Acids and Bases

CONCEPTS TO REVIEW

Acids, Bases, and Neutralization Reactions
(Sections 4.11 and 6.10)

Reversible Reactions and Chemical Equilibrium
(Section 7.7)

Equilibrium Equations and Equilibrium Constants
(Section 7.8)

Units of Concentration; Molarity
(Section 9.7)

Ion Equivalents
(Section 9.10)

▲ Acids are found in many of the foods we eat, including tomatoes, peppers, and these citrus fruits.

CONTENTS

CHAPTER GOALS

We have already touched on the subject of acids and bases on several occasions, but the time has come for a more detailed study that will answer the following questions:

1. What are acids and bases?

THE GOAL: Be able to recognize acids and bases and write equations for common acid–base reactions.

2. What effect does the strength of acids and bases have on their reactions?

THE GOAL: Be able to interpret acid strength using acid dissociation constants K_a and predict the favored direction of acid–base equilibria.

3. What is the ion-product constant for water?

THE GOAL: Be able to write the equation for this constant and use it to find the concentration of H_3O^+ or OH^-.

4. What is the pH scale for measuring acidity?

THE GOAL: Be able to explain the pH scale and find pH from the H_3O^+ concentration.

5. What is a buffer?

THE GOAL: Be able to explain how a buffer maintains pH and how the bicarbonate buffer functions in the body.

6. How is the acid or base concentration of a solution determined?

THE GOAL: Be able to explain how a titration procedure works and use the results of a titration to calculate acid or base concentration in a solution.
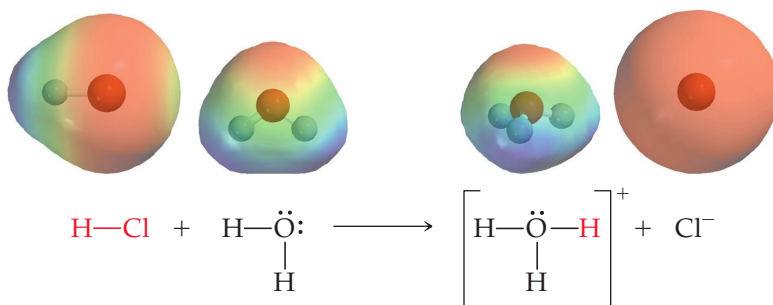
A cids! The word evokes images of dangerous, corrosive liquids that eat away everything they touch. Although a few well-known substances such as sulfuric acid (H_2SO_4) do indeed fit this description, most acids are relatively harmless. In fact, many acids, such as ascorbic acid (vitamin C), are necessary for life.

10.1 Acids and Bases in Aqueous Solution

Let us take a moment to review what we said about acids and bases in Sections 4.11 and 6.10 before going on to a more systematic study:

- An acid is a substance that produces hydrogen ions, H^+, when dissolved in water.

- A base is a substance that produces hydroxide ions, OH^-, when dissolved in water.

- The neutralization reaction of an acid with a base yields water plus a *salt*, an ionic compound composed of the cation from the base and the anion from the acid.
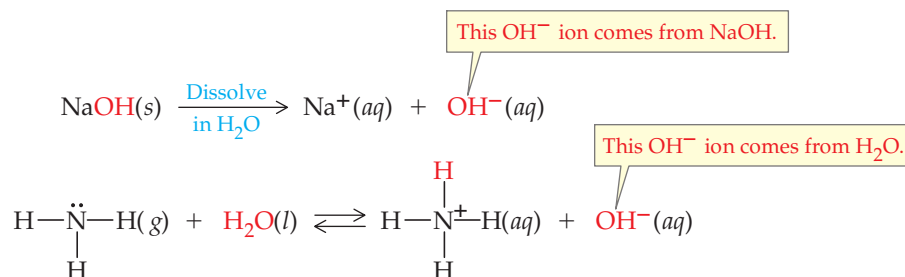
The above definitions of acids and bases were proposed in 1887 by the Swedish chemist Svante Arrhenius and are useful for many purposes. The definitions are limited, however, because they refer only to reactions that take place in aqueous solution. (We will see shortly how the definitions can be broadened.) Another issue is that the H^+ ion is so reactive it does not exist in water. Instead, H^+ reacts with H_2O to give the **hydronium ion**, H_3O^+, as mentioned in Section 4.11. When gaseous HCl dissolves in water, for instance, H_3O^+ and Cl^- are formed. As described in Section 5.8, electrostatic potential maps show that the hydrogen of HCl is positively polarized and electron-poor (blue), whereas the oxygen of water is negatively polarized and electron-rich (red):

Hydronium ion The H_3O^+ ion, formed when an acid reacts with water.

$$H-Cl \ + \ H-\ddot{O}: \ \longrightarrow \ \left[H-\ddot{O}-H \right]^+ \ + \ Cl^-$$
$$ \underset{H}{|} \underset{H}{|}$$

Thus, the Arrhenius definition is updated to acknowledge that an acid yields H_3O^+ in water rather than H^+. In practice, however, the notations H_3O^+ and $H^+(aq)$ are often used interchangeably.

The Arrhenius definition of a base is correct as far as it goes, but it is important to realize that the OH^- ions "produced" by the base can come from either of two sources. Metal hydroxides, such as NaOH, KOH, and $Ba(OH)_2$, are ionic compounds that already contain OH^- ions and merely release those ions when they dissolve in water. Ammonia, however, is not ionic and contains no OH^- ions in its structure. Nonetheless, ammonia is a base because it undergoes a reaction with water when it dissolves, producing NH_4^+ and OH^- ions:

This OH^- ion comes from NaOH.

$$NaOH(s) \xrightarrow[\text{in } H_2O]{\text{Dissolve}} Na^+(aq) + OH^-(aq)$$

This OH^- ion comes from H_2O.

$$H-\ddot{N}-H(g) + H_2O(l) \rightleftharpoons H-\overset{+}{N}-H(aq) + OH^-(aq)$$

The reaction of ammonia with water is a reversible process (Section 7.7) whose equilibrium strongly favors unreacted ammonia. (⊂⊃, p. 198) Nevertheless, *some* OH^- ions are produced, so NH_3 is a base.

10.2 Some Common Acids and Bases

Acids and bases are present in a variety of foods and consumer products. Acids generally have a sour taste, and nearly every sour food contains an acid: Lemons, oranges, and grapefruit contain citric acid, for instance, and sour milk contains lactic acid. Bases are not so obvious in foods, but most of us have them stored under the kitchen or bathroom sink. Bases are present in many household cleaning agents, from perfumed toilet soap, to ammonia-based window cleaners, to the substance you put down the drain to dissolve hair, grease, and other materials that clog it.

Some of the most common acids and bases are listed below. It is a good idea at this point to learn their names and formulas, because we will refer to them often.

▲ Hydrochloric acid, also known as muriatic acid, has many industrial applications.

- **Sulfuric acid, H_2SO_4,** is probably the most important raw material in the chemical and pharmaceutical industries, and is manufactured in greater quantity worldwide than any other industrial chemical. Over 45 million tons are prepared in the United States annually for use in many hundreds of industrial processes, including the preparation of phosphate fertilizers. Its most common consumer use is as the acid found in automobile batteries. As anyone who has splashed battery acid on their skin or clothing knows, sulfuric acid is highly corrosive and can cause painful burns.

- **Hydrochloric acid, HCl,** or *muriatic acid* as it was historically known, has many industrial applications, including its use in metal cleaning and in the manufacture of high-fructose corn syrup. Aqueous HCl is also present as "stomach acid" in the digestive systems of most mammals.

- **Phosphoric acid, H_3PO_4,** is used in vast quantities in the manufacture of phosphate fertilizers. In addition, it is also used as an additive in foods and toothpastes. The tart taste of many soft drinks is due to the presence of phosphoric acid.

- **Nitric acid, HNO_3,** is a strong oxidizing agent that is used for many purposes, including the manufacture of ammonium nitrate fertilizer and military explosives. When spilled on the skin, it leaves a characteristic yellow coloration because of its reaction with skin proteins.

- **Acetic acid, CH_3CO_2H,** is the primary organic constituent of vinegar. It also occurs in all living cells and is used in many industrial processes such as the preparation of solvents, lacquers, and coatings.

- **Sodium hydroxide, NaOH,** also called *caustic soda* or *lye*, is the most commonly used of all bases. Industrially, it is used in the production of aluminum from its ore, in the production of glass, and in the manufacture of soap from animal fat. Concentrated solutions of NaOH can cause severe burns if allowed to sit on the skin for long. Drain cleaners often contain NaOH because it reacts with the fats and proteins found in grease and hair.

- **Calcium hydroxide, Ca(OH)$_2$,** or *slaked lime*, is made industrially by treating lime (CaO) with water. It has many applications, including its use in mortars and cements. An aqueous solution of Ca(OH)$_2$ is often called *limewater*.

- **Magnesium hydroxide, Mg(OH)$_2$,** or *milk of magnesia*, is an additive in foods, toothpaste, and many over-the-counter medications. Antacids such as Rolaids, Mylanta, and Maalox, for instance, all contain magnesium hydroxide.

- **Ammonia, NH$_3$,** is used primarily as a fertilizer, but it also has many other industrial applications including the manufacture of pharmaceuticals and explosives. A dilute solution of ammonia is frequently used around the house as a glass cleaner.
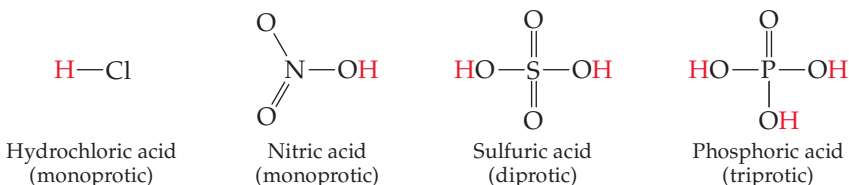
▲ Soap is manufactured by the reaction of vegetable oils and animal fats with the bases NaOH and KOH.
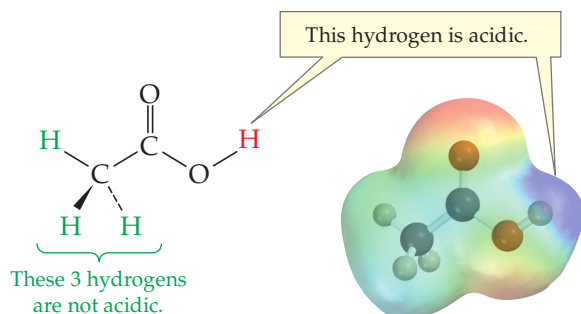
10.3 The Brønsted–Lowry Definition of Acids and Bases

The Arrhenius definition of acids and bases discussed in Section 10.1 applies only to reactions that take place in aqueous solution. A far more general definition was proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. A **Brønsted–Lowry acid** is any substance that is able to give a hydrogen ion, H$^+$, to another molecule or ion. A hydrogen *atom* consists of a proton and an electron, so a hydrogen *ion*, H$^+$, is simply a proton. Thus, we often refer to acids as *proton donors*. The reaction need not occur in water, and a Brønsted–Lowry acid need not give appreciable concentrations of H$_3$O$^+$ ions in water.

Different acids can supply different numbers of H$^+$ ions, as we saw in Section 4.11. (⬤⬤, p. 98) Acids with one proton to donate, such as HCl and HNO$_3$, are called *monoprotic acids*; H$_2$SO$_4$ is a *diprotic acid* because it has two protons to donate, and H$_3$PO$_4$ is a *triprotic acid* because it has three protons to donate. Notice that the acidic H atoms (that is, the H atoms that are donated as protons) are bonded to electronegative atoms, such as chlorine or oxygen.
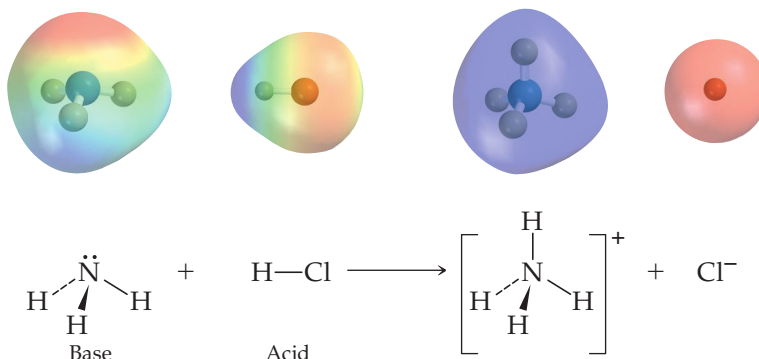
Brønsted–Lowry acid A substance that can donate a hydrogen ion, H$^+$, to another molecule or ion.

H—Cl

Hydrochloric acid
(monoprotic)

Nitric acid
(monoprotic)

Sulfuric acid
(diprotic)

Phosphoric acid
(triprotic)

Acetic acid (CH$_3$CO$_2$H), an example of an organic acid, actually has a total of 4 hydrogens, but only the one bonded to the electronegative oxygen is positively polarized and therefore acidic. The 3 hydrogens bonded to carbon are not acidic. Most organic acids are similar in that they contain many hydrogen atoms, but only the one in the —CO$_2$H group (blue in the electrostatic potential map) is acidic:
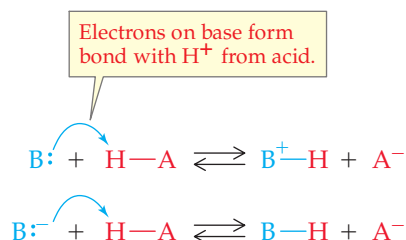
This hydrogen is acidic.

These 3 hydrogens are not acidic.

Brønsted–Lowry base A substance that can accept H^+ from an acid.

Whereas a Brønsted–Lowry acid is a substance that *donates* H^+ ions, a **Brønsted–Lowry base** is a substance that *accepts* H^+ from an acid. The reaction need not occur in water, and the Brønsted–Lowry base need not give appreciable concentrations of OH^- ions in water. Gaseous NH_3, for example, acts as a base to accept H^+ from gaseous HCl and yield the ionic solid $NH_4^+Cl^-$:

$$ \underset{\text{Base}}{\overset{\ddot{N}}{H\diagdown\diagup H}} \;+\; \underset{\text{Acid}}{H\!-\!Cl} \longrightarrow \left[\overset{H}{\underset{H}{H\diagdown\overset{|}{N}\diagup H}} \right]^{+} \;+\; Cl^- $$
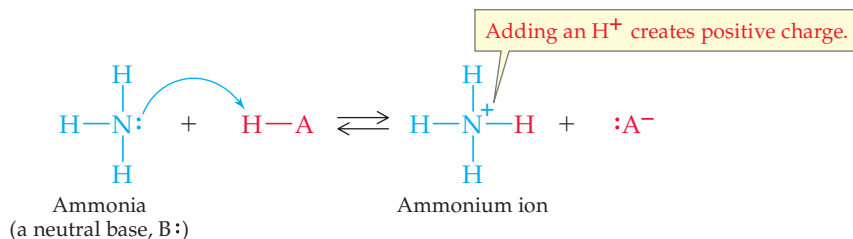
Putting the acid and base definitions together, *an acid–base reaction is one in which a proton is transferred*. The general reaction between proton-donor acids and proton-acceptor bases can be represented as
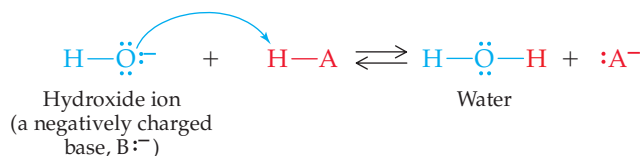
> Electrons on base form bond with H^+ from acid.

$$ B{:} \;+\; H\!-\!A \;\rightleftarrows\; B\overset{+}{-}H \;+\; A^- $$

$$ B{:}^- \;+\; H\!-\!A \;\rightleftarrows\; B\!-\!H \;+\; A^- $$

where the abbreviation HA represents a Brønsted–Lowry acid and B: or B:$^-$ represents a Brønsted–Lowry base. Notice in these acid–base reactions that both electrons in the product B—H bond come from the base, as indicated by the curved arrow flowing from the electron pair of the base to the hydrogen atom of the acid. Thus, the B—H bond that forms is a coordinate covalent bond (Section 5.4). (⬤⬤, p. 115) In fact, a Brønsted–Lowry base *must* have such a lone pair of electrons; without them, it could not accept H^+ from an acid.

