CHAPTER



ACIDS AND BASES



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7.2

6.8

or health reasons, swimming pools are regularly treated with chemicals that are usually called "chlorine." However, the chemicals are more likely to be hypochlorites or similar compounds. The effectiveness of these disinfectants depends on how acidic or basic the water is. Pool owners must therefore measure and, if necessary, adjust, the acidity of their pool. A pH test kit, such as the one shown at left, can measure the balance of acids and bases dissolved in the pool water to ensure that it is in a healthy range.

START-UPACTIVITY

What Does an Antacid Do?

PROCEDURE





- Pour 100 mL of water into a 150 mL beaker. Use a plastic pipet to add vinegar one drop at a time while stirring with a glass stirrer. Keep a piece of blue litmus paper dipped in the solution, and record the number of drops needed to make the solution turn the litmus paper bright red.
- 2. Use a mortar and pestle to crush an antacid tablet until the tablet is powdered. Pour 100 mL of water into another 150 mL beaker, add the powdered tablet, and stir until the tablet is at least mostly dissolved.
- **3.** Add vinegar dropwise to the antacid solution and monitor the solution by using **another piece of blue litmus paper.** Record the number of drops needed to turn the litmus paper bright red.

ANALYSIS

- **1.** Which required more acid to turn the blue litmus paper red: the water or the antacid solution?
- 2. How does an antacid work to counteract excess stomach acid?

Pre-Reading Questions

- **1** Give examples of acids and bases that you encounter in your everyday life.
- What polyatomic ion does the hydrogen ion, H⁺, form in aqueous solution?
- 3 Acids are said to "neutralize" bases, and vice versa. How would you define the term *neutralize*?



<u>SECTION 1</u> What Are Acids and Bases?

SECTION 2

Acidity, Basicity, and pH

SECTION 3

Neutralization and Titrations

SECTION 4

Equilibria of Weak Acids and Bases



S E C T I O N

What Are Acids and Bases?

Key Terms

- strong acid
- weak acid
- strong base
- weak base
- Brønsted-Lowry acid
- Brønsted-Lowry base
- conjugate acid
- conjugate base
- amphoteric

OBJECTIVES

- **Describe** the distinctive properties of strong and weak acids, and relate their properties to the Arrhenius definition of an acid.
- **Describe** the distinctive properties of strong and weak bases, and relate their properties to the Arrhenius definition of a base.
- **Compare** the Brønsted-Lowry definitions of acids and bases with the Arrhenius definitions of acids and bases.
- **Identify** conjugate acid-base pairs.
- **Write** chemical equations that show how an amphoteric species can behave as either an acid or a base.

Acids

Vinegar is acidic. So are the juices of the fruits that you see in **Figure 1**. Colas and some other soft drinks are also acidic. You can recognize these liquids as acidic by their tart, sour, or sharp taste. What they have in common is that they contain dissolved compounds that chemists describe as *acids*. Many other acids are highly caustic and should not be put to the taste test. One example of a hazardous acid is sulfuric acid, H_2SO_4 , which is important in car batteries. Another example is hydrochloric acid, HCl, which is used to treat the water in swimming pools.

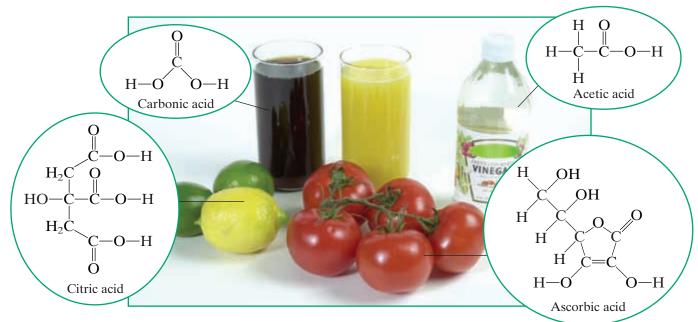


Figure 1

Fruits and fruit juices contain a variety of acids, including those shown here. Carbonic acid is found in cola. Vinegar contains acetic acid.

