are diprotic, meaning that they have two ionizable protons, and one is a **triprotic acid** (three ionizable protons). We discuss polyprotic acids in more detail in Section 17.9.

TABLE 17.4 ■ Some Weak Acids

Hydrofluoric acid (HF)	Sulfurous acid (H_2SO_3) (<i>diprotic</i>)
Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)	Carbonic acid (H_2CO_3) (<i>diprotic</i>)
Formic acid (HCHO_2)	Phosphoric acid (H_3PO_4) (<i>triprotic</i>)

The Acid Ionization Constant (K_a)

We quantify the relative strength of a weak acid with the **acid ionization constant** (K_a), which is the equilibrium constant for the ionization reaction of the weak acid. As we saw in Section 16.3, for the two equivalent reactions:



the equilibrium constant is:

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

Since $[\text{H}_3\text{O}^+]$ is equivalent to $[\text{H}^+]$, both forms of the expression are equal. Although the ionization constants for all weak acids are relatively small (otherwise the acid would not be a weak acid), they do vary in magnitude. The smaller the constant, the less the acid ionizes, and the weaker the acid. Table 17.5 lists the acid ionization constants for a number of common weak acids in order of decreasing acid strength. Appendix IIC contains a more complete list.

Sometimes K_a is referred to as the acid dissociation constant.

Recall from Chapter 16 that the concentrations of pure solids or pure liquids are not included in the expression for K_c ; therefore, $\text{H}_2\text{O}(l)$ is not included in the expression for K_a .

TABLE 17.5 ■ Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25 °C

Acid	Formula	Structural Formula	Ionization Reaction	K_a	pK_a
Chlorous acid	HClO_2	$\text{H}-\text{O}-\text{Cl}=\text{O}$	$\text{HClO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq)$	1.1×10^{-2}	1.96
Nitrous acid	HNO_2	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$	4.6×10^{-4}	3.34
Hydrofluoric acid	HF	$\text{H}-\text{F}$	$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$	6.8×10^{-4}	3.17
Formic acid	HCHO_2	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	$\text{HCHO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CHO}_2^-(aq)$	1.8×10^{-4}	3.74
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{C}(\text{H})=\text{C}(\text{H})-\text{CH}_3$	$\text{HC}_7\text{H}_5\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_7\text{H}_5\text{O}_2^-(aq)$	6.5×10^{-5}	4.19
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$	$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$	1.8×10^{-5}	4.74
Hypochlorous acid	HClO	$\text{H}-\text{O}-\text{Cl}$	$\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$	2.9×10^{-8}	7.54
Hydrocyanic acid	HCN	$\text{H}-\text{C}\equiv\text{N}$	$\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$	4.9×10^{-10}	9.31
Phenol	$\text{HC}_6\text{H}_5\text{O}$	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{C}(\text{H})=\text{C}(\text{H})-\text{CH}_3$	$\text{HC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{O}^-(aq)$	1.3×10^{-10}	9.89

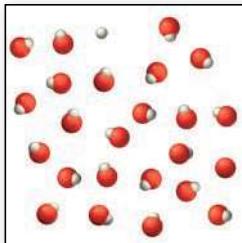
ANSWER NOW!



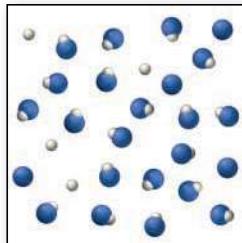
17.3 Cc Conceptual Connection

THE MAGNITUDE OF THE ACID IONIZATION CONSTANT

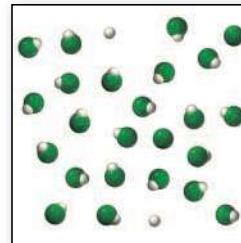
Consider the three generic weak acids HA, HB, and HC. The images shown here represent the ionization of each acid at room temperature. Which acid has the largest K_a ?



(a) HA



(b) HB



(c) HC

ANSWER NOW!



17.4 Cc Conceptual Connection

RELATIVE STRENGTHS OF WEAK ACIDS

Consider these two acids and their K_a values:

$$\text{(a)} \text{ HF} \quad K_a = 6.8 \times 10^{-4}$$

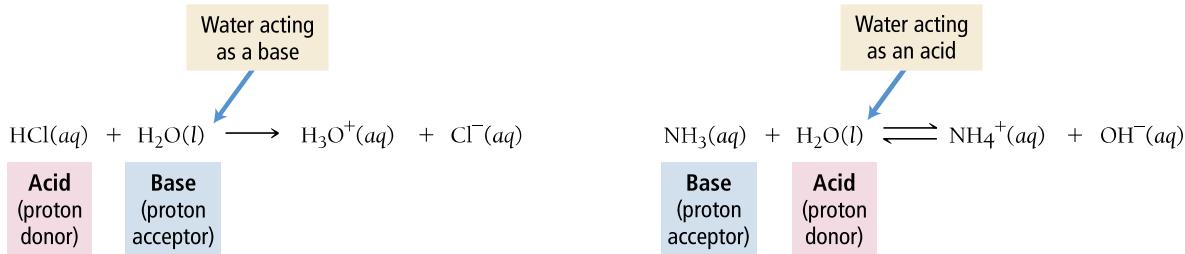
$$\text{(b)} \text{ HClO} \quad K_a = 2.9 \times 10^{-8}$$

Which acid is stronger?

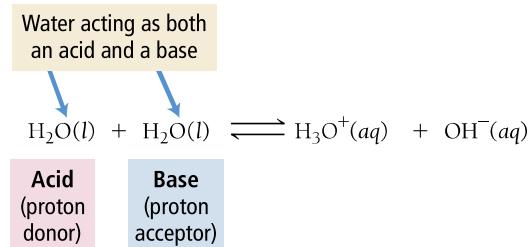
17.5

Autoionization of Water and pH

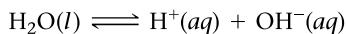
We saw previously that water acts as a base when it reacts with HCl and as an acid when it reacts with NH_3 :



Water is *amphoteric*; it can act as either an acid or a base. Even when pure, water acts as an acid and a base with itself, a process called **autoionization**:



We can write the autoionization reaction as:



The equilibrium constant expression for this reaction is the product of the concentration of the two ions:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-]$$

This equilibrium constant is called the **ion product constant for water (K_w)** (sometimes called the *dissociation constant for water*). At 25 °C, $K_w = 1.0 \times 10^{-14}$. In pure water, since H₂O is the only source of these ions, the concentrations of H₃O⁺ and OH⁻ are equal, and the solution is **neutral**. Since the concentrations of the two ions are equal, we can easily calculate them from K_w .

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 1.0 \times 10^{-7} \quad (\text{in pure water at } 25^\circ\text{C})$$

As you can see, in pure water, the concentrations of H₃O⁺ and OH⁻ are *very small* ($1.0 \times 10^{-7}\text{M}$) at room temperature.

An **acidic solution** contains an acid that creates additional H₃O⁺ ions, causing [H₃O⁺] to increase. However, the *ion product constant still applies*:

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

The concentration of H₃O⁺ times the concentration of OH⁻ is always 1.0×10^{-14} at 25 °C.

If [H₃O⁺] increases, then [OH⁻] must decrease for the ion product constant to remain 1.0×10^{-14} . For example, if [H₃O⁺] = 1.0×10^{-3} , then we can find [OH⁻] by solving the ion product constant expression for [OH⁻]:

$$\begin{aligned} (1.0 \times 10^{-3})[\text{OH}^-] &= 1.0 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\text{ M} \end{aligned}$$

In an acidic solution [H₃O⁺] > [OH⁻].

A **basic solution** contains a base that creates additional OH⁻ ions, causing [OH⁻] to increase and [H₃O⁺] to decrease, but again the *ion product constant still applies*. Suppose [OH⁻] = 1.0×10^{-2} ; we can find [H₃O⁺] by solving the ion product constant expression for [H₃O⁺]:

$$\begin{aligned} [\text{H}_3\text{O}^+](1.0 \times 10^{-2}) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\text{ M} \end{aligned}$$

In a basic solution [OH⁻] > [H₃O⁺].

Notice that changing [H₃O⁺] in an aqueous solution produces an inverse change in [OH⁻] and vice versa.

Summarizing K_w :

- A *neutral solution* contains [H₃O⁺] = [OH⁻] = $1.0 \times 10^{-7}\text{ M}$ (at 25 °C).
- An *acidic solution* contains [H₃O⁺] > [OH⁻].
- A *basic solution* contains [OH⁻] > [H₃O⁺].
- In *all aqueous solutions* both H₃O⁺ and OH⁻ are present, with [H₃O⁺][OH⁻] = $K_w = 1.0 \times 10^{-14}$ (at 25 °C).

The ion product constant K_w depends on temperature. For all calculations in this book, assume 25 °C unless otherwise noted.

ACIDITY OF SOLUTIONS The H₃O⁺ concentrations of three solutions at room temperature are as follows. Which solution is acidic?

- (a) [H₃O⁺] = $1 \times 10^{-3}\text{ M}$ (b) [H₃O⁺] = $1 \times 10^{-7}\text{ M}$
 (c) [H₃O⁺] = $1 \times 10^{-9}\text{ M}$



ANSWER NOW!



EXAMPLE 17.2 Using K_w in Calculations

Calculate [OH⁻] at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

(a) [H₃O⁺] = $7.5 \times 10^{-5}\text{ M}$ (b) [H₃O⁺] = $1.5 \times 10^{-9}\text{ M}$ (c) [H₃O⁺] = $1.0 \times 10^{-7}\text{ M}$

SOLUTION

- (a) To find [OH⁻], use the ion product constant. Substitute the given value for [H₃O⁺] and solve the equation for [OH⁻].

Since [H₃O⁺] > [OH⁻], the solution is acidic.

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

$$(7.5 \times 10^{-5})[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-5}} = 1.3 \times 10^{-10}\text{ M}$$

Acidic solution

—Continued on the next page

Continued—

- (b) Substitute the given value for $[H_3O^+]$ and solve the acid ionization equation for $[OH^-]$.
Since $[H_3O^+] < [OH^-]$, the solution is basic.

$$(1.5 \times 10^{-9})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6} M$$

Basic solution

- (c) Substitute the given value for $[H_3O^+]$ and solve the acid ionization equation for $[OH^-]$.
Since $[H_3O^+] = 1.0 \times 10^{-7}$ and $[OH^-] = 1.0 \times 10^{-7}$, the solution is neutral.

$$(1.0 \times 10^{-7})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} M$$

Neutral solution

FOR PRACTICE 17.2 Calculate $[H_3O^+]$ at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

(a) $[OH^-] = 1.5 \times 10^{-2} M$

(b) $[OH^-] = 1.0 \times 10^{-7} M$

(c) $[OH^-] = 8.2 \times 10^{-10} M$

WATCH NOW!

KEY CONCEPT VIDEO 17.5



The log of a number is the exponent to which 10 must be raised to obtain that number. Thus, $\log 10^1 = 1$; $\log 10^2 = 2$; $\log 10^{-1} = -1$; $\log 10^{-2} = -2$, and so (see Appendix I).

When we take the log of a quantity, the result has the same number of decimal places as the number of significant figures in the original quantity.

Concentrated acid solutions can have negative pH. For example, if $[H_3O^+] = 2.0 M$, the pH is -0.30 .

TABLE 17.6 ■ The pH of Some Common Substances

Substance	pH
Gastric juice (human stomach)	1.0–3.0
Limes	1.8–2.0
Lemons	2.2–2.4
Soft drinks	2.0–4.0
Plums	2.8–3.0
Wines	2.8–3.8
Apples	2.9–3.3
Peaches	3.4–3.6
Cherries	3.2–4.0
Beers	4.0–5.0
Rainwater (unpolluted)	5.6
Human blood	7.3–7.4
Egg whites	7.6–8.0
Milk of magnesia	10.5
Household ammonia	10.5–11.5
4% NaOH solution	14

The pH Scale: A Way to Quantify Acidity and Basicity

The pH scale is a compact way to specify the acidity of a solution. We define **pH** as the negative of the logarithm of the hydronium ion concentration:

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

A solution with $[H_3O^+] = 1.0 \times 10^{-3} M$ (acidic) has a pH of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.0 \times 10^{-3}) \\ &= -(-3.00) \\ &= 3.00 \end{aligned}$$

Notice that we report the pH to two *decimal places* in this example. This is because only the numbers to the right of the decimal point are significant in a logarithm. Because our original value for the concentration had two significant figures, the log of that number has two decimal places:

$$\begin{array}{ccc} 2 \text{ significant digits} & & 2 \text{ decimal places} \\ \downarrow & & \downarrow \\ \log 1.0 \times 10^{-3} & = & 3.00 \end{array}$$

If the original number has three significant digits, we report the log to three decimal places:

$$\begin{array}{ccc} 3 \text{ significant digits} & & 3 \text{ decimal places} \\ \downarrow & & \downarrow \\ \log 1.00 \times 10^{-3} & = & 3.000 \end{array}$$

A solution with $[H_3O^+] = 1.0 \times 10^{-7} M$ (neutral at 25 °C) has a pH of:

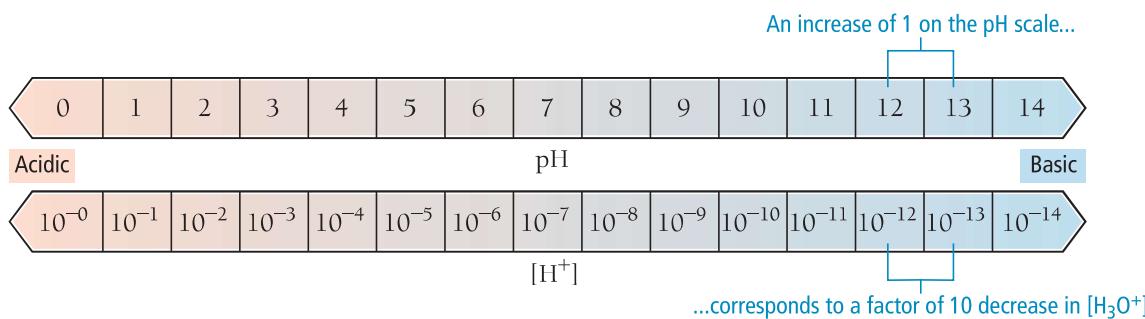
$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.0 \times 10^{-7}) \\ &= -(-7.00) \\ &= 7.00 \end{aligned}$$

In general, at 25 °C:

- pH < 7 The solution is *acidic*.
- pH > 7 The solution is *basic*.
- pH = 7 The solution is *neutral*.

Table 17.6 lists the pH of some common substances. As we discussed in Section 17.2, many foods, especially fruits, are acidic and have low pH values. Relatively few foods are basic. The foods with the lowest pH values are limes and lemons, and they are among the sourest. Because the pH scale is a *logarithmic scale*, a change of 1 pH unit corresponds to a 10-fold change in H_3O^+ concentration (Figure 17.7►). For example, a lime with a pH of 2.0 is 10 times more acidic than a plum with a pH of 3.0 and 100 times more acidic than a cherry with a pH of 4.0.

The pH Scale



▲ FIGURE 17.7 The pH Scale An increase of 1 on the pH scale corresponds to a factor of 10 decrease in $[H_3O^+]$.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.3

EXAMPLE 17.3 Calculating pH from $[H_3O^+]$ or $[OH^-]$



Calculate the pH of each solution at 25 °C and indicate whether the solution is acidic or basic.

(a) $[H_3O^+] = 1.8 \times 10^{-4} M$

(b) $[OH^-] = 1.3 \times 10^{-2} M$

SOLUTION

- (a) To calculate pH, substitute the given $[H_3O^+]$ into the pH equation. Since $pH < 7$, this solution is acidic.

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(1.8 \times 10^{-4}) \\ &= -(-3.74) \\ &= 3.74 \text{ (acidic)} \end{aligned}$$

- (b) First use K_w to find $[H_3O^+]$ from $[OH^-]$.

$$\begin{aligned} [H_3O^+][OH^-] &= K_w = 1.0 \times 10^{-14} \\ [H_3O^+](1.3 \times 10^{-2}) &= 1.0 \times 10^{-14} \\ [H_3O^+] &= \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13} M \\ \text{pH} &= -\log[H_3O^+] \\ &= -\log(7.7 \times 10^{-13}) \\ &= -(-12.11) \\ &= 12.11 \text{ (basic)} \end{aligned}$$

Then substitute $[H_3O^+]$ into the pH expression to find pH.

Since $pH > 7$, this solution is basic.

FOR PRACTICE 17.3 Calculate the pH of each solution and indicate whether the solution is acidic or basic.

(a) $[H_3O^+] = 9.5 \times 10^{-9} M$

(b) $[OH^-] = 7.1 \times 10^{-3} M$

EXAMPLE 17.4 Calculating $[H_3O^+]$ from pH

Calculate $[H_3O^+]$ for a solution with a pH of 4.80.

SOLUTION

- (a) To find $[H_3O^+]$ from pH, start with the equation that defines pH. Substitute the given value of pH and then solve for $[H_3O^+]$. Since the given pH value was reported to two decimal places, report the $[H_3O^+]$ to two significant figures. (Remember that $10^{\log x} = x$ (see Appendix I). Some calculators use an inv log key to represent this function.)

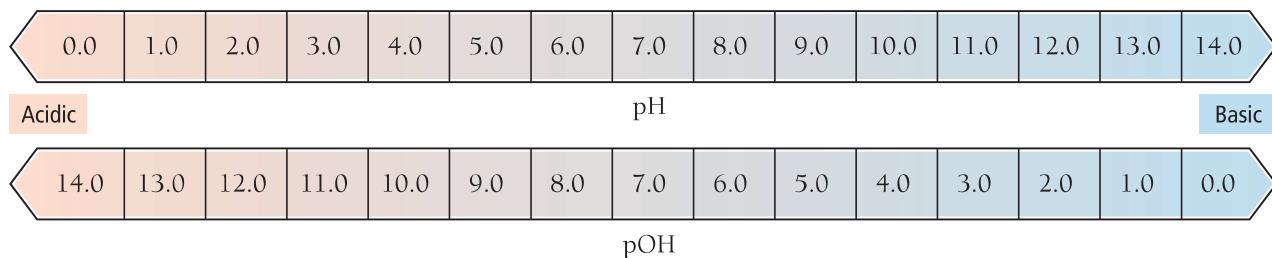
$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ 4.80 &= -\log[H_3O^+] \\ -4.80 &= \log[H_3O^+] \\ 10^{-4.80} &= 10^{\log[H_3O^+]} \\ 10^{-4.80} &= [H_3O^+] \\ [H_3O^+] &= 1.6 \times 10^{-5} M \end{aligned}$$

FOR PRACTICE 17.4 Calculate $[H_3O^+]$ for a solution with a pH of 8.37.

pOH and Other p Scales

The pOH scale is analogous to the pH scale but is defined with respect to $[OH^-]$ instead of $[H_3O^+]$:

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

**▲ FIGURE 17.8** pH and pOH

Notice that p is the mathematical operator $-\log$; thus, $pX = -\log X$.

A solution with an $[\text{OH}^-]$ of 1.0×10^{-3} M (basic) has a pOH of 3.00. On the pOH scale, a pOH less than 7 is basic and a pOH greater than 7 is acidic. A pOH of 7 is neutral (Figure 17.8▲). We can derive a relationship between pH and pOH at 25°C from the expression for K_w :

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

Taking the log of both sides, we get:

$$\begin{aligned}\log([\text{H}_3\text{O}^+][\text{OH}^-]) &= \log(1.0 \times 10^{-14}) \\ \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-] &= -14.00 \\ -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] &= 14.00 \\ \text{pH} + \text{pOH} &= 14.00\end{aligned}$$

The sum of pH and pOH is always equal to 14.00 at 25°C . Therefore, a solution with a pH of 3 has a pOH of 11.

Another common p scale is the $\text{p}K_a$ scale defined as:

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

The $\text{p}K_a$ of a weak acid is another way to quantify its strength. The smaller the $\text{p}K_a$, the stronger the acid. For example, chlorous acid, with a K_a of 1.1×10^{-2} , has a $\text{p}K_a$ of 1.96; and formic acid, with a K_a of 1.8×10^{-4} , has a $\text{p}K_a$ of 3.74 (see Table 17.5).

ANSWER NOW!



17.6 Cc Conceptual Connection

pH AND ACIDITY As the pH of a solution increases (gets higher), what happens to the acidity of the solution?

- (a) The acidity increases.
- (b) The acidity decreases.
- (c) The acidity remains constant.



CHEMISTRY AND MEDICINE

Ulcers

An ulcer is a lesion on the wall of the stomach or small intestine. Under normal circumstances, a thick layer of mucus lines the stomach wall and protects it from the hydrochloric acid and other gastric juices in the stomach. If that mucous layer is damaged, however, stomach juices come in direct contact with the stomach wall and begin to digest it, creating an ulcer. The main symptom of an ulcer is a burning or gnawing pain in the stomach.

Acidic drugs, such as aspirin, and acidic foods, such as citrus fruits and pickling fluids, irritate ulcers. When consumed, these substances increase the acidity of the stomach juices, exacerbating the irritation to the stomach wall. On the other hand, antacids—which contain bases—relieve ulcers. Common antacids include Tums and milk of magnesia.