A base can be either neutral (B:) or negatively charged (B:$^-$). If the base is neutral, then the product has a positive charge (BH^+) after H^+ has added. Ammonia is an example:

> Adding an H^+ creates positive charge.

$$ \underset{\substack{\text{Ammonia}\\ \text{(a neutral base, B{:})}}}{\overset{H}{\underset{H}{H\!-\!N{:}}}} \;+\; H\!-\!A \;\rightleftarrows\; \underset{\substack{\text{Ammonium ion}}}{\overset{H}{\underset{H}{H\!-\!\overset{+}{N}\!-\!H}}} \;+\; {:}A^- $$

If the base is negatively charged, then the product is neutral (BH). Hydroxide ion is an example:

$$ \underset{\substack{\text{Hydroxide ion}\\ \text{(a negatively charged}\\ \text{base, B{:}}^-)}}{H\!-\!\ddot{O}{:}^-} \;+\; H\!-\!A \;\rightleftarrows\; \underset{\text{Water}}{H\!-\!\ddot{O}\!-\!H} \;+\; {:}A^- $$

An important consequence of the Brønsted–Lowry definitions is that the *products* of an acid–base reaction can also behave as acids and bases. Many acid–base reactions are reversible (Section 7.8), although in some cases the equilibrium constant for the reaction is quite large. (⊂◯◯⊃, p. 200) For example, suppose we have as a forward reaction an acid HA donating a proton to a base B to produce A⁻. This product A⁻ is a base because it can act as a proton acceptor in the reverse reaction. At the same time, the product BH⁺ acts as an acid because it donates a proton in the reverse reaction:
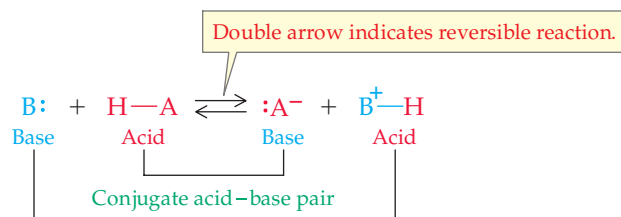
Pairs of chemical species such as B, BH⁺ and HA, A⁻ are called **conjugate acid–base pairs**. They are species that are found on opposite sides of a chemical reaction whose formulas differ by only one H⁺. Thus, the product anion A⁻ is the **conjugate base** of the reactant acid HA, and HA is the **conjugate acid** of the base A⁻. Similarly, the reactant B is the conjugate base of the product acid BH⁺, and BH⁺ is the conjugate acid of the base B. The number of protons in a conjugate acid–base pair is always one greater than the number of protons in the base of the pair. To give some examples, acetic acid and acetate ion, the hydronium ion and water, and the ammonium ion and ammonia all make conjugate acid–base pairs:
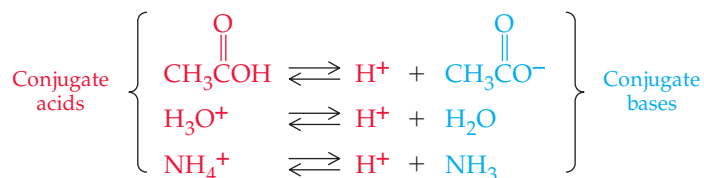
Conjugate acid–base pair Two substances whose formulas differ by only a hydrogen ion, H^+.

Conjugate base The substance formed by loss of H^+ from an acid.

Conjugate acid The substance formed by addition of H^+ to a base.

| **WORKED EXAMPLE** | **10.1** Acids and Bases: Identifying Brønsted–Lowry Acids and Bases |

Identify each of the following as a Brønsted–Lowry acid or base:

(a) PO_4^{3-}
(b) $HClO_4$
(c) CN^-

ANALYSIS A Brønsted–Lowry acid must have a hydrogen that it can donate as H^+, and a Brønsted–Lowry base must have an atom with a lone pair of electrons that can bond to H^+. Typically, a Brønsted–Lowry base is an anion derived by loss of H^+ from an acid.

SOLUTION

(a) The phosphate anion (PO_4^{3-}) is a Brønsted–Lowry base derived by loss of 3 H^+ ions from phosphoric acid, H_3PO_4.
(b) Perchloric acid ($HClO_4$) is a Brønsted–Lowry acid because it can donate an H^+ ion.
(c) The cyanide ion (CN^-) is a Brønsted–Lowry base derived by removal of an H^+ ion from hydrogen cyanide, HCN.

> **WORKED EXAMPLE** **10.2** Acids and Bases: Identifying Conjugate Acid–Base Pairs
>
> Write formulas for
>
>   **(a)** The conjugate acid of the cyanide ion, CN^-
>   **(b)** The conjugate base of perchloric acid, $HClO_4$
>
> **ANALYSIS** A conjugate acid is formed by adding H^+ to a base; a conjugate base is formed by removing H^+ from an acid.
>
> **SOLUTION**
>
>   **(a)** HCN is the conjugate acid of CN^-.
>   **(b)** ClO_4^- is the conjugate base of $HClO_4$.

PROBLEM 10.1

Which of the following would you expect to be Brønsted–Lowry acids?

(a) HCO_2H **(b)** H_2S **(c)** $SnCl_2$

PROBLEM 10.2

Which of the following would you expect to be Brønsted–Lowry bases?

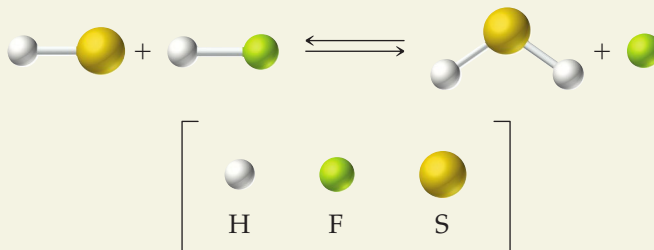**(a)** SO_3^{2-} **(b)** Ag^+ **(c)** F^-

PROBLEM 10.3

Write formulas for:

(a) The conjugate acid of HS^- **(b)** The conjugate acid of PO_4^{3-}
(c) The conjugate base of H_2CO_3 **(d)** The conjugate base of NH_4^+

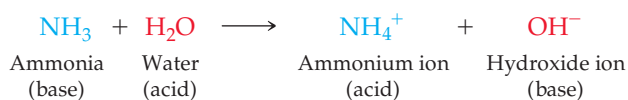**⚯ KEY CONCEPT PROBLEM 10.4**

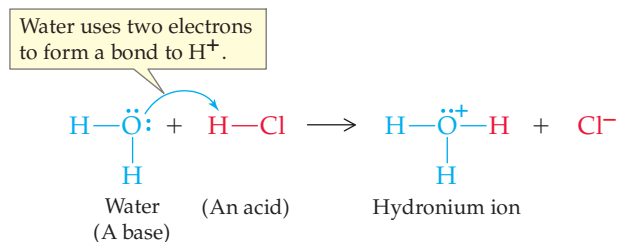For the reaction shown here, identify the Brønsted–Lowry acids, bases, and conjugate acid–base pairs.

10.4 Water as Both an Acid and a Base

Water is neither an acid nor a base in the Arrhenius sense because it does not contain appreciable concentrations of either H_3O^+ or OH^-. In the Brønsted–Lowry sense, however, water can act as *both* an acid and a base. When in contact with a base, water reacts as a Brønsted–Lowry acid and *donates* a proton to the base. In its

reaction with ammonia, for example, water donates H^+ to ammonia to form the ammonium ion:

$$NH_3 \ + \ H_2O \ \longrightarrow \ NH_4^+ \ + \ OH^-$$

Ammonia	Water	Ammonium ion	Hydroxide ion
(base)	(acid)	(acid)	(base)

When in contact with an acid, water reacts as a Brønsted–Lowry base and *accepts* H^+ from the acid. This, of course, is exactly what happens when an acid such as HCl dissolves in water, as discussed in Section 10.1.

Water uses two electrons to form a bond to H^+.

$$H\!-\!\ddot{O}\!: \ + \ H\!-\!Cl \ \longrightarrow \ H\!-\!\overset{+}{\ddot{O}}\!-\!H \ + \ Cl^-$$

Water	(An acid)	Hydronium ion
(A base)		

Substances like water, which can react as either an acid or a base depending on the circumstances, are said to be **amphoteric** (am-pho-**tare**-ic). When water acts as an acid, it donates H^+ and becomes OH^-; when it acts as a base, it accepts H^+ and becomes H_3O^+.

Amphoteric Describing a substance that can react as either an acid or a base.

PROBLEM 10.5
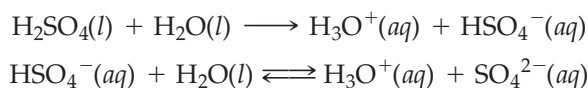
Is water an acid or a base in the following reactions?

(a) $H_3PO_4(aq) + H_2O(l) \longrightarrow H_2PO_4^-(aq) + H_3O^+(aq)$

(b) $F^-(aq) + H_2O(l) \longrightarrow HF(aq) + OH^-(aq)$

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

10.5 Acid and Base Strength

Some acids and bases, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), or sodium hydroxide (NaOH), are highly corrosive. They react readily and, in contact with skin, can cause serious burns. Other acids and bases are not nearly as reactive. Acetic acid (CH_3COOH, the major component in vinegar) and phosphoric acid (H_3PO_4) are found in many food products. Why are some acids and bases relatively "safe," while others must be handled with extreme caution? The answer lies in how easily they produce the active ions for an acid (H^+) or a base (OH^-).

As indicated in Table 10.1, acids differ in their ability to give up a proton. The six acids at the top of the table are **strong acids**, meaning that they give up a proton easily and are essentially 100% **dissociated**, or split apart into ions, in water. Those remaining are **weak acids**, meaning that they give up a proton with difficulty and are substantially less than 100% dissociated in water. In a similar way, the bases at the top of the table are **weak bases** because they have little affinity for a proton, and the bases at the bottom of the table are **strong bases** because they grab and hold a proton tightly.

Note that diprotic acids, such as sulfuric acid, undergo two stepwise dissociations in water. The first dissociation yields HSO_4^- and occurs to the extent of nearly 100%, so H_2SO_4 is a strong acid. The second dissociation yields SO_4^{2-} and takes place to a much lesser extent because separation of a positively charged H^+ from the negatively charged HSO_4^- anion is difficult. Thus, HSO_4^- is a weak acid:

$$H_2SO_4(l) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

Strong acid An acid that gives up H^+ easily and is essentially 100% dissociated in water.

Dissociation The splitting apart of an acid in water to give H^+ and an anion.

Weak acid An acid that gives up H^+ with difficulty and is less than 100% dissociated in water.

Weak base A base that has only a slight affinity for H^+ and holds it weakly.

Strong base A base that has a high affinity for H^+ and holds it tightly.

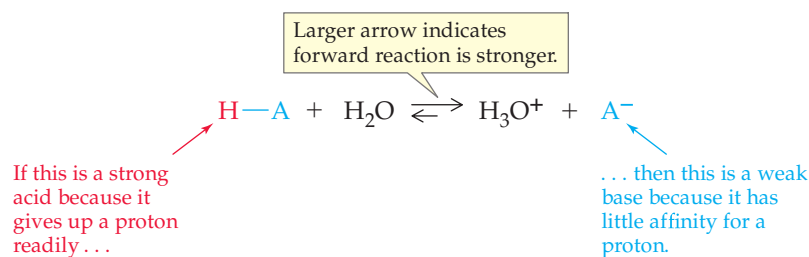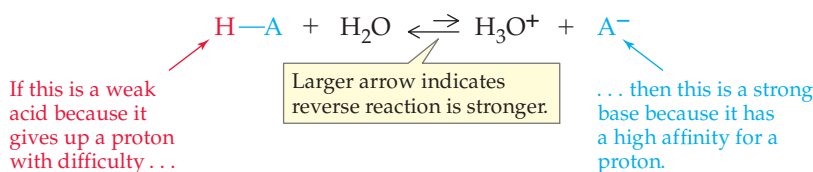**TABLE 10.1** Relative Strengths of Acids and Conjugate Bases

		ACID		CONJUGATE BASE		
Increasing acid strength	Strong acids: 100% dissociated	Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion	**Increasing base strength**
		Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion	Little or no reaction as bases
		Hydriodic acid	HI	I^-	Iodide ion	
		Hydrobromic acid	HBr	Br^-	Bromide ion	
		Hydrochloric acid	HCl	Cl^-	Chloride ion	
		Nitric acid	HNO_3	NO_3^-	Nitrate ion	
		Hydronium ion	H_3O^+	H_2O	**Water**	
	Weak acids	Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion	Very weak bases
		Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion	
		Nitrous acid	HNO_2	NO_2^-	Nitrite ion	
		Hydrofluoric acid	HF	F^-	Fluoride ion	
		Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion	
	Very weak acids	Carbonic acid	H_2CO_3	HCO_3^-	Bicarbonate ion	Weak bases
		Dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	Hydrogen phosphate ion	
		Ammonium ion	NH_4^+	NH_3	Ammonia	
		Hydrocyanic acid	HCN	CN^-	Cyanide ion	
		Bicarbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion	
		Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	Phosphate ion	
		Water	H_2O	OH^-	**Hydroxide ion**	Strong base

Perhaps the most striking feature of Table 10.1 is the inverse relationship between acid strength and base strength. *The stronger the acid, the weaker its conjugate base; the weaker the acid, the stronger its conjugate base.* HCl, for example, is a strong acid, so Cl^- is a very weak base. H_2O, however, is a very weak acid, so OH^- is a strong base.

Why is there an inverse relationship between acid strength and base strength? To answer this question, think about what it means for an acid or base to be strong or weak. A strong acid $H—A$ is one that readily gives up a proton, meaning that its conjugate base A^- has little affinity for the proton. But this is exactly the definition of a weak base—a substance that has little affinity for a proton. As a result, the reverse reaction occurs to a lesser extent, as indicated by the size of the forward and reverse arrows in the reaction:

Larger arrow indicates forward reaction is stronger.

$$H—A + H_2O \rightleftharpoons H_3O^+ + A^-$$

If this is a strong acid because it gives up a proton readily . . .

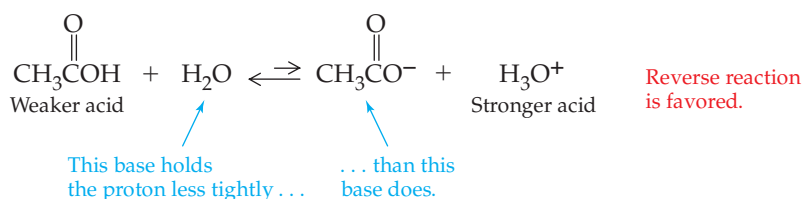. . . then this is a weak base because it has little affinity for a proton.

In the same way, a weak acid is one that gives up a proton with difficulty, meaning that its conjugate base has a high affinity for the proton. But this is just the definition of a strong base—a substance that has a high affinity for the proton. The reverse reaction now occurs more readily.

$$H-A \ + \ H_2O \ \underset{\longrightarrow}{\overset{\longleftarrow}{}} \ H_3O^+ \ + \ A^-$$

If this is a weak
acid because it
gives up a proton
with difficulty . . .

Larger arrow indicates
reverse reaction is stronger.

. . . then this is a strong
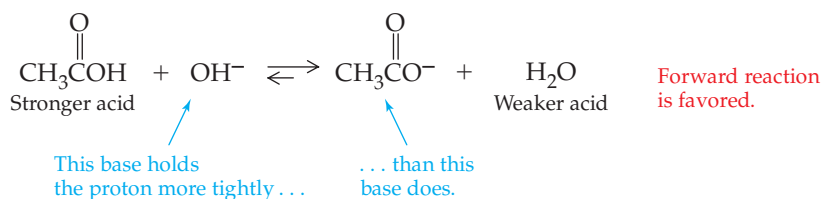base because it has
a high affinity for a
proton.

Knowing the relative strengths of different acids as shown in Table 10.1 makes it possible to predict the direction of proton-transfer reactions. *An acid–base proton-transfer equilibrium always favors reaction of the stronger acid with the stronger base, and formation of the weaker acid and base.* That is, the proton always leaves the stronger acid (whose weaker conjugate base cannot hold the proton) and always ends up in the weaker acid (whose stronger conjugate base holds the proton tightly). Put another way, in a contest for the proton, the stronger base always wins.

Stronger acid + Stronger base $\rightleftharpoons$ Weaker base + Weaker acid
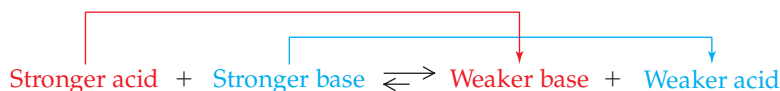
To try out this rule, compare the reactions of acetic acid with water and with hydroxide ion. The idea is to write the equation, identify the acid on each side of the arrow, and then decide which acid is stronger and which is weaker. For example, the reaction of acetic acid with water to give acetate ion and hydronium ion is favored in the reverse direction, because acetic acid is a weaker acid than H_3O^+:

$$\overset{O}{\underset{\parallel}{CH_3COH}} \ + \ H_2O \ \underset{\longrightarrow}{\overset{\longleftarrow}{}} \ \overset{O}{\underset{\parallel}{CH_3CO^-}} \ + \ H_3O^+$$

Weaker acid   Stronger acid

Reverse reaction
is favored.

This base holds
the proton less tightly . . .

. . . than this
base does.

On the other hand, the reaction of acetic acid with hydroxide ion to give acetate ion and water is favored in the forward direction, because acetic acid is a stronger acid than H_2O:

$$\overset{O}{\underset{\parallel}{CH_3COH}} \ + \ OH^- \ \underset{\longleftarrow}{\overset{\longrightarrow}{}} \ \overset{O}{\underset{\parallel}{CH_3CO^-}} \ + \ H_2O$$

Stronger acid   Weaker acid

Forward reaction
is favored.

This base holds
the proton more tightly . . .
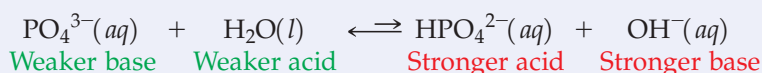
. . . than this
base does.

WORKED EXAMPLE   **10.3** Acid/Base Strength: Predicting Direction
of H-transfer Reactions

Write a balanced equation for the proton-transfer reaction between phosphate ion (PO_4^{3-}) and water, and determine in which direction the equilibrium is favored.

ANALYSIS Look in Table 10.1 to see the relative acid and base strengths of the species involved in the reaction. The acid–base proton-transfer equilibrium will favor reaction of the stronger acid and formation of the weaker acid.

SOLUTION
Phosphate ion is the conjugate base of a weak acid (HPO_4^{2-}) and is therefore a relatively strong base. Table 10.1 shows that HPO_4^{2-} is a stronger acid than H_2O, and OH^- is a stronger base than PO_4^{3-}, so the reaction is favored in the reverse direction:

$$PO_4^{3-}(aq) \ + \ H_2O(l) \ \underset{\longleftarrow}{\overset{\longrightarrow}{}} \ HPO_4^{2-}(aq) \ + \ OH^-(aq)$$

Weaker base   Weaker acid   Stronger acid   Stronger base

APPLICATION ▶

GERD—Too Much Acid or Not Enough?