Acid Solutions Conduct Electricity Well

Acids are electrolytes, so their solutions in water are conductors of electric current, as **Figure 2** demonstrates. To understand why, consider what happens as hydrogen chloride, HCl, dissolves in water. Like other electrolytes, hydrogen chloride dissociates to produce ions. The hydrogen ion immediately reacts with a water molecule to form a hydronium ion, as shown in the equation below.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

The resulting solution is called *hydrochloric acid*.

The hydronium ion, H_3O^+ , is able to transfer charge through aqueous solutions much faster than other ions do. The positive charge is simply passed from water molecule to water molecule. The result is that acid solutions are excellent conductors of electricity.

Acids React with Many Metals

Another property shared by aqueous solutions of acids is that they react with many metals. All metals that are above hydrogen in the activity series react with acids to produce hydrogen gas. The reaction is caused by the hydronium ion present in the solution. The presence of the hydronium ion explains why all acids behave in this way. An example is the reaction of hydrochloric acid with zinc, which is shown in **Figure 3** and is represented by the following net ionic equation.

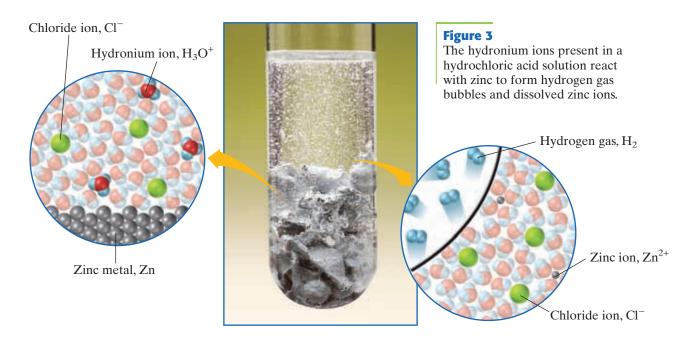
$$2H_3O^+(aq) + Zn(s) \longrightarrow 2H_2O(l) + H_2(g) + Zn^{2+}(aq)$$

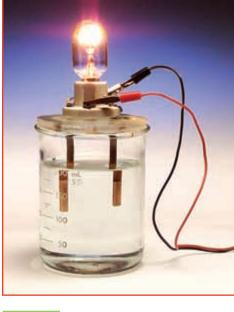
Notice that even though hydrochloric acid is often represented by the formula HCl(aq), in aqueous solution hydrochloric acid actually consists of dissolved $H_3O^+(aq)$ and $Cl^-(aq)$ ions. The chloride ions do not play a part in the reaction and so do not appear in the net ionic equation. The beaker of hydrochloric acid solution contains $H_3O^+(aq)$ and $Cl^-(aq)$ ions. Because the solution is a good conductor, electricity can pass through the solution to cause the bulb to be brightly lit.

Figure 2



Refer to the "Solutions" chapter for a discussion of strong and weak electrolytes.







strong acid

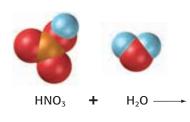
an acid that ionizes completely in a solvent

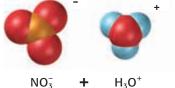
weak acid

an acid that releases few hydrogen ions in aqueous solution

Figure 4

According to Arrhenius, an acid in aqueous solution ionizes to form hydronium ions, H_3O^+ , as shown here for nitric acid, HNO₃.





NO₃

Some Strong Acids and Some Weak Acids Table 1

Strong acids	Weak acids
hydrochloric acid, HCl	acetic acid, CH ₃ COOH
hydrobromic acid, HBr	hydrocyanic acid, HCN
hydriodic acid, HI	hydrofluoric acid, HF
nitric acid, HNO ₃	nitrous acid, HNO ₂
sulfuric acid, H ₂ SO ₄	sulfurous acid, H ₂ SO ₃
perchloric acid, HClO ₄	hypochlorous acid, HOCl
periodic acid, HIO ₄	phosphoric acid, H ₃ PO ₄

Acids Generate Hydronium Ions

Recall that some electrolytes are strong and others are weak, depending on whether they dissociate completely or partially. Because acids are also electrolytes, they can be classified as strong or weak. Table 1 lists the names and formulas of several strong acids and several weak acids.