The causes of ulcers are manifold. For many years, a stressful lifestyle and a rich diet were blamed. More recent research, however, has shown that a bacterial infection of the stomach lining is

responsible for many ulcers. (The 2005 Nobel Prize in Physiology or Medicine was awarded to Australians Barry J. Marshall and J. Robin Warren, for their discovery of the bacterial cause of ulcers.) Long-term use of some over-the-counter pain relievers, such as aspirin, is also believed to produce ulcers.



▲ An ulcer is a lesion in the stomach wall.

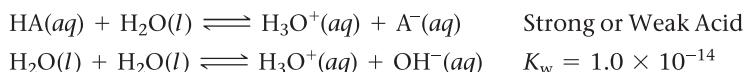
QUESTION Which dessert is less likely to irritate an ulcer, key lime pie or meringue (made of egg whites)?



17.6

Finding the $[H_3O^+]$ and pH of Strong and Weak Acid Solutions

A solution containing a strong or weak acid has two potential sources of H_3O^+ : the ionization of the acid itself and the autoionization of water. If we let HA be a strong or weak acid, the ionization equations are:



Except in extremely dilute acid solutions, the autoionization of water contributes a negligibly small amount of H_3O^+ compared to the ionization of the strong or weak acid. Recall from Section 17.5 that autoionization in pure water at 25 °C produces an H_3O^+ concentration of 1.0×10^{-7} M. In a strong or weak acid solution, the additional H_3O^+ from the acid causes the autoionization of water equilibrium to shift left (as described by Le Châtelier's principle). Consequently, in most strong or weak acid solutions, the autoionization of water produces even less H_3O^+ than in pure water and can be ignored. Therefore we can focus exclusively on the amount of H_3O^+ produced by the acid.

WATCH NOW!

KEY CONCEPT VIDEO 17.6

Finding the $[H_3O^+]$ and pH of Strong and Weak Acid Solutions

The only exceptions would be extremely dilute ($< 10^{-5}$ M) strong acid solutions.

Strong Acids

Because strong acids, by definition, completely ionize in solution and because we can (in nearly all cases) ignore the contribution of the autoionization of water, *the concentration of H_3O^+ in a strong acid solution is equal to the concentration of the strong acid*. For example, a 0.10 M HCl solution has an H_3O^+ concentration of 0.10 M and a pH of 1.00:

$$0.10 \text{ M HCl} \Rightarrow [H_3O^+] = 0.10 \text{ M} \Rightarrow \text{pH} = -\log(0.10) = 1.00$$

Weak Acids

Finding the pH of a weak acid solution is more complicated because the concentration of H_3O^+ is *not equal* to the concentration of the weak acid. For example, if we make a solution of 0.10 M HCl (a strong acid) and a solution of 0.10 M acetic acid (a weak acid) in the laboratory and measure the pH of each, we get the following results:

0.10 M HCl	pH = 1.00
0.10 M HC ₂ H ₃ O ₂	pH = 2.87

The pH of the acetic acid solution is higher (it is less acidic) because acetic acid only partially ionizes. Calculating the $[H_3O^+]$ formed by the ionization of a weak acid requires solving an equilibrium problem similar to those in Chapter 16. Consider, for example, a 0.10 M solution of the generic weak acid HA with an acid ionization constant K_a . Since we can ignore the contribution of the autoionization of water, we only have to determine the concentration of H_3O^+ formed by the following equilibrium:



We can summarize the initial conditions, the changes, and the equilibrium conditions in the following ICE table:

	[HA]	[H ₃ O ⁺]	[A ⁻]
Initial	0.10	≈ 0.00	0.00
Change	-x	+x	+x
Equilibrium	0.10 - x	x	x

The initial H_3O^+ concentration is listed as *approximately* zero because of the negligibly small contribution of H_3O^+ due to the autoionization of water (discussed previously). The variable x represents the amount of HA that ionizes. As discussed in Chapter 16, each *equilibrium* concentration is the sum of the two entries above it in the ICE table. In order to find the

ICE tables were first introduced in Section 16.6. The reactant $\text{H}_2\text{O}(l)$ is a pure liquid and is therefore not included either in the equilibrium constant or in the ICE table (see Section 16.5).

equilibrium concentration of H_3O^+ , we must find the value of the variable x . We can use the equilibrium expression to set up an equation in which x is the only variable:

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

$$= \frac{x^2}{0.10 - x}$$

As is often the case with equilibrium problems, we arrive at a quadratic equation in x , which we can solve using the quadratic formula (see Appendix IC). However, in many cases we can apply the x is small approximation (first discussed in Section 16.8). In Examples 17.5 and 17.6, we examine the general procedure for solving weak acid equilibrium problems. In both of these examples, the x is small approximation works well. In Example 17.7, we solve a problem in which the x is small approximation does not work. In such cases, we can solve the quadratic equation explicitly, or apply the method of successive approximations (also discussed in Section 16.8). Finally, in Example 17.8, we work a problem in which we find the equilibrium constant of a weak acid from its pH.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE VIDEO 17.5

HOW TO: Find the pH (or $[\text{H}_3\text{O}^+]$) of a Weak Acid Solution

To solve these types of problems, follow the outlined procedure.

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration. Leave room in the table for the changes in concentrations and for the equilibrium concentrations. (Note that $[\text{H}_3\text{O}^+]$ is listed as approximately zero because the autoionization of water produces a negligibly small amount of H_3O^+ .)

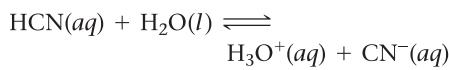
2. Represent the change in the concentration of H_3O^+ with the variable x . Define the changes in the concentrations of the other reactants and products in terms of x . Always keep in mind the stoichiometry of the reaction.

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .

EXAMPLE 17.5

Finding the $[\text{H}_3\text{O}^+]$ of a Weak Acid Solution

Find the $[\text{H}_3\text{O}^+]$ of a 0.100 M HCN solution.

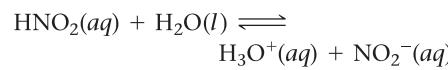


	[HCN]	$[\text{H}_3\text{O}^+]$	$[\text{CN}^-]$
Initial	0.100	≈ 0.00	0.00
Change			
Equil			

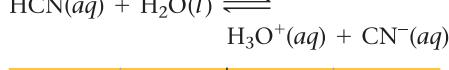
EXAMPLE 17.6

Finding the pH of a Weak Acid Solution

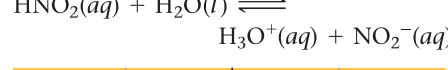
Find the pH of a 0.200 M HNO_2 solution.



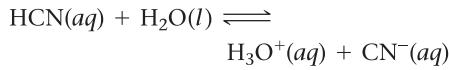
	[HNO_2]	$[\text{H}_3\text{O}^+]$	$[\text{NO}_2^-]$
Initial	0.200	≈ 0.00	0.00
Change			
Equil			



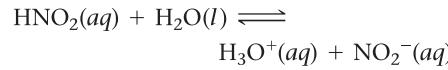
	[HCN]	$[\text{H}_3\text{O}^+]$	$[\text{CN}^-]$
Initial	0.100	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil			



	[HNO_2]	$[\text{H}_3\text{O}^+]$	$[\text{NO}_2^-]$
Initial	0.200	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil			



	[HCN]	$[\text{H}_3\text{O}^+]$	$[\text{CN}^-]$
Initial	0.100	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x



	[HNO_2]	$[\text{H}_3\text{O}^+]$	$[\text{NO}_2^-]$
Initial	0.200	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.200 - x$	x	x

- 4. Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant (K_a).** In many cases, you can make the approximation that x is small (as discussed in Section 16.8). **Substitute the value of the acid ionization constant (from Table 17.5) into the K_a expression and solve for x .**

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

$$= \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.100}$$

$$\sqrt{4.9 \times 10^{-10}} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(4.9 \times 10^{-10})} \\ = 7.0 \times 10^{-6}$$

$$\frac{7.0 \times 10^{-6}}{0.100} \times 100\% = 7.0 \times 10^{-3}\%$$

Therefore, the approximation is valid.

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$= \frac{x^2}{0.200 - x} \quad (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{0.200}$$

$$\sqrt{4.6 \times 10^{-4}} = \sqrt{\frac{x^2}{0.200}}$$

$$x = \sqrt{(0.200)(4.6 \times 10^{-4})} \\ = 9.6 \times 10^{-3}$$

$$\frac{9.6 \times 10^{-3}}{0.200} \times 100\% = 4.8\%$$

Therefore, the approximation is valid (but barely so).

- 5. Determine $[H_3O^+]$ from the calculated value of x and calculate the pH if necessary.**

$$[H_3O^+] = 7.0 \times 10^{-6} \text{ M}$$

(pH was not asked for in this problem.)

$$[H_3O^+] = 9.6 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [H_3O^+]$$

$$= -\log(9.6 \times 10^{-3})$$

$$= 2.02$$

- 6. Check your answer by substituting the calculated equilibrium values into the acid ionization expression.**

The calculated value of K_a should match the given value of K_a . Note that rounding errors and the x is small approximation may result in a difference in the least significant digit when comparing values of K_a .

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(7.0 \times 10^{-6})^2}{0.100}$$

$$= 4.9 \times 10^{-10}$$

Since the calculated value of K_a matches the given value, the answer is valid.

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(9.6 \times 10^{-3})^2}{0.200}$$

$$= 4.6 \times 10^{-4}$$

Since the calculated value of K_a matches the given value, the answer is valid.

FOR PRACTICE 17.5

Find the H_3O^+ concentration of a 0.250 M hydrofluoric acid solution.

FOR PRACTICE 17.6

Find the pH of a 0.0150 M acetic acid solution.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.7

EXAMPLE 17.7

Finding the pH of a Weak Acid Solution in Cases Where the x is small Approximation Does Not Work



Find the pH of a 0.100 M $HClO_2$ solution.

SOLUTION

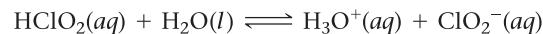
1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration.

(Note that the H_3O^+ concentration is listed as approximately zero. Although a little H_3O^+ is present from the autoionization of water, this amount is negligibly small compared to the amount of $HClO_2$ or H_3O^+ formed by the acid.)

2. Represent the change in $[H_3O^+]$ with the variable x . Define the changes in the concentrations of the other reactants and products in terms of x .



	$[HClO_2]$	$[H_3O^+]$	$[ClO_2^-]$
Initial	0.100	≈ 0.00	0.00
Change			
Equil			



	$[HClO_2]$	$[H_3O^+]$	$[ClO_2^-]$
Initial	0.100	≈ 0.00	0.00
Change	- x	+ x	+ x
Equil			

—Continued on the next page

Continued—

- 3.** Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .



	[HClO ₂]	[H ₃ O ⁺]	[ClO ₂ ⁻]
Initial	0.100	≈ 0.00	0.00
Change	- x	+ x	+ x
Equil	0.100 - x	x	x

- 4.** Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant (K_a). Make the x is small approximation and substitute the value of the acid ionization constant (from Table 17.5) into the K_a expression. Solve for x .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]}$$

$$= \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$0.011 = \frac{x^2}{0.100}$$

$$\sqrt{0.011} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(0.011)} \\ = 0.033$$

$$\frac{0.033}{0.100} \times 100\% = 33\%$$

Therefore, the x is small approximation is not valid.

- 4a.** If the x is small approximation is not valid, solve the quadratic equation explicitly or use the method of successive approximations to find x . In this case, you solve the quadratic equation.

$$0.011 = \frac{x^2}{0.100 - x}$$

$$0.011(0.100 - x) = x^2$$

$$0.0011 - 0.011x = x^2$$

$$x^2 + 0.011x - 0.0011 = 0$$

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

$$= \frac{-(0.011) \pm \sqrt{(0.011)^2 - 4(1)(-0.0011)}}{2(1)}$$

$$= \frac{-0.011 \pm 0.0672}{2}$$

$$x = -0.039 \text{ or } x = 0.028$$

Since x represents the concentration of H₃O⁺, and since concentrations cannot be negative, you reject the negative root.

$$x = 0.028$$

- 5.** Determine the H₃O⁺ concentration from the calculated value of x and calculate the pH (if necessary).

$$[\text{H}_3\text{O}^+] = 0.028 \text{ M}$$

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

$$= -\log 0.028$$

$$= 1.55$$

- 6.** Check your answer by substituting the calculated equilibrium values into the acid ionization expression. The calculated value of K_a should match the given value of K_a . Note that rounding errors could result in a difference in the least significant digit when comparing values of K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{0.028^2}{0.100 - 0.028}$$

$$= 0.011$$

Since the calculated value of K_a matches the given value, the answer is valid.

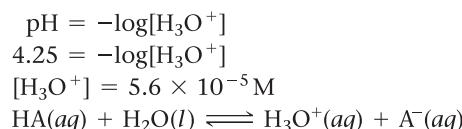
FOR PRACTICE 17.7 Find the pH of a 0.010 M HNO₂ solution.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.8

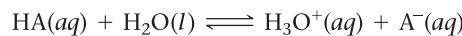
EXAMPLE 17.8 Finding the Equilibrium Constant from pHA 0.100 M weak acid (HA) solution has a pH of 4.25. Find K_a for the acid.**SOLUTION**

Use the given pH to find the equilibrium concentration of H_3O^+ . Then write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing all known concentrations.



	[HA]	$[H_3O^+]$	$[\text{A}^-]$
Initial	0.100	≈ 0.00	0.00
Change			
Equil		5.6×10^{-5}	

Use the equilibrium concentration of H_3O^+ and the stoichiometry of the reaction to predict the changes and equilibrium concentration for all species. For most weak acids, the initial and equilibrium concentrations of the weak acid (HA) are effectively equal because the amount that ionizes is usually very small compared to the initial concentration.



	[HA]	$[H_3O^+]$	$[\text{A}^-]$
Initial	0.100	≈ 0.00	0.00
Change	-5.6×10^{-5}	$+5.6 \times 10^{-5}$	$+5.6 \times 10^{-5}$
Equil	$(0.100 - 5.6 \times 10^{-5})$ ≈ 0.100	5.6×10^{-5}	5.6×10^{-5}

Substitute the equilibrium concentrations into the expression for K_a and calculate its value.

$$\begin{aligned} K_a &= \frac{[H_3O^+][\text{A}^-]}{[\text{HA}]} \\ &= \frac{(5.6 \times 10^{-5})(5.6 \times 10^{-5})}{0.100} \\ &= 3.1 \times 10^{-8} \end{aligned}$$

FOR PRACTICE 17.8 A 0.175 M weak acid solution has a pH of 3.25. Find K_a for the acid.

THE X IS SMALL APPROXIMATION The initial concentration and K_a of several weak acid (HA) solutions are listed. For which solution is the *x is small* approximation least likely to work in finding the pH?

- (a) initial [HA] = 0.100 M; $K_a = 1.0 \times 10^{-5}$
- (b) initial [HA] = 1.00 M; $K_a = 1.0 \times 10^{-6}$
- (c) initial [HA] = 0.0100 M; $K_a = 1.0 \times 10^{-3}$
- (d) initial [HA] = 1.0 M; $K_a = 1.5 \times 10^{-3}$



ANSWER NOW!



STRONG AND WEAK ACIDS Which solution is most acidic (that is, which one has the lowest pH)?

- (a) 0.10 M HCl
- (b) 0.10 M HF
- (c) 0.20 M HF



ANSWER NOW!



Percent Ionization of a Weak Acid

We can quantify the ionization of a weak acid according to the percentage of acid molecules that actually ionizes. We define the **percent ionization** of a weak acid as the ratio of the ionized acid concentration to the initial acid concentration, multiplied by 100%:

$$\text{Percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% = \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\%$$

Since the concentration of ionized acid is equal to the H_3O^+ concentration at equilibrium (for a monoprotic acid), we can use $[\text{H}_3\text{O}^+]_{\text{equil}}$ and $[\text{HA}]_{\text{init}}$ in the formula to calculate the percent ionization. For example, in Example 17.6, we found that a 0.200 M HNO_2 solution contains 9.6×10^{-3} M H_3O^+ . The 0.200 M HNO_2 solution therefore has the following percent ionization:

$$\begin{aligned}\% \text{ionization} &= \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\% \\ &= \frac{9.6 \times 10^{-3} \text{ M}}{0.200 \text{ M}} \times 100\% \\ &= 4.8\%\end{aligned}$$

As you can see, the percent ionization is relatively small. In this case, even though HNO_2 has the second largest K_a in Table 17.5, fewer than 5 molecules out of 100 ionize. For most other weak acids (with smaller K_a values) the percent ionization is even less.

In Example 17.9, we calculate the percent ionization of a more concentrated HNO_2 solution. In the example, notice that the calculated H_3O^+ concentration is much greater (as we would expect for a more concentrated solution), but the *percent ionization* is actually smaller.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.9

EXAMPLE 17.9 Finding the Percent Ionization of a Weak Acid

Find the percent ionization of a 2.5 M HNO_2 solution.

SOLUTION

To find the percent ionization, you must find the equilibrium concentration of H_3O^+ . Follow the procedure in Example 17.5, shown in condensed form here.

	$[\text{HNO}_2]$	$[\text{H}_3\text{O}^+]$	$[\text{NO}_2^-]$
Initial	2.5	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$2.5 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{2.5 - x} \quad (x \text{ is small})$$

$$\begin{aligned}4.6 \times 10^{-4} &= \frac{x^2}{2.5} \\ x &= 0.034\end{aligned}$$

Therefore, $[\text{H}_3\text{O}^+] = 0.034 \text{ M}$.

Use the definition of percent ionization to calculate it. (Since the percent ionization is less than 5%, the x is small approximation is valid.)

$$\begin{aligned}\% \text{ionization} &= \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\% \\ &= \frac{0.034 \text{ M}}{2.5 \text{ M}} \times 100\% \\ &= 1.4\%\end{aligned}$$

FOR PRACTICE 17.9 Find the percent ionization of a 0.250 M $\text{HC}_2\text{H}_3\text{O}_2$ solution at 25 °C.

We can now compare the results of Examples 17.6 and 17.9. From the table shown here, we can see that the more concentrated HNO_2 solution has a lower percent ionization. This trend applies to all weak acid solutions.

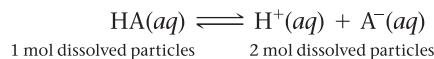
$[HNO_2]$	$[H_3O^+]$	Percent Ionization
0.200	0.0096	4.8%
2.5	0.034	1.4%

Summarizing $[H_3O^+]$ and Percent Ionization:

- The equilibrium H_3O^+ concentration of a weak acid increases with increasing initial concentration of the acid.
- The percent ionization of a weak acid decreases with increasing concentration of the acid.

In other words, as the concentration of a weak acid solution increases, the concentration of the hydronium ion also increases, but the increase is not linear. The H_3O^+ concentration increases less than the concentration of the acid because as the acid concentration increases, a smaller fraction of weak acid molecules ionize.

We can understand this behavior by analogy with Le Châtelier's principle. Consider the following weak acid ionization equilibrium:



If we dilute a weak acid solution initially at equilibrium, the system (according to Le Châtelier's principle) responds to minimize the disturbance. The equilibrium shifts to the right because the right side of the equation contains more particles in solution (2 mol versus 1 mol) than the left side. If the system shifts to the right, the percent ionization is greater in the more dilute solution, which is what we observe.

PERCENT IONIZATION Which weak acid solution has the greatest percent ionization?

- 0.100 M $HC_2H_3O_2$
- 0.500 M $HC_2H_3O_2$
- 0.0100 M $HC_2H_3O_2$



ANSWER NOW!

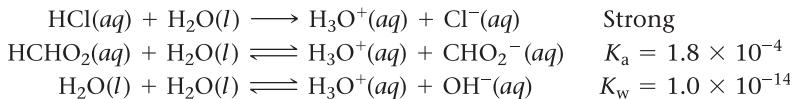


Mixtures of Acids

Finding the pH of a mixture of acids may seem difficult at first. However, in many cases, the relative strengths of the acids in the mixture allow us to neglect the weaker acid and focus only on the stronger one. Here, we consider two possible acid mixtures: a strong acid with a weak acid and a weak acid with another weak acid.

A Strong Acid and a Weak Acid

Consider a mixture that is 0.10 M in HCl and 0.10 M in $HCHO_2$. There are three sources of H_3O^+ ions: the strong acid (HCl), the weak acid ($HCHO_2$), and the autoionization of water:

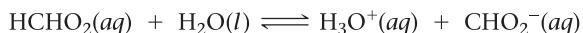


Since HCl is strong, we know that it completely ionizes to produce a significant concentration of H_3O^+ (0.10 M). The H_3O^+ formed by HCl then suppresses the formation of additional H_3O^+ formed by the ionization of $HCHO_2$ or the autoionization of water. In other words, according to Le Châtelier's principle, the formation of H_3O^+ by the strong acid causes the weak acid to ionize even less than it would in the absence of the strong acid. To see this clearly, we calculate $[\text{H}_3\text{O}^+]$ and $[\text{CHO}_2^-]$ in this solution.