S trong acids are very caustic substances that can dissolve even metals, and no one would think of ingesting them. However, the major component of the gastric juices secreted in the stomach is hydrochloric acid—a strong acid—and the acidic environment in the stomach is vital to good health and nutrition.

Stomach acid is essential for the digestion of proteins and for the absorption of certain micronutrients, such as calcium, magnesium, iron, and vitamin B_{12}. It also creates a sterile environment in the gut by killing yeast and bacteria that may be ingested. If these gastric juices leak up into the esophagus, the tube through which food and drink enter the stomach, they can cause the burning sensation in the chest or throat known as either heartburn or acid indigestion. Persistent irritation of the esophagus is known as gastro-esophageal reflux disease (GERD) and, if untreated, can lead to more serious health problems.

Hydrogen ions and chloride ions are secreted separately from the cytoplasm of cells lining the stomach and then combine to form HCl that is usually close to 0.10 M. The HCl is then released into the stomach cavity, where the concentration is diluted to about 0.01–0.001 M. Unlike the esophagus, the stomach is coated by a thick mucus layer that protects the stomach wall from damage by this caustic solution.

Those who suffer from acid indigestion can obtain relief using over-the-counter antacids, such as Tums or Rolaids (see Section 10.14, p. 320). Chronic conditions such as GERD, however, are often treated with prescription medications. GERD can be treated by two classes of drugs. Proton-pump inhibitors (PPI), such as Prevacid and Prilosec, prevent the production the H^+ ions in the parietal cells, while H2-receptor blockers (Tagamet, Zantac, and Pepcid) prevent the release of stomach acid into the lumen. Both drugs effectively decrease the production of stomach acid to ease the symptoms of GERD.

Ironically, GERD can also be caused by not having enough stomach acid—a condition known as *hypochlorhydria*. The valve that controls the release of stomach contents to the small intestine is triggered by acidity. If this valve fails to open because the stomach is not acidic enough, the contents of the stomach can be churned up into the esophagus.
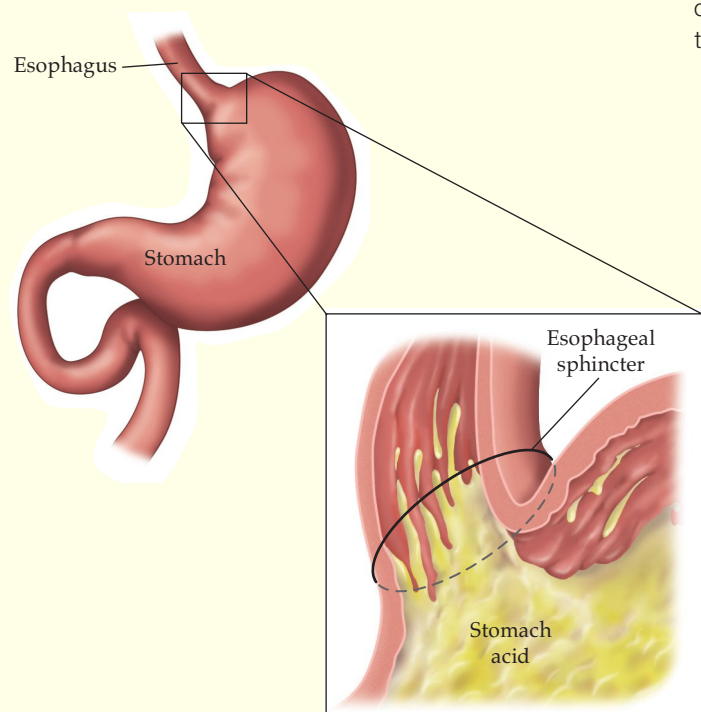
▲ The burning sensation and other symptoms associated with GERD are caused by the reflux of the acidic contents of the stomach into the esophagus.
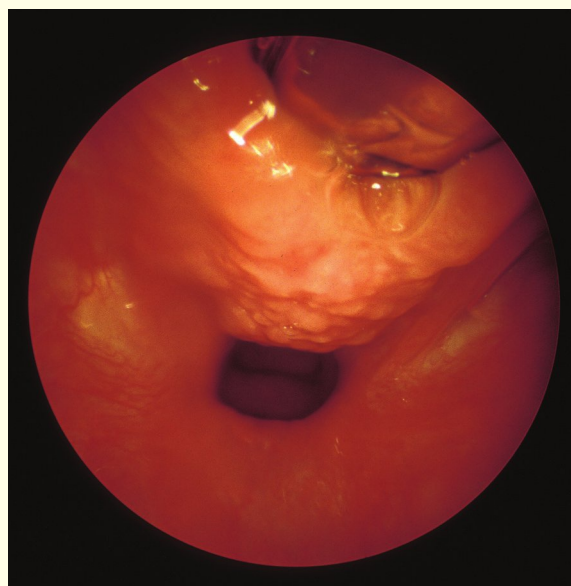
▲ If not treated, GERD can cause ulcers and scarring of esophageal tissue.

See Additional Problem 10.96 at the end of the chapter.

PROBLEM 10.6

Use Table 10.1 to identify the stronger acid in the following pairs:

(a) H_2O or NH_4^+
(b) H_2SO_4 or CH_3CO_2H
(c) HCN or H_2CO_3

PROBLEM 10.7

Use Table 10.1 to identify the stronger base in the following pairs:

(a) F^- or Br^- **(b)** OH^- or HCO_3^-

PROBLEM 10.8

Write a balanced equation for the proton-transfer reaction between a hydrogen phosphate ion and a hydroxide ion. Identify each acid–base pair, and determine in which direction the equilibrium is favored.

KEY CONCEPT PROBLEM 10.9

From this electrostatic potential map of the amino acid alanine, identify the most acidic hydrogens in the molecule:

Alanine
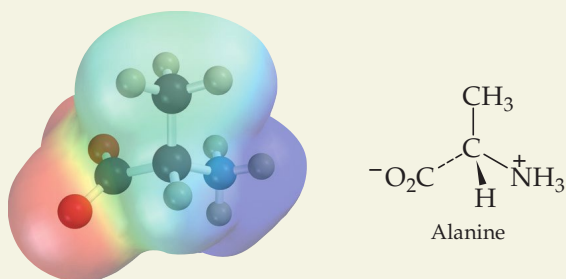
10.6 Acid Dissociation Constants

The reaction of a weak acid with water, like any chemical equilibrium, can be described by an equilibrium equation (Section 7.8), where square brackets indicate the concentrations of the enclosed species in molarity (moles per liter). (, p. 200)

For the reaction $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

We have $K = \dfrac{[H_3O^+][A^-]}{[HA][H_2O]}$

Because water is a solvent as well as a participant for the reaction, its concentration is essentially constant and has no effect on the equilibrium. Therefore, we usually put the equilibrium constant K and the water concentration $[H_2O]$ together to make a new constant called the **acid dissociation constant, K_a**. The acid dissociation constant is simply the hydronium ion concentration $[H_3O^+]$ times the conjugate base concentration $[A^-]$ divided by the undissociated acid concentration $[HA]$:

Acid dissociation constant $K_a = K[H_2O] = \dfrac{[H_3O^+][A^-]}{[HA]}$

For a strong acid, the H_3O^+ and A^- concentrations are much larger than the HA concentration, so K_a is very large. In fact, the K_a values for strong acids such as HCl are so large that it is difficult and not very useful to measure them. For a weak acid, however, the H_3O^+ and A^- concentrations are smaller than the HA concentration, so K_a is small. Table 10.2 gives K_a values for some common acids and illustrates several important points:

- Strong acids have K_a values much greater than 1 because dissociation is favored.
- Weak acids have K_a values much less than 1 because dissociation is not favored.

TABLE 10.2 Some Acid Dissociation Constants, K_a, at 25 °C

ACID	K_a	ACID	K_a
Hydrofluoric acid (HF)	3.5×10^{-4}	*Polyprotic acids*	
Hydrocyanic acid (HCN)	4.9×10^{-10}	Sulfuric acid	
Ammonium ion (NH_4^+)	5.6×10^{-10}	H_2SO_4	Large
		HSO_4^-	1.2×10^{-2}
Organic acids		Phosphoric acid	
Formic acid (HCOOH)	1.8×10^{-4}	H_3PO_4	7.5×10^{-3}
Acetic acid (CH_3COOH)	1.8×10^{-5}	$H_2PO_4^-$	6.2×10^{-8}
Propanoic acid	1.3×10^{-5}	HPO_4^{2-}	2.2×10^{-13}
(CH_3CH_2COOH)		Carbonic acid	
Ascorbic acid (vitamin C)	7.9×10^{-5}	H_2CO_3	4.3×10^{-7}
		HCO_3^-	5.6×10^{-11}

- Donation of each successive H^+ from a polyprotic acid is more difficult than the one before it, so K_a values become successively lower.
- Most organic acids, which contain the $-CO_2H$ group, have K_a values near 10^{-5}.

PROBLEM 10.10

Benzoic acid has $K_a = 6.5 \times 10^{-5}$, and citric acid has $K_a = 7.2 \times 10^{-4}$. Which of the two is the stronger acid?

10.7 Dissociation of Water

We saw previously that water is amphoteric – it can act as an acid when a base is present and as a base when an acid is present. What about when no other acids or bases are present, however? In this case, one water molecule acts as an acid while another water molecule acts as a base, reacting to form the hydronium and hydroxide ions:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
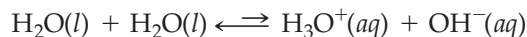
Because each dissociation reaction yields one H_3O^+ ion and one OH^- ion, the concentrations of the two ions are identical. At 25 °C, the concentration of each is 1.00×10^{-7} M. We can write the equilibrium constant expression for the dissociation of water as

$$K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

and $$K_a = K[H_2O] = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

where $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ M (at 25 °C)

As both a reactant and a solvent, the concentration of water is essentially constant. We can therefore put the acid dissociation constant K_a and the water concentration $[H_2O]$ together to make a new constant called the **ion-product constant for water (K_w)**, which is simply the H_3O^+ concentration times the OH^- concentration. At 25 °C, $K_w = 1.00 \times 10^{-14}$.

$$\textit{Ion-product constant for water} \quad K_w = K_a[H_2O] = [H_3O^+][OH^-]$$
$$= (1.00 \times 10^{-7})(1.00 \times 10^{-7})$$
$$= 1.00 \times 10^{-14} \quad (\text{at } 25\,°C)$$

The importance of the equation $K_w = [H_3O^+][OH^-]$ is that it applies to all aqueous solutions, not just to pure water. Since the product of $[H_3O^+]$ times $[OH^-]$ is always constant for any solution, we can determine the concentration of one species if we know the concentration of the other. If an acid is present in solution, for instance, so that $[H_3O^+]$ is large, then $[OH^-]$ must be small. If a base is present in solution so that $[OH^-]$ is large, then $[H_3O^+]$ must be small. For example, for a 0.10 M HCl solution, we know that $[H_3O^+] = 0.10$ M because HCl is 100% dissociated. Thus, we can calculate that $[OH^-] = 1.0 \times 10^{-13}$ M:

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

$$\text{we have} \quad [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

Similarly, for a 0.10 M NaOH solution, we know that $[OH^-] = 0.10$ M, so $[H_3O^+] = 1.0 \times 10^{-13}$ M:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

Solutions are identified as acidic, neutral, or basic (*alkaline*) according to the value of their H_3O^+ and OH^- concentrations:

Acidic solution: $[H_3O^+] > 10^{-7}$ M   and $[OH^-] < 10^{-7}$ M

Neutral solution: $[H_3O^+] = 10^{-7}$ M   and $[OH^-] = 10^{-7}$ M

Basic solution: $[H_3O^+] < 10^{-7}$ M   and $[OH^-] > 10^{-7}$ M

WORKED EXAMPLE   **10.4** Water Dissociation Constant: Using K_w to Calculate $[OH^-]$

Milk has an H_3O^+ concentration of 4.5×10^{-7} M. What is the value of $[OH^-]$? Is milk acidic, neutral, or basic?

ANALYSIS The OH^- concentration can be found by dividing K_w by $[H_3O^+]$. An acidic solution has $[H_3O^+] > 10^{-7}$ M, a neutral solution has $[H_3O^+] = 10^{-7}$ M, and a basic solution has $[H_3O^+] < 10^{-7}$ M.
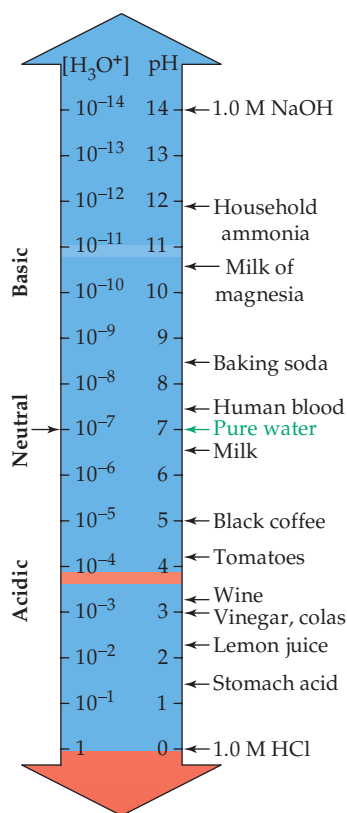
BALLPARK ESTIMATE Since the H_3O^+ concentration is slightly *greater* than 10^{-7} M, the OH^- concentration must be slightly *less* than 10^{-7} M, on the order of 10^{-8}.

SOLUTION

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8} \text{ M}$$

Milk is slightly acidic because its H_3O^+ concentration is slightly larger than 1×10^{-7} M.

BALLPARK CHECK The OH^- concentration is of the same order of magnitude as our estimate.

[H₃O⁺] pH

- 10^{-14} 14 ← 1.0 M NaOH
- 10^{-13} 13
- 10^{-12} 12 ← Household ammonia
- 10^{-11} 11
- 10^{-10} 10 ← Milk of magnesia
- 10^{-9} 9
- 10^{-8} 8 ← Baking soda
- 10^{-7} 7 ← Human blood ← Pure water ← Milk
- 10^{-6} 6
- 10^{-5} 5 ← Black coffee
- 10^{-4} 4 ← Tomatoes
- 10^{-3} 3 ← Wine ← Vinegar, colas
- 10^{-2} 2 ← Lemon juice
- 10^{-1} 1 ← Stomach acid
- 1 0 ← 1.0 M HCl

Basic — Neutral — Acidic

▲ **FIGURE 10.1 The pH scale and the pH values of some common substances.** A low pH corresponds to a strongly acidic solution, a high pH corresponds to a strongly basic solution, and a pH of 7 corresponds to a neutral solution.

p function The negative common logarithm of some variable, pX = −log(X).

pH A measure of the acid strength of a solution; the negative common logarithm of the H_3O^+ concentration.

▲ Adding only a teaspoonful of concentrated (6 M) hydrochloric acid lowers the pH of this pool from 7 to 6. Lowering the pH from 7 to 1 would take 400 gallons.

PROBLEM 10.11

Identify the following solutions as either acidic or basic. What is the value of $[OH^-]$ in each?

(a) Beer, $[H_3O^+] = 3.2 \times 10^{-5}$ M
(b) Household ammonia, $[H_3O^+] = 3.1 \times 10^{-12}$ M

10.8 Measuring Acidity in Aqueous Solution: pH

In many fields, from medicine to chemistry to winemaking, it is necessary to know the exact concentration of H_3O^+ or OH^- in a solution. If, for example, the H_3O^+ concentration in blood varies only slightly from a value of 4.0×10^{-8} M, death can result.

Although correct, it is nevertheless awkward to refer to low concentrations of H_3O^+ using molarity. If you were asked which concentration is higher, 9.0×10^{-8} M or 3.5×10^{-7} M, you would probably have to stop and think for a moment before answering. Fortunately, there is an easier way to express and compare H_3O^+ concentrations—the *pH scale*.

The pH of an aqueous solution is a number, usually between 0 and 14, that indicates the H_3O^+ concentration of the solution. A pH smaller than 7 corresponds to an acidic solution, a pH larger than 7 corresponds to a basic solution, and a pH of exactly 7 corresponds to a neutral solution. The pH scale and pH values of some common substances are shown in Figure 10.1.

Mathematically, a **p function** is defined as the negative common logarithm of some variable. The **pH** of a solution, therefore, is the negative common logarithm of the H_3O^+ concentration:

$$pH = -\log[H^+] \quad (or\,[H_3O^+])$$

If you have studied logarithms, you may remember that the common logarithm of a number is the power to which 10 must be raised to equal the number. The pH definition can therefore be restated as

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

For example, in neutral water at 25 °C, where $[H_3O^+] = 1 \times 10^{-7}$ M, the pH is 7; in a strong acid solution where $[H_3O^+] = 1 \times 10^{-1}$ M, the pH is 1; and in a strong base solution where $[H_3O^+] = 1 \times 10^{-14}$ M, the pH is 14:

Acidic solution: pH < 7, $[H_3O^+] > 1 \times 10^{-7}$ M
Neutral solution: pH = 7, $[H_3O^+] = 1 \times 10^{-7}$ M
Basic solution: pH > 7, $[H_3O^+] < 1 \times 10^{-7}$ M

Keep in mind that the pH scale covers an enormous range of acidities because it is a *logarithmic* scale, which involves powers of 10 (Figure 10.2). A change of only 1 pH unit means a tenfold change in $[H_3O^+]$, a change of 2 pH units means a hundredfold change in $[H_3O^+]$, and a change of 12 pH units means a change of 10^{12} (a million) in $[H_3O^+]$.

To get a feel for the size of the quantities involved, think of a typical backyard swimming pool, which contains about 100,000 L of water. You would have to add only 0.10 mol of HCl (3.7 g) to lower the pH of the pool from 7.0 (neutral) to 6.0, but you would have to add 10,000 mol of HCl (370 kg!) to lower the pH of the pool from 7.0 to 1.0.