Nitric acid, HNO₃, is an example of a **strong acid**. Its reaction with water is shown in **Figure 4** and is represented by the following equation:

$$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

No HNO₃ molecules are present in a solution of nitric acid.

When a **weak acid** is dissolved in water, only a small fraction of its molecules are ionized at any given time. Hypochlorous acid, HOCl, is a weak acid. Its reaction with water is described by the equation below.

$$HOCl(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$

Recall that the opposed arrows in this equation indicate equilibrium. Hypochlorite ions, ClO⁻, react with hydronium ions to form HOCl at exactly the same rate that HOCl molecules react with water to form ions.

The presence of a considerable number of hydronium ions identifies an aqueous solution as acidic. A Swedish chemist, Svante Arrhenius, was among the first to recognize this fact. In 1890, he proposed that an acid be defined as any substance that, when added to water, increases the hydronium ion concentration. Later, you will learn about another way to define acids that goes beyond aqueous solutions.

In some acids, a single molecule can react to form more than one hydronium ion. This happens when sulfuric acid dissolves in water, as described by the following equations:

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

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

As shown above, sulfuric acid has two ionizable hydrogens. One of them ionizes completely, after which the other ionizes partially as a weak acid.

Table 2 Some Strong Bases and Some Weak Bases			
Strong bases	Weak bases		
sodium hydroxide, NaOH	ammonia, NH ₃		
potassium hydroxide, KOH	sodium carbonate, Na ₂ CO ₃		
calcium hydroxide, Ca(OH) ₂	potassium carbonate, K ₂ CO ₃		
barium hydroxide, Ba(OH) ₂	aniline, C ₆ H ₅ NH ₂		
sodium phosphate, Na ₃ PO ₄	trimethylamine, (CH ₃) ₃ N		



Bases

Bases are another class of electrolytes. Unlike acids, which are usually liquids or gases, many common bases are solids. Solutions of bases are slippery to the touch, but touching bases is an unsafe way to identify them. The slippery feel comes about because bases react with oils in your skin, converting them into soaps. This property of attacking oils and greases makes bases useful in cleaning agents, such as those in **Figure 5**.

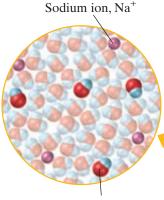
Some bases, such as magnesium hydroxide, $Mg(OH)_2$, are almost insoluble in water. Other bases, such as potassium hydroxide, are so soluble that they will absorb water vapor from the air and dissolve in the water. A base that is very soluble in water is called an *alkali*, a term that you also know describes the Group 1 metals of the periodic table. These metals react with water to form hydroxides that are water-soluble alkalis. The hydroxide-rich solutions that form when bases dissolve in water are said to be *basic* or *alkaline*.

Just as acids may be strong or weak depending on whether they ionize completely or reach an equilibrium between ionized and un-ionized forms, bases are also classified as strong or weak. **Table 2** lists several bases of each class.



Figure 5

A variety of bases, including ammonia, sodium hydroxide, and sodium bicarbonate, can be found in products used around the home. **Figure 6 a** Sodium hydroxide is a strong base. It dissociates completely in aqueous solution.

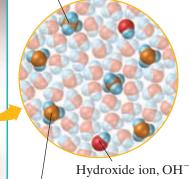


Hydroxide ion, OH-



b Only a small portion of the dissolved molecules of ammonia, a weak base, react with water. Most of the ammonia remains as neutral molecules.

Ammonium ion, NH₄⁺



Ammonia molecule, NH₃

Bases Generate Hydroxide Ions

The following equation can be used to describe the dissolving of sodium hydroxide, a **strong base**, in water.

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

The ions dissociate in solution as they become surrounded by water molecules and float away independently.