In an initial estimate of $[H_3O^+]$, we can neglect the contribution of $HCHO_2$ and H_2O . The concentration of H_3O^+ is then equal to the initial concentration of HCl:

$$[H_3O^+] = [HCl] = 0.10 \text{ M}$$

To find $[CHO_2^-]$ we must solve an equilibrium problem. However, the initial concentration of H_3O^+ in this case is not negligible (as it has been in all the other weak acid equilibrium problems that we have worked so far) because HCl has formed a significant amount of H_3O^+ . The concentration of H_3O^+ formed by HCl becomes the *initial* concentration of H_3O^+ in the ICE table for $HCHO_2$ as shown here:



	$[HCHO_2]$	$[H_3O^+]$	$[CHO_2^-]$
Initial	0.10	0.10	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.10 - x$	$0.10 + x$	x

We then use the equilibrium expression to set up an equation in which x is the only variable:

$$\begin{aligned} K_a &= \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} \\ &= \frac{(0.10 + x)x}{0.10 - x} \end{aligned}$$

Since the equilibrium constant is small relative to the initial concentration of the acid, we can make the x is *small* approximation:

$$K_a = \frac{(0.10 + x)x}{0.10 - x}$$

$$1.8 \times 10^{-4} = \frac{(0.10)x}{0.10}$$

$$x = 1.8 \times 10^{-4}$$

Checking the x is *small* approximation:

$$\frac{1.8 \times 10^{-4}}{0.10} \times 100\% = 0.18\%$$

We find that the approximation is valid. Therefore, $[CHO_2^-] = 1.8 \times 10^{-4} \text{ M}$. We can now see that we can completely ignore the ionization of the weak acid ($HCHO_2$) in calculating $[H_3O^+]$ for the mixture. The contribution to the concentration of H_3O^+ by the weak acid must necessarily be equal to the concentration of CHO_2^- that we just calculated (because of the stoichiometry of the ionization reaction). Therefore, we have the following contributions to $[H_3O^+]$:

HCl contributes 0.10 M

$HCHO_2$ contributes $1.8 \times 10^{-4} \text{ M}$ or 0.00018 M

Total $[H_3O^+] = 0.10 \text{ M} + 0.00018 \text{ M} = 0.10 \text{ M}$

As we can see, since the significant figure rules for addition limit the answer to two decimal places, the amount of H_3O^+ contributed by $HCHO_2$ is completely negligible. The amount of H_3O^+ contributed by the autoionization of water is even smaller and therefore similarly negligible.

A Mixture of Two Weak Acids

When two weak acids are mixed, we again have three potential sources of H_3O^+ to consider: each of the two weak acids and the autoionization of water. However, if the values of K_a for the two weak acids are sufficiently different in magnitude (if they differ by more than a factor of several hundred), then as long as the concentrations of the two acids are similar in magnitude (or the concentration of the stronger one is greater than that of the weaker), we can assume that the weaker acid will not make a significant contribution to

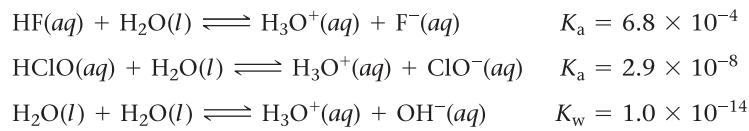
the concentration of H_3O^+ . We make this assumption for the same reason that we made a similar assumption for a mixture of a strong acid and a weak one: the H_3O^+ formed by the stronger acid suppresses the ionization of the weaker one, in accordance with Le Châtelier's principle. Example 17.10 shows how to calculate the concentration of H_3O^+ in a mixture of two weak acids.

EXAMPLE 17.10 Mixtures of Weak Acids

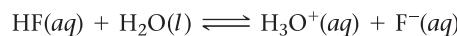
Find the pH of a mixture that is 0.300 M in HF and 0.100 M in HClO.

SOLUTION

The three possible sources of H_3O^+ ions are HF, HClO, and H_2O . Write the ionization equations for the three sources and their corresponding equilibrium constants. Since the equilibrium constant for the ionization of HF is about 24,000 times larger than that for the ionization of HClO, the contribution of HF to $[H_3O^+]$ is by far the greatest. You can therefore just calculate the $[H_3O^+]$ formed by HF and neglect the other two potential sources of H_3O^+ .



Write the balanced equation for the ionization of HF and use it as a guide to prepare an ICE table.



	[HF]	[H_3O^+]	[F ⁻]
Initial	0.300	≈ 0.00	0.00
Change	-x	+x	+x
Equil	0.300 - x	x	x

Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant (K_a). Since the equilibrium constant is small relative to the initial concentration of HF, you can make the x is small approximation. Substitute the value of the acid ionization constant (from Table 17.5) into the K_a expression and solve for x .

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.300 - x} \quad (x \text{ is small})$$

$$6.8 \times 10^{-4} = \frac{x^2}{0.300}$$

$$\sqrt{(0.300)(6.8 \times 10^{-4})} = \sqrt{x^2}$$

$$x = 1.428 \times 10^{-2}$$

$$\frac{1.428 \times 10^{-2}}{0.300} \times 100\% = 4.8\%$$

Therefore, the approximation is valid (though barely so).

Determine the H_3O^+ concentration from the calculated value of x and find the pH.

$$\begin{aligned} [H_3O^+] &= 1.4 \times 10^{-2} \text{ M} \\ \text{pH} &= -\log(1.4 \times 10^{-2}) = 1.85 \end{aligned}$$

FOR PRACTICE 17.10 Find the ClO^- concentration of the mixture of HF and HClO discussed in Example 17.10.

JUDGING RELATIVE pH Which solution is most acidic (that is, has the lowest pH)?

- (a) 1.0 M HCl
- (b) 2.0 M HF
- (c) A solution that is 1.0 M in HF and 1.0 M in HClO



ANSWER NOW!



17.7 Base Solutions

We have seen that bases are solutions that produce OH^- in solution (Arrhenius definition) or accept protons (Brønsted-Lowry definition). In analogy to acids, which can be strong or weak, bases can also be strong or weak.

Strong Bases

Just as we define a strong acid as one that completely ionizes in solution, analogously we define a **strong base** as a base that completely dissociates in solution. NaOH , for example, is a strong base:



An NaOH solution contains no intact NaOH —it has all dissociated to form $\text{Na}^+(aq)$ and $\text{OH}^-(aq)$ (Figure 17.9▼). In other words, a 1.0 M NaOH solution has $[\text{OH}^-] = 1.0 \text{ M}$ and $[\text{Na}^+] = 1.0 \text{ M}$. Table 17.7 lists the common strong bases.

► **FIGURE 17.9** Ionization of a Strong Base

Strong Base NaOH dissociates completely in water to form Na^+ and OH^- . The solution contains virtually no intact NaOH .

A Strong Base

When NaOH dissolves in water, it dissociates completely.

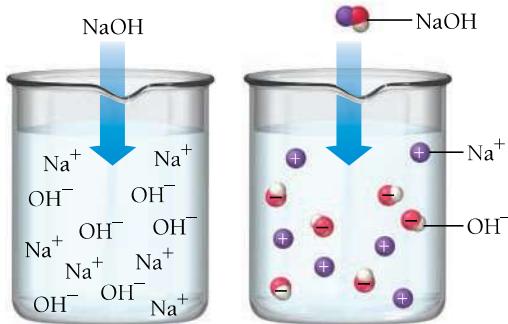
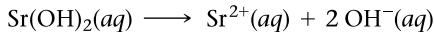


TABLE 17.7 ■ Strong Bases

Lithium hydroxide (LiOH)
Sodium hydroxide (NaOH)
Potassium hydroxide (KOH)
Strontium hydroxide ($\text{Sr}(\text{OH})_2$)
Calcium hydroxide ($\text{Ca}(\text{OH})_2$)
Barium hydroxide ($\text{Ba}(\text{OH})_2$)

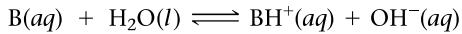
As we can see in the table, most strong bases are group 1A or group 2A metal hydroxides. The group 1A metal hydroxides are highly soluble in water and can form concentrated base solutions. The group 2A metal hydroxides, however, are only slightly soluble, a useful property for some applications (see *Chemistry and Medicine: What's in My Antacid?* in this section). Notice that the general formula for the group 2A metal hydroxides is $\text{M}(\text{OH})_2$. When they dissolve in water, they produce 2 mol of OH^- per mole of the base. For example, $\text{Sr}(\text{OH})_2$ dissociates as follows:



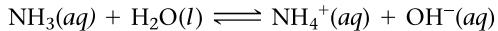
Unlike diprotic acids, which ionize in two steps, bases containing two OH^- ions dissociate in one step.

Weak Bases

The behavior of a **weak base** is analogous to that of a weak acid. Unlike strong bases that contain OH^- and *dissociate* in water, the most common weak bases produce OH^- by accepting a proton from water, ionizing water to form OH^- according to the general equation:



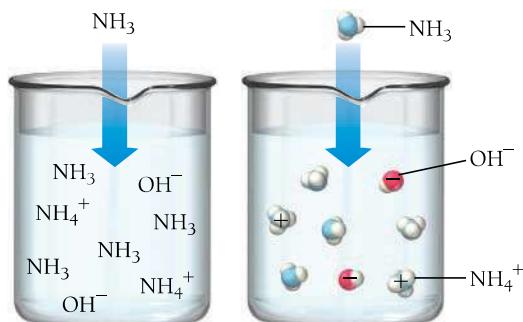
In this equation, B is a generic symbol for a weak base. Ammonia, for example, ionizes water as follows:



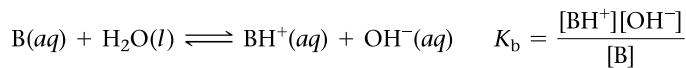
The double arrow indicates that the ionization is not complete. An NH_3 solution contains mostly NH_3 with only some NH_4^+ and OH^- (Figure 17.10►). A 1.0 M NH_3 solution will have $[\text{OH}^-] < 1.0 \text{ M}$.

A Weak Base

When NH_3 dissolves in water, it partially ionizes.



The extent of ionization of a weak base is quantified with the **base ionization constant (K_b)**. For the general reaction in which a weak base ionizes water, we define K_b as follows:



By analogy with K_a , the smaller the value of K_b , the weaker the base. Table 17.8 lists some common weak bases, their ionization reactions, and values for K_b . Appendix II C contains a more complete table. We can also apply the “p” scale to K_b , so that $pK_b = -\log K_b$.

All but two of the weak bases listed in Table 17.8 are either ammonia or an amine, which we can think of as ammonia with one or more hydrocarbon groups substituted for one or more hydrogen atoms. All of these bases have a nitrogen atom with a lone pair (Figure 17.11▶). This lone pair acts as the proton acceptor that makes the substance a base, as shown in the reactions for ammonia and methylamine:

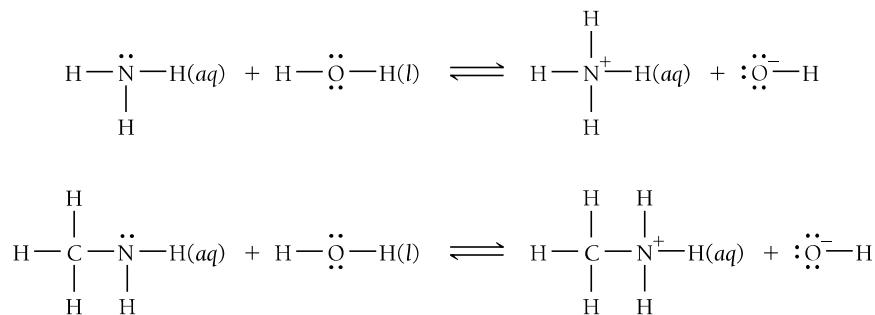


TABLE 17.8 ■ Some Common Weak Bases

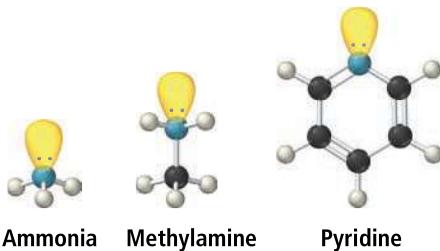
Weak Base	Ionization Reaction	K_b (at 25 °C)
Carbonate ion (CO_3^{2-})*	$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$	4.4×10^{-4}
Ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$)	$\text{C}_2\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$	5.6×10^{-4}
Ammonia (NH_3)	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$	1.76×10^{-5}
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)	$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$	2.3×10^{-8}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)	$\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$	1.7×10^{-9}
Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)	$\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$	3.9×10^{-10}

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate (NaHCO_3) basic. We look more closely at ionic bases in Section 17.8.

◀ FIGURE 17.10 Ionization of a Weak Base NH_3 partially ionizes in water to form NH_4^+ and OH^- . Most of the NH_3 molecules in solution remain as NH_3 .

► FIGURE 17.11 Lone Pairs in Weak Bases

Weak Bases Many weak bases have a nitrogen atom with a lone pair that acts as the proton acceptor.



Finding the $[OH^-]$ and pH of Basic Solutions

Finding the $[OH^-]$ and pH of a strong base solution is relatively straightforward, as shown in Example 17.11. As we did in calculating the $[H_3O^+]$ in strong acid solutions, we can neglect the contribution of the autoionization of water to the $[OH^-]$ and focus solely on the strong base itself.

EXAMPLE 17.11 Finding the $[OH^-]$ and pH of a Strong Base Solution

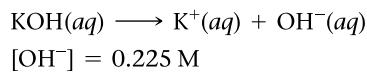
Determine the OH^- concentration and pH in each solution.

- (a) 0.225 M KOH
- (b) 0.0015 M $Sr(OH)_2$

SOLUTION

- (a) Since KOH is a strong base, it completely dissociates into K^+ and OH^- in solution. The concentration of OH^- is therefore the same as the given concentration of KOH. Use this concentration and K_w to find $[H_3O^+]$.

Then substitute $[H_3O^+]$ into the pH expression to find the pH.



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

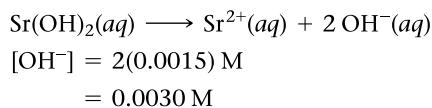
$$[H_3O^+](0.225) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = 4.44 \times 10^{-14} \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(4.44 \times 10^{-14}) \\ &= 13.35 \end{aligned}$$

- (b) Since $Sr(OH)_2$ is a strong base, 1 mol of $Sr(OH)_2$ completely dissociates into 1 mol of Sr^{2+} and 2 mol of OH^- in solution. The concentration of OH^- is therefore twice the given concentration of $Sr(OH)_2$.

Use this concentration and K_w to find $[H_3O^+]$.



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

$$[H_3O^+](0.0030) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = 3.3 \times 10^{-12} \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(3.3 \times 10^{-12}) \\ &= 11.48 \end{aligned}$$

FOR PRACTICE 17.11 Find the $[OH^-]$ and pH of a 0.010 M $Ba(OH)_2$ solution.

Finding the $[OH^-]$ and pH of a *weak base* solution is analogous to finding the $[H_3O^+]$ and pH of a weak acid. Similarly, we neglect the contribution of the autoionization of water to the $[OH^-]$ and focus solely on the weak base itself. We find the contribution of the weak base by preparing an ICE table showing the relevant concentrations of all species and then use the base ionization constant expression to find the $[OH^-]$. Example 17.12 demonstrates how to find the $[OH^-]$ and pH of a weak base solution.

WATCH NOW!

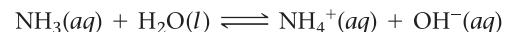
INTERACTIVE WORKED EXAMPLE 17.12

EXAMPLE 17.12 Finding the $[OH^-]$ and pH of a Weak Base Solution

Find the $[OH^-]$ and pH of a 0.100 M NH_3 solution.

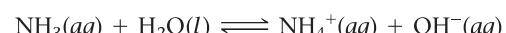
SOLUTION

- 1.** Write the balanced equation for the ionization of water by the base and use it as a guide to prepare an ICE table showing the given concentration of the weak base as its initial concentration. Leave room in the table for the changes in concentrations and for the equilibrium concentrations. (Note that you should list the OH^- concentration as approximately zero. Although a little OH^- is present from the autoionization of water, this amount is negligibly small compared to the amount of OH^- formed by the base.)



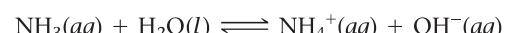
	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.100	0.00	≈ 0.00
Change			
Equil			

- 2.** Represent the change in the concentration of OH^- with the variable x . Define the changes in the concentrations of the other reactants and products in terms of x .



	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.100	0.00	≈ 0.00
Change	$-x$	$+x$	$+x$
Equil			

- 3.** Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .



	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.100	0.00	≈ 0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

- 4.** Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the base ionization constant. In many cases, you can make the approximation that x is small (as discussed in Chapter 16).

Substitute the value of the base ionization constant (from Table 17.8) into the K_b expression and solve for x .

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$1.76 \times 10^{-5} = \frac{x^2}{0.100}$$

$$\sqrt{1.76 \times 10^{-5}} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(1.76 \times 10^{-5})}$$

$$= 1.33 \times 10^{-3}$$

$$\frac{1.33 \times 10^{-3}}{0.100} \times 100\% = 1.33\%$$

Therefore, the approximation is valid.

- 5.** Determine the OH^- concentration from the calculated value of x . Use the expression for K_w to find $[H_3O^+]$.

Substitute $[H_3O^+]$ into the pH equation to find pH.

$$[OH^-] = 1.33 \times 10^{-3} \text{ M}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

$$[H_3O^+](1.33 \times 10^{-3}) = 1.00 \times 10^{-14}$$

$$[H_3O^+] = 7.52 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[H_3O^+]$$

$$= -\log(7.52 \times 10^{-12})$$

$$= 11.124$$

FOR PRACTICE 17.12 Find the $[OH^-]$ and pH of a 0.33 M methylamine solution.



CHEMISTRY AND MEDICINE

What's in My Antacid?

In the opening section of this chapter, we discussed heartburn and its treatment with antacids. Some common antacids and their active ingredients include the following:

Amphogel	Al(OH)_3
Milk of magnesia	Mg(OH)_2
Maalox	Mg(OH)_2 and Al(OH)_3
Mylanta	Mg(OH)_2 and Al(OH)_3
Tums	CaCO_3

We categorize antacids into three main groups: calcium-based, magnesium-based, and aluminum-based. Calcium-based antacids may cause acid rebound—which means that, although they initially relieve heartburn, they can also cause the stomach to produce more acid, resulting in a quick return of the symptoms. Aluminum- and magnesium-based antacids do not cause acid rebound but have downsides of their own. Aluminum-based antacids tend to cause constipation, and magnesium-based ones tend to cause diarrhea. (In fact, milk of magnesia is sometimes used as a laxative.) A person who takes repeated doses of these antacids should alternate between the two or choose a product that contains both.

Notice the absence of group 1A metal hydroxides, such as KOH or NaOH, in the list of antacids. Why are those substances—which are completely soluble and act as strong bases—not used in antacids? Because a solution that contains sufficient KOH or NaOH to neutralize stomach acid would also burn the mouth and throat. In contrast, Mg(OH)_2 and Al(OH)_3 are only slightly soluble. Therefore

liquid antacids containing these are actually suspensions of Mg(OH)_2 and Al(OH)_3 —they are heterogeneous mixtures in which the solid is finely divided into the liquid. As a result, the concentration of OH^- in these suspensions is relatively small compared to what it would be with a group 1A metal hydroxide.

► Antacids contain a variety of bases that effectively neutralize excess stomach acid.



Initially, it might seem as though the relatively lower OH^- concentration would make the antacid much less effective. However, the solid Mg(OH)_2 or Al(OH)_3 continues to dissolve as the OH^- neutralizes stomach acid. For example, a suspension of magnesium hydroxide contains solid Mg(OH)_2 in equilibrium with dissolved Mg^{2+} and OH^- ions:



As stomach acid is neutralized, OH^- is used up, and the equilibrium shifts to the right providing additional OH^- ions. In this way, a suspension of Mg(OH)_2 provides a steady concentration of dissolved OH^- ions to neutralize stomach acid.

QUESTION Write chemical equations showing the reactions of each of the bases in the antacids discussed here with stomach acid (HCl).



WATCH NOW!

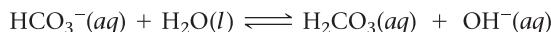
KEY CONCEPT VIDEO 17.8

The Acid–Base Properties of Ions and Salts

17.8

The Acid–Base Properties of Ions and Salts

We have already seen that some ions act as bases. For example, the bicarbonate ion acts as a base according to the following equation:



The bicarbonate ion, like any ion, does not exist by itself—in order to be charge-neutral, it must pair with a counterion (in this case a cation) to form an ionic compound, called a *salt*. For example, the sodium salt of bicarbonate is sodium bicarbonate. Like all soluble salts, sodium bicarbonate dissociates in solution to form a sodium cation and bicarbonate anion:



The sodium ion has neither acidic nor basic properties (it does not ionize water), as we will see shortly. The bicarbonate ion, by contrast, acts as a weak base, ionizing water as just shown to form a basic solution. Consequently, the pH of a sodium bicarbonate solution is above 7 (the solution is basic). In this section, we consider some of the acid–base properties of salts and the ions they contain. Some salts are pH-neutral when put into water, others are acidic, and still others are basic, depending on their constituent anions and cations. In general, anions tend to form either *basic* or neutral solutions, while cations tend to form either *acidic* or neutral solutions.