The logarithmic pH scale is a convenient way of reporting the relative acidity of solutions, but using logarithms can also be useful when calculating H_3O^+ and

OH^- concentrations. Remember that the equilibrium between H_3O^+ and OH^- in aqueous solutions is expressed by K_w, where

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \quad \text{(at 25 °C)}$$

If we convert this equation to its negative logarithmic form, we obtain

$$-\log(K_w) = -\log(H_3O^+) - \log(OH^-)$$

$$-\log(1 \times 10^{-14}) = -\log(H_3O^+) - \log(OH^-)$$

$$or \quad 14.00 = pH + pOH$$

The logarithmic form of the K_w equation can simplify the calculation of solution pH from OH^- concentration, as demonstrated in Worked Example 10.7.

WORKED EXAMPLE **10.5** Measuring Acidity: Calculating pH from $[H_3O^+]$

The H_3O^+ concentration in coffee is about 1×10^{-5} M. What pH is this?

ANALYSIS The pH is the negative common logarithm of the H_3O^+ concentration: $pH = -\log[H_3O^+]$.

SOLUTION
Since the common logarithm of 1×10^{-5} M is -5, the pH is 5.0.

WORKED EXAMPLE **10.6** Measuring Acidity: Calculating $[H_3O^+]$ from pH

Lemon juice has a pH of about 2. What $[H_3O^+]$ is this?

ANALYSIS In this case, we are looking for the $[H_3O^+]$, where $[H_3O^+] = 10^{-pH}$.

SOLUTION
Since pH $= 2.0$, $[H_3O^+] = 10^{-2} = 1 \times 10^{-2}$ M.

WORKED EXAMPLE **10.7** Measuring Acidity: Using K_w to Calculate $[H_3O^+]$ and pH

A cleaning solution is found to have $[OH^-] = 1 \times 10^{-3}$ M. What is the pH?

ANALYSIS To find pH, we must first find the value of $[H_3O^+]$ by using the equation $[H_3O^+] = K_w/[OH^-]$. Alternatively, we can calculate the pOH of the solution and then use the logarithmic form of the K_w equation: $pH = 14.00 - pOH$.

SOLUTION
Rearranging the K_w equation, we have

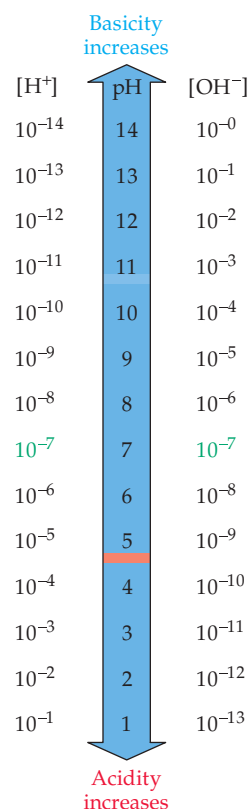$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1 \times 10^{-3}} = 1 \times 10^{-11} \text{ M}$$

$$pH = -\log(1 \times 10^{-11}) = 11.0$$

Using the logarithmic form of the K_w equation, we have

$$pH = 14.0 - pOH = 14.0 - (-\log(OH^-))$$

$$pH = 14.0 - (-\log(1 \times 10^{-3}))$$

$$pH = 14.0 - 3.0 = 11.0$$

▲ **FIGURE 10.2** The relationship of the pH scale to H^+ and OH^- concentrations.

WORKED EXAMPLE **10.8** Measuring Acidity: Calculating pH of Strong Acid Solutions

What is the pH of a 0.01 M solution of HCl?

ANALYSIS To find pH, we must first find the value of $[H_3O^+]$.

SOLUTION
Since HCl is a strong acid (Table 10.1), it is 100% dissociated, and the H_3O^+ concentration is the same as the HCl concentration: $[H_3O^+] = 0.01$ M, or 1×10^{-2} M, and pH $= 2.0$.

PROBLEM 10.12

Which solution has the higher H_3O^+ concentration, one with pH $= 5$ or one with pH $= 9$? Which has the higher OH^- concentration?

PROBLEM 10.13

Give the pH of solutions with the following concentrations:

(a) $[H_3O^+] = 1 \times 10^{-5}$ M

(b) $[OH^-] = 1 \times 10^{-9}$ M

PROBLEM 10.14

Give the hydronium ion concentrations of solutions with the following values of pH. Which of the solutions is most acidic? Which is most basic?

(a) pH 13.0   (b) pH 3.0   (c) pH 8.0

PROBLEM 10.15

What is the pH of a 1×10^{-4} M solution of HNO_3?

10.9 Working with pH

Converting between pH and H_3O^+ concentration is easy when the pH is a whole number, but how do you find the H_3O^+ concentration of blood, which has a pH of 7.4, or the pH of a solution with $[H_3O^+] = 4.6 \times 10^{-3}$ M? Sometimes it is sufficient to make an estimate. The pH of blood (7.4) is between 7 and 8, so the H_3O^+ concentration of blood must be between 1×10^{-7} and 1×10^{-8} M. To be exact about finding pH values, though, requires a calculator.

Converting from pH to $[H_3O^+]$ requires finding the *antilogarithm* of the negative pH, which is done on many calculators with an "INV" key and a "log" key. Converting from $[H_3O^+]$ to pH requires finding the logarithm, which is commonly done with a "log" key and an "expo" or "EE" key for entering exponents of 10. Consult your calculator instructions if you are not sure how to use these keys. Remember that the sign of the number given by the calculator must be changed from minus to plus to get the pH.

The H_3O^+ concentration in blood with pH $= 7.4$ is

$$[H_3O^+] = \text{antilog}(-7.4) = 4 \times 10^{-8} \text{ M}$$

The pH of a solution with $[H_3O^+] = 4.6 \times 10^{-3}$ M is

$$pH = -\log(4.6 \times 10^{-3}) = -(-2.34) = 2.34$$

A note about significant figures: An antilogarithm contains the same number of digits that the original number has to the right of the decimal point. A logarithm contains the same number of digits to the right of the decimal point that the original number has

$$\text{antilog}(-7.\underline{4}) = \underline{4} \times 10^{-8} \qquad \log(\underline{4.6} \times 10^{-3}) = -2.\underline{34}$$

| 1 digit after decimal point | 1 digit | 2 digits | 2 digits after decimal point |

WORKED EXAMPLE   **10.9** Working with pH: Converting a pH to $[H_3O^+]$

Soft drinks usually have a pH of approximately 3.1. What is the $[H_3O^+]$ concentration in a soft drink?

ANALYSIS To convert from a pH value to an $[H_3O^+]$ concentration requires using the equation $[H_3O^+] = 10^{-pH}$, which requires finding an antilogarithm on a calculator.

BALLPARK ESTIMATE Because the pH is between 3.0 and 4.0, the $[H_3O^+]$ must be between 1×10^{-3} and 1×10^{-4}. A pH of 3.1 is very close to 3.0, so the $[H_3O^+]$ must be just slightly below 1×10^{-3} M.

SOLUTION
Entering the negative pH on a calculator (-3.1) and pressing the "INV" and "log" keys gives the answer 7.943×10^{-4}, which must be rounded off to 8×10^{-4} since the pH has only one digit to the right of the decimal point.

BALLPARK CHECK The calculated $[H_3O^+]$ of 8×10^{-4} M is between 1×10^{-3} M and 1×10^{-4} M and, as we estimated, just slightly below 1×10^{-3} M. (Remember, 8×10^{-4} is 0.8×10^{-3}.)

WORKED EXAMPLE   **10.10** Working with pH: Calculating pH for Strong Acid Solutions

What is the pH of a 0.0045 M solution of $HClO_4$?

ANALYSIS Finding pH requires first finding $[H_3O^+]$ and then using the equation $pH = -\log[H_3O^+]$. Since $HClO_4$ is a strong acid (see Table 10.1), it is 100% dissociated, and so the H_3O^+ concentration is the same as the $HClO_4$ concentration.

BALLPARK ESTIMATE Because $[H^+] = 4.5 \times 10^{-3}$ M is close to midway between 1×10^{-2} M and 1×10^{-3} M, the pH must be close to the midway point between 2.0 and 3.0. (Unfortunately, because the logarithm scale is not linear, trying to estimate the midway point is not a simple process.)

SOLUTION
$[H_3O^+] = 0.0045$ M $= 4.5 \times 10^{-3}$ M. Taking the negative logarithm gives $pH = 2.35$.

BALLPARK CHECK The calculated pH is consistent with our estimate.

WORKED EXAMPLE **10.11** Working with pH: Calculating pH for Strong Base Solutions

What is the pH of a 0.0032 M solution of NaOH?

ANALYSIS Since NaOH is a strong base, the OH^- concentration is the same as the NaOH concentration. Starting with the OH^- concentration, finding pH requires either using the K_w equation to find $[H_3O^+]$ or calculating pOH and then using the logarithmic form of the K_w equation.

BALLPARK ESTIMATE Because $[OH^-] = 3.2 \times 10^{-3}$ M is close to midway between 1×10^{-2} M and 1×10^{-3} M, the pOH must be close to the midway point between 2.0 and 3.0. Subtracting the pOH from 14 would therefore yield a pH between 11 and 12.

SOLUTION

$$[OH^-] = 0.0032 \text{ M} = 3.2 \times 10^{-3} \text{ M}$$

$$[H_3O^+] = \frac{K_w}{(3.2 \times 10^{-3})} = 3.1 \times 10^{-12} \text{ M}$$

Taking the negative logarithm gives pH $= -\log(3.1 \times 10^{-12}) = 11.51$. Alternatively, we can calculate pOH and subtract from 14.00 using the logarithmic form of the K_w equation. For $[OH^-] = 0.0032$ M,

$$pOH = -\log(3.2 \times 10^{-3}) = 2.49$$

$$pH = 14.00 - 2.49 = 11.51$$

Since the given OH^- concentration included two significant figures, the final pH includes two significant figures beyond the decimal point.

BALLPARK CHECK The calculated pH is consistent with our estimate.

PROBLEM 10.16

Identify the following solutions as acidic or basic, estimate $[H_3O^+]$ values for each, and rank them in order of increasing acidity:

(a) Saliva, pH $= 6.5$ **(b)** Pancreatic juice, pH $= 7.9$

(c) Orange juice, pH $= 3.7$ **(d)** Wine, pH $= 3.5$

PROBLEM 10.17

Find the pH of the following solutions:

(a) Seawater with $[H_3O^+] = 5.3 \times 10^{-9}$ M

**(b)** A urine sample with $[H_3O^+] = 8.9 \times 10^{-6}$ M

PROBLEM 10.18

What is the pH of a 0.0025 M solution of HCl?

## 10.10 Laboratory Determination of Acidity

The pH of water is an important indicator of water quality in applications ranging from swimming pool and spa maintenance to municipal water treatment. There are several ways to measure the pH of a solution. The simplest but least accurate method is to use an **acid–base indicator**, a dye that changes color depending on

Acid–base indicator A dye that changes color depending on the pH of a solution.

(a)

(b)
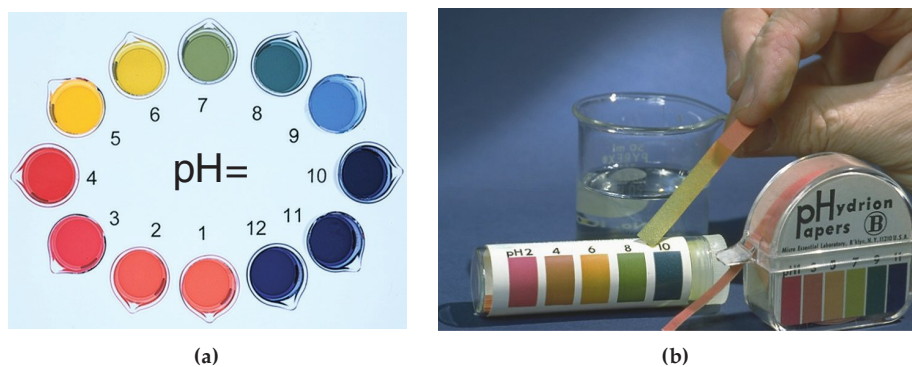
▲ **FIGURE 10.3** **Finding pH.** (a) The color of universal indicator in solutions of known pH from 1 to 12. (b) Testing pH with a paper strip. Comparing the color of the strip with the code on the package gives the approximate pH.

the pH of the solution. For example, the well-known dye *litmus* is red below pH 4.8 but blue above pH 7.8 and the indicator *phenolphthalein* (fee-nol-**thay**-lean) is color-less below pH 8.2 but red above pH 10. To make pH determination particularly easy, test kits are available that contain a mixture of indicators known as *universal indicator* to give approximate pH measurements in the range 2–10 (Figure 10.3a). Also available are rolls of "pH paper," which make it possible to determine pH simply by putting a drop of solution on the paper and comparing the color that appears to the color on a calibration chart (Figure 10.3b).

A much more accurate way to determine pH uses an electronic pH meter like the one shown in Figure 10.4. Electrodes are dipped into the solution, and the pH is read from the meter.
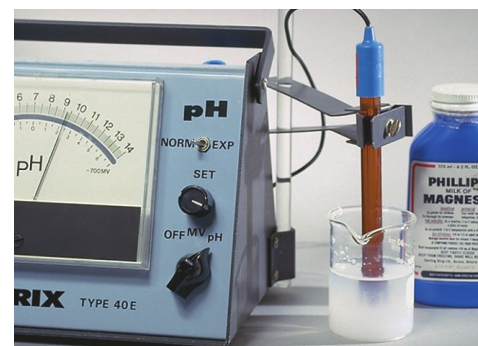
▲ **FIGURE 10.4** **Using a pH meter to obtain an accurate reading of pH.** Is milk of magnesia acidic or basic?

APPLICATION ▶ pH of Body Fluids

Each fluid in our bodies has a pH range suited to its function, as shown in the accompanying table. The stability of cell membranes, the shapes of huge protein molecules that must be folded in certain ways to function, and the activities of enzymes are all dependent on appropriate H_3O^+ concentrations.

pH of Body Fluids

FLUID	pH
Blood plasma	7.4
Interstitial fluid	7.4
Cytosol	7.0
Saliva	5.8–7.1
Gastric juice	1.6–1.8
Pancreatic juice	7.5–8.8
Intestinal juice	6.3–8.0
Urine	4.6–8.0
Sweat	4.0–6.8

Blood plasma and the interstitial fluid surrounding cells, which together comprise one-third of body water, have a slightly basic pH of 7.4. In fact, one of the functions of blood is to neutralize the acid by-products of cellular metabolism. The fluid within cells, called the *cytosol*, is slightly more acidic than the fluid outside, so a pH differential exists.

The strongly acidic gastric juice in the stomach has three important functions. First, gastric juice aids in the digestion of proteins by causing them to denature, or unfold. Second, it kills most of the bacteria we consume along with our food. Third, it converts the enzyme that breaks down proteins from an inactive form to the active form.

When the acidic mixture of partially digested food (*chyme*) leaves the stomach and enters the small intestine, it triggers secretion by the pancreas of an alkaline fluid contain-ing bicarbonate ions, HCO_3^-. A principal function of this pancreatic juice and other intestinal fluids is to dilute and neu-tralize the hydrochloric acid carried along from the stomach.

Urine has a wide normal pH range, depending on the diet and recent activities. It is generally acidic, though, because one important function of urine is to eliminate a quantity of hydrogen ion equal to that produced by the body each day. Without this elimination, the body would soon be over-whelmed by acid.

*See Additional Problem 10.97 at the end of the chapter.*

10.11 Buffer Solutions

Much of the body's chemistry depends on maintaining the pH of blood and other fluids within narrow limits. This is accomplished through the use of **buffers**—combinations of substances that act together to prevent a drastic change in pH.

Buffer A combination of substances that act together to prevent a drastic change in pH; usually a weak acid and its conjugate base.

Most buffers are mixtures of a weak acid and a roughly equal concentration of its conjugate base—for example, a solution that contains 0.10 M acetic acid and 0.10 M acetate ion. If a small amount of OH^- is added to a buffer solution, the pH increases, but not by much because the acid component of the buffer neutralizes the added OH^-. If a small amount of H_3O^+ is added to a buffer solution, the pH decreases, but again not by much because the base component of the buffer neutralizes the added H_3O^+.

To see why buffer solutions work, look at the equation for the acid dissociation constant of an acid HA.

For the reaction: $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$
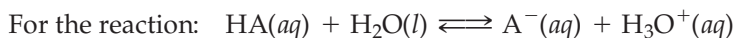
we have $\quad K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

Rearranging this equation shows that the value of $[H_3O^+]$, and thus the pH, depends on the ratio of the undissociated acid concentration to the conjugate base concentration, $[HA]/[A^-]$:

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

In the case of the acetic acid–acetate ion buffer, for instance, we have

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
$$(0.10 \text{ M}) \qquad\qquad\qquad\qquad\qquad (0.10 \text{ M})$$
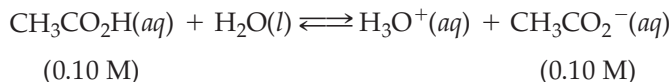
and $\quad [H_3O^+] = K_a\dfrac{[CH_3CO_2H]}{[CH_3CO_2^-]}$

Initially, the pH of the 0.10 M acetic acid–0.10 M acetate ion buffer solution is 4.74. When acid is added, most is removed by reaction with $CH_3CO_2^-$. The equilibrium reaction shifts to the left, and as a result the concentration of CH_3CO_2H increases and the concentration of $CH_3CO_2^-$ decreases. As long as the changes in $[CH_3CO_2H]$ and $[CH_3CO_2^-]$ are relatively small, however, the ratio of $[CH_3CO_2H]$ to $[CH_3CO_2^-]$ changes only slightly, and there is little change in the pH.