Ammonia is a typical **weak base.** At room temperature, ammonia is a gas, $NH_3(g)$, but it is very soluble in water, forming $NH_3(aq)$. A few of the ammonia molecules in solution react with water to reach the equilibrium system described by the equation below.

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

 $NH_4^+(aq)$ is the ammonium ion. The vast majority of ammonia molecules, however, remain un-ionized at any given time.

Both strong and weak bases generate hydroxide ions when they dissolve in water, as **Figure 6** shows. This property is the basis of the Arrhenius definitions of a base.

Many oxides, carbonates, and phosphates are bases, too. Potassium oxide is a strong base. It reacts with water as shown below:

$$K_2O(s) + H_2O(l) \longrightarrow 2K^+(aq) + 2OH^-(aq)$$

Soluble carbonates are weak bases, however, because the dissolved carbonate ion establishes the following equilibrium in water:

$$\operatorname{CO}_3^{2-}(aq) + \operatorname{H}_2\operatorname{O}(l) \rightleftharpoons \operatorname{HCO}_3^{-}(aq) + \operatorname{OH}^{-}(aq)$$

The equilibrium system contains a low concentration of hydroxide ions, a low concentration of hydrogen carbonate ions, $HCO_3^-(aq)$, and a greater concentration of unreacted carbonate ions, $CO_3^{2-}(aq)$.

strong base

a base that ionizes completely in a solvent

weak base

a base that releases few hydroxide ions in aqueous solution



SAFETY PRECAUTIONS

Acids and Bases in the Home

Because taste and feel are not safe ways to determine whether a substance is an acid or a base, you should use an indicator to recognize acids and bases. As its name suggests, an *indicator* indicates whether a solution is acidic or basic. It does this by changing color.

PROCEDURE

1. Using a **blender**, grind **red cabbage** with **water**.

- **2.** Strain the liquid into a **large beaker**, and dilute it with water. You now have an indicator.
- **3.** Using your indicator, test **various household products** by adding each product to a separate **small beaker** containing a sample of the indicator. Start with an item that you know is an acid and an item that you know is a base.



ANALYSIS

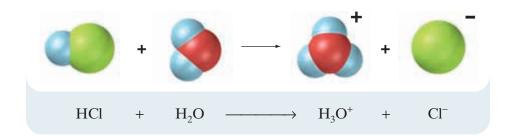
- **1.** What color is the indicator in acidic solution? in basic solution?
- **2.** Are cleaning products more likely to be acidic or basic?
- **3.** Are food products more likely to be acidic or basic?

Brønsted-Lowry Classification

The definitions of *Arrhenius acid* and *Arrhenius base* given earlier in this book are variants of the definitions of *acid* and *base* originally proposed by Arrhenius in the late 19th century. One drawback that the Arrhenius definitions have is that they are limited to aqueous solutions: HCl, for instance, should be considered an acid whether it is in the form of a pure gas or in aqueous solution. Another limitation is that the Arrhenius definition cannot classify substances that sometimes act as acids and sometimes act as bases.

Brønsted-Lowry Acids Donate Protons

In 1923, the Danish chemist Johannes Brønsted proposed a broader definition of *acid*. Surprisingly, the same year, the British scientist Thomas Lowry happened to make exactly the same proposal independently. Their idea was to apply the name *acid* to any species that can donate a proton. Recall that a proton is a hydrogen atom that has lost its electron; it is a hydrogen ion and can be represented as H⁺. Such molecules or ions are now called **Brønsted-Lowry acids.** A reaction showing hydrochloric acid, a representative Brønsted-Lowry acid, is depicted in **Figure 7**.



Brønsted-Lowry acid

a substance that donates a proton to another substance

Figure 7

When hydrogen chloride dissolves in water, a proton is transferred from the HCl molecule (leaving behind Cl^{-}) to an H₂O molecule (forming H₃O⁺).