Anions as Weak Bases

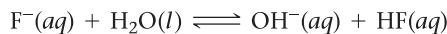
We can think of any anion as the conjugate base of an acid. Consider the following anions and their corresponding acids:

This anion	is the conjugate base of	this acid
Cl^-		HCl
F^-		HF
NO_3^-		HNO_3
$\text{C}_2\text{H}_3\text{O}_2^-$		$\text{HC}_2\text{H}_3\text{O}_2$

In general, the anion A^- is the conjugate base of the acid HA . Since every anion can be regarded as the conjugate base of an acid, every anion itself can potentially act as a base. However, *not every anion does act as a base*—it depends on the strength of the corresponding acid. In general:

- An anion that is the conjugate base of a *weak acid* is itself a *weak base*.
- An anion that is the conjugate base of a *strong acid* is pH-*neutral* (forms solutions that are neither acidic nor basic).

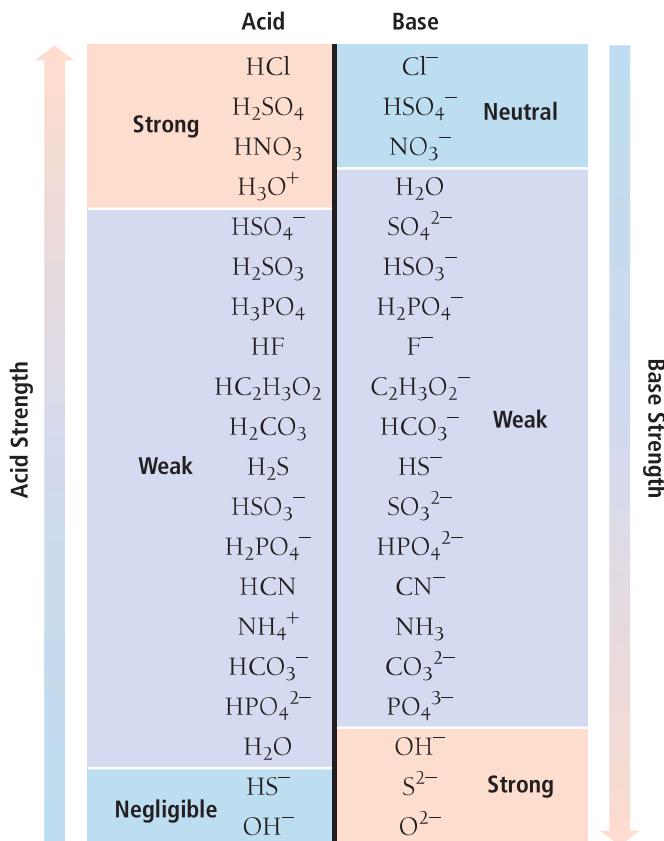
For example, the Cl^- anion is the conjugate base of HCl, a strong acid. Therefore, the Cl^- anion is pH-neutral (neither acidic nor basic). The F^- anion, however, is the conjugate base of HF, a weak acid. Therefore, the F^- ion is itself a weak base and ionizes water according to the reaction:



We can understand why the conjugate base of a weak acid is basic by asking ourselves why an acid is weak to begin with. Hydrofluoric acid is a weak acid because the following reaction lies to the left:

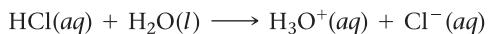


The equilibrium lies to the left because the F^- ion has a significant affinity for H^+ ions. Consequently, when F^- is put into water, its affinity for H^+ ions allows it to remove H^+ ions from water molecules, thus acting as a weak base. In general, as shown in Figure 17.12▼,



◀ FIGURE 17.12 Strength of Conjugate Acid–Base Pairs The stronger an acid, the weaker its conjugate base.

the weaker the acid, the stronger the conjugate base (as we saw in Section 17.4). In contrast, the conjugate base of a strong acid, such as Cl^- , does not act as a base because this reaction lies far to the right:



The reaction lies far to the right because the Cl^- ion has a low affinity for H^+ ions. Consequently, when Cl^- is put into water, it does not remove H^+ ions from water molecules.

EXAMPLE 17.13
Determining Whether an Anion Is Basic or pH-Neutral

Classify each anion as a weak base or pH-neutral.

- (a) NO_3^- (b) NO_2^- (c) $\text{C}_2\text{H}_3\text{O}_2^-$

SOLUTION

- (a) From Table 17.3, you can see that NO_3^- is the conjugate base of a *strong* acid (HNO_3) and is therefore pH-neutral.
- (b) From Table 17.5 (or from its absence in Table 17.3), you know that NO_2^- is the conjugate base of a weak acid (HNO_2) and is therefore a weak base.
- (c) From Table 17.5 (or from its absence in Table 17.3), you know that $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base of a weak acid ($\text{HC}_2\text{H}_3\text{O}_2$) and is therefore a weak base.

FOR PRACTICE 17.13 Classify each anion as a weak base or pH-neutral.

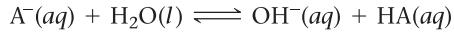
- (a) CHO_2^- (b) ClO_4^-

We can determine the pH of a solution containing an anion that acts as a weak base in a manner similar to how we determine the pH of any weak base solution. However, we need to know K_b for the anion acting as a base, which we can readily determine from K_a of the corresponding acid. Recall from Section 17.4 the expression for K_a for a generic acid HA:



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

Similarly, the expression for K_b for the conjugate base (A^-) is:



$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]}$$

If we multiply the expressions for K_a and K_b , we get K_w :

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

Or simply,

$$K_a \times K_b = K_w$$

The product of K_a for an acid and K_b for its conjugate base is K_w (1.0×10^{-14} at 25 °C). Consequently, we can find K_b for an anion acting as a base from the value of K_a for the corresponding acid. For example, for acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), $K_a = 1.8 \times 10^{-5}$. We calculate K_b for the conjugate base ($\text{C}_2\text{H}_3\text{O}_2^-$) by substituting into the equation:

$$K_a \times K_b = K_w$$

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

Knowing K_b , we can find the pH of a solution containing an anion acting as a base, as Example 17.14 demonstrates.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.14

EXAMPLE 17.14**Determining the pH of a Solution Containing an Anion Acting as a Base**

Find the pH of a 0.100 M NaCHO_2 solution. The salt completely dissociates into $\text{Na}^+(aq)$ and $\text{CHO}_2^-(aq)$, and the Na^+ ion has no acid or base properties.

SOLUTION

- 1.** Since the Na^+ ion does not have any acidic or basic properties, you can ignore it. Write the balanced equation for the ionization of water by the basic anion and use it as a guide to prepare an ICE table showing the given concentration of the weak base as its initial concentration.



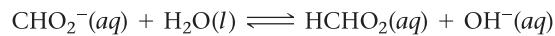
	$[\text{CHO}_2^-]$	$[\text{HCHO}_2]$	$[\text{OH}^-]$
Initial	0.100	0.00	≈ 0.00
Change			
Equil			

- 2.** Represent the change in the concentration of OH^- with the variable x . Define the changes in the concentrations of the other reactants and products in terms of x .



	$[\text{CHO}_2^-]$	$[\text{HCHO}_2]$	$[\text{OH}^-]$
Initial	0.100	0.00	≈ 0.00
Change	$-x$	$+x$	$+x$
Equil			

- 3.** Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .



	$[\text{CHO}_2^-]$	$[\text{HCHO}_2]$	$[\text{OH}^-]$
Initial	0.100	0.00	≈ 0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

- 4.** Find K_b from K_a (for the conjugate acid).

Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for K_b . In many cases, you can make the approximation that x is small.

Substitute the value of K_b into the K_b expression and solve for x .

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a \times K_b = K_w$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

$$K_b = \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]}$$

$$= \frac{x^2}{0.100 - x}$$

$$5.6 \times 10^{-11} = \frac{x^2}{0.100}$$

$$x = 2.4 \times 10^{-6}$$

$$\frac{2.4 \times 10^{-6}}{0.100} \times 100\% = 0.0024\%$$

Therefore, the approximation is valid.

- 5.** Determine the OH^- concentration from the calculated value of x .

Use the expression for K_w to find $[\text{H}_3\text{O}^+]$.

Substitute $[\text{H}_3\text{O}^+]$ into the pH equation to find pH.

$$[\text{OH}^-] = 2.4 \times 10^{-6} \text{ M}$$

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

$$[\text{H}_3\text{O}^+](2.4 \times 10^{-6}) = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 4.2 \times 10^{-9} \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(4.2 \times 10^{-9}) \\ &= 8.38 \end{aligned}$$

FOR PRACTICE 17.14 Find the pH of a 0.250 M $\text{NaC}_2\text{H}_3\text{O}_2$ solution.

We can also express the relationship between K_a and K_b in terms of pK_a and pK_b . By taking the log of both sides of $K_a \times K_b = K_w$, we get:

$$\log(K_a \times K_b) = \log K_w$$

$$\log K_a + \log K_b = \log K_w$$

Since $K_w = 10^{-14}$, we can rearrange the equation to get:

$$\log K_a + \log K_b = \log 10^{-14} = -14$$

Rearranging further:

$$-\log K_a - \log K_b = 14$$

Since $-\log K = pK$, we get:

$$pK_a + pK_b = 14$$

ANSWER NOW!



17.11 Cc Conceptual Connection

ANIONS AS WEAK BASES

Which anion acts as a weak base?

- (a) Cl⁻
- (b) Br⁻
- (c) F⁻

Cations as Weak Acids

In contrast to anions, which in some cases act as weak bases, cations can in some cases act as *weak acids*. Although some exceptions exist, we can generally divide cations into three categories: cations that are the counterions of strong bases; cations that are the conjugate acids of *weak bases*; and cations that are small, highly charged metals. We examine each individually.

Cations That Are the Counterions of Strong Bases

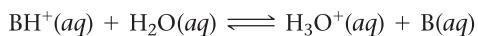
Strong bases such as NaOH or Ca(OH)₂ generally contain hydroxide ions and a counterion. In solution, a strong base completely dissociates to form OH⁻(*aq*) and the solvated (in solution) counterion. Although these counterions interact with water molecules via ion-dipole forces, they do not ionize water and they do not contribute to the acidity or basicity of the solution. In general, *cations that are the counterions of strong bases are themselves pH-neutral* (they form solutions that are neither acidic nor basic). For example, Na⁺, K⁺, and Ca²⁺ are the counterions of the strong bases NaOH, KOH, and Ca(OH)₂ and are therefore themselves pH-neutral.

Cations That Are the Conjugate Acids of Weak Bases

A cation can be formed from any nonionic weak base by adding a proton (H⁺) to its formula. The cation is the conjugate acid of the base. Consider the following cations and their corresponding weak bases:

This cation	is the conjugate acid of	this weak base
NH ₄ ⁺		NH ₃
C ₂ H ₅ NH ₃ ⁺		C ₂ H ₅ NH ₂
CH ₃ NH ₃ ⁺		CH ₃ NH ₂

Any of these cations, with the general formula BH⁺, will act as a weak acid according to the equation:

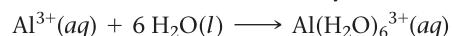


In general, *a cation that is the conjugate acid of a weak base is a weak acid*.

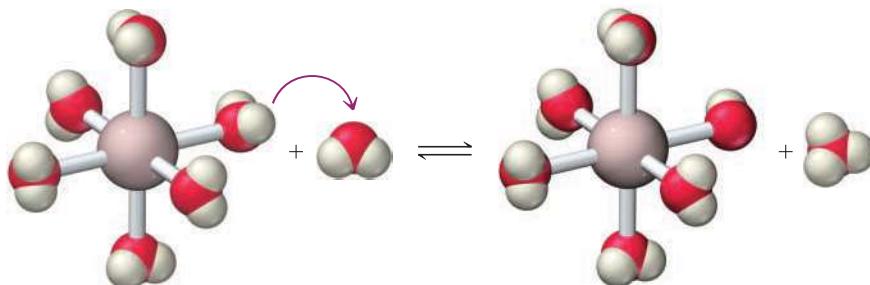
We can calculate the pH of a solution containing the conjugate acid of a weak base just like that of any other weak acidic solution. However, we must derive the value of K_a for the acid from K_b using the previously derived relationship: $K_a \times K_b = K_w$.

Cations That Are Small, Highly Charged Metals

Small, highly charged metal cations such as Al³⁺ and Fe³⁺ form weakly acidic solutions. For example, when Al³⁺ is dissolved in water, it becomes hydrated according to the equation:



The hydrated form of the ion then acts as a Brønsted–Lowry acid:



In effect, the binding of a water molecule to the cation makes the water more acidic. See Section 17.10.

Neither the alkali metal cations nor the alkaline earth metal cations ionize water in this way, but the cations of many other metals do. The smaller and more highly charged the cation, the more acidic its behavior.

EXAMPLE 17.15

Determining Whether a Cation Is Acidic or pH-Neutral

Classify each cation as a weak acid or pH-neutral.

- (a) $\text{C}_5\text{H}_5\text{NH}^+$ (b) Ca^{2+} (c) Cr^{3+}

SOLUTION

- (a) The $\text{C}_5\text{H}_5\text{NH}^+$ cation is the conjugate acid of a weak base and is therefore a weak acid.
- (b) The Ca^{2+} cation is the counterion of a strong base and is therefore pH-neutral (neither acidic nor basic).
- (c) The Cr^{3+} cation is a small, highly charged metal cation and is therefore a weak acid.

FOR PRACTICE 17.15 Classify each cation as a weak acid or pH-neutral.

- (a) Li^+ (b) CH_3NH_3^+ (c) Fe^{3+}

Classifying Salt Solutions as Acidic, Basic, or Neutral

Since salts contain both a cation and an anion, they can form acidic, basic, or neutral solutions when dissolved in water. The pH of the solution depends on the specific cation and anion involved. We examine the four possibilities individually.

1. **Salts in which neither the cation nor the anion acts as an acid or a base form pH-neutral solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of strong acid forms a *neutral* solution. Some salts in this category include:

NaCl
sodium chloride

$\text{Ca}(\text{NO}_3)_2$
calcium nitrate

KBr
potassium bromide

Cations are pH-neutral.

Anions are conjugate bases of strong acids.

2. **Salts in which the cation does not act as an acid and the anion acts as a base form basic solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of *weak* acid forms a *basic* solution. Salts in this category include:

NaF
sodium fluoride

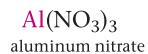
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$
calcium acetate

KNO_2
potassium nitrite

Cations are pH-neutral.

Anions are conjugate bases of weak acids.

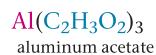
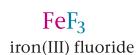
- 3. Salts in which the cation acts as an acid and the anion does not act as a base form acidic solutions.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of *strong* acid forms an *acidic* solution. Salts in this category include:



Cations are conjugate acids
of *weak* bases or small,
highly charged metal ions.

Anions are conjugate bases of *strong* acids.

- 4. Salts in which the cation acts as an acid and the anion acts as a base form solutions in which the pH depends on the relative strengths of the acid and the base.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of a *weak* acid forms a solution in which the pH depends on the relative strengths of the acid and base. Salts in this category include:



Cations are conjugate acids
of *weak* bases or small,
highly charged metal ions.

Anions are conjugate bases of *weak* acids.

We can determine the overall acidity or basicity of a solution containing one of these salts by comparing the K_a of the acid to the K_b of the base—the ion with the higher value of K dominates and determines whether the solution will be acidic or basic, as shown in part (e) of Example 17.16. Table 17.9 summarizes all of these possibilities.

TABLE 17.9 ■ pH of Salt Solutions

		ANION	
		Conjugate base of strong acid	Conjugate base of weak acid
CATION	Conjugate acid of weak base	Acidic	Depends on relative strengths
	Small, highly charged metal ion	Acidic	Depends on relative strengths
	Counterion of strong base	Neutral	Basic

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 17.16

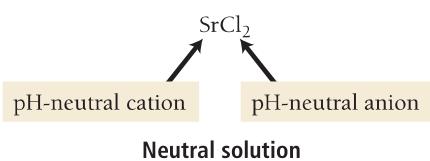
EXAMPLE 17.16 Determining the Overall Acidity or Basicity of Salt Solutions

Determine if the solution formed by each salt is acidic, basic, or neutral.

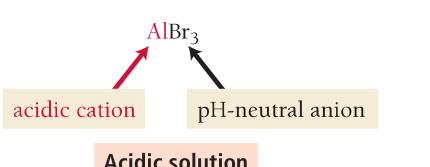
- (a) SrCl_2 (b) AlBr_3 (c) $\text{CH}_3\text{NH}_3\text{NO}_3$
 (d) NaCHO_2 (e) NH_4F

SOLUTION

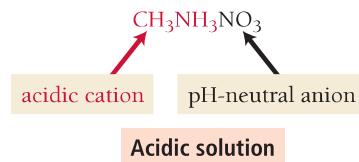
- (a) The Sr^{2+} cation is the counterion of a strong base ($\text{Sr}(\text{OH})_2$) and is pH-neutral. The Cl^- anion is the conjugate base of a strong acid (HCl) and is pH-neutral as well. The SrCl_2 solution is therefore pH-neutral (neither acidic nor basic).



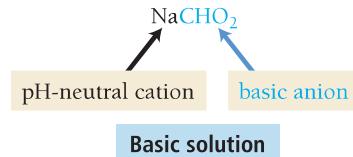
- (b) The Al^{3+} cation is a small, highly charged metal ion (that is not an alkali metal or an alkaline earth metal) and is a weak acid. The Br^- anion is the conjugate base of a strong acid (HBr) and is pH-neutral. The AlBr_3 solution is therefore acidic.



- (c) The CH_3NH_3^+ ion is the conjugate acid of a weak base (CH_3NH_2) and is acidic. The NO_3^- anion is the conjugate base of a strong acid (HNO_3) and is pH-neutral. The $\text{CH}_3\text{NH}_3\text{NO}_3$ solution is therefore acidic.



- (d) The Na^+ cation is the counterion of a strong base and is pH-neutral. The CHO_2^- anion is the conjugate base of a weak acid and is basic. The NaCHO_2 solution is therefore basic.



- (e) The NH_4^+ ion is the conjugate acid of a weak base (NH_3) and is acidic. The F^- ion is the conjugate base of a weak acid and is basic. To determine the overall acidity or basicity of the solution, compare the values of K_a for the acidic cation and K_b for the basic anion. Obtain each value of K from the conjugate by using $K_a \times K_b = K_w$.

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

$$K_b(\text{F}^-) = \frac{K_w}{K_a(\text{HF})} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

$K_a > K_b$ Acidic solution

Since K_a is greater than K_b , the solution is acidic.

FOR PRACTICE 17.16 Determine if the solution formed by each salt is acidic, basic, or neutral.

- (a) NaHCO_3 (b) $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$ (c) KNO_3 (d) $\text{Fe}(\text{NO}_3)_3$

ACIDITY OR BASICITY OF IONIC COMPOUNDS

Which ionic compound forms an acidic solution when dissolved in water?

- (a) NH_4Br (b) KCl (c) NaHCO_3



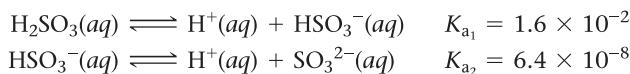
ANSWER NOW!



17.9 Polyprotic Acids

In Section 17.4, we discussed that some acids, called polyprotic acids, contain two or more ionizable protons. Recall that sulfuric acid (H_2SO_4) is a diprotic acid containing two ionizable protons and that phosphoric acid (H_3PO_4) is a triprotic acid containing three ionizable protons.

Typically, a **polyprotic acid** ionizes in successive steps, each with its own K_a . For example, sulfuric acid ionizes in two steps:

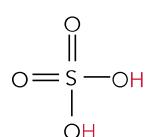
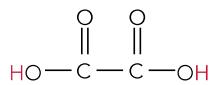
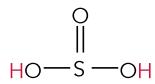
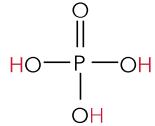
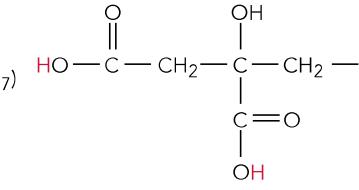
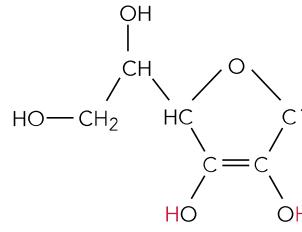
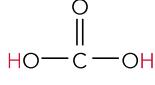


K_{a_1} is the acid ionization constant for the first step, and K_{a_2} is the acid ionization constant for the second step. Notice that K_{a_2} is much smaller than K_{a_1} . This is true for all polyprotic acids and makes sense because the first proton separates from a neutral molecule, while

the second must separate from an anion. The negatively charged anion holds the positively charged proton more tightly, making the proton more difficult to remove and resulting in a smaller value of K_a .

Table 17.10 lists some common polyprotic acids and their acid ionization constants. Notice that in all cases, the value of K_a for each step becomes successively smaller. The value of K_{a_1} for sulfuric acid is identified as strong because sulfuric acid is strong in the first step and weak in the second.