When base is added to the buffer, most is removed by reaction with CH_3CO_2H. The equilibrium shifts to the right, and so the concentration of CH_3CO_2H decreases and the concentration of $CH_3CO_2^-$ increases. Here too, though, as long as the concentration changes are relatively small, there is little change in the pH.

The ability of a buffer solution to resist changes in pH when acid or base is added is illustrated in Figure 10.5. Addition of 0.010 mol of H_3O^+ to 1.0 L of pure water changes the pH from 7 to 2, and addition of 0.010 mol of OH^- changes the pH from 7 to 12. A similar addition of acid to 1.0 L of a 0.10 M acetic acid–0.10 M acetate ion buffer, however, changes the pH only from 4.74 to 4.68, and addition of base changes the pH only from 4.74 to 4.85.

As we did with K_w, we can convert the rearranged K_a equation to its logarithmic form to obtain

$$pH = pK_a - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$\text{or} \quad pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$
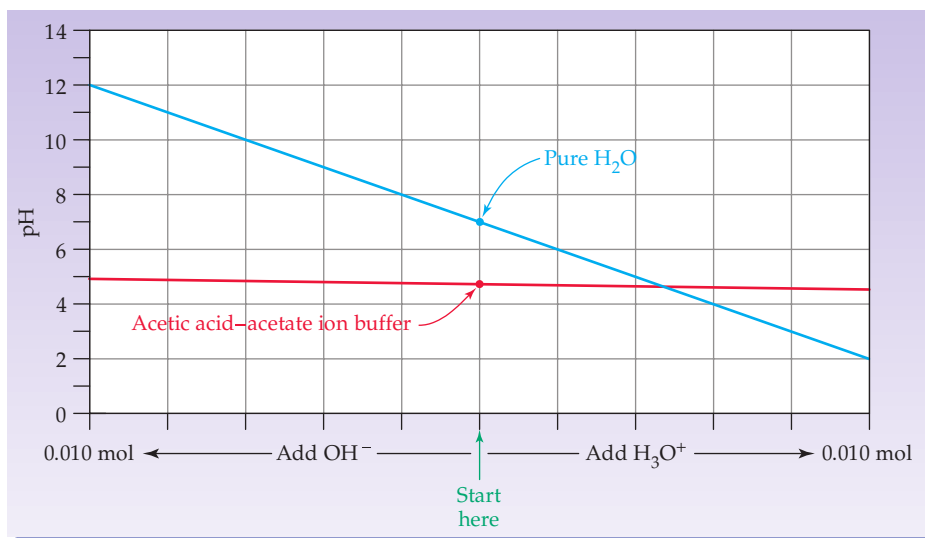
▲ **FIGURE 10.5 A comparison of the change in pH.** When 0.010 mol of acid and 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of a 0.10 M acetic acid–0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.

This expression is known as the **Henderson–Hasselbalch equation** and is very useful in buffer applications, particularly in biology and biochemistry. Examination of the Henderson–Hasselbalch equation provides useful insights into how to prepare a buffer and into the factors that affect the pH of a buffer solution.

Henderson–Hasselbalch equation The logarithmic form of the K_a equation for a weak acid, used in applications involving buffer solutions.

The effective pH range of a buffer will depend on the pK_a of the acid HA and on the relative concentrations of HA and conjugate base A^-. In general, the most effective buffers meet the following conditions:

- The pK_a for the weak acid should be close to the desired pH of the buffer solution.
- The ratio of [HA] to $[A^-]$ should be close to 1, so that neither additional acid nor additional base changes the pH of the solution dramatically.
- The molar amounts of HA and A^- in the buffer should be approximately 10 times greater than the molar amounts of either acid or base you expect to add so that the ratio $[A^-]/[HA]$ does not undergo a large change.

WORKED EXAMPLE **10.12** Buffers: Selecting a Weak Acid for a Buffer Solution

Which of the organic acids in Table 10.2 would be the most appropriate for preparing a pH 4.15 buffer solution?

ANALYSIS The pH of the buffer solution depends on the pK_a of the weak acid. Remember that $pK_a = -\log(K_a)$.

SOLUTION
The K_a and pK_a values for the four organic acids in Table 10.2 are tabulated below. The ascorbic acid ($pK_a = 4.10$) will produce a buffer solution closest to the desired pH of 4.15.

ORGANIC ACID	K_a	pK_a
Formic acid (HCOOH)	1.8×10^{-4}	3.74
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Propanoic acid (CH_3CH_2COOH)	1.3×10^{-5}	4.89
Ascorbic acid (vitamin C)	7.9×10^{-5}	4.10

WORKED EXAMPLE 10.13 Buffers: Calculating the pH of a Buffer Solution

What is the pH of a buffer solution that contains 0.100 M HF and 0.120 M NaF? The K_a of HF is 3.5×10^{-4}, and so $pK_a = 3.46$.

ANALYSIS The Henderson–Hasselbalch equation can be used to calculate the pH of a buffer solution: $pH = pK_a + \log\left(\dfrac{[F^-]}{[HF]}\right)$.

BALLPARK ESTIMATE If the concentrations of F^- and HF were equal, the log term in our equation would be zero, and the pH of the solution would be equal to the pK_a for HF, which means pH = 3.46. However, since the concentration of the conjugate base ($[F^-] = 0.120$ M) is slightly higher than the concentration of the conjugate acid ($[HF] = 0.100$ M), then the pH of the buffer solution will be slightly higher (more basic) than the pK_a.

SOLUTION

$$pH = pK_a + \log\left(\frac{[F^-]}{[HF]}\right)$$

$$pH = 3.46 + \log\left(\frac{(0.120)}{(0.100)}\right) = 3.46 + 0.08 = 3.54$$

BALLPARK CHECK The calculated pH of 3.54 is consistent with the prediction that the final pH will be slightly higher than the pK_a of 3.46.

WORKED EXAMPLE 10.14 Buffers: Measuring the Effect of Added Base on pH

What is the pH of 1.00 L of the 0.100 M hydrofluoric acid–0.120 M fluoride ion buffer system described in Worked Example 10.13 after 0.020 mol of NaOH is added?

ANALYSIS Initially, the 0.100 M HF–0.120 M NaF buffer has pH = 3.54, as calculated in Worked Example 10.13. The added base will react with the acid as indicated in the neutralization reaction,

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

which means $[HF]$ decreases and $[F^-]$ increases. With the pK_a and the concentrations of HF and F^- known, pH can be calculated using the Henderson–Hasselbalch equation.

BALLPARK ESTIMATE After the neutralization reaction, there is more conjugate base (F^-) and less conjugate acid (HF), and so we expect the pH to increase slightly from the initial value of 3.54.

SOLUTION
When 0.020 mol of NaOH is added to 1.00 L of the buffer, the HF concentration *decreases* from 0.100 M to 0.080 M as a result of an acid–base reaction. At the same time, the F^- concentration *increases* from 0.120 M to 0.140 M because additional F^- is produced by the neutralization. Using these new values gives

$$pH = 3.46 + \log\left(\frac{(0.140)}{(0.080)}\right) = 3.46 + 0.24 = 3.70$$

The addition of 0.020 mol of base causes the pH of the buffer to rise only from 3.54 to 3.70.

BALLPARK CHECK The final pH, 3.70, is slightly more basic than the initial pH of 3.54, consistent with our prediction.

PROBLEM 10.19

What is the pH of 1.00 L of the 0.100 M hydrofluoric acid–0.120 M fluoride ion buffer system described in Worked Example 10.13 after 0.020 mol of HNO_3 is added?

PROBLEM 10.20

The ammonia/ammonium buffer system is used to optimize polymerase chain reactions (PCR) used in DNA studies. The equilibrium for this buffer can be written as

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

Calculate the pH of a buffer that contains 0.050 M ammonium chloride and 0.080 M ammonia. The K_a of ammonium is 5.6×10^{-10}.

KEY CONCEPT PROBLEM 10.21

A buffer solution is prepared using CN^- (from NaCN salt) and HCN in the amounts indicated. The K_a for HCN is 4.9×10^{-10}. Calculate the pH of the buffer solution.

= HCN   = CN^-
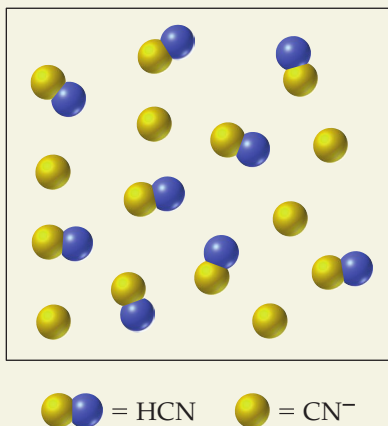
10.12 Buffers in the Body

The pH of body fluids is maintained by three major buffer systems. Two of these buffers, the carbonic acid–bicarbonate (H_2CO_3–HCO_3^-) system and the dihydrogen phosphate–hydrogen phosphate system, depend on weak acid–conjugate base interactions exactly like those of the acetate buffer system described in the preceding section:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \qquad pK_a = 6.37$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad pK_a = 7.21$$
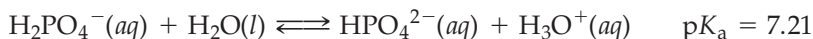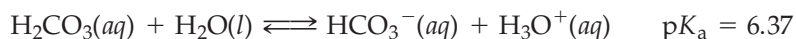
The third buffer system depends on the ability of proteins to act as either proton acceptors or proton donors at different pH values.

To illustrate the action of buffers in the body, take a look at the carbonic acid–bicarbonate system, the principal buffer in blood serum and other extracellular fluids. (The hydrogen phosphate system is the major buffer within cells.) Because carbonic acid is unstable and therefore in equilibrium with CO_2 and water, there is an extra step in the bicarbonate buffer mechanism:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
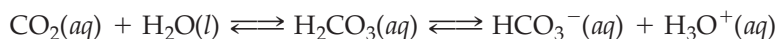
As a result, the bicarbonate buffer system is intimately related to the elimination of CO_2, which is continuously produced in cells and transported to the lungs to be exhaled.

Because most CO_2 is present simply as the dissolved gas rather than as H_2CO_3, the acid dissociation constant for carbonic acid in blood can be written using $[CO_2]$:

$$K_a = \frac{[H_3O^+][HCO_3{}^-]}{[CO_2]}$$

which can be rearranged to

$$[H_3O^+] = K_a \frac{[CO_2]}{[HCO_3{}^-]}$$

An increase in $[CO_2]$ raises $[H_3O^+]$ and lowers pH.

A decrease in $[CO_2]$ lowers $[H_3O^+]$ and raises pH.

Converting this rearranged equation to the logarithmic form of the Henderson–Hasselbalch equation yields

$$pH = pK_a + \log\left(\frac{[HCO_3{}^-]}{[CO_2]}\right)$$

This rearranged equation shows that an increase in $[CO_2]$ makes the ratio of $[HCO_3{}^-]$ to $[CO_2]$ smaller, thereby decreasing the pH; that is, the blood becomes more acidic. Similarly, a decrease in $[CO_2]$ makes the ratio of $[HCO_3{}^-]$ to $[CO_2]$ larger, thereby increasing the pH; that is, the blood becomes more basic. At the normal blood pH of 7.4, the ratio $[HCO_3{}^-]/[CO_2]$ is about 20 to 1.

The relationships between the bicarbonate buffer system, the lungs, and the kidneys are shown in Figure 10.6. Under normal circumstances, the reactions shown in the figure are at equilibrium. Addition of excess acid (red arrows) causes formation of H_2CO_3 and results in lowering of H_3O^+ concentration. Removal of acid (blue arrows) causes formation of more H_3O^+ by dissociation of H_2CO_3. The maintenance of pH by this mechanism is supported by a reserve of bicarbonate ions in body fluids. Such a buffer can accommodate large additions of H_3O^+ before there is a significant change in the pH, a condition that meets the body's needs because excessive production of acid is a more common body condition than excessive loss of acid.
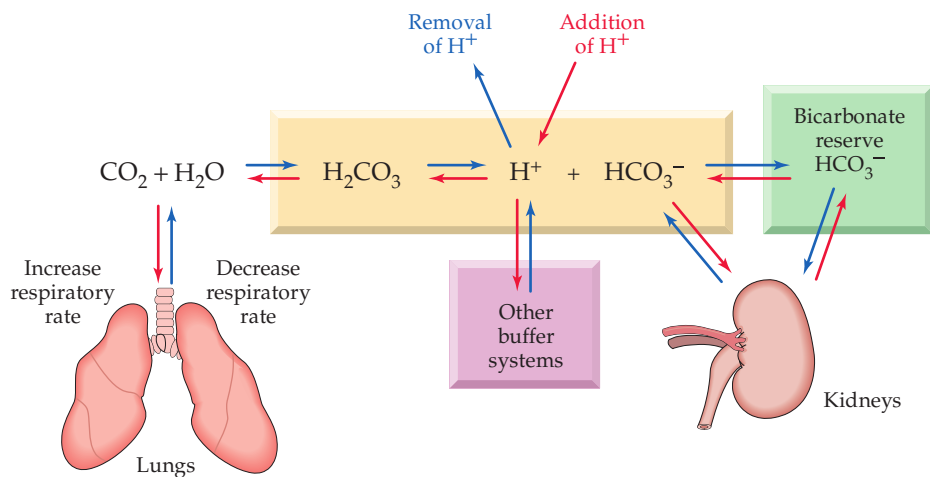
▶ **FIGURE 10.6 Relationships of the bicarbonate buffer system to the lungs and the kidneys.** The red and blue arrows show the responses to the stresses of increased or decreased respiratory rate and removal or addition of acid.

A change in the breathing rate provides a quick further adjustment in the bicarbonate buffer system. When the CO_2 concentration in the blood starts to rise, the breathing rate increases to remove CO_2, thereby decreasing the acid concentration (red arrows in Figure 10.6). When the CO_2 concentration in the blood starts to

APPLICATION ▶ Buffers in the Body: Acidosis and Alkalosis

A group of teenagers at a rock concert experience a collective fainting spell. A person taking high doses of aspirin for chronic pain appears disoriented and is having trouble breathing. An insulin-dependent diabetic patient complains of tiredness and stomach pains. An athlete who recently completed a highly strenuous workout suffers from muscle cramps and nausea. A patient on an HIV drug regimen experiences increasing weakness and numbness in the hands and feet. What do all these individuals have in common? They are all suffering from abnormal fluctuations in blood pH, resulting in conditions known as *acidosis* (pH < 7.35) or *alkalosis* (pH > 7.45).

The highly complex series of reactions and equilibria that take place throughout the body are very sensitive to pH—variations of even a few tenths of a pH unit can produce severe physiological symptoms. The carbonate–bicarbonate buffer system (Section 10.12) maintains the pH of blood serum at a fairly constant value of 7.4. The effective pH depends on the relative amounts of CO_2 and bicarbonate dissolved in the blood:

$$CO_2(aq) + H_2O(l)$$
$$\rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3{}^-(aq) + H_3O^+(aq)$$
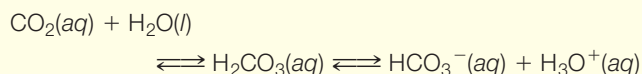
Anything that significantly shifts the balance between dissolved CO_2 and $HCO_3{}^-$ can raise or lower the pH. How does this happen, and how does the body compensate?

Respiratory acidosis can be caused by a decrease in respiration, which leads to a buildup of excess CO_2 in the blood and a corresponding decrease in pH. This could be caused by a blocked air passage due to inhaled food—removal of the blockage restores normal breathing and a return to the optimal pH. *Metabolic acidosis* results from an excess of other acids in the blood that reduce the bicarbonate concentration. High doses of aspirin (acetyl salicylic acid, Section 17.5), for example, increase the hydronium ion concentration and decrease the pH. Strenuous exercise generates excess lactate in the muscles, which is released into the bloodstream (Section 23.11). The liver converts lactate into glucose, which is the body's major source of energy; this process consumes bicarbonate ions, which decreases the pH. Some HIV drug therapies can damage cellular mitochondria (Section 21.3),

resulting in a buildup of lactic acid in the cells and blood stream. In the case of the diabetic patient, lack of insulin causes the body to start burning fat, which generates ketones and keto acids (Chapter 16), organic compounds that lower the blood pH.

The body attempts to correct acidosis by increasing the rate and depth of respiration—breathing faster "blows off" CO_2, shifting the CO_2–bicarbonate equilibrium to the left and lowering the pH. The net effect is rapid reversal of the acidosis. Although this may be sufficient for cases of respiratory acidosis, it provides only temporary relief for metabolic acidosis. A long-term solution depends on removal of excess acid by the kidneys, which can take several hours.

What about our teenage fans? In their excitement they have hyperventilated—their increased breathing rate has removed too much CO_2 from their blood and they are suffering from *respiratory alkalosis*. The body responds by "fainting" to decrease respiration and restore the CO_2 levels in the blood. When they regain consciousness, they will be ready to rock once again.

▲ **Hyperventilation, the rapid breathing due to excitement or stress, removes CO_2 and increases blood pH resulting in respiratory alkalosis.**

See Additional Problems 10.98 and 10.99 at the end of the chapter.

fall, the breathing rate decreases and acid concentration increases (blue arrows in Figure 10.6).

Additional backup to the bicarbonate buffer system is provided by the kidneys. Each day a quantity of acid equal to that produced in the body is excreted in the urine. In the process, the kidney returns $HCO_3{}^-$ to the extracellular fluids, where it becomes part of the bicarbonate reserve.