We might also think of the reaction occurring when HCl dissolves in water as proceeding in two steps:

> $HCl \rightarrow H^+ + Cl^$ followed by $H^+ + H_2O \longrightarrow H_3O^+$

The reaction shows HCl acting as an Arrhenius acid, forming a hydronium ion. Because the reaction also involves a proton transfer, hydrochloric acid is also a Brønsted-Lowry acid. All Arrhenius acids are, by definition, also Brønsted-Lowry acids.

Brønsted-Lowry Bases Accept Protons

As you might expect based on their definition of an acid, Brønsted and Lowry defined a base as a proton acceptor. In the reaction taking place in Figure 8, ammonia, NH₃, serves as the proton acceptor and is therefore a **Brønsted-Lowry base.** Ammonia also functions as a proton acceptor when it dissolves in water, as in the equation below.

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

Again, notice that ammonia, a Brønsted-Lowry base, is also an Arrhenius base. All Arrhenius bases are also Brønsted-Lowry bases. Ammonia does not have to react in aqueous solution to be considered a Brønsted-Lowry base. Even as a gas, ammonia accepts a proton from hydrogen chloride, as Figure 8 shows.



Brønsted-Lowry base

a substance that accepts a proton

Figure 8

each escaped from aqueous solution combine to form a cloud of solid ammonium chloride, $NH_4Cl(s)$

Conjugate Acids and Bases

In the language of Brønsted and Lowry, an acid-base reaction is very simple: one molecule or ion passes a proton to another molecule or ion. Whatever loses the proton is an acid, and whatever accepts the proton is a base.

Look again at the equation for the reversible reaction of ammonia, NH_3 , with water:

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

base acid

Water donates a proton to ammonia, so it is an acid. Ammonia accepts the proton, so it is a base. The ammonium ion forms when NH_3 receives the proton, and the hydroxide ion forms when H_2O has lost the proton.

Notice that the reaction is reversible, so it can be written with the products as reactants. When the reaction is written that way, we can identify another acid and another base.

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

acid base

In this reaction, the ammonium ion donates a proton to the hydroxide ion. NH_4^+ is the acid, and OH^- is the base. The ammonium ion is called the **conjugate acid** of the base, ammonia. The hydroxide ion is called the **conjugate base** of the acid, water.

$$\begin{array}{rcl} \mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O}(l) & \rightleftharpoons & \mathrm{NH}_4^+(aq) & + & \mathrm{OH}^-(aq) \\ & & & & \mathrm{acid} & & & \mathrm{conjugate \ acid} & & & & \mathrm{conjugate \ base} \end{array}$$

Every Brønsted-Lowry acid has a conjugate base, and every Brønsted-Lowry base has a conjugate acid. **Table 3** lists many such acid-base pairs.

conjugate acid

an acid that forms when a base gains a proton

conjugate base

a base that forms when an acid loses a proton

Table 3 Conjugate Acid-Base Pairs			
Acid	Conjugate base		
hydrochloric acid, HCl	chloride ion, Cl ⁻		
sulfuric acid, H ₂ SO ₄	hydrogen sulfate ion, HSO ₄		
hydronium ion, H ₃ O ⁺	water, H ₂ O		
hydrogen sulfate ion, HSO ₄	sulfate ion, SO ₄ ²⁻		
hypochlorous acid, HOCl	hypochlorite ion, ClO ⁻		
dihydrogen phosphate ion, $H_2PO_4^-$	monohydrogen phosphate ion, HPO ₄ ²⁻		
ammonium ion, NH ₄ ⁺	ammonia, NH ₃		
hydrogen carbonate ion, HCO ₃	carbonate ion, CO_3^{2-}		
water, H ₂ O	hydroxide ion, OH ⁻		
Conjugate acid	Base		

amphoteric

describes a substance, such as water, that has the properties of an acid and the properties of a base

Amphoteric Species Are Both Acids and Bases

Did you notice that some species appear in both the "Acid" and the "Base" columns in **Table 3?** Several species can both donate and accept protons. Such species are described as **amphoteric.** The hydrogen carbonate ion, HCO_3^- , is amphoteric in aqueous solution, for example. It can act as an acid by donating a proton to an ammonia molecule, as represented by the following equation:

 $\begin{array}{c} \mathrm{HCO}_{3}^{-}(aq) + \mathrm{NH}_{3}(aq) \rightleftharpoons \mathrm{CO}_{3}^{2-}(aq) + \mathrm{NH}_{4}^{+}(aq) \\ \text{acid} & \text{base} \end{array}$

Alternatively, the hydrogen carbonate ion can act as a base when, for example, it accepts a proton from a hydronium ion in the reaction described by the equation below.

 $\begin{array}{c} \mathrm{HCO}_{3}^{-}(aq) + \mathrm{H}_{3}\mathrm{O}^{+}(aq) \rightleftharpoons \mathrm{H}_{2}\mathrm{CO}_{3}(aq) + \mathrm{H}_{2}\mathrm{O}(l) \\ \text{base} & \text{acid} \end{array}$

Water itself is amphoteric. A water molecule can donate a proton and become a hydroxide ion in the process. Or it can accept a proton to become a hydronium ion. The consequences of this fact are described in the next section.



UNDERSTANDING KEY IDEAS

- **1.** List the observable properties of an acid.
- 2. How did Arrhenius define a base?
- **3.** Giving examples, explain how strong acids and weak acids differ.
- **4.** How does the Brønsted-Lowry definition of an acid differ from the Arrhenius definition of an acid?
- **5.** Write an equation that demonstrates the properties of acids and bases, as defined by Brønsted and Lowry.
- **6.** Define a conjugate acid-base pair, and give an example.
- 7. Show chemical equations for the reaction of water with (a) an acid of your choosing and (b) a base of your choosing.

CRITICAL THINKING

- **8.** Could a Brønsted-Lowry acid *not* be an Arrhenius acid? Explain.
- **9.** How would [OH⁻] in an ammonia solution compare with [OH⁻] in a sodium hydroxide solution of similar concentration?
- **10.** Write the formulas of the conjugate acid and the conjugate base of the $H_2PO_4^-$ ion.
- **11.** Write an equation describing a proton transfer between $H_2SO_4(aq)$ and $SO_4^{2-}(aq)$.
- **12.** Why can magnesium hydroxide be described as a strong base even though it is only slightly soluble in water?
- **13.** Identify two acids and their conjugate bases in the following reaction.

 $H_2SO_4(aq) + SO_3^{2-}(aq) \rightleftharpoons HSO_4(aq) + HSO_3(aq)$

S E C T I O N



Acidity, Basicity, and pH

Key Terms

OBJECTIVES

- self-ionization constant of water, K_w
- neutral
- ۰pH
- indicator

- **Use** *K_w* in calculations.
- **Explain** the relationship between pH and H₃O⁺ concentration.
- **Perform** calculations using pH, $[H_3O^+]$, $[OH^-]$, and K_w .
- Describe two methods of measuring pH.

The Self-Ionization of Water

You have just learned that water is both an acid and a base. This means that a water molecule can either give or receive a proton. So what happens when one molecule of water donates a proton to another molecule of water? The reaction is described by the equation below.

> $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ base acid

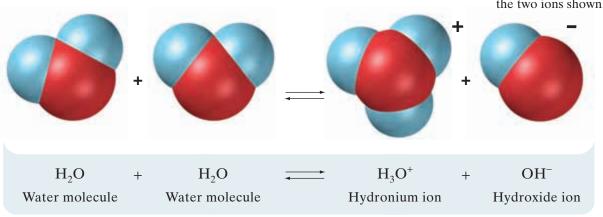
As also shown in **Figure 9**, a pair of water molecules are in equilibrium with two ions—a hydronium ion and a hydroxide ion—in a reaction known as the *self-ionization of water*.

Thus, even pure water contains ions. The chemical equation shows that the two ions are produced in equal numbers. Therefore, in pure water, the two ions must share the same concentration. Experiments show that this concentration is 1.00×10^{-7} M at 25°C.