TABLE 17.10 ■ Common Polyprotic Acids and Ionization Constants at 25 °C

Name (Formula)	Structure	Space-Filling Model	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric Acid (H_2SO_4)			Strong	1.2×10^{-2}	
Oxalic Acid ($H_2C_2O_4$)			6.0×10^{-2}	6.1×10^{-5}	
Sulfurous Acid (H_2SO_3)			1.6×10^{-2}	6.4×10^{-8}	
Phosphoric Acid (H_3PO_4)			7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric Acid ($H_3C_6H_5O_7$)			7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Ascorbic Acid ($H_2C_6H_6O_6$)			8.0×10^{-5}	1.6×10^{-12}	
Carbonic Acid (H_2CO_3)			4.3×10^{-7}	5.6×10^{-11}	

Finding the pH of Polyprotic Acid Solutions

Finding the pH of a polyprotic acid solution is less difficult than we might first imagine because, for most polyprotic acids, K_{a_1} is much larger than K_{a_2} (or K_{a_3} for triprotic acids). Therefore, the amount of H_3O^+ formed by the first ionization step is much larger than

that formed by the second or third ionization step. In addition, the formation of H_3O^+ in the first step inhibits the formation of additional H_3O^+ in the second step (because of Le Châtelier's principle). Consequently, we treat most polyprotic acid solutions as if the first step were the only one that contributes to the H_3O^+ concentration, as illustrated in Example 17.17. A major exception is a dilute solution of sulfuric acid, which we examine in Example 17.18.

EXAMPLE 17.17 Finding the pH of a Polyprotic Acid Solution

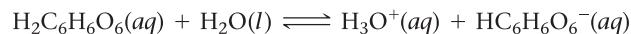
Find the pH of a 0.100 M ascorbic acid ($\text{H}_2\text{C}_6\text{H}_6\text{O}_6$) solution.

SOLUTION

To find the pH, you must find the equilibrium concentration of H_3O^+ . Treat the problem as a weak acid pH problem with a single ionizable proton. The second proton contributes a negligible amount to the concentration of H_3O^+ and can be ignored. Follow the procedure from Example 17.6, shown in condensed form here. Use K_{a_1} for ascorbic acid from Table 17.10.

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

Calculate the pH from H_3O^+ concentration.



	$[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]$	$[\text{H}_3\text{O}^+]$	$[\text{HC}_6\text{H}_6\text{O}_6^-]$
Initial	0.100	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

$$\begin{aligned} K_{\text{a}_1} &= \frac{[\text{H}_3\text{O}^+][\text{HC}_6\text{H}_6\text{O}_6^-]}{[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]} \\ &= \frac{x^2}{0.100 - x} \quad (x \text{ is small}) \\ 8.0 \times 10^{-5} &= \frac{x^2}{0.100} \\ x &= 2.8 \times 10^{-3} \\ \frac{2.8 \times 10^{-3}}{0.100} \times 100\% &= 2.8\% \end{aligned}$$

The approximation is valid. Therefore,

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 2.8 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log(2.8 \times 10^{-3}) = 2.55 \end{aligned}$$

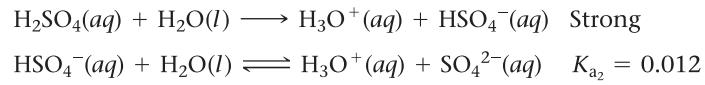
FOR PRACTICE 17.17 Find the pH of a 0.050 M H_2CO_3 solution.

EXAMPLE 17.18 Dilute H_2SO_4 Solutions

Find the pH of a 0.0100 M sulfuric acid (H_2SO_4) solution.

SOLUTION

Sulfuric acid is strong in its first ionization step and weak in its second. Begin by writing the equations for the two steps. As the concentration of an H_2SO_4 solution becomes smaller, the second ionization step becomes more significant because the percent ionization increases (as discussed in Section 17.6). Therefore, for a concentration of 0.0100 M, you can't neglect the H_3O^+ contribution from the second step, as you can for other polyprotic acids. You must calculate the H_3O^+ contributions from both steps.



—Continued on the next page

Continued—

The $[\text{H}_3\text{O}^+]$ that results from the first ionization step is 0.0100 M (because the first step is strong). To determine the $[\text{H}_3\text{O}^+]$ formed by the second step, prepare an ICE table for the second step in which the initial concentration of H_3O^+ is 0.0100 M. The initial concentration of HSO_4^- must also be 0.0100 M (due to the stoichiometry of the ionization reaction).

	$[\text{HSO}_4^-]$	$[\text{H}_3\text{O}^+]$	$[\text{SO}_4^{2-}]$
Initial	0.0100	≈ 0.0100	0.000
Change	$-x$	$+x$	$+x$
Equil	$0.0100 - x$	$0.0100 + x$	x

Substitute the expressions for the equilibrium concentrations (from the table just shown) into the expression for K_{a_2} . In this case, you cannot make the x is small approximation because the equilibrium constant (0.012) is not small relative to the initial concentration (0.0100).

Substitute the value of K_{a_2} and multiply out the expression to arrive at the standard quadratic form.

$$\begin{aligned} K_{a_2} &= \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \\ &= \frac{(0.0100 + x)x}{0.0100 - x} \\ 0.012 &= \frac{0.0100x + x^2}{0.0100 - x} \\ 0.012(0.0100 - x) &= 0.0100x + x^2 \\ 0.00012 - 0.012x &= 0.0100x + x^2 \\ x^2 + 0.022x - 0.00012 &= 0 \end{aligned}$$

Solve the quadratic equation using the quadratic formula.

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-(0.022) \pm \sqrt{(0.022)^2 - 4(1)(-0.00012)}}{2(1)} \\ &= \frac{-0.022 \pm 0.031}{2} \\ x &= -0.027 \text{ or } x = 0.0045 \end{aligned}$$

Since x represents a concentration and since concentrations cannot be negative, we reject the negative root.

$$x = 0.0045$$

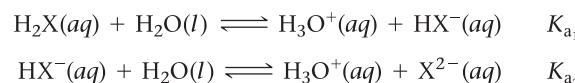
Determine the H_3O^+ concentration from the calculated value of x and calculate the pH. Notice that the second step produces almost half as much H_3O^+ as the first step—an amount that must not be ignored. This is always the case with dilute H_2SO_4 solutions.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0.0100 + x \\ &= 0.0100 + 0.0045 \\ &= 0.0145 \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(0.0145) \\ &= 1.84 \end{aligned}$$

FOR PRACTICE 17.18 Find the pH and $[\text{SO}_4^{2-}]$ of a 0.0075 M sulfuric acid solution.

Finding the Concentration of the Anions for a Weak Diprotic Acid Solution

In some cases, we may want to know the concentrations of the anions formed by a polyprotic acid. Consider the following generic polyprotic acid H_2X and its ionization steps:



In Examples 17.17 and 17.18, we illustrated how to find the concentration of H_3O^+ for such a solution, which is equal to the concentration of HX^- . What if instead we needed to find the concentration of X^{2-} ? To find the concentration of X^{2-} , we use the concentration of HX^- and H_3O^+ (from the first ionization step) as the initial concentrations for the second ionization step. We then solve a second equilibrium problem using the second ionization equation and K_{a_2} , as demonstrated in Example 17.19.

EXAMPLE 17.19**Finding the Concentration of the Anions for a Weak Diprotic Acid Solution**

Find the $[C_6H_6O_6^{2-}]$ of the 0.100 M ascorbic acid ($H_2C_6H_6O_6$) solution in Example 17.17.

SOLUTION

To find the $[C_6H_6O_6^{2-}]$, use the concentrations of $[HC_6H_6O_6^-]$ and H_3O^+ produced by the first ionization step (as calculated in Example 17.17) as the initial concentrations for the second step. Because of the 1:1 stoichiometry, $[HC_6H_6O_6^-] = [H_3O^+]$. Then solve an equilibrium problem for the second step similar to that of Example 17.5, shown in condensed form here. You can find the value of K_{a_2} for ascorbic acid in Table 17.10.



	$[HC_6H_6O_6^-]$	$[H_3O^+]$	$[C_6H_6O_6^{2-}]$
Initial	2.8×10^{-3}	2.8×10^{-3}	0.000
Change	$-x$	$+x$	$+x$
Equil	$2.8 \times 10^{-3} - x$	$2.8 \times 10^{-3} + x$	x

$$\begin{aligned} K_{a_2} &= \frac{[H_3O^+][C_6H_6O_6^{2-}]}{[HC_6H_6O_6^-]} \\ &= \frac{(2.8 \times 10^{-3} + x)x}{2.8 \times 10^{-3} - x} \quad (x \text{ is small}) \\ &= \frac{(2.8 \times 10^{-3})x}{2.8 \times 10^{-3}} \end{aligned}$$

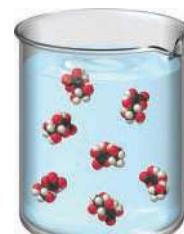
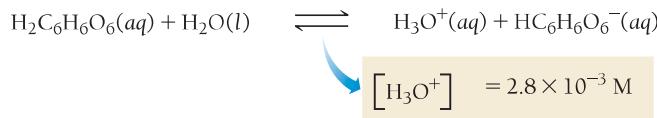
$$x = K_{a_2} = 1.6 \times 10^{-12} \text{ M}$$

Since x is much smaller than 2.8×10^{-3} , the x is small approximation is valid. Therefore,

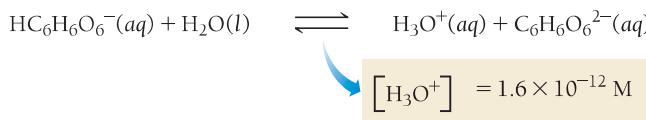
$$[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12} \text{ M}$$

FOR PRACTICE 17.19 Find the $[CO_3^{2-}]$ of the 0.050 M carbonic acid (H_2CO_3) solution in For Practice 17.17.

Notice from the results of Example 17.19 that the concentration of X^{2-} for a weak diprotic acid H_2X is equal to K_{a_2} . This general result applies to all diprotic acids in which the x is small approximation is valid. Notice also that the concentration of H_3O^+ produced by the second ionization step of a diprotic acid is very small compared to the concentration produced by the first step, as shown in Figure 17.13▼.

Dissociation of a Polyprotic Acid

0.100 M $H_2C_6H_6O_6$



$$\begin{aligned} \text{Total } [H_3O^+] &= 2.8 \times 10^{-3} \text{ M} + 1.6 \times 10^{-12} \text{ M} \\ &= 2.8 \times 10^{-3} \text{ M} \end{aligned}$$

▲ FIGURE 17.13 Dissociation of a Polyprotic Acid A 0.100 M $H_2C_6H_6O_6$ solution contains an H_3O^+ concentration of 2.8×10^{-3} M from the first step. The amount of H_3O^+ contributed by the second step is only 1.6×10^{-12} M, which is insignificant compared to the amount produced by the first step.

17.10 Acid Strength and Molecular Structure

We have learned that a Brønsted-Lowry acid is a proton (H^+) donor. However, we have not explored why some hydrogen-containing molecules act as acids while others do not, or why some acids are strong and others weak. For example, why is H_2S acidic while CH_4 is not? Or why is HF a weak acid while HCl is a strong acid? We divide our discussion about these issues into two categories: binary acids (those containing hydrogen and only one other element) and oxyacids (those containing hydrogen bonded to an oxygen atom that is bonded to another element).

Binary Acids

Consider the bond between a hydrogen atom and some other generic element (which we call Y):



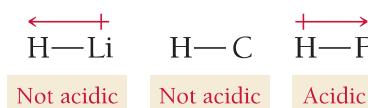
The factors affecting the ease with which this hydrogen is donated (and therefore will be acidic) are the *polarity* of the bond and the *strength* of the bond.

Bond Polarity

Using the notation introduced in Chapter 10, the H—Y bond must be polarized with the hydrogen atom as the positive pole in order for HY to be acidic:



This requirement makes physical sense because the hydrogen atom must be lost as a positively charged ion (H^+). A partial positive charge on the hydrogen atom facilitates its loss. Consider the following three bonds and their corresponding dipole moments:



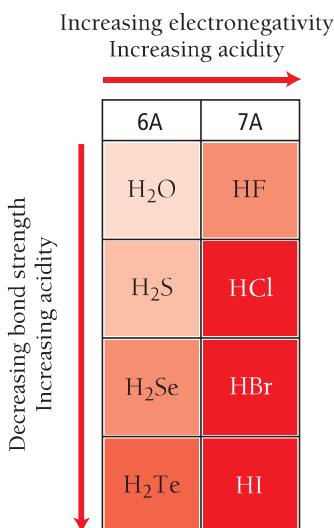
LiH is ionic with the *negative charge on the hydrogen atom*; therefore, LiH is not acidic. The C—H bond is virtually nonpolar because the electronegativities of carbon and hydrogen are similar; therefore C—H is not acidic. In contrast, the H—F bond is polar with the positive charge on the hydrogen atom. As we have discussed in this chapter, HF is an acid. This is because the partial positive charge on the hydrogen atom makes it easier for the hydrogen to be lost as an H^+ ion.

Bond Strength

The strength of the H—Y bond also affects the strength of the corresponding acid. As we might expect, the stronger the bond, the weaker the acid—the more tightly the hydrogen atom is held, the less likely it is to come off. We can see the effect of bond strength by comparing the bond strengths and acidities of the hydrogen halides:

Acid	Bond Energy (kJ/mol)	Type of Acid
H—F	565	Weak
H—Cl	431	Strong
H—Br	364	Strong

HCl and HBr have weaker bonds and are both strong acids. HF, however, has a stronger bond and is therefore a weak acid, despite the greater bond polarity of HF.



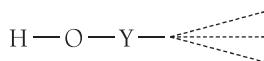
▲ FIGURE 17.14 Acidity of the Group 6A and 7A Hydrides From left to right, the hydrides become more acidic because the H—Y bond becomes more polar. From top to bottom, these hydrides become more acidic because the H—Y bond becomes weaker.

The Combined Effect of Bond Polarity and Bond Strength

We can see the combined effect of bond polarity and bond strength by examining the trends in acidity of the group 6A and 7A hydrides as shown in Figure 17.14 ▲. The hydrides become more acidic from left to right as the H—Y bond becomes more polar. The hydrides also become more acidic from top to bottom as the H—Y bond becomes weaker.

Oxyacids

Oxyacids contain a hydrogen atom bonded to an oxygen atom. The oxygen atom is in turn bonded to another atom (which we call Y):



Oxyacids are sometimes called oxoacids.

Y may or may not be bonded to yet other atoms. The factors affecting the ease with which the hydrogen in an oxyacid is donated (and therefore is acidic) are the *electronegativity of the element Y* and the *number of oxygen atoms attached to the element Y*.

The Electronegativity of Y

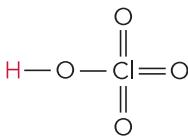
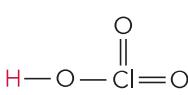
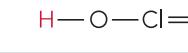
The more electronegative the element Y, the more it weakens and polarizes the H—O bond and the more acidic the oxyacid is. We can see this effect by comparing the electronegativity of Y and the acid ionization constants of the following oxyacids:

Acid	Electronegativity of Y	K_a
H—O—I	2.5	2.3×10^{-11}
H—O—Br	2.8	2.0×10^{-9}
H—O—Cl	3.0	2.9×10^{-8}

Chlorine is the most electronegative of the three elements, and the corresponding acid has the greatest K_a .

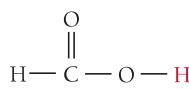
The Number of Oxygen Atoms Bonded to Y

Oxyacids may contain additional oxygen atoms bonded to the element Y. Because these additional oxygen atoms are electronegative, they draw electron density away from Y, which in turn draws electron density away from the H—O bond, further weakening and polarizing it, and leading to increasing acidity. We can see this effect by comparing the following series of acid ionization constants:

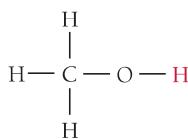
Acid	Structure	K_a
HClO ₄	$\text{H}—\text{O}—\text{Cl}=\text{O}$ 	Strong
HClO ₃	$\text{H}—\text{O}—\text{Cl}=\text{O}$ 	1
HClO ₂	$\text{H}—\text{O}—\text{Cl}=\text{O}$ 	1.1×10^{-2}
HClO	$\text{H}—\text{O}—\text{Cl}$ 	2.9×10^{-8}

The greater the number of oxygen atoms bonded to Y, the stronger the acid. On this basis we would predict that H₂SO₄ is a stronger acid than H₂SO₃ and that HNO₃ is stronger than HNO₂. As we have seen in this chapter, both H₂SO₄ and HNO₃ are strong acids, while H₂SO₃ and HNO₂ are weak acids, as predicted.

ACID STRENGTH AND MOLECULAR STRUCTURE Which of the protons shown in red is more acidic?



(a)



(b)

17.13
Cc

Conceptual Connection

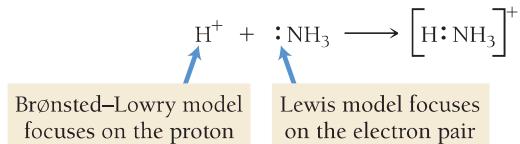
ANSWER NOW!



17.11 Lewis Acids and Bases

We began our definitions of acids and bases with the Arrhenius model. We then saw how the Brønsted–Lowry model, by introducing the concept of a proton donor and proton acceptor, expands the range of substances that we consider acids and bases. We now introduce a third model, which further broadens the range of substances that we can consider acids. This third model is the *Lewis model*, named after G. N. Lewis, the American chemist who devised the electron-dot representation of chemical bonding (Section 10.1).

While the Brønsted–Lowry model focuses on the transfer of a proton, the Lewis model focuses on the transfer of an electron pair. Consider the simple acid–base reaction between the H^+ ion and NH_3 , shown here with Lewis structures:



According to the Brønsted–Lowry model, the ammonia accepts a proton, thus acting as a base. According to the Lewis model, the ammonia acts as a base by *donating an electron pair*. The general definitions of acids and bases according to the Lewis model focus on the electron pair:

Lewis acid: electron pair acceptor

Lewis base: electron pair donor

According to the Lewis definition, H^+ in the reaction just shown is acting as an acid because it is accepting an electron pair from NH_3 . NH_3 is acting as a Lewis base because it is donating an electron pair to H^+ .

Although the Lewis model does not significantly expand the substances that can be considered bases—because all proton acceptors must have an electron pair to bind the proton—it does significantly expand the substances that can be considered acids. According to the Lewis model, a substance need not even contain hydrogen to be an acid. For example, consider the gas-phase reaction between boron trifluoride and ammonia shown here:



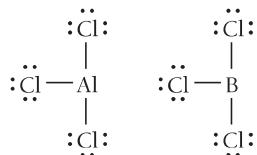
Boron trifluoride has an empty orbital that can accept the electron pair from ammonia and form the product (the product of a Lewis acid–base reaction is sometimes called an *adduct*). The reaction just shown demonstrates an important property of Lewis acids:

A Lewis acid has an empty orbital (or can rearrange electrons to create an empty orbital) that can accept an electron pair.

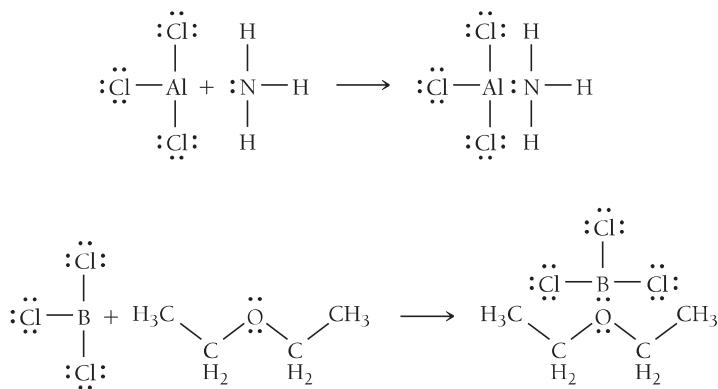
Consequently, the Lewis definition subsumes a whole new class of acids. Next we examine a few examples.

Molecules That Act as Lewis Acids

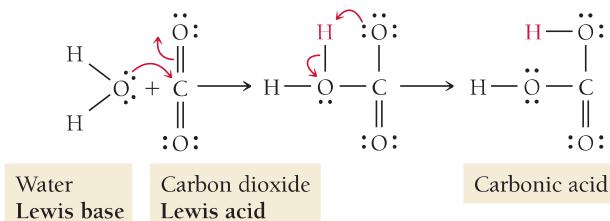
Since molecules with incomplete octets have empty orbitals, they can serve as Lewis acids. For example, both AlCl_3 and BCl_3 have incomplete octets:



These both act as Lewis acids, as shown in the following reactions:



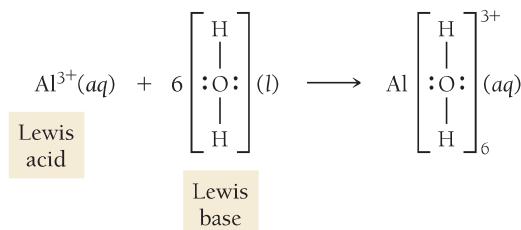
Some molecules that may not initially contain empty orbitals can rearrange their electrons to act as Lewis acids. Consider the reaction between carbon dioxide and water:



The electrons in the double bond on carbon move to the terminal oxygen atom, allowing carbon dioxide to act as a Lewis acid by accepting an electron pair from water. The molecule then undergoes a rearrangement in which the hydrogen atom shown in red bonds with the terminal oxygen atom instead of the internal one.