⊂⊃ Looking Ahead

In Chapter 29, we will see how the regulation of blood pH by the bicarbonate buffer system is particularly important in preventing *acidosis* and *alkalosis*.   ⊂⊃

10.13 Acid and Base Equivalents

We said in Section 9.10 that it is sometimes useful to think in terms of ion *equivalents* (Eq) and *gram-equivalents* (g-Eq) when we are primarily interested in an ion itself rather than the compound that produced the ion. (⬤⬤, p. 276) For similar reasons, it can also be useful to consider acid or base equivalents and gram-equivalents.

When dealing with ions, the property of interest was the charge on the ion. Therefore, 1 Eq of an ion was defined as the number of ions that carry 1 mol of charge, and 1 g-Eq of any ion was defined as the molar mass of the ion divided by the ionic charge. For acids and bases, the property of interest is the number of H^+ ions (for an acid) or the number of OH^- ions (for a base) per formula unit. Thus, 1 **equivalent of acid** contains 1 mol of H^+ ions, and 1 g-Eq of an acid is the mass in grams that contains 1 mol of H^+ ions. Similarly, 1 **equivalent of base** contains 1 mol of OH^- ions, and 1 g-Eq of a base is the mass in grams that contains 1 mol of OH^- ions:

Equivalent of acid Amount of an acid that contains 1 mole of H^+ ions.

Equivalent of base Amount of base that contains 1 mole of OH^- ions.

$$\text{One gram-equivalent of acid} = \frac{\text{Molar mass of acid (g)}}{\text{Number of } H^+ \text{ ions per formula unit}}$$

$$\text{One gram-equivalent of base} = \frac{\text{Molar mass of base (g)}}{\text{Number of } OH^- \text{ ions per formula unit}}$$

Thus 1 g-Eq of the monoprotic acid HCl is

$$1 \text{ g-Eq HCl} = \frac{36.5 \text{ g}}{1 \text{ } H^+ \text{ per HCl}} = 36.5 \text{ g}$$

which is the molar mass of the acid, but one gram-equivalent of the diprotic acid H_2SO_4 is

$$1 \text{ g-Eq } H_2SO_4 = \frac{98.0 \text{ g}}{2 \text{ } H^+ \text{ per } H_2SO_4} = 49.0 \text{ g}$$

which is the molar mass divided by 2 because 1 mol of H_2SO_4 contains 2 mol of H^+.

$$\text{One equivalent of } H_2SO_4 = \frac{\text{Molar mass of } H_2SO_4}{2} = \frac{98.0 \text{ g}}{2} = 49.0 \text{ g}$$

Divide by 2 because H_2SO_4 is diprotic.

Using acid–base equivalents has two practical advantages: First, they are convenient when only the acidity or basicity of a solution is of interest rather than the identity of the acid or base. Second, they show quantities that are chemically equivalent in their properties; 36.5 g of HCl and 49.0 g of H_2SO_4 are chemically equivalent quantities because each reacts with 1 Eq of base. *One equivalent of any acid neutralizes one equivalent of any base.*

Because acid–base equivalents are so useful, clinical chemists sometimes express acid and base concentrations in *normality* rather than molarity. The **normality (N)** of an acid or base solution is defined as the number of equivalents (or milliequivalents) of acid or base per liter of solution. For example, a solution made by dissolving 1.0 g-Eq (49.0 g) of H_2SO_4 in water to give 1.0 L of solution has a concentration of 1.0 Eq/L, which is 1.0 N. Similarly, a solution that contains 0.010 Eq/L of acid is 0.010 N and has an acid concentration of 10 mEq/L:

$$\text{Normality (N)} = \frac{\text{Equivalents of acid or base}}{\text{Liters of solution}}$$

The values of molarity (M) and normality (N) are the same for monoprotic acids, such as HCl, but are not the same for diprotic or triprotic acids. A solution made by diluting 1.0 g-Eq (49.0 g = 0.50 mol) of the diprotic acid H_2SO_4 to a volume of 1.0 L has a *normality* of 1.0 N but a *molarity* of 0.50 M. For any acid or base,

normality is always equal to molarity times the number of H^+ or OH^- ions produced per formula unit:

Normality of acid = (Molarity of acid) × (Number of H^+ ions produced per formula unit)

Normality of base = (Molarity of base) × (Number of OH^- ions produced per formula unit)

WORKED EXAMPLE **10.15** Equivalents: Mass to Equivalent Conversion for Diprotic Acid

How many equivalents are in 3.1 g of the diprotic acid H_2S? The molar mass of H_2S is 34.0 g.

ANALYSIS The number of acid or base equivalents is calculated by doing a gram to mole conversion using molar mass as the conversion factor and then multiplying by the number of H^+ ions produced.

BALLPARK ESTIMATE The 3.1 g is a little less than 0.10 mol of H_2S. Since it is a diprotic acid, (two H^+ per mole), this represents a little less than 0.2 Eq of H_2S.

SOLUTION

$$(3.1 \text{ g } H_2S)\left(\frac{1 \text{ mol } H_2S}{34.0 \text{ g } H_2S}\right)\left(\frac{2 \text{ Eq } H_2S}{1 \text{ mol } H_2S}\right) = 0.18 \text{ Eq } H_2S$$

BALLPARK CHECK The calculated value of 0.18 is consistent with our prediction of a little less than 0.2 Eq of H_2S.

WORKED EXAMPLE **10.16** Equivalents: Calculating Equivalent Concentrations

What is the normality of a solution made by diluting 6.5 g of H_2SO_4 to a volume of 200 mL? What is the concentration of this solution in milliequivalents per liter? The molar mass of H_2SO_4 is 98.0 g.

ANALYSIS Calculate how many equivalents of H_2SO_4 are in 6.5 g by using the molar mass of the acid as a conversion factor and then determine the normality of the acid.

SOLUTION

STEP 1: Identify known information. We know the molar mass of H_2SO_4, the mass of H_2SO_4 to be dissolved, and the final volume of solution.

MW of H_2SO_4 = 98.0 g/mol
Mass of H_2SO_4 = 6.5 g
Volume of solution = 200 mL

STEP 2: Identify answer including units. We need to calculate the normality of the final solution.

Normality = ?? (equiv./L)

STEP 3: Identify conversion factors. We will need to convert the mass of H_2SO_4 to moles, and then to equivalents of H_2SO_4. We will then need to convert volume from mL to L.

$$(6.5 \text{ g } H_2SO_4)\left(\frac{1 \text{ mol } H_2SO_4}{98.0 \text{ g } H_2SO_4}\right)\left(\frac{2 \text{ Eq } H_2SO_4}{1 \text{ mol } H_2SO_4}\right)$$
$$= 0.132 \text{ Eq } H_2SO_4 \text{(don't round yet!)}$$

$$(200 \text{ mL})\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) = 0.200 \text{ L}$$

STEP 4: Solve. Dividing the number of equivalents by the volume yields the Normality.

$$\frac{0.132 \text{ Eq } H_2SO_4}{0.200 \text{ L}} = 0.66 \text{ N}$$

The concentration of the sulfuric acid solution is 0.66 N, or 660 mEq/L.

10.14 Some Common Acid–Base Reactions

Among the most common of the many kinds of Brønsted–Lowry acid–base reactions are those of an acid with hydroxide ion, an acid with bicarbonate or carbonate ion, and an acid with ammonia or a related nitrogen-containing compound. Let us look briefly at each of the three types.

Reaction of Acids with Hydroxide Ion

One equivalent of an acid reacts with 1 Eq of a metal hydroxide to yield water and a salt in a neutralization reaction (Section 6.10): (⊂⊃, p. 165)

$$HCl(aq) + KOH(aq) \longrightarrow H_2O(l) + KCl(aq)$$
(An acid) (A base) (Water) (A salt)
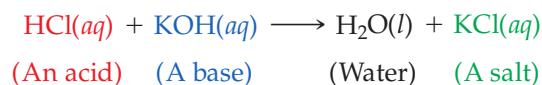
Such reactions are usually written with a single arrow because their equilibria lie far to the right and they have very large equilibrium constants ($K = 5 \times 10^{15}$; Section 7.8). The net ionic equation (Section 6.13) for all such reactions makes clear why acid-base equivalents are useful and why the properties of the acid and base disappear in neutralization reactions: The equivalent ions for the acid (H^+) and the base (OH^-) are used up in the formation of water.
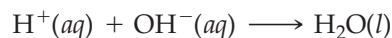
$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Reaction of Acids with Bicarbonate and Carbonate Ion

Bicarbonate ion reacts with acid by accepting H^+ to yield carbonic acid, H_2CO_3. Similarly, carbonate ion accepts two protons in its reaction with acid. As mentioned on p. 315, though, that H_2CO_3 is unstable, rapidly decomposing to carbon dioxide gas and water:

$$H^+(aq) + HCO_3^-(aq) \longrightarrow [H_2CO_3(aq)] \longrightarrow H_2O(l) + CO_2(g)$$
$$2\,H^+(aq) + CO_3^{2-}(aq) \longrightarrow [H_2CO_3(aq)] \longrightarrow H_2O(l) + CO_2(g)$$
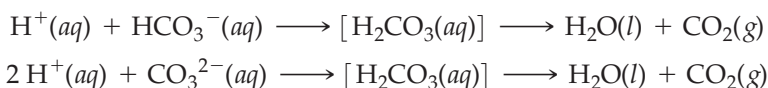
Most metal carbonates are insoluble in water—marble, for example, is almost pure calcium carbonate, $CaCO_3$—but they nevertheless react easily with aqueous acid. In fact, geologists often test for carbonate-bearing rocks by putting a few drops of aqueous HCl on the rock and watching to see if bubbles of CO_2 form (Figure 10.7). This reaction is also responsible for the damage to marble and


▲ **FIGURE 10.7 Marble.** Marble, which is primarily $CaCO_3$, releases bubbles of CO_2 when treated with hydrochloric acid.

limestone artwork caused by acid rain (See Application, p. 324). The most common application involving carbonates and acid, however, is the use of antacids that contain carbonates, such as Tums or Rolaids, to neutralize excess stomach acid.
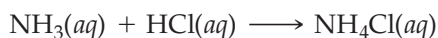

PROBLEM 10.25

Write a balanced equation for each of the following reactions:

(a) $KHCO_3(aq) + H_2SO_4(aq) \longrightarrow$?
(b) $MgCO_3(aq) + HNO_3(aq) \longrightarrow$?
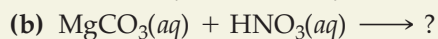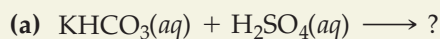
Reaction of Acids with Ammonia

Acids react with ammonia to yield ammonium salts, such as ammonium chloride, NH_4Cl, most of which are water-soluble:

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

Living organisms contain a group of compounds called *amines*, which contain nitrogen atoms bonded to carbon. Amines react with acids just as ammonia does, yielding water-soluble salts. Methylamine, for example, an organic compound found in rotting fish, reacts with HCl:

Methylamine   Methylammonium chloride
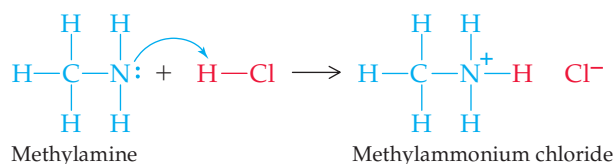
Looking Ahead

In Chapter 15, we will see that amines occur in all living organisms, both plant and animal, as well as in many pharmaceutical agents. Amines called amino acids form the building blocks from which proteins are made, as we will see in Chapter 18.

PROBLEM 10.26

What products would you expect from the reaction of ammonia and sulfuric acid in aqueous solution?

$$NH_3(aq) + H_2SO_4(aq) \longrightarrow ?$$
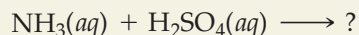
PROBLEM 10.27

Show how ethylamine ($C_2H_5NH_2$) reacts with hydrochloric acid to form an ethylammonium salt.

10.15 Titration

Determining the pH of a solution gives the solution's H_3O^+ concentration but not necessarily its total acid concentration. That is because the two are not the same thing. The H_3O^+ concentration gives only the amount of acid that has dissociated into ions, whereas total acid concentration gives the sum of dissociated plus undissociated acid. In a 0.10 M solution of acetic acid, for instance, the total acid concentration is 0.10 M, yet the H_3O^+ concentration is only 0.0013 M (pH = 2.89) because acetic acid is a weak acid that is only about 1% dissociated.

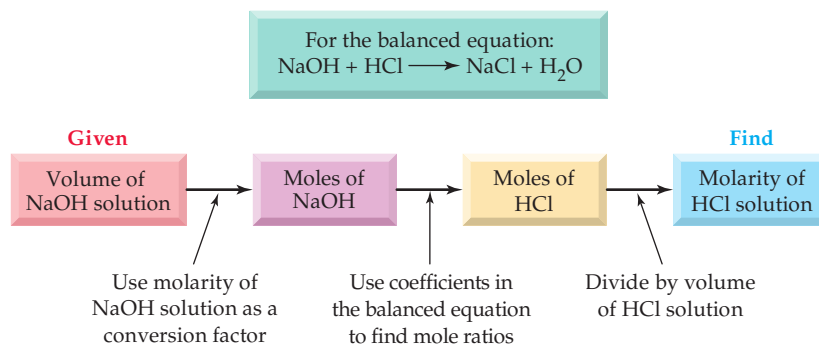▲ This limestone statue adorning the Rheims Cathedral in France has been severely eroded by acid rain.

Titration A procedure for determining the total acid or base concentration of a solution.

The total acid or base concentration of a solution can be found by carrying out a **titration** procedure, as shown in Figure 10.8. Let us assume, for instance, that we want to find the acid concentration of an HCl solution. (We could equally well need to find the base concentration of an NaOH solution.) We begin by measuring out a known volume of the HCl solution and adding an acid–base indicator. Next, we fill a calibrated glass tube called a *buret* with an NaOH solution of known concentration, and we slowly add the NaOH to the HCl until neutralization is complete (the *end point*), identified by a color change in the indicator.

(a)   (b)
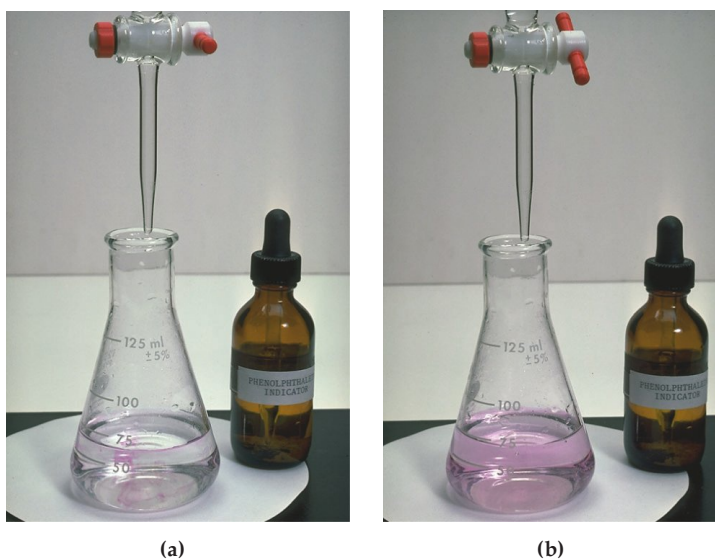
▲ **FIGURE 10.8   Titration of an acid solution of unknown concentration with a base solution of known concentration.**   (a) A measured volume of the acid solution is placed in the flask along with an indicator. (b) The base of known concentration is then added from a buret until the color change of the indicator shows that neutralization is complete (the *end point*).

Reading from the buret gives the volume of the NaOH solution that has reacted with the known volume of HCl. Knowing both the concentration and volume of the NaOH solution then allows us to calculate the molar amount of NaOH, and the coefficients in the balanced equation allow us to find the molar amount of HCl that has been neutralized. Dividing the molar amount of HCl by the volume of the HCl solution gives the concentration. The calculation thus involves mole–volume conversions just like those done in Section 9.7. (⬭, p. 265) Figure 10.9 shows a flow diagram of the strategy, and Worked Example 10.17 shows how to calculate total acid concentration.

For the balanced equation:
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Given			**Find**
Volume of NaOH solution	Moles of NaOH	Moles of HCl	Molarity of HCl solution

Use molarity of NaOH solution as a conversion factor

Use coefficients in the balanced equation to find mole ratios
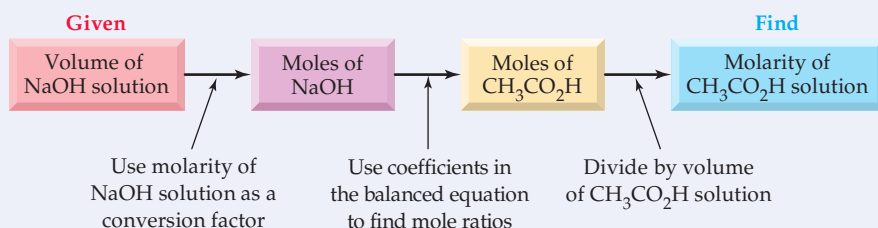
Divide by volume of HCl solution

▲ **FIGURE 10.9   A flow diagram for an acid–base titration.**   This diagram summarizes the calculations needed to determine the concentration of an HCl solution by titration with an NaOH solution of known concentration. The steps are similar to those shown in Figure 9.7.

WORKED EXAMPLE **10.17** Titrations: Calculating Total Acid Concentration

When a 5.00 mL sample of household vinegar (dilute aqueous acetic acid) is titrated, 44.5 mL of 0.100 M NaOH solution is required to reach the end point. What is the acid concentration of the vinegar in moles per liter, equivalents per liter, and milliequivalents per liter? The neutralization reaction is

$$CH_3CO_2H(aq) + NaOH(aq) \longrightarrow CH_3CO_2{}^-Na^+(aq) + H_2O(l)$$

ANALYSIS To find the molarity of the vinegar, we need to know the number of moles of acetic acid dissolved in the 5.00 mL sample. Following a flow diagram similar to Figure 10.9, we use the volume and molarity of NaOH to find the number of moles. From the chemical equation, we use the mole ratio to find the number of moles of acid, and then divide by the volume of the acid solution. Because acetic acid is a monoprotic acid, the normality of the solution is numerically the same as its molarity.

Given

| Volume of NaOH solution | Moles of NaOH | Moles of CH_3CO_2H | **Find** Molarity of CH_3CO_2H solution |

Use molarity of NaOH solution as a conversion factor

Use coefficients in the balanced equation to find mole ratios

Divide by volume of CH_3CO_2H solution

BALLPARK ESTIMATE The 5.00 mL of vinegar required nearly nine times as much NaOH solution (44.5 mL) for complete reaction. Since the neutralization stoichiometry is 1:1, the molarity of the acetic acid in the vinegar must be nine times greater than the molarity of NaOH, or 0.90 M.

SOLUTION
Substitute the known information and appropriate conversion factors into the flow diagram, and solve for the molarity of the acetic acid:

$$(44.5 \text{ mL NaOH})\left(\frac{0.100 \text{ mol NaOH}}{1000 \text{ mL}}\right)\left(\frac{1 \text{ mol } CH_3CO_2H}{1 \text{ mol NaOH}}\right)$$

$$\times \left(\frac{1}{0.005\ 00 \text{ L}}\right) = 0.890 \text{ M } CH_3CO_2H$$

$$= 0.890 \text{ N } CH_3CO_2H$$

Expressed in milliequivalents, this concentration is

$$\frac{0.890 \text{ Eq}}{L} \times \frac{1000 \text{ mEq}}{1 \text{ Eq}} = 890 \text{ mEq/L}$$

BALLPARK CHECK The calculated result (0.890 M) is very close to our estimate of 0.90 M.

PROBLEM 10.28

A titration is carried out to determine the concentration of the acid in an old bottle of aqueous HCl whose label has become unreadable. What is the HCl concentration if 58.4 mL of 0.250 M NaOH is required to titrate a 20.0 mL sample of the acid?

APPLICATION ▶   Acid Rain

As the water that evaporates from oceans and lakes condenses into raindrops, it dissolves small quantities of gases from the atmosphere. Under normal conditions, rain is slightly acidic, with a pH close to 5.6, because of atmospheric CO_2 that dissolves to form carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons$$
$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
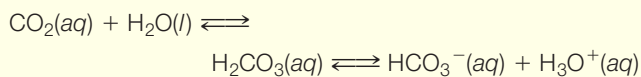
In recent decades, however, the acidity of rainwater in many industrialized areas of the world has increased by a factor of over 100, to a pH between 3 and 3.5.

The primary cause of this so-called *acid rain* is industrial and automotive pollution. Each year, large power plants and smelters pour millions of tons of sulfur dioxide (SO_2) gas into the atmosphere, where some is oxidized by air to produce sulfur trioxide (SO_3). Sulfur oxides then dissolve in rain to form dilute sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4):

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$
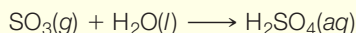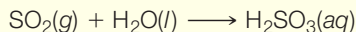
Nitrogen oxides produced by the high-temperature reaction of N_2 with O_2 in coal-burning plants and in automobile engines further contribute to the problem. Nitrogen dioxide (NO_2) dissolves in water to form dilute nitric acid (HNO_3) and nitric oxide (NO):

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$
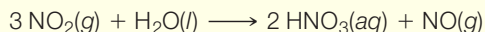
Oxides of both sulfur and nitrogen have always been present in the atmosphere, produced by such natural sources as volcanoes and lightning bolts, but their amounts have increased dramatically over the last century because of industrialization. The result is a notable decrease in the pH of rainwater in more densely populated regions, including Europe and the eastern United States.

Many processes in nature require such a fine pH balance that they are dramatically upset by the shift that has occurred in the pH of rain. Some watersheds contain soils that have high "buffering capacity" and so are able to neutralize acidic compounds in acid rain (Section 10.11). Other areas, such as the northeastern United States and eastern Canada, where soil buffering capacity is poor, have experienced negative ecological effects. Acid rain releases aluminum salts from soil, and the ions then wash into streams. The low pH and increased aluminum levels are so toxic to fish and other organisms that many lakes and streams in these areas are devoid of aquatic life. Massive tree die-offs have occurred throughout central and eastern Europe as acid rain has lowered the pH of the soil and has leached nutrients from leaves.
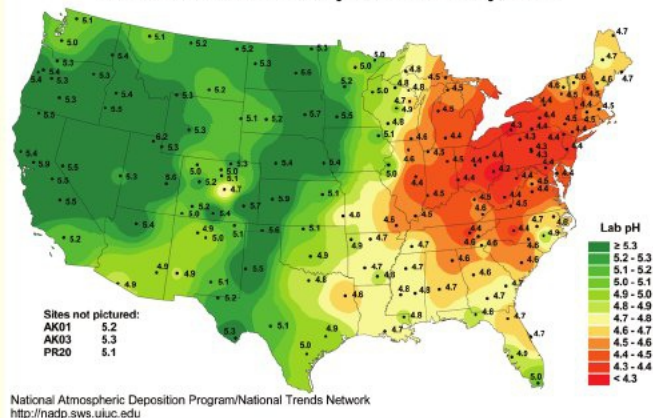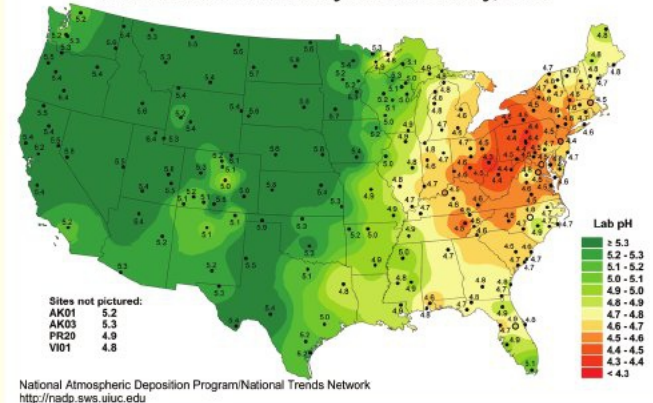
▲ These maps compare the average pH of precipitation in the United States in 1996 and in 2006. During this period, total acid deposition in much of the eastern United States decreased substantially.

Fortunately, acidic emissions in the United States have been greatly reduced in recent years as a result of the Clean Air Act Amendments of 1990. Industrial emissions of SO_2 and nitrogen oxides decreased by over 40% from 1990 to 2007, resulting in a decrease in acid rain depositions, particularly in the eastern United States and Canada (see accompanying figure). While significant reductions have been realized, most environmental scientists agree that additional reductions in these pollutant emissions are necessary to ensure the recovery of affected lakes and streams.

See Additional Problems 10.100 and 10.101 at the end of the chapter.

PROBLEM 10.29

How many milliliters of 0.150 M NaOH are required to neutralize 50.0 mL of 0.200 M H_2SO_4? The balanced neutralization reaction is:

$$H_2SO_4(aq) + 2\,NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2\,H_2O(l).$$

PROBLEM 10.30

A 21.5 mL sample of a KOH solution of unknown concentration requires 16.1 mL of 0.150 M H_2SO_4 solution to reach the end point in a titration. What is the molarity of the KOH solution?

10.16 Acidity and Basicity of Salt Solutions

It is tempting to think of all salt solutions as neutral; after all, they come from the neutralization reaction between an acid and a base. In fact, salt solutions can be neutral, acidic, or basic, depending on the ions present, because some ions react with water to produce H_3O^+ and some ions react with water to produce OH^-. To predict the acidity of a salt solution, it is convenient to classify salts according to the acid and base from which they are formed in a neutralization reaction. The classification and some examples are given in Table 10.3.

TABLE 10.3 Acidity and Basicity of Salt Solutions

ANION DERIVED FROM ACID THAT IS:	CATION DERIVED FROM BASE THAT IS:	SOLUTION	EXAMPLE
Strong	Weak	Acidic	NH_4Cl, NH_4NO_3
Weak	Strong	Basic	$NaHCO_3$, KCH_3CO_2
Strong	Strong	Neutral	$NaCl$, KBr, $Ca(NO_3)_2$
Weak	Weak	More information needed	

The general rule for predicting the acidity or basicity of a salt solution is that the stronger partner from which the salt is formed dominates. That is, a salt formed from a strong acid and a weak base yields an acidic solution because the strong acid dominates; a salt formed from a weak acid and a strong base yields a basic solution because the base dominates; and a salt formed from a strong acid and a strong base yields a neutral solution because neither acid nor base dominates. Here are some examples.
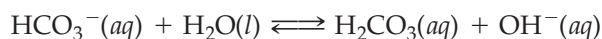
Salt of Strong Acid + Weak Base $\longrightarrow$ Acidic Solution

A salt such as NH_4Cl, which can be formed by reaction of a strong acid (HCl) with a weak base (NH_3), yields an acidic solution. The Cl^- ion does not react with water, but the NH_4^+ ion is a weak acid that gives H_3O^+ ions:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$
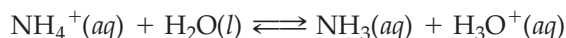
Salt of Weak Acid + Strong Base $\longrightarrow$ Basic Solution

A salt such as sodium bicarbonate, which can be formed by reaction of a weak acid (H_2CO_3) with a strong base (NaOH), yields a basic solution. The Na^+ ion does not react with water, but the HCO_3^- ion is a weak base that gives OH^- ions:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Salt of Strong Acid + Strong Base ⟶ Neutral Solution

A salt such as NaCl, which can be formed by reaction of a strong acid (HCl) with a strong base (NaOH), yields a neutral solution. Neither the Cl^- ion nor the Na^+ ion reacts with water.

Salt of Weak Acid + Weak Base

Both cation and anion in this type of salt react with water, so we cannot predict whether the resulting solution will be acidic or basic without quantitative information. The ion that reacts to the greater extent with water will govern the pH—it may be either the cation or the anion.

WORKED EXAMPLE **10.18** Acidity and Basicity of Salt Solutions

Predict whether the following salts produce an acidic, basic, or neutral solution:

(a) $BaCl_2$ (b) NaCN   (c) NH_4NO_3

ANALYSIS Look in Table 10.1 (p. 300) to see the classification of acids and bases as strong or weak.

SOLUTION

(a) $BaCl_2$ gives a neutral solution because it is formed from a strong acid (HCl) and a strong base $[Ba(OH)_2]$.

(b) NaCN gives a basic solution because it is formed from a weak acid (HCN) and a strong base (NaOH).

(c) NH_4NO_3 gives an acidic solution because it is formed from a strong acid (HNO_3) and a weak base (NH_3).

PROBLEM 10.31

Predict whether the following salts produce an acidic, basic, or neutral solution:

(a) K_2SO_4 (b) Na_2HPO_4 (c) MgF_2 (d) NH_4Br


SUMMARY: REVISITING THE CHAPTER GOALS

1. **What are acids and bases?** According to the *Brønsted–Lowry definition*, an acid is a substance that donates a hydrogen ion (a proton, H^+) and a base is a substance that accepts a hydrogen ion. Thus, the generalized reaction of an acid with a base involves the reversible transfer of a proton:

$$B: + H-A \rightleftharpoons A:^- + H-B^+$$
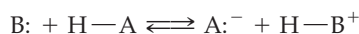
In aqueous solution, water acts as a base and accepts a proton from an acid to yield a *hydronium ion*, H_3O^+. Reaction of an acid with a metal hydroxide, such as KOH, yields water and a salt; reaction with bicarbonate ion (HCO_3^-) or carbonate ion (CO_3^{2-}) yields water, a salt, and CO_2 gas; and reaction with ammonia yields an ammonium salt.

2. **What effect does the strength of acids and bases have on their reactions?** Different acids and bases differ in their ability to give up or accept a proton. A *strong acid* gives up a proton easily and is 100% *dissociated* in aqueous solution; a *weak acid* gives up a proton with difficulty, is only slightly dissociated in water, and establishes an equilibrium between dissociated and undissociated forms. Similarly, a *strong base* accepts and holds a proton

readily, whereas a *weak base* has a low affinity for a proton and establishes an equilibrium in aqueous solution. The two substances that are related by the gain or loss of a proton are called a *conjugate acid–base pair*. The exact strength of an acid is defined by an *acid dissociation constant*, K_a:

$$\text{For the reaction} \quad HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
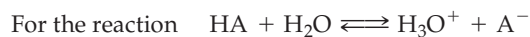
$$\text{we have} \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

A proton-transfer reaction always takes place in the direction that favors formation of the weaker acid.

3. **What is the ion-product constant for water?** Water is *amphoteric*; that is, it can act as either an acid or a base. Water also dissociates slightly into H_3O^+ ions and OH^- ions; the product of whose concentrations in any aqueous solution is the *ion-product constant for water*, $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ at 25 °C.

4. **What is the pH scale for measuring acidity?** The acidity or basicity of an aqueous solution is given by its *pH*, defined as the negative logarithm of the hydronium ion concentration, $[H_3O^+]$. A pH below 7 means an acidic solution; a pH equal to 7 means a neutral solution; and a pH above 7 means a basic solution.

5. **What is a buffer?** The pH of a solution can be controlled through the use of a *buffer* that acts to remove either added H^+ ions or added OH^- ions. Most buffer solutions consist of roughly equal amounts of a weak acid and its conjugate base. The bicarbonate buffer present in blood and the hydrogen phosphate buffer present in cells are particularly important examples.

6. **How is the acid or base concentration of a solution determined?** Acid (or base) concentrations are determined in the laboratory by *titration* of a solution of unknown concentration with a base (or acid) solution of known strength until an indicator signals that neutralization is complete.

Dissociation, *p. 299*

Equivalent of acid, *p. 318*

Equivalent of base, *p. 318*

Gram-equivalent of acid, *p. 318*

Gram-equivalent of base, *p. 318*

Henderson–Hasselbalch equation, *p. 313*

Hydronium ion, *p. 293*

Ion-product constant for water (K_w), *p. 305*

Normality (N), *p. 318*

p function, *p. 306*

pH, *p. 306*

Strong acid, *p. 299*
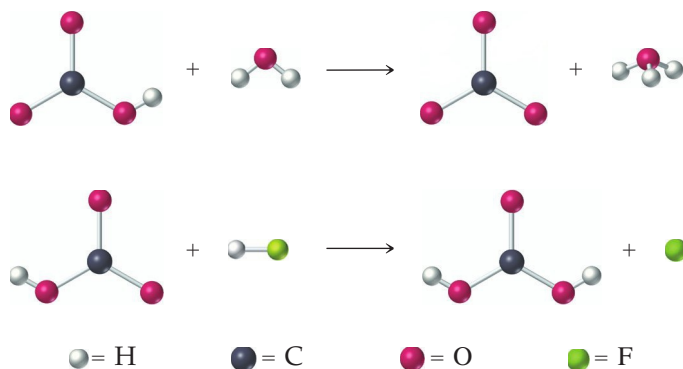
Strong base, *p. 299*

Titration, *p. 322*

Weak acid, *p. 299*
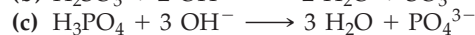
Weak base, *p. 299*

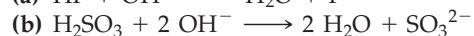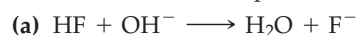## UNDERSTANDING KEY CONCEPTS

**10.32** Identify the Brønsted–Lowry acid and base in the following reactions:

= H   = C   = O   = F

10.33 An aqueous solution of OH^-, represented as a blue sphere, is allowed to mix with a solution of an acid H_nA, represented as a red sphere. Three possible outcomes are depicted by boxes (1)–(3), where the green spheres represent A^{n-}, the anion of the acid:


(1)   (2)   (3)
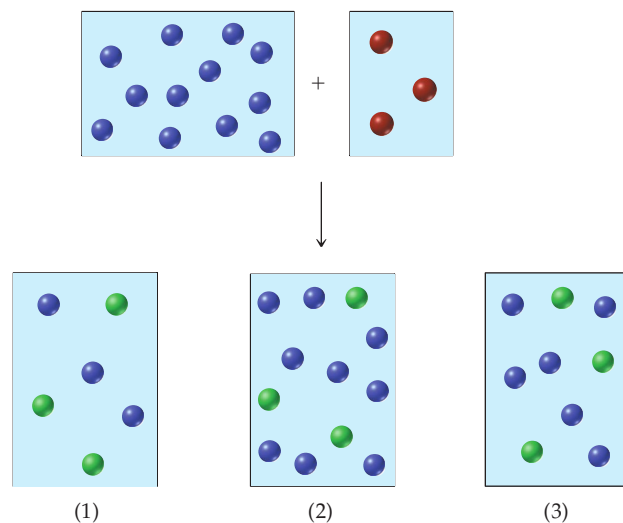
Which outcome corresponds to the following reactions?

(a) $HF + OH^- \longrightarrow H_2O + F^-$

(b) $H_2SO_3 + 2\ OH^- \longrightarrow 2\ H_2O + SO_3^{2-}$

(c) $H_3PO_4 + 3\ OH^- \longrightarrow 3\ H_2O + PO_4^{3-}$

10.34 Electrostatic potential maps of acetic acid (CH_3CO_2H) and ethyl alcohol (CH_3CH_2OH) are shown. Identify the most acidic hydrogen in each, and tell which of the two is likely to be the stronger acid.


CH_3CO_2H CH_3CH_2OH
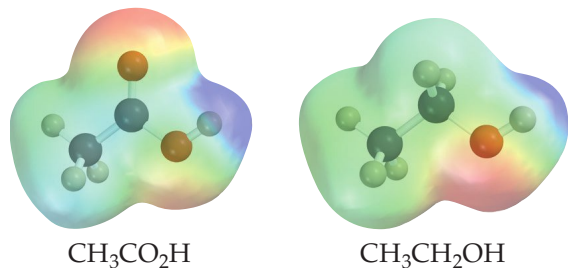
10.35 The following pictures represent aqueous acid solutions. Water molecules are not shown.