Cations That Act as Lewis Acids

Some cations, because they are positively charged and have lost some electrons, have empty orbitals that allow them to also act as Lewis acids. Consider the hydration process of the Al^{3+} ion discussed in Section 17.8 and shown here:



The aluminum ion acts as a Lewis acid, accepting lone pairs from six water molecules to form the hydrated ion. Many other small, highly charged metal ions also act as Lewis acids in this way.

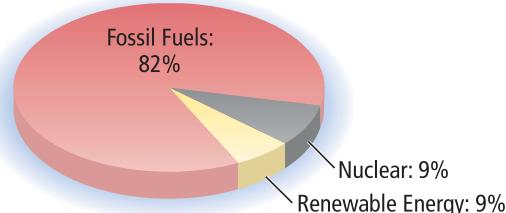
17.12 Acid Rain

About 82% of U.S. energy comes from the combustion of fossil fuels, including petroleum, natural gas, and coal (Figure 17.15▶).

Some fossil fuels, especially coal, contain small amounts of sulfur impurities. During combustion, these impurities react with oxygen to form SO_2 . In addition, during combustion of any fossil fuel, nitrogen from the air reacts with oxygen to form NO_2 . Sulfur dioxide and nitrogen dioxide react with water and diatomic oxygen (O_2) in the atmosphere to form sulfuric acid and nitric acid:



U.S. Energy Consumption by Source, 2017

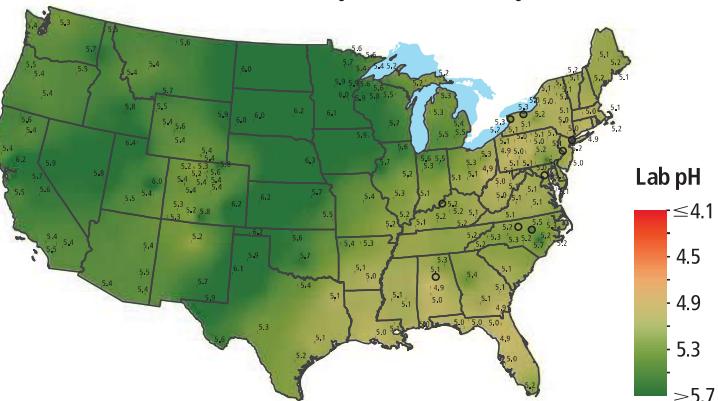


▲ FIGURE 17.15 Sources of U.S. Energy

About 82% of U.S. energy comes from fossil fuel combustion.

Source: U.S. EIA Annual Energy Review 2017

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2015



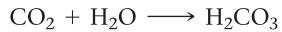
▲ FIGURE 17.16 Acid Rain

Acid rain is a significant problem in the northeastern United States. The map shows the pH of rain that falls across the United States.

Source: National Atmospheric Deposition Program, National Trends Network

These acids combine with rain to form *acid rain*. The problem is greatest in the northeastern portion of the United States, where the rain is significantly acidic because the sulfur and nitrogen oxides produced by coal combustion in the Midwest are carried toward the Northeast by natural air currents.

Even in relatively unpolluted areas, rain is naturally somewhat acidic because of atmospheric carbon dioxide. Carbon dioxide combines with rainwater to form carbonic acid:



However, carbonic acid is a relatively weak acid. Rain that is saturated with CO_2 has a pH of about 5.6, which is only mildly acidic. When nitric acid and sulfuric acid mix with rain, the pH of the rain can fall below 4.3 (Figure 17.16▲). Remember that because of the logarithmic nature of the pH scale, rain with a pH of 4.3 has an $[\text{H}_3\text{O}^+]$ that is 20 times greater than rain with a pH of 5.6. Rain that is this acidic has a harmful impact.

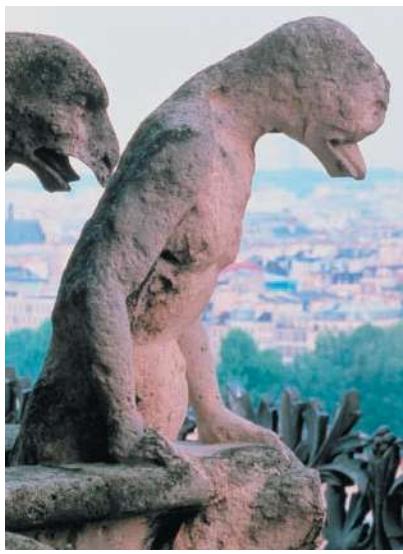
Effects of Acid Rain

Acids dissolve metals and acid rain degrades metal structures. Bridges, railroads, and even automobiles can be damaged by acid rain. Since acids react with carbonates, acid rain also harms building materials that contain carbonates (CO_3^{2-}), including marble, cement, and limestone. Statues, buildings, and pathways in the Northeast show significant signs of acid rain damage (Figure 17.17a▼).

Acid rain also accumulates in lakes and rivers and affects aquatic life. Many lakes, especially those that are surrounded by land that contains significant amounts of limestone (CaCO_3), have the ability to neutralize acidic rain. In the Midwest, for example, limestone-rich soils prevent most lakes from becoming acidified. In the northeastern United States, however, the lack of limestone makes lakes more susceptible, and over 2000 lakes and streams have increased acidity levels due to acid rain. Aquatic plants, frogs, salamanders, and some species of fish are sensitive to acid levels and cannot survive in the acidified water. Trees can also be affected by acid rain because the acid removes nutrients from the soil, making survival difficult (Figure 17.17b▼).

▼ FIGURE 17.17 The Effects of Acid Rain

(a) Buildings, gravestones, and statues damaged by acid rain are a common sight in the northeastern United States and in many other industrialized nations. (b) Some species of trees are highly susceptible to the effects of acid rain.



(a)

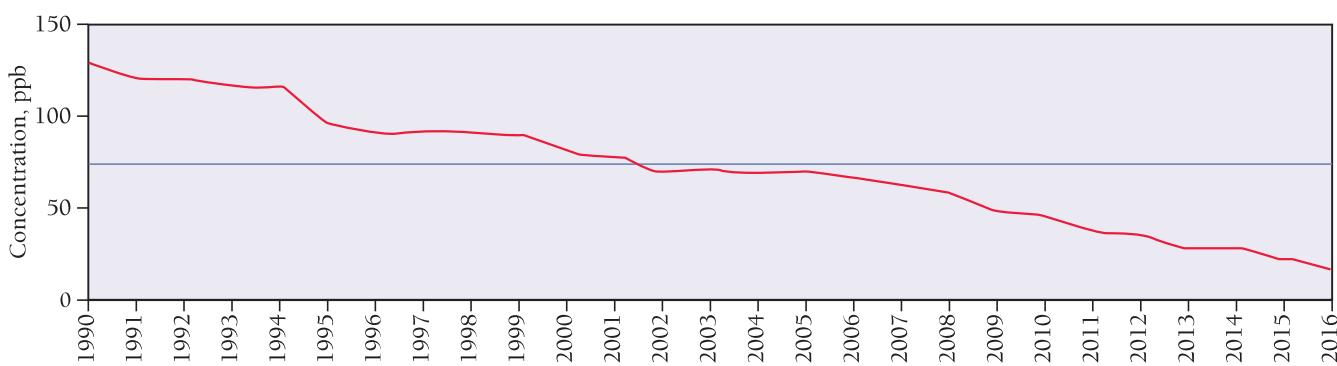


(b)

Acid Rain Legislation

In 1990, the U.S. Congress passed amendments to the Clean Air Act specifically targeted at reducing acid rain. These amendments force electrical utilities—which are the most significant source of SO_2 —to lower their SO_2 emissions gradually over time. The result has been a 76% decrease in SO_2 pollutant levels in the United States since 1990 (Figure 17.18▼). The acidity of rain over the northeastern United States has begun to decrease, and lakes are beginning to recover. In the early 1990s, scientists categorized 30% of the lakes in the Northeast as being of *acute concern*, which means that a complete loss of fish population is expected. Today, the fraction of lakes in this category has been reduced to less than 18%. The acid rain program has been a dramatic success, and today's environmental legislation—such as legislation aimed at global warming—is using the acid rain legislation as a model for what can work.

SO₂ AIR QUALITY, 1990–2016



▲ FIGURE 17.18 U.S. Sulfur Dioxide Pollutant Levels As a result of amendments to the Clean Air Act passed in 1990, SO_2 levels continue to decrease.
Source: U.S. EPA Air Trends

QUIZ YOURSELF NOW!

Self-Assessment Quiz



- Q1.** Identify the conjugate base in the reaction shown here:



MISSED THIS? Read Section 17.3; Watch KCV 17.3, IWE 17.1

- a) HClO_2 b) H_2O c) H_3O^+ d) ClO_2^-

- Q2.** Which pair is a Brønsted-Lowry conjugate acid-base pair?

MISSED THIS? Read Section 17.3; Watch KCV 17.3, IWE 17.1

- a) NH_3 ; NH_4^+ b) H_3O^+ ; OH^-
c) HCl ; HBr d) ClO_4^- ; ClO_3^-

- Q3.** Consider the given acid ionization constants. Identify the strongest conjugate base.

MISSED THIS? Read Sections 17.4, 17.8

Acid	K_a
$\text{HNO}_2(aq)$	4.6×10^{-4}
$\text{HCHO}_2(aq)$	1.8×10^{-4}
$\text{HClO}(aq)$	2.9×10^{-8}
$\text{HCN}(aq)$	4.9×10^{-10}

- a) $\text{NO}_2^-(aq)$ b) $\text{CHO}_2^-(aq)$
c) $\text{ClO}^-(aq)$ d) $\text{CN}^-(aq)$

- Q4.** What is the OH^- concentration in an aqueous solution at 25 °C in which $[\text{H}_3\text{O}^+] = 1.9 \times 10^{-9} \text{ M}$?

MISSED THIS? Read Section 17.5

- a) $1.9 \times 10^{-9} \text{ M}$ b) $5.3 \times 10^{-6} \text{ M}$
c) $5.3 \times 10^6 \text{ M}$ d) $1.9 \times 10^{-23} \text{ M}$

- Q5.** An $\text{HNO}_3(aq)$ solution has a pH of 1.75. What is the molar concentration of the $\text{HNO}_3(aq)$ solution?

MISSED THIS? Read Section 17.6; Watch KCV 17.6

- a) 1.75 M b) $5.6 \times 10^{-13} \text{ M}$
c) 56 M d) 0.018 M

- Q6.** Find the pH of a 0.350 M aqueous benzoic acid solution. For benzoic acid, $K_a = 6.5 \times 10^{-5}$.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.5

- a) 4.64 b) 4.19
c) 2.32 d) 11.68

- Q7.** Find the pH of a 0.155 M $\text{HClO}_2(aq)$ solution. For HClO_2 , $K_a = 0.011$.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.7

- a) 0.92 b) 1.44
c) 1.39 d) 0.69

Continued—

- Q8.** Calculate the percent ionization of 1.45 M aqueous acetic acid solution. For acetic acid, $K_a = 1.8 \times 10^{-5}$.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.9

- a) 0.35% b) 0.0018%
c) 0.29% d) 0.0051%

- Q9.** Consider two aqueous solutions of nitrous acid (HNO_2). Solution A has a concentration of $[\text{HNO}_2] = 0.55\text{ M}$ and solution B has a concentration of $[\text{HNO}_2] = 1.25\text{ M}$. Which statement about the two solutions is true?

MISSED THIS? Read Section 17.6

- a) Solution A has the higher percent ionization and the higher pH.
b) Solution B has the higher percent ionization and the higher pH.
c) Solution A has the higher percent ionization and solution B has the higher pH.
d) Solution B has the higher percent ionization and solution A has the higher pH.

- Q10.** Find the $[\text{OH}^-]$ in a 0.200 M solution of ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$). For ethylamine, $K_b = 5.6 \times 10^{-4}$.

MISSED THIS? Read Section 17.7; Watch IWE 17.12

- a) 11.52 M b) 2.48 M
c) 0.033 M d) 0.011 M

- Q11.** Which ion forms a basic solution when dissolved in water?

MISSED THIS? Read Section 17.8; Watch KCV 17.8

- a) Br^- b) NO_3^- c) HSO_4^- d) SO_3^{2-}

- Q12.** Which compound forms an acidic solution when dissolved in water?

MISSED THIS? Read Section 17.8; Watch KCV 17.8, IWE 17.16

- a) NH_4Cl b) NaCl c) KNO_2 d) $\text{Ca}(\text{NO}_3)_2$

- Q13.** Find the pH of 0.175 M NaCN solution. For HCN, $K_a = 4.9 \times 10^{-10}$.

MISSED THIS? Read Section 17.8; Watch KCV 17.8, IWE 17.14

- a) 5.03 b) 11.28 c) 2.31 d) 8.97

- Q14.** What is the concentration of X^{2-} in a 0.150 M solution of the diprotic acid H_2X ? For H_2X , $K_{a_1} = 4.5 \times 10^{-6}$ and $K_{a_2} = 1.2 \times 10^{-11}$.

MISSED THIS? Read Section 17.9

- a) $9.9 \times 10^{-8}\text{ M}$ b) $2.0 \times 10^{-9}\text{ M}$
c) $8.2 \times 10^{-4}\text{ M}$ d) $1.2 \times 10^{-11}\text{ M}$

- Q15.** Which acid has the largest K_a : $\text{HClO}_2(aq)$, $\text{HBrO}_2(aq)$, or $\text{HIO}_2(aq)$?

MISSED THIS? Read Section 17.10

- a) $\text{HClO}_2(aq)$
b) $\text{HBrO}_2(aq)$
c) $\text{HIO}_2(aq)$
d) All three acids have the same K_a .

Answers: 1. (d) 2. (a) 3. (d) 4. (b) 5. (d) 6. (c) 7. (b) 8. (a) 9. (a) 10. (d) 11. (d) 12. (a) 13. (b) 14. (d) 15. (a)

CHAPTER 17 IN REVIEW

TERMS

Section 17.2

carboxylic acid (733)
alkaloid (734)

Section 17.3

Arrhenius definitions
(of acids and bases) (735)
hydronium ion (735)
Brønsted-Lowry
definitions (of acids and
bases) (735)
amphoteric (735)

conjugate acid-base pair (736)

conjugate acid (736)
conjugate base (736)

Section 17.4

strong acid (737)
weak acid (737)
monoprotic acid (737)
diprotic acid (737)
triprotic acid (738)
acid ionization
constant (K_a) (739)

Section 17.5

autoionization (740)
ion product constant for
water (K_w) (741)
neutral (741)
acidic solution (741)
basic solution (741)
pH (742)

Section 17.6

percent ionization (750)

Section 17.7

strong base (754)
weak base (754)
base ionization
constant (K_b) (755)

Section 17.9

polyprotic acid (765)

Section 17.11

Lewis acid (772)
Lewis base (772)

CONCEPTS

Heartburn (17.1)

- Hydrochloric acid from the stomach sometimes comes in contact with the esophageal lining, resulting in irritation, called heartburn. Heartburn is treated with antacids, bases that neutralize stomach acid.

The Nature of Acids and Bases (17.2)

- Acids generally taste sour, dissolve metals, turn blue litmus paper red, and neutralize bases. Common acids are hydrochloric, sulfuric, nitric, and carboxylic acids.

- Bases generally taste bitter, feel slippery, turn red litmus paper blue, and neutralize acids. Common bases are sodium hydroxide, sodium bicarbonate, and potassium hydroxide.

Definitions of Acids and Bases (17.3)

- The Arrhenius definition of acids and bases states that in an aqueous solution, an acid produces hydrogen ions and a base produces hydroxide ions.
- The Brønsted-Lowry definition states that an acid is a proton (hydrogen ion) donor and a base is a proton acceptor. According to the Brønsted-Lowry definition, two substances related by the transfer of a proton are a conjugate acid-base pair.

Acid Strength and the Acid Dissociation Constant, K_a (17.4)

- In a solution, a strong acid completely ionizes but a weak acid only partially ionizes.
- Generally, the stronger the acid, the weaker the conjugate base, and vice versa.
- The extent of dissociation of a weak acid is quantified by the acid dissociation constant, K_a , which is the equilibrium constant for the ionization of the weak acid.

Autoionization of Water and pH (17.5)

- In an acidic solution, the concentration of hydrogen ions is always greater than the concentration of hydroxide ions. $[H_3O^+]$ multiplied by $[OH^-]$ is always constant at a constant temperature.
- There are two types of logarithmic acid-base scales: pH and pOH. At 25 °C, the sum of a solution's pH and pOH is always 14.

Finding the $[H_3O^+]$ and pH of Strong and Weak Acid Solutions (17.6)

- In a strong acid solution, the hydrogen ion concentration equals the initial concentration of the acid.
- In a weak acid solution, the hydrogen ion concentration—which can be determined by solving an equilibrium problem—is lower than the initial acid concentration.
- The percent ionization of weak acids decreases as the acid (and hydrogen ion) concentration increases.
- In mixtures of two acids with large K_a differences, the concentration of hydrogen ions can usually be determined by considering only the stronger of the two acids.

EQUATIONS AND RELATIONSHIPS

Note: In all of these equations $[H^+]$ is interchangeable with $[H_3O^+]$.

Expression for the Acid Ionization Constant, K_a (17.4)

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

The Ion Product Constant for Water, K_w (17.5)

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

Expression for the pH Scale (17.5)

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

Expression for the pOH Scale (17.5)

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

Base Solutions (17.7)

- A strong base dissociates completely; a weak base does not.
- Most weak bases produce hydroxide ions through the ionization of water. The base ionization constant, K_b , indicates the extent of ionization.

Ions as Acids and Bases (17.8)

- A cation is a weak acid if it is the conjugate acid of a weak base; it is neutral if it is the counterion of a strong base.
- An anion is a weak base if it is the conjugate base of a weak acid; it is neutral if it is the conjugate base of a strong acid.
- To calculate the pH of a solution of an acidic cation or basic anion, we determine K_a or K_b from the equation $K_a \times K_b = K_w$.

Polyprotic Acids (17.9)

- Polyprotic acids contain two or more ionizable protons.
- Generally, polyprotic acids ionize in successive steps, and the value of K_a becomes smaller for each step.
- In many cases, we can determine the $[H_3O^+]$ of a polyprotic acid solution by considering only the first ionization step; then, the concentration of the anion formed in the second ionization step is equivalent to the value of K_{a_2} .

Acid Strength and Molecular Structure (17.10)

- For binary acids, acid strength decreases with increasing bond energy and increases with increasing bond polarity.
- For oxyacids, acid strength increases with the electronegativity of the atoms bonded to the oxygen atom and also increases with the number of oxygen atoms in the molecule.

Lewis Acids and Bases (17.11)

- A third model of acids and bases, the Lewis model, defines a base as an electron pair donor and an acid as an electron pair acceptor. According to this definition, an acid does not have to contain hydrogen. A Lewis acid can be a compound with an empty orbital—or one that will rearrange to make an empty orbital—or a cation.

Acid Rain (17.12)

- The combustion of fossil fuels produces oxides of sulfur and nitrogen, which react with oxygen and water to form sulfuric and nitric acids. These acids combine with rain to form acid rain.
- Acid rain corrodes human-made structures and damages aquatic environments and forests. Environmental legislation has helped stabilize the amount of acid rain being produced.