● = HA   ● = H_3O^+ ● = A^-

(1)   (2)   (3)
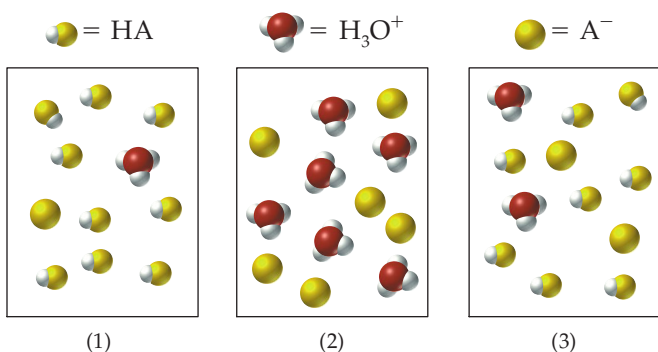
(a) Which picture represents the weakest acid?
(b) Which picture represents the strongest acid?
(c) Which picture represents the acid with the smallest value of K_a?

10.36 The following pictures represent aqueous solutions of a diprotic acid H_2A. Water molecules are not shown.

● = H_2A ● = H_3O^+ ● = HA^- ● = A^{2-}

(1)   (2)   (3)
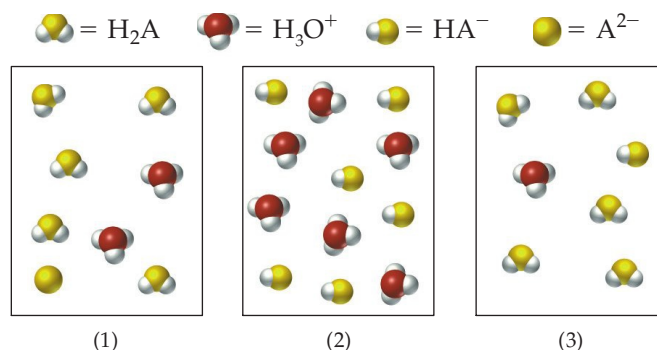
(a) Which picture represents a solution of a weak diprotic acid?
(b) Which picture represents an impossible situation?

10.37 Assume that the red spheres in the buret represent H^+ ions, the blue spheres in the flask represent OH^- ions, and you are carrying out a titration of the base with the acid. If the volumes in the buret and the flask are identical and the concentration of the acid in the buret is 1.00 M, what is the concentration of the base in the flask?
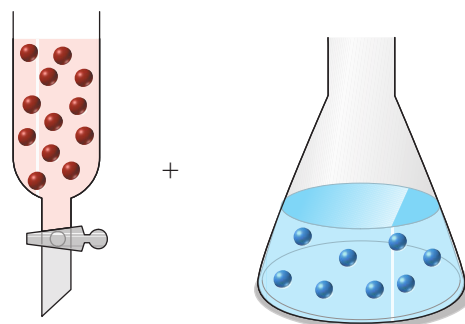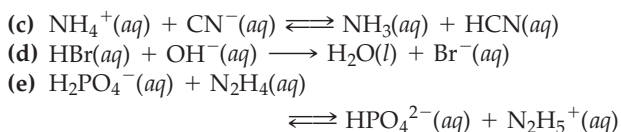

ADDITIONAL PROBLEMS

ACIDS AND BASES

10.38 What happens when a strong acid such as HBr is dissolved in water?

10.39 What happens when a weak acid such as CH_3CO_2H is dissolved in water?

10.40 What happens when a strong base such as KOH is dissolved in water?

10.41 What happens when a weak base such as NH_3 is dissolved in water?

10.42 What is the difference between a monoprotic acid and a diprotic acid? Give an example of each.

10.43 What is the difference between H^+ and H_3O^+?

10.44 Which of the following are strong acids? Look at Table 10.1 (*p. 300*) if necessary.
(a) $HClO_4$ **(b)** H_2CO_3
(c) H_3PO_4 **(d)** NH_4^+
(e) HI   **(f)** $H_2PO_4^-$

10.45 Which of the following are weak bases? Look at Table 10.1 (*p. 300*) if necessary.
(a) NH_3 **(b)** $Ca(OH)_2$
(c) HPO_4^{2-} **(d)** LiOH
(e) CN^- **(f)** NH_2^-

BRØNSTED–LOWRY ACIDS AND BASES

10.46 Identify the following substances as a Brønsted–Lowry base, a Brønsted–Lowry acid, or neither:
(a) HCN   **(b)** $CH_3CO_2^-$
(c) $AlCl_3$ **(d)** H_2CO_3
(e) Mg^{2+} **(f)** $CH_3NH_3^+$

10.47 Label the Brønsted–Lowry acids and bases in the following equations, and tell which substances are conjugate acid–base pairs.
(a) $CO_3^{2-}(aq) + HCl(aq) \longrightarrow HCO_3^-(aq) + Cl^-(aq)$
(b) $H_3PO_4(aq) + NH_3(aq) \longrightarrow H_2PO_4^-(aq) + NH_4^+(aq)$

(c) $NH_4^+(aq) + CN^-(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$
(d) $HBr(aq) + OH^-(aq) \longrightarrow H_2O(l) + Br^-(aq)$
(e) $H_2PO_4^-(aq) + N_2H_4(aq)$

$$\rightleftharpoons HPO_4^{2-}(aq) + N_2H_5^+(aq)$$

10.48 Write the formulas of the conjugate acids of the following Brønsted–Lowry bases:

(a) $ClCH_2CO_2^-$
(b) C_5H_5N
(c) SeO_4^{2-}
(d) $(CH_3)_3N$

10.49 Write the formulas of the conjugate bases of the following Brønsted–Lowry acids:

(a) HCN
(b) $(CH_3)_2NH_2^+$
(c) H_3PO_4
(d) $HSeO_3^-$

10.50 The hydrogen-containing anions of many polyprotic acids are amphoteric. Write equations for HCO_3^- and $H_2PO_4^-$ acting as bases with the strong acid HCl and as acids with the strong base NaOH.

10.51 Write balanced equations for proton-transfer reactions between the listed pairs. Indicate the conjugate pairs, and determine the favored direction for each equilibrium.

(a) HCl and PO_4^{3-}
(b) HCN and SO_4^{2-}
(c) $HClO_4$ and NO_2^-
(d) CH_3O^- and HF

10.52 Tums, a drugstore remedy for acid indigestion, contains $CaCO_3$. Write an equation for the reaction of Tums with gastric juice (HCl).

10.53 Write balanced equations for the following acid–base reactions:

(a) $LiOH + HNO_3 \longrightarrow$
(b) $BaCO_3 + HI \longrightarrow$
(c) $H_3PO_4 + KOH \longrightarrow$
(d) $Ca(HCO_3)_2 + HCl \longrightarrow$
(e) $Ba(OH_2) + H_2SO_4 \longrightarrow$

ACID AND BASE STRENGTH: K_a AND pH

10.54 How is K_a defined? Write the equation for K_a for the generalized acid HA.

10.55 Rearrange the equation you wrote in Problem 10.54 to solve for $[H_3O^+]$ in terms of K_a.

10.56 How is K_w defined, and what is its numerical value at 25 °C?

10.57 How is pH defined?

10.58 A solution of 0.10 M HCl has a pH = 1.00, whereas a solution of 0.10 M CH_3COOH has a pH = 2.88. Explain.

10.59 Calculate $[H_3O^+]$ for the 0.10 M CH_3COOH solution in Problem 10.58. What percent of the weak acid is dissociated?

10.60 Write the expressions for the acid dissociation constants for the three successive dissociations of phosphoric acid, H_3PO_4, in water.

10.61 Find K_a values in Table 10.2, and decide which acid in the following pairs is stronger:

(a) HCO_3H or HF
(b) HSO_4^- or HCN
(c) $H_3PO_4^-$ or HPO_4^{2-}
(d) $CH_3CH_2CO_2H$ or CH_3CO_2H

10.62 Which substance in the following pairs is the stronger base? Look at Table 10.1 if necessary.

(a) OH^- or PO_4^{3-}
(b) Br^- or NO_2^-
(c) NH_3 or OH^-
(d) CN^- or H_2O
(e) I^- or HPO_4^{2-}

10.63 Based on the K_a values in Table 10.1, rank the following solutions in order of increasing pH: 0.10 M HCOOH, 0.10 M HF, 0.10 M H_2CO_3, 0.10 M HSO_4^-, 0.10 M NH_4^+.

10.64 The electrode of a pH meter is placed in a sample of urine, and a reading of 7.9 is obtained. Is the sample acidic, basic, or neutral? What is the concentration of H_3O^+ in the urine sample?

10.65 A 0.10 M solution of the deadly poison hydrogen cyanide, HCN, has a pH of 5.2. Is HCN acidic or basic? Is it strong or weak?

10.66 Normal gastric juice has a pH of about 2. Assuming that gastric juice is primarily aqueous HCl, what is the HCl concentration?

10.67 Human spinal fluid has a pH of 7.4. Approximately what is the H_3O^+ concentration of spinal fluid?

10.68 What is the approximate pH of a 0.10 M solution of a strong monoprotic acid? Of a 0.10 M solution of a strong base, such as KOH?

10.69 Calculate the pOH of each solution in Problems 10.64–10.67.

10.70 Approximately what pH do the following H_3O^+ concentrations correspond to?

(a) Fresh egg white: $[H_3O^+] = 2.5 \times 10^{-8}$ M
(b) Apple cider: $[H_3O^+] = 5.0 \times 10^{-4}$ M
(c) Household ammonia: $[H_3O^+] = 2.3 \times 10^{-12}$ M

10.71 What are the OH^- concentration and pOH for each solution in Problem 10.70? Rank the solutions according to increasing acidity.

10.72 What are the H_3O^+ and OH^- concentrations of solutions that have the following pH values?

(a) pH 4
(b) pH 11
(c) pH 0
(d) pH 1.38
(e) pH 7.96

10.73 About 12% of the acid in a 0.10 M solution of a weak acid dissociates to form ions. What are the H_3O^+ and OH^- concentrations? What is the pH of the solution?

BUFFERS

10.74 What are the two components of a buffer system? How does a buffer work to hold pH nearly constant?

10.75 Which system would you expect to be a better buffer: $HNO_3 + Na^+NO_3^-$, or $CH_3CO_2H + CH_3CO_2^-Na^+$? Explain.

10.76 The pH of a buffer solution containing 0.10 M acetic acid and 0.10 M sodium acetate is 4.74.

(a) Write the Henderson–Hasselbalch equation for this buffer.

(b) Write the equations for reaction of this buffer with a small amount of HNO_3 and with a small amount of NaOH.

10.77 Which of the following buffer systems would you use if you wanted to prepare a solution having a pH of approximately 9.5?

(a) 0.08 M $H_2PO_4^-$/0.12 M HPO_4^{2-}

(b) 0.08 M NH_4^+/0.12 M NH_3

10.78 What is the pH of a buffer system that contains 0.200 M hydrocyanic acid (HCN) and 0.150 M sodium cyanide (NaCN)? The pK_a of hydrocyanic acid is 9.31.

10.79 What is the pH of 1.00 L of the 0.200 M hydrocyanic acid–0.150 M cyanide ion buffer system described in Problem 10.78 after 0.020 mol of HCl is added? After 0.020 mol of NaOH is added?

10.80 What is the pH of a buffer system that contains 0.15 M NH_4^+ and 0.10 M NH_3? The pK_a of NH_4^+ is 9.25.

10.81 How many moles of NaOH must be added to 1.00 L of the solution described in Problem 10.80 to increase the pH to 9.25?

CONCENTRATIONS OF ACID AND BASE SOLUTIONS

10.82 What does it mean when we talk about acid *equivalents* and base *equivalents*?

10.83 How is normality defined as a means of expressing acid or base concentration?

10.84 Calculate the gram-equivalent for each of the following acids and bases.

(a) HNO_3 (b) H_3PO_4

(c) KOH   (d) $Mg(OH)_2$

10.85 What mass of each of the acids and bases in Problem 10.84 is needed to prepare 500 mL of 0.15 N solution?

10.86 How many milliliters of 0.0050 N KOH are required to neutralize 25 mL of 0.0050 N H_2SO_4? To neutralize 25 mL of 0.0050 N HCl?

10.87 What is the normality of a 0.12 M H_2SO_4 solution? Of a 0.12 M H_3PO_4 solution?

10.88 How many equivalents of an acid or base are in the following?

(a) 0.25 mol $Mg(OH)_2$

(b) 2.5 g $Mg(OH)_2$

(c) 15 g CH_3CO_2H

10.89 What mass of citric acid (triprotic, $C_6H_5O_7H_3$) contains 152 mEq of citric acid?

10.90 What are the molarity and the normality of a solution made by dissolving 5.0 g of $Ca(OH)_2$ in enough water to make 500.0 mL of solution?

10.91 What are the molarity and the normality of a solution made by dissolving 25 g of citric acid (triprotic, $C_6H_5O_7H_3$) in enough water to make 800 mL of solution?

10.92 Titration of a 12.0 mL solution of HCl requires 22.4 mL of 0.12 M NaOH. What is the molarity of the HCl solution?

10.93 What volume of 0.085 M HNO_3 is required to titrate 15.0 mL of 0.12 M $Ba(OH)_2$ solution?

10.94 Titration of a 10.0 mL solution of KOH requires 15.0 mL of 0.0250 M H_2SO_4 solution. What is the molarity of the KOH solution?

10.95 If 35.0 mL of a 0.100 N acid solution is needed to reach the end point in titration of 21.5 mL of a base solution, what is the normality of the base solution?

Applications

10.96 The concentration of HCl when released to the stomach cavity is diluted to between 0.01 and 0.001 M [*GERD— Too Much Acid or Not Enough? p. 302*]

(a) What is the pH range in the stomach cavity?

(b) Write a balanced equation for the neutralization of stomach acid by $NaHCO_3$.

(c) How many grams of $NaHCO_3$ are required to neutralize 15.0 mL of a solution having a pH of 1.8?

10.97 Which body fluid is most acidic? Which is most basic? [*pH of Body Fluids, p. 311*]

10.98 Metabolic acidosis is often treated by administering bicarbonate intravenously. Explain how this treatment can increase blood serum pH. [*Buffers in the Body: Acidosis and Alkalosis, p. 317*]

10.99 The normal $[HCO_3^-]/[CO_2]$ ratio in the blood is about 20 to 1 at a pH = 7.4. What is this ratio at pH = 7.3 (acidosis) and at pH = 7.5 (alkalosis)? [*Buffers in the Body: Acidosis and Alkalosis, p. 317*]

10.100 Rain typically has a pH of about 5.6. What is the H_3O^+ concentration in rain? [*Acid Rain, p. 324*]

10.101 Acid rain with a pH as low as 1.5 has been recorded in West Virginia. [*Acid Rain, p. 324*]

(a) What is the H_3O^+ concentration in this acid rain?

(b) How many grams of HNO_3 must be dissolved to make 25 L of solution that has a pH of 1.5?

General Questions and Problems

10.102 Alka-Seltzer, a drugstore antacid, contains a mixture of $NaHCO_3$, aspirin, and citric acid, $C_6H_5O_7H_3$. Why does Alka-Seltzer foam and bubble when dissolved in water? Which ingredient is the antacid?

10.103 How many milliliters of 0.50 M NaOH solution are required to titrate 40.0 mL of a 0.10 M H_2SO_4 solution to an end point?

10.104 Which solution contains more acid, 50 mL of a 0.20 N HCl solution or 50 mL of a 0.20 N acetic acid solution? Which has a higher hydronium ion concentration? Which has a lower pH?

10.105 One of the buffer systems used to control the pH of blood involves the equilibrium between $H_2PO_4^-$ and HPO_4^{2-}. The pK_a for $H_2PO_4^-$ is 7.21.

(a) Write the Henderson–Hasselbalch equation for this buffer system.

(b) What HPO_4^{2-} to $H_2PO_4^-$ ratio is needed to maintain the optimum blood pH of 7.40?

10.106 A 0.15 M solution of HCl is used to titrate 30.0 mL of a $Ca(OH)_2$ solution of unknown concentration. If 140 mL of HCl is required, what is the concentration (in molarity) of the $Ca(OH)_2$ solution?

10.107 Which of the following combinations produces an effective buffer solution? Assuming equal concentrations of each acid and its conjugate base, calculate the pH of each buffer solution.

(a) NaF and HF

(b) $HClO_4$ and $NaClO_4$

(c) NH_4Cl and NH_3

(d) KBr and HBr

10.108 One method of analyzing ammonium salts is to treat them with NaOH and then heat the solution to remove the NH_3 gas formed.

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

(a) Label the Brønsted–Lowry acid–base pairs.

(b) If 2.86 L of NH_3 at 60 °C and 755 mmHg is produced by the reaction of NH_4Cl, how many grams of NH_4Cl were in the original sample?

10.109 One method of reducing acid rain is *scrubbing* the combustion products before they are emitted from power plant smoke stacks. The process involves addition of an aqueous suspension of lime (CaO) to the combustion chamber and stack, where the lime reacts with SO_2 to give calcium sulfite ($CaSO_3$).

(a) Write the balanced chemical equation for this reaction.

(b) How much lime is needed to remove 1 kg of SO_2?

10.110 Sodium oxide, Na_2O, reacts with water to give NaOH.

(a) Write a balanced equation for the reaction.

(b) What is the pH of the solution prepared by allowing 1.55 g of Na_2O to react with 500.0 mL of water? Assume that there is no volume change.

(c) How many milliliters of 0.0100 M HCl are needed to neutralize the NaOH solution prepared in (b)?