Relationship between pH and pOH (17.5)

$$pH + pOH = 14.00$$

Expression for the pK_a Scale (17.5)

$$pK_a = -\log K_a$$

Expression for Percent Ionization (17.6)

$$\begin{aligned} \text{Percent ionization} &= \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% \\ &= \frac{[H_3O^+]_{\text{equil}}}{[HA]_{\text{init}}} \times 100\% \end{aligned}$$

Relationship between K_a , K_b , and K_w (17.8)

$$K_a \times K_b = K_w$$

LEARNING OUTCOMES

Chapter Objectives	Assessment
Analyze acids and bases by definition (Arrhenius or Brønsted–Lowry) and their corresponding properties (17.2, 17.3)	Example 17.1 For Practice 17.1 Exercises 33–40
Perform calculations involving K_a (17.4)	Exercises 41–46
Perform calculations involving K_w (17.5)	Example 17.2 For Practice 17.2 Exercises 47–48
Quantify the acidity of a solution using the pH scale (17.5)	Examples 17.3, 17.4 For Practice 17.3, 17.4 Exercises 49–56
Perform pH calculations of strong acids and weak acids (17.6)	Examples 17.5–17.8 For Practice 17.5–17.8 Exercises 57–70
Perform percent ionization calculations for acids (17.6)	Example 17.9 For Practice 17.9 Exercises 71–78
Perform pH calculations for mixtures of acids (17.6)	Example 17.10 For Practice 17.10 Exercises 79–80
Perform pH calculations for a strong base (17.7)	Example 17.11 For Practice 17.11 Exercises 81–86
Perform pH calculations for a weak base (17.7)	Example 17.12 For Practice 17.12 Exercises 87–94
Classify an anion in solution as basic or neutral (17.8)	Example 17.13 For Practice 17.13 Exercises 95–96
Perform pH calculations for solutions containing anions that act as a base (17.8)	Example 17.14 For Practice 17.14 Exercises 97–98
Classify a cation in solution as acidic or neutral (17.8)	Example 17.15 For Practice 17.15 Exercises 99–100
Classify salts solutions as acidic, basic, or neutral (17.8)	Example 17.16 For Practice 17.16 Exercises 101–108
Perform pH calculations of polyprotic acid solutions (17.9)	Examples 17.17, 17.18 For Practice 17.17, 17.18 Exercises 109–112
Calculate the concentration of anions for weak diprotic acid solutions (17.9)	Example 17.19 For Practice 17.19 Exercises 113–116
Predict acidity based on molecular structure (17.10)	Exercises 117–122
Analyze acids and bases in terms of the Lewis model definition (17.11)	Exercises 123–126

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- What causes heartburn? What are some possible ways to alleviate heartburn?
- What are the general physical and chemical properties of acids? Of bases?
- What is a carboxylic acid? Give an example.
- What is the Arrhenius definition of an acid? Of a base?
- What is a hydronium ion? Does H^+ exist in solution by itself?
- What is the Brønsted–Lowry definition of an acid? Of a base?
- Why is there more than one definition of acid–base behavior? Which definition is the right one?
- Describe amphoteric behavior and give an example.
- What is a conjugate acid–base pair? Provide an example.
- Explain the difference between a strong acid and a weak acid and list one example of each.
- What are diprotic and triprotic acids? List an example of each.
- Define the acid ionization constant and explain its significance.
- Write an equation for the autoionization of water and an expression for the ion product constant for water (K_w). What is the value of K_w at 25 °C?
- What happens to the $[OH^-]$ of a solution when the $[H_3O^+]$ is increased? Decreased?
- Define pH. What pH range is considered acidic? Basic? Neutral? (Assume 25 °C.)
- Define pOH. What pOH range is considered acidic? Basic? Neutral? (Assume 25 °C.)
- In most solutions containing a strong or weak acid, the autoionization of water can be neglected when calculating $[H_3O^+]$. Explain why this statement is valid.
- When calculating $[H_3O^+]$ for weak acid solutions, we can often use the *x is small* approximation. Explain the nature of this approximation and why it is valid.
- What is the percent ionization of an acid? Explain what happens to the percent ionization of a weak acid as a function of the concentration of the weak acid solution.

20. In calculating $[\text{H}_3\text{O}^+]$ for a mixture of a strong acid and weak acid, the weak acid can often be neglected. Explain why this statement is valid.
21. Write a generic equation showing how a weak base ionizes water.
22. How can you determine if an anion will act as a weak base? Write a generic equation showing the reaction by which an anion, A^- , acts as a weak base.
23. What is the relationship between the acid ionization constant for a weak acid (K_a) and the base ionization constant for its conjugate base (K_b)?
24. What kinds of cations act as weak acids? List some examples.
25. When calculating the $[\text{H}_3\text{O}^+]$ for a polyprotic acid, the second ionization step can often be neglected. Explain why this statement is valid.
26. For a weak diprotic acid H_2X , what is the relationship between $[\text{X}^{2-}]$ and K_{a_2} ? Under what conditions does this relationship exist?
27. For a binary acid, $\text{H}-\text{Y}$, which factors affect the relative ease with which the acid ionizes?
28. Which factors affect the relative acidity of an oxyacid?
29. What is the Lewis definition of an acid? Of a base?
30. What is a general characteristic of a Lewis acid? Of a Lewis base?
31. What is acid rain? What causes it, and where is the problem the greatest?
32. What are the main detrimental effects of acid rain? What is being done to address the problem of acid rain?

PROBLEMS BY TOPIC

The Nature and Definitions of Acids and Base

33. Identify each substance as an acid or a base and write a chemical equation showing how it is an acid or a base according to the Arrhenius definition.

MISSED THIS? Read Section 17.3; Watch KCV 17.3

- a. $\text{HNO}_3(aq)$ b. $\text{NH}_4^+(aq)$
c. $\text{KOH}(aq)$ d. $\text{HC}_2\text{H}_3\text{O}_2(aq)$

34. Identify each substance as an acid or a base and write a chemical equation showing how it is an acid or a base in aqueous solution according to the Arrhenius definition.

- a. $\text{NaOH}(aq)$ b. $\text{H}_2\text{SO}_4(aq)$
c. $\text{HBr}(aq)$ d. $\text{Sr}(\text{OH})_2(aq)$

35. In each reaction, identify the Brønsted-Lowry acid, the Brønsted-Lowry base, the conjugate acid, and the conjugate base.

MISSED THIS? Read Section 17.3; Watch KCV 17.3, IWE 17.1

- a. $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$
b. $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$
c. $\text{HNO}_3(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)$
d. $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$

36. In each reaction, identify the Brønsted-Lowry acid, the Brønsted-Lowry base, the conjugate acid, and the conjugate base.

- a. $\text{HI}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{I}^-(aq)$
b. $\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$
c. $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$
d. $\text{HBr}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{Br}^-(aq)$

37. Write the formula for the conjugate base of each acid.

MISSED THIS? Read Section 17.3; Watch KCV 17.3, IWE 17.1

- a. HCl b. H_2SO_3 c. HCHO_2 d. HF

38. Write the formula for the conjugate acid of each base.

- a. NH_3 b. ClO_4^- c. HSO_4^- d. CO_3^{2-}

39. Both H_2O and H_2PO_4^- are amphoteric. Write an equation to show how each substance can act as an acid and another equation to show how each can act as a base.

MISSED THIS? Read Sections 17.3, 17.5; Watch KCV 17.3, IWE 17.1

40. Both HCO_3^- and HS^- are amphoteric. Write an equation to show how each substance can act as an acid and another equation to show how each can act as a base.

MISSED THIS? Read Sections 17.3, 17.5; Watch KCV 17.3, IWE 17.1

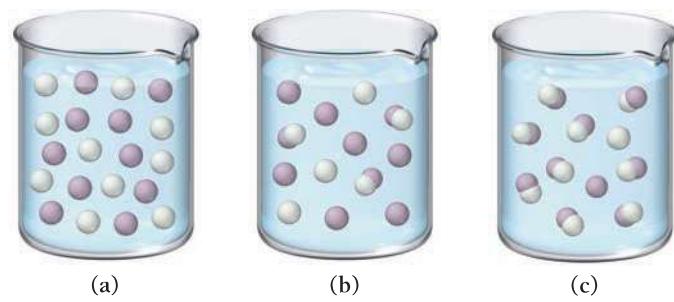
Acid Strength and K_a

41. Classify each acid as strong or weak. If the acid is weak, write an expression for the acid ionization constant (K_a).

MISSED THIS? Read Section 17.4; Watch KCV 17.4

- a. HNO_3 b. HCl c. HBr d. H_2SO_3

42. For a weak diprotic acid H_2X , what is the relationship between $[\text{X}^{2-}]$ and K_{a_2} ? Under what conditions does this relationship exist?
43. For a binary acid, $\text{H}-\text{Y}$, which factors affect the relative ease with which the acid ionizes?
44. Which factors affect the relative acidity of an oxyacid?
45. What is the Lewis definition of an acid? Of a base?
46. What is a general characteristic of a Lewis acid? Of a Lewis base?
47. What is acid rain? What causes it, and where is the problem the greatest?
48. What are the main detrimental effects of acid rain? What is being done to address the problem of acid rain?



49. Rank the solutions in order of decreasing $[\text{H}_3\text{O}^+]$: 0.10 M HCl ; 0.10 M HF ; 0.10 M HClO ; 0.10 M $\text{HC}_6\text{H}_5\text{O}$.

50. Pick the stronger base from each pair.

MISSED THIS? Read Sections 17.4, 17.8

- a. F^- or Cl^- b. NO_2^- or NO_3^- c. F^- or ClO^-

51. Pick the stronger base from each pair.

- a. ClO_4^- or ClO_2^- b. Cl^- or H_2O c. CN^- or ClO^-

Autoionization of Water and pH

52. Calculate $[\text{OH}^-]$ in each aqueous solution at 25 °C, and classify the solution as acidic or basic.

MISSED THIS? Read Section 17.5

- a. $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-8} \text{ M}$ b. $[\text{H}_3\text{O}^+] = 8.5 \times 10^{-5} \text{ M}$
c. $[\text{H}_3\text{O}^+] = 3.5 \times 10^{-2} \text{ M}$

53. Calculate $[\text{H}_3\text{O}^+]$ in each aqueous solution at 25 °C, and classify each solution as acidic or basic.

- a. $[\text{OH}^-] = 1.1 \times 10^{-9} \text{ M}$ b. $[\text{OH}^-] = 2.9 \times 10^{-2} \text{ M}$
c. $[\text{OH}^-] = 6.9 \times 10^{-12} \text{ M}$

54. Calculate the pH and pOH of each solution at 25 °C.

MISSED THIS? Read Section 17.5; Watch IWE 17.3

- a. $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-8} \text{ M}$ b. $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$
c. $[\text{H}_3\text{O}^+] = 2.2 \times 10^{-6} \text{ M}$

55. Calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ for each solution at 25 °C.

- a. $\text{pH} = 8.55$ b. $\text{pH} = 11.23$ c. $\text{pH} = 2.87$

51. Complete the table. (All solutions are at 25 °C.)

MISSED THIS? Read Section 17.5; Watch IWE 17.3

[H ₃ O ⁺]	[OH ⁻]	pH	Acidic or Basic
_____	_____	3.15	_____
3.7 × 10 ⁻⁹	_____	_____	_____
_____	_____	11.1	_____
_____	1.6 × 10 ⁻¹¹	_____	_____

52. Complete the table. (All solutions are at 25 °C.)

[H ₃ O ⁺]	[OH ⁻]	pH	Acidic or Basic
3.5 × 10 ⁻³	_____	_____	_____
_____	3.8 × 10 ⁻⁷	_____	_____
1.8 × 10 ⁻⁹	_____	_____	_____
_____	_____	7.15	_____

53. Like all equilibrium constants, the value of K_w depends on temperature. At body temperature (37 °C), $K_w = 2.4 \times 10^{-14}$. What are the [H₃O⁺] and pH of pure water at body temperature?

MISSED THIS? Read Sections 17.5, 17.6; Watch KCV 17.6, IWE 17.5

54. The value of K_w increases with increasing temperature. Is the autoionization of water endothermic or exothermic?

55. Calculate the pH of each acid solution. Explain how the resulting pH values demonstrate that the pH of an acid solution should carry as many digits to the right of the decimal place as the number of significant figures in the concentration of the solution.

MISSED THIS? Read Section 17.5

$$[\text{H}_3\text{O}^+] = 0.044 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.045 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.046 \text{ M}$$

56. Determine the concentration of H₃O⁺ to the correct number of significant figures in a solution with each pH. Describe how these calculations show the relationship between the number of digits to the right of the decimal place in pH and the number of significant figures in concentration.

$$\text{pH} = 2.50$$

$$\text{pH} = 2.51$$

$$\text{pH} = 2.52$$

Acid Solutions

57. For each strong acid solution, determine [H₃O⁺], [OH⁻], and pH.

MISSED THIS? Read Section 17.6

- a. 0.25 M HCl
- b. 0.015 M HNO₃
- c. a solution that is 0.052 M in HBr and 0.020 M in HNO₃
- d. a solution that is 0.655% HNO₃ by mass (assume a density of 1.01 g/mL for the solution)

58. Determine the pH of each solution.

- a. 0.048 M HI
- b. 0.0895 M HClO₄
- c. a solution that is 0.045 M in HClO₄ and 0.048 M in HCl
- d. a solution that is 1.09% HCl by mass (assume a density of 1.01 g/mL for the solution)

59. What mass of HI must be present in 0.250 L of solution to obtain a solution with each pH value?

MISSED THIS? Read Section 17.6

- a. pH = 1.25
- b. pH = 1.75
- c. pH = 2.85

60. What mass of HClO₄ must be present in 0.500 L of solution to obtain a solution with each pH value?

- a. pH = 2.50
- b. pH = 1.50
- c. pH = 0.50

61. What is the pH of a solution in which 224 mL of HCl(g), measured at 27.2 °C and 1.02 atm, is dissolved in 1.5 L of aqueous solution?

MISSED THIS? Read Section 17.6

62. What volume of a concentrated HCl solution, which is 36.0% HCl by mass and has a density of 1.179 g/mL, should be used to make 5.00 L of an HCl solution with a pH of 1.8?

63. Determine the [H₃O⁺] and pH of a 0.100 M solution of benzoic acid. **MISSED THIS?** Read Section 17.6; Watch KCV 17.6, IWE 17.5

64. Determine the [H₃O⁺] and pH of a 0.200 M solution of formic acid.

65. Determine the pH of an HNO₂ solution of each concentration. In which cases can you *not* make the simplifying assumption that x is small?

- MISSED THIS?** Read Section 17.6; Watch KCV 17.6, IWE 17.5, 17.7
- a. 0.500 M
 - b. 0.100 M
 - c. 0.0100 M

66. Determine the pH of an HF solution of each concentration. In which cases can you *not* make the simplifying assumption that x is small? (K_a for HF is 6.8×10^{-4} .)

- a. 0.250 M
- b. 0.0500 M
- c. 0.0250 M

67. If 15.0 mL of glacial acetic acid (pure HC₂H₃O₂) is diluted to 1.50 L with water, what is the pH of the resulting solution? The density of glacial acetic acid is 1.05 g/mL.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.5

68. Calculate the pH of a formic acid solution that contains 1.35% formic acid by mass. (Assume a density of 1.01 g/mL for the solution.)

69. A 0.185 M solution of a weak acid (HA) has a pH of 2.95. Calculate the acid ionization constant (K_a) for the acid.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.8

70. A 0.115 M solution of a weak acid (HA) has a pH of 3.29. Calculate the acid ionization constant (K_a) for the acid.

71. Determine the percent ionization of a 0.125 M HCN solution. **MISSED THIS?** Read Section 17.6; Watch KCV 17.6, IWE 17.9

72. Determine the percent ionization of a 0.225 M solution of benzoic acid.

73. Calculate the percent ionization of an acetic acid solution having the given concentration.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.9

- a. 1.00 M
- b. 0.500 M
- c. 0.100 M
- d. 0.0500 M

74. Calculate the percent ionization of a formic acid solution having the given concentration.

- a. 1.00 M
- b. 0.500 M
- c. 0.100 M
- d. 0.0500 M

75. A 0.148 M solution of a monoprotic acid has a percent ionization of 1.55%. Determine the acid ionization constant (K_a) for the acid.

MISSED THIS? Read Section 17.6; Watch KCV 17.6, IWE 17.9

76. A 0.085 M solution of a monoprotic acid has a percent ionization of 0.59%. Determine the acid ionization constant (K_a) for the acid.

77. Find the pH and percent ionization of each HF solution. (K_a for HF is 6.8×10^{-4} .) **MISSED THIS?** Read Section 17.6; Watch KCV 17.6, IWE 17.5, 17.7, 17.9

- a. 0.250 M HF
- b. 0.100 M HF
- c. 0.050 M HF

78. Find the pH and percent ionization of a 0.100 M solution of a weak monoprotic acid having the given K_a values.
- $K_a = 1.0 \times 10^{-5}$
 - $K_a = 1.0 \times 10^{-3}$
 - $K_a = 1.0 \times 10^{-1}$
79. Find the pH of each mixture of acids.
- MISSED THIS? Read Section 17.6**
- 0.115 M in HBr and 0.125 M in HCHO_2
 - 0.150 M in HNO_2 and 0.085 M in HNO_3
 - 0.185 M in HCHO_2 and 0.225 M in $\text{HC}_2\text{H}_3\text{O}_2$
 - 0.050 M in acetic acid and 0.050 M in hydrocyanic acid
80. Find the pH of each mixture of acids.
- 0.075 M in HNO_3 and 0.175 M in $\text{HC}_7\text{H}_5\text{O}_2$
 - 0.020 M in HBr and 0.015 M in HClO_4
 - 0.095 M in HF and 0.225 M in $\text{HC}_6\text{H}_5\text{O}$
 - 0.100 M in formic acid and 0.050 M in hypochlorous acid

Base Solutions

81. For each strong base solution, determine $[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$, pH, and pOH. **MISSED THIS? Read Section 17.7**
- 0.15 M NaOH
 - 1.5×10^{-3} M $\text{Ca}(\text{OH})_2$
 - 4.8×10^{-4} M $\text{Sr}(\text{OH})_2$
 - 8.7×10^{-5} M KOH
82. For each strong base solution, determine $[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$, pH, and pOH.
- 8.77×10^{-3} M LiOH
 - 0.0112 M $\text{Ba}(\text{OH})_2$
 - 1.9×10^{-4} M KOH
 - 5.0×10^{-4} M $\text{Ca}(\text{OH})_2$
83. Determine the pH of a solution that is 3.85% KOH by mass. Assume that the solution has density of 1.01 g/mL.
- MISSED THIS? Read Section 17.7**
84. Determine the pH of a solution that is 1.55% NaOH by mass. Assume that the solution has density of 1.01 g/mL.
85. What volume of 0.855 M KOH solution is required to make 3.55 L of a solution with pH of 12.4?
- MISSED THIS? Read Section 17.7**
86. What volume of a 15.0% by mass NaOH solution, which has a density of 1.116 g/mL, should be used to make 5.00 L of an NaOH solution with a pH of 10.8?
87. Write equations showing how each weak base ionizes water to form OH^- . Also write the corresponding expression for K_b .
- MISSED THIS? Read Section 17.7**
- NH_3
 - HCO_3^-
 - CH_3NH_2
88. Write equations showing how each weak base ionizes water to form OH^- . Also write the corresponding expression for K_b .
- CO_3^{2-}
 - $\text{C}_6\text{H}_5\text{NH}_2$
 - $\text{C}_2\text{H}_5\text{NH}_2$
89. Determine the $[\text{OH}^-]$, pH, and pOH of a 0.15 M ammonia solution. **MISSED THIS? Read Section 17.7; Watch IWE 17.12**
90. Determine the $[\text{OH}^-]$, pH, and pOH of a solution that is 0.125 M in CO_3^{2-} .
91. Caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) is a weak base with a pK_b of 10.4. Calculate the pH of a solution containing a caffeine concentration of 455 mg/L.
- MISSED THIS? Read Section 17.7; Watch IWE 17.12**
92. Amphetamine ($\text{C}_9\text{H}_{13}\text{N}$) is a weak base with a pK_b of 4.2. Calculate the pH of a solution containing an amphetamine concentration of 225 mg/L.
93. Morphine is a weak base. A 0.150 M solution of morphine has a pH of 10.7. What is K_b for morphine?
- MISSED THIS? Read Section 17.7; Watch IWE 17.8, 17.12**
94. A 0.135 M solution of a weak base has a pH of 11.23. Determine K_b for the base.

Acid–Base Properties of Ions and Salts

95. Determine if each anion acts as a weak base in solution. For those anions that are basic, write an equation that shows how the anion acts as a base.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8**
- Br^-
 - ClO^-
 - CN^-
 - Cl^-
96. Determine whether each anion is basic or neutral. For those anions that are basic, write an equation that shows how the anion acts as a base.
- $\text{C}_7\text{H}_5\text{O}_2^-$
 - I^-
 - NO_3^-
 - F^-
97. Determine the $[\text{OH}^-]$ and pH of a solution that is 0.140 M in F^- . **MISSED THIS? Read Section 17.8; Watch KCV 17.8, IWE 17.14**
98. Determine the $[\text{OH}^-]$ and pH of a solution that is 0.250 M in HCO_3^- .
99. Determine whether each cation is acidic or pH-neutral. For those cations that are acidic, write an equation that shows how the cation acts as an acid.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8**
- NH_4^+
 - Na^+
 - Co^{3+}
 - CH_2NH_3^+
100. Determine whether each cation is acidic or pH-neutral. For each cation that is acidic, write an equation that shows how the cation acts as an acid.
- Sr^{2+}
 - Mn^{3+}
 - $\text{C}_5\text{H}_5\text{NH}^+$
 - Li^+
101. Determine if each salt will form a solution that is acidic, basic, or pH-neutral.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8, IWE 17.16**
- FeCl_3
 - NaF
 - CaBr_2
 - NH_4Br
 - $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_2$
102. Determine if each salt will form a solution that is acidic, basic, or pH-neutral.
- $\text{Al}(\text{NO}_3)_3$
 - $\text{C}_2\text{H}_5\text{NH}_3\text{NO}_3$
 - K_2CO_3
 - RbI
 - NH_4ClO
103. Arrange the solutions in order of increasing acidity.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8**
- NaCl
 - NH_4Cl
 - NaHCO_3
 - NH_4ClO_2
 - NaOH
104. Arrange the solutions in order of increasing basicity.
- $\text{CH}_3\text{NH}_3\text{Br}$
 - KOH
 - KBr
 - KCN
 - $\text{C}_5\text{H}_5\text{NHNO}_2$
105. Determine the pH of each solution.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8, 17.14, 17.16**
- 0.10 M NH_4Cl
 - 0.10 M $\text{NaC}_2\text{H}_3\text{O}_2$
 - 0.10 M NaCl
106. Determine the pH of each solution.
- 0.20 M KCHO_2
 - 0.20 M $\text{CH}_3\text{NH}_3\text{I}$
 - 0.20 M KI
107. Calculate the concentration of all species in a 0.15 M KF solution.
- MISSED THIS? Read Section 17.8; Watch KCV 17.8, 17.14, 17.16**
108. Calculate the concentration of all species in a 0.225 M $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ solution.

Polyprotic Acids

109. Write chemical equations and corresponding equilibrium expressions for each of the three ionization steps of phosphoric acid.
- MISSED THIS? Read Section 17.9**
110. Write chemical equations and corresponding equilibrium expressions for each of the two ionization steps of carbonic acid.
111. Calculate the $[\text{H}_3\text{O}^+]$ and pH of each polyprotic acid solution.
- MISSED THIS? Read Section 17.9**
- 0.350 M H_3PO_4
 - 0.350 M $\text{H}_2\text{C}_2\text{O}_4$
112. Calculate the $[\text{H}_3\text{O}^+]$ and pH of each polyprotic acid solution.
- 0.125 M H_2CO_3
 - 0.125 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$

- 113.** Calculate the concentration of all species in a 0.500 M solution of H_2SO_3 .

MISSED THIS? Read Section 17.9

- 114.** Calculate the concentration of all species in a 0.155 M solution of H_2CO_3 .

- 115.** Calculate the $[\text{H}_3\text{O}^+]$ and pH of each H_2SO_4 solution. At approximately what concentration does the x is small approximation break down?

MISSED THIS? Read Section 17.9

- 0.50 M
- 0.10 M
- 0.050 M

- 116.** Consider a 0.10 M solution of a weak polyprotic acid (H_2A) with the possible values of K_{a_1} and K_{a_2} given here.

- $K_{\text{a}_1} = 1.0 \times 10^{-4}$; $K_{\text{a}_2} = 5.0 \times 10^{-5}$
- $K_{\text{a}_1} = 1.0 \times 10^{-4}$; $K_{\text{a}_2} = 1.0 \times 10^{-5}$
- $K_{\text{a}_1} = 1.0 \times 10^{-4}$; $K_{\text{a}_2} = 1.0 \times 10^{-6}$

Calculate the contributions to $[\text{H}_3\text{O}^+]$ from each ionization step. At what point can the contribution of the second step be neglected?

Molecular Structure and Acid Strength

- 117.** Based on their molecular structure, pick the stronger acid from each pair of binary acids. Explain your choice.

MISSED THIS? Read Section 17.10

- HF and HCl
- H_2O or HF
- H_2Se or H_2S

- 118.** Based on molecular structure, arrange the binary compounds in order of increasing acid strength. Explain your choice.



- 119.** Based on their molecular structure, pick the stronger acid from each pair of oxyacids. Explain your choice.

MISSED THIS? Read Section 17.10

- H_2SO_4 or H_2SO_3
- HClO_2 or HClO
- HClO or HBrO
- CCl_3COOH or CH_3COOH

- 120.** Based on molecular structure, arrange the oxyacids in order of increasing acid strength. Explain your choice.



- 121.** Which is a stronger base, S^{2-} or Se^{2-} ? Explain.

MISSED THIS? Read Section 17.10

- 122.** Which is a stronger base, PO_4^{3-} or AsO_4^{3-} ? Explain.

Lewis Acids and Bases

- 123.** Classify each species as either a Lewis acid or a Lewis base.

MISSED THIS? Read Section 17.11

- Fe^{3+}
- BH_3
- NH_3
- F^-

- 124.** Classify each species as either a Lewis acid or a Lewis base.

- BeCl_2
- OH^-
- $\text{B}(\text{OH})_3$
- CN^-

- 125.** Identify the Lewis acid and Lewis base from among the reactants in each equation.

MISSED THIS? Read Section 17.11

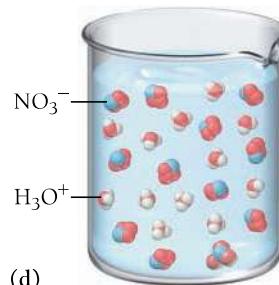
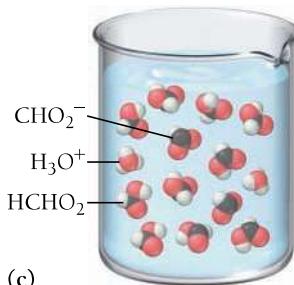
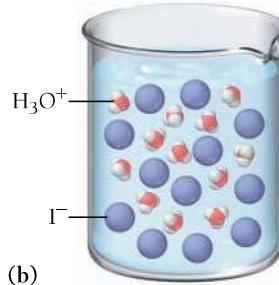
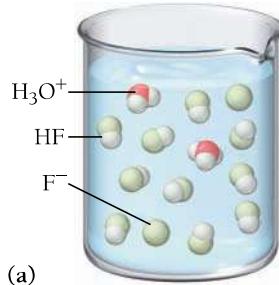
- $\text{Fe}^{3+}(aq) + 6 \text{H}_2\text{O}(l) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{3+}(aq)$
- $\text{Zn}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}(aq)$
- $(\text{CH}_3)_3\text{N}(g) + \text{BF}_3(g) \rightleftharpoons (\text{CH}_3)_3\text{NBF}_3(s)$

- 126.** Identify the Lewis acid and Lewis base from among the reactants in each equation.

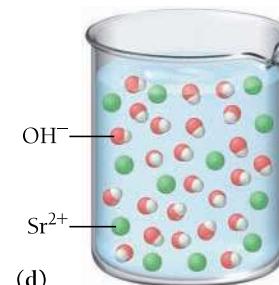
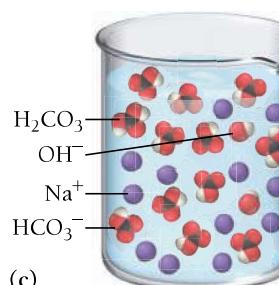
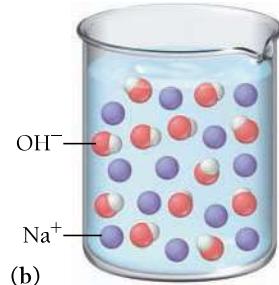
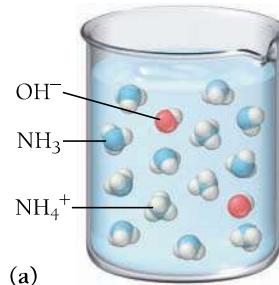
- $\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
- $\text{AlBr}_3 + \text{NH}_3 \rightleftharpoons \text{H}_3\text{NAlBr}_3$
- $\text{F}^-(aq) + \text{BF}_3(aq) \rightleftharpoons \text{BF}_4^-(aq)$

CUMULATIVE PROBLEMS

- 127.** Based on these molecular views, determine whether each pictured acid is weak or strong.



- 128.** Based on these molecular views, determine whether each pictured base is weak or strong.

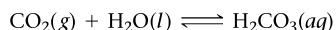


- 129.** The binding of oxygen by hemoglobin in the blood involves the equilibrium reaction:



In this equation, Hb is hemoglobin. The pH of normal human blood is highly controlled within a range of 7.35 to 7.45. Given the above equilibrium, why is this important? What would happen to the oxygen-carrying capacity of hemoglobin if blood became too acidic (a dangerous condition known as acidosis)?

- 130.** Carbon dioxide dissolves in water according to the equations:



Carbon dioxide levels in the atmosphere have increased about 20% over the last century. Given that Earth's oceans are exposed to atmospheric carbon dioxide, what effect might the increased CO₂ be having on the pH of the world's oceans? What effect might this change be having on the limestone structures (primarily CaCO₃) of coral reefs and marine shells?

- 131.** People often take milk of magnesia to reduce the discomfort associated with acid stomach or heartburn. The recommended dose is 1 teaspoon, which contains 4.00×10^2 mg of Mg(OH)₂. What volume of an HCl solution with a pH of 1.3 can be neutralized by one dose of milk of magnesia? If the stomach contains 2.00×10^2 mL of pH 1.3 solution, is all the acid neutralized? If not, what fraction is neutralized?

- 132.** Lakes that have been acidified by acid rain can be neutralized by liming, the addition of limestone (CaCO₃). How much limestone (in kg) is required to completely neutralize a 4.3 billion liter lake with a pH of 5.5?

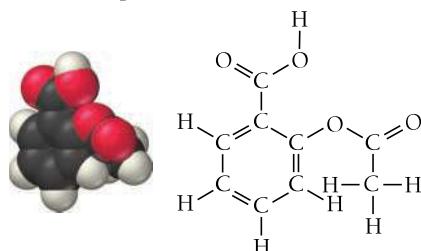


▲ Liming a lake.

- 133.** Acid rain over the Great Lakes has a pH of about 4.5. Calculate the [H₃O⁺] of this rain and compare that value to the [H₃O⁺] of rain over the West Coast that has a pH of 5.4. How many times more concentrated is the acid in rain over the Great Lakes?

- 134.** White wines tend to be more acidic than red wines. Find the [H₃O⁺] in a Sauvignon Blanc with a pH of 3.23 and a Cabernet Sauvignon with a pH of 3.64. How many times more acidic is the Sauvignon Blanc?

- 135.** Common aspirin is acetylsalicylic acid, which has the structure shown here and a pK_a of 3.5.



Calculate the pH of a solution in which one normal adult dose of aspirin (6.5×10^2 mg) is dissolved in 8.0 ounces of water.

- 136.** The AIDS drug zalcitabine (also known as ddC) is a weak base with a pK_b of 9.8.

What percentage of the base is protonated in an aqueous zalcitabine solution containing 565 mg/L?

- 137.** Determine the pH of each solution.

- 0.0100 M HClO₄
- 0.115 M HClO₂
- 0.045 M Sr(OH)₂
- 0.0852 M KCN
- 0.155 M NH₄Cl

- 138.** Determine the pH of each solution.

- 0.0650 M HNO₃
- 0.150 M HNO₂
- 0.0195 M KOH
- 0.245 M CH₃NH₃I
- 0.318 M KC₆H₅O

- 139.** Determine the pH of each two-component solution.

- 0.0550 M in HI and 0.00850 M in HF
- 0.112 M in NaCl and 0.0953 M in KF
- 0.132 M in NH₄Cl and 0.150 M HNO₃
- 0.0887 M in sodium benzoate and 0.225 M in potassium bromide
- 0.0450 M in HCl and 0.0225 M in HNO₃

- 140.** Determine the pH of each two-component solution.

- 0.050 M KOH and 0.015 M Ba(OH)₂
- 0.265 M NH₄NO₃ and 0.102 M HCN
- 0.075 M RbOH and 0.100 M NaHCO₃
- 0.088 M HClO₄ and 0.022 M KOH
- 0.115 M NaClO and 0.0500 M KI

- 141.** Write net ionic equations for the reactions that take place when aqueous solutions of the following substances are mixed:

- sodium cyanide and nitric acid
- ammonium chloride and sodium hydroxide
- sodium cyanide and ammonium bromide
- potassium hydrogen sulfate and lithium acetate
- sodium hypochlorite and ammonia

- 142.** Morphine has the formula C₁₇H₁₉NO₃. It is a base and accepts one proton per molecule. It is isolated from opium. A 0.682-g sample of opium is found to require 8.92 mL of a 0.0116 M solution of sulfuric acid for neutralization. Assuming that morphine is the only acid or base present in opium, calculate the percent morphine in the sample of opium.

- 143.** The pH of a 1.00 M solution of urea, a weak organic base, is 7.050. Calculate the K_a of protonated urea.

- 144.** A solution is prepared by dissolving 0.10 mol of acetic acid and 0.10 mol of ammonium chloride in enough water to make 1.0 L of solution. Find the concentration of ammonia in the solution.

- 145.** Lactic acid is a weak acid found in milk. Its calcium salt is a source of calcium for growing animals. A saturated solution of this salt, which we can represent as Ca(Lact)₂, has a [Ca²⁺] = 0.26 M and a pH = 8.78. Assuming the salt is completely dissociated, calculate the K_a of lactic acid.

- 146.** A solution of 0.23 mol of the chloride salt of protonated quinine (QH⁺), a weak organic base, in 1.0 L of solution has pH = 4.58. Find the K_b of quinine (Q).

CHALLENGE PROBLEMS

- 147.** A student mistakenly calculates the pH of a 1.0×10^{-7} M HI solution to be 7.0. Explain why the student is incorrect and calculate the correct pH.
- 148.** When 2.55 g of an unknown weak acid (HA) with a molar mass of 85.0 g/mol is dissolved in 250.0 g of water, the freezing point of the resulting solution is -0.257°C . Calculate K_a for the unknown weak acid.
- 149.** Calculate the pH of a solution that is 0.00115 M in HCl and 0.0100 M in HClO_2 .
- 150.** To what volume should you dilute 1 L of a solution of a weak acid HA to reduce the $[\text{H}^+]$ to one-half of that in the original solution?
- 151.** HA, a weak acid, with $K_a = 1.0 \times 10^{-8}$, also forms the ion HA_2^- . The reaction is $\text{HA}(aq) + \text{A}^-(aq) \rightleftharpoons \text{HA}_2^-(aq)$ and its $K = 4.0$. Calculate the $[\text{H}^+]$, $[\text{A}^-]$, and $[\text{HA}_2^-]$ in a 1.0 M solution of HA.
- 152.** Basicity in the gas phase can be defined as the proton affinity of the base, for example, $\text{CH}_3\text{NH}_2(g) + \text{H}^+(g) \rightleftharpoons \text{CH}_3\text{NH}_3^+(g)$. In the gas phase, $(\text{CH}_3)_3\text{N}$ is more basic than CH_3NH_2 , while in solution the reverse is true. Explain this observation.
- 153.** Calculate the pH of a solution prepared from 0.200 mol of NH_4CN and enough water to make 1.00 L of solution.
- 154.** To 1.0 L of a 0.30 M solution of HClO_2 is added 0.20 mol of NaF. Calculate the $[\text{HClO}_2]$ at equilibrium.
- 155.** A mixture of Na_2CO_3 and NaHCO_3 has a mass of 82.2 g. It is dissolved in 1.00 L of water, and the pH is found to be 9.95. Find the mass of NaHCO_3 in the mixture.
- 156.** A mixture of NaCN and NaHSO_4 consists of a total of 0.60 mol. When the mixture is dissolved in 1.0 L of water and comes to equilibrium, the pH is found to be 9.9. Find the amount of NaCN in the mixture.

CONCEPTUAL PROBLEMS

- 157.** Without doing any calculations, determine which solution in each pair is more acidic.
- 0.0100 M in HCl and 0.0100 M in KOH
 - 0.0100 M in HF and 0.0100 M in KBr
 - 0.0100 M in NH_4Cl and 0.0100 M in $\text{CH}_3\text{NH}_3\text{Br}$
 - 0.100 M in NaCN and 0.100 M in CaCl_2
- 158.** Without doing any calculations, determine which solution in each pair is more basic.
- 0.100 M in NaClO and 0.100 M in NaF
 - 0.0100 M in KCl and 0.0100 M in KClO_2
- 159.** Rank the acids in order of increasing acid strength.
- CH_3COOH CH_2ClCOOH CHCl_2COOH CCl_3COOH
- 160.** Without using a calculator, determine the pH and pOH of each solution. Rank the solutions from most acidic to most basic.
- | | |
|-------------------------------|--------------------------------|
| a. 1.0×10^{-2} M HCl | b. 1.0×10^{-4} M HCl |
| c. 1.0 M NaOH | d. 1.0×10^{-4} M NaOH |

QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 161.** Without referring to the text, have each member of your group mention a different property of either an acid or a base, such as “Acids turn blue litmus paper red.” Record as many properties as your group can recall without the text.
- 162.** Have each group member make two flashcards with an acid or base on one side and its conjugate on the other side. Check each other’s cards and quiz each other until each group member is proficient at identifying conjugate pairs.
- 163.** Answer the following questions in a complete sentence or two:
- How do you know if an acid is strong or weak?
 - How do you calculate the pH of a strong acid solution?

Active Classroom Learning

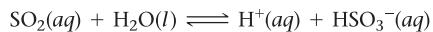
- c. How do you calculate the pH of a weak acid solution?
- d. If you know the K_a of an acid, how do you determine the K_b of its conjugate base?
- e. If you know $[\text{OH}^-]$ for a solution, how do you determine $[\text{H}_3\text{O}^+]$?
- 164.** Solve the following problem, taking turns in your group to explain how to do the next step: What is the pH when 5.3 g of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, is dissolved in 100.0 mL of water? (The K_a of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is 1.8×10^{-5} .)
- 165.** Define each of the following with complete sentences, and provide an example chemical equation: an Arrhenius acid, a Brønsted-Lowry base, and a Lewis acid.



DATA INTERPRETATION AND ANALYSIS

Sulfur Dioxide in Wine

- 166.** Sulfur dioxide is a common preservative in wine; it prevents oxidation and bacterial growth. When SO_2 is added to wine, it reacts with water to form an equilibrium system with the bisulfite ion:



In this equilibrium system, SO_2 is called “molecular SO_2 ;”; in its HSO_3^- form, it is called “free SO_2 .” Only molecular SO_2 acts as a preservative. The amount of molecular SO_2 in the equilibrium

system is highly pH dependent—the lower the pH, the more the equilibrium shifts to the left and the greater the amount of free SO_2 . The recommended amount of free SO_2 is 0.8 ppm for white wine and 0.5 ppm for red wine. The table shows the amount of free SO_2 required to obtain the correct amount of molecular SO_2 as a function of pH for both red and white wine. For dilute solutions such as these, 1 ppm = 1 mg/L.

Study the table and answer the questions.

pH	White Wine 0.8 ppm molecular SO ₂	Red Wine 0.5 ppm molecular SO ₂
3	13	8
3.05	15	9
3.1	16	10
3.15	19	12
3.2	21	13
3.25	23	15
3.3	26	16
3.35	29	18
3.4	32	20
3.45	37	23
3.5	40	25
3.55	46	29
3.6	50	31
3.65	57	36
3.7	63	39
3.75	72	45
3.8	79	49
3.85	91	57
3.9	99	62

Amount of Free SO₂ Required to Maintain Correct Amount of Molecular SO₂ in White and Red Wine.

Cc ANSWERS TO CONCEPTUAL CONNECTIONS

Acid Properties

17.1 (c) Acids typically have a sour taste. The bitter taste is associated with bases.

Conjugate Acid–Base Pairs

17.2 (b) H₂SO₄ and H₂SO₃ are both acids; this is not a conjugate acid–base pair.

The Magnitude of the Acid Ionization Constant

17.3 (b) HB has the largest K_a .

Relative Strengths of Weak Acids

17.4 (a) HF is stronger because it has a larger acid ionization constant.

Acidity of Solutions

17.5 (a) Since the H₃O⁺ concentration is greater than 10⁻⁷ M at room temperature, this solution is acidic.

pH and Acidity

17.6 (b) As pH increases, acidity decreases.

The *x* is small Approximation

17.7 (c) The validity of the *x* is small approximation depends on both the value of the equilibrium constant and the initial concentration—the closer that these are to one another, the less likely the approximation is valid.

Strong and Weak Acids

17.8 (a) A weak acid solution is usually less than 5% dissociated. Since HCl is a strong acid, the 0.10 M solution is much more acidic than either a weak acid with the same concentration or even a weak acid that is twice as concentrated.

a. A 225-L barrel of white wine has an initial free SO₂ concentration of 22 ppm and a pH of 3.70. How much SO₂ (in grams) should be added to the barrel to result in the required SO₂ level?

b. A 225-L barrel of red wine has an initial free SO₂ concentration of 11 ppm and a pH of 3.80. How much SO₂ (in grams) should be added to this barrel to result in the required SO₂ level?

c. Gaseous SO₂ is highly toxic and can be difficult to handle, so winemakers often use potassium metabisulfite (K₂S₂O₅), also known as KMBS, as a source of SO₂ in wine. When KMBS is added to wine, the metabisulfite ion (S₂O₅²⁻) reacts with water to form the bisulfite ion (HSO₃⁻). Write the balanced equation for the reaction that occurs when the metabisulfite ion reacts with water.

d. Determine the percent by mass of SO₂ in KMBS.

e. How much KMBS must a winemaker add to the barrels of wine in problems (a) and (b) to achieve the required amount of molecular SO₂?

Percent Ionization

17.9 Solution (c) has the greatest percent ionization because percent ionization increases with decreasing weak acid concentration.

Judging Relative pH

17.10 (a) A weak acid solution is usually less than 5% dissociated. Therefore, since HCl is the only strong acid, the 1.0 M solution is much more acidic than either a weak acid that is twice as concentrated or a combination of two weak acids with the same concentrations.

Anions as Weak Bases

17.11 (c) The F⁻ ion is the conjugate base of a *weak* acid (HF) and is therefore a weak base.

Acidity or Basicity of Ionic Compounds

17.12 (a) The NH₄⁺ cation is the conjugate acid of a weak base and is therefore a weak acid. The Br⁻ ion is the conjugate base of a *strong* acid (HBr) and is therefore pH-neutral. Therefore, the compound forms an acidic solution when dissolved in water.

Acid Strength and Molecular Structure

17.13 (a) Since the carbon atom in (a) is bonded to another oxygen atom, which draws electron density away from the O—H bond (weakening and polarizing it), and the carbon atom in (b) is bonded only to other hydrogen atoms, the proton in structure (a) is more acidic.