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} M$$

Figure 9

In water and aqueous solutions, an equilibrium exists between H_2O and the two ions shown.



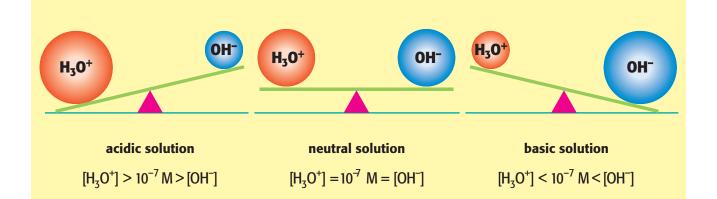


Figure 10

When the concentration of H_3O^+ goes up, the concentration of $OH^$ goes down, and vice versa.

the self-ionization constant of water, *K*_w

the product of the concentrations of the two ions that are in equilibrium with water; $[H_3O^+][OH^-]$

Topic Link

Refer to the "Chemical Equilibrium" chapter for a discussion of equilibrium constants.

The Self-Ionization Constant of Water

The equilibrium between water and the ions it forms is described by the following equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Recall that an equilibrium-constant expression relates the concentrations of species involved in an equilibrium. The relationship for the water equilibrium is simply $[H_3O^+][OH^-] = K_{eq}$. This equilibrium constant, called the **self-ionization constant of water**, is so important that it has a special symbol, K_w . Its value can be found from the known concentrations of the hydronium and hydroxide ions in pure water, as follows:

$$[H_3O^+][OH^-] = K_w = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) = 1.00 \times 10^{-14}$$

The product of these two ion concentrations is always a constant. Thus, anything that increases one of the ion concentrations decreases the other, as elaborated in **Table 4** and illustrated in **Figure 10**. Likewise, if you know one of the ion concentrations, you can calculate the other. The concentration of hydronium ions in a solution expresses its *acidity*. The concentration of hydroxide ions in a solution expresses its *basicity*.

Table 4Concentrations and Kw

Solution	[H ₃ O ⁺] (M)	[OH [_]] (M)	$K_w = [\mathrm{H}_3\mathrm{O}^+][\mathrm{OH}^-]$
Pure water	1.0×10^{-7}	1.0×10^{-7}	1.0×10^{-14}
0.10 M strong acid	1.0×10^{-1}	1.0×10^{-13}	1.0×10^{-14}
0.010 M strong acid	1.0×10^{-2}	1.0×10^{-12}	1.0×10^{-14}
0.10 M strong base	1.0×10^{-13}	1.0×10^{-1}	1.0×10^{-14}
0.010 M strong base	1.0×10^{-12}	1.0×10^{-2}	1.0×10^{-14}
0.025 M strong acid	2.5×10^{-2}	4.0×10^{-13}	1.0×10^{-14}
0.025 M strong base	4.0×10^{-13}	2.5×10^{-2}	1.0×10^{-14}

SAMPLE PROBLEM A

Determining $[OH^-]$ or $[H_3O^+]$ Using K_w

What is $[OH^-]$ in a 3.00×10^{-5} M solution of HCl?

1 Gather information.

Because HCl is a strong acid, all HCl in an aqueous solution ionizes according to the equation below.

$$\operatorname{HCl}(g) + \operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{H}_3\operatorname{O}^+(aq) + \operatorname{Cl}^-(aq)$$

Therefore, a 3.00×10^{-5} M solution of HCl has

$$[H_3O^+] = 3.00 \times 10^{-5} \text{ M}.$$

The self-ionization constant of water is

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

2 Plan your work.

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = (3.00 \times 10^{-5})[OH^-]$$

Values of $[H_3O^+]$ and of $[H_3O^+][OH^-]$, K_w , are known. Therefore, $[OH^-]$ can be found by division.

3 Calculate.

$$[OH^{-}] = \frac{K_w}{[H_3O^{+}]} = \frac{1.00 \times 10^{-14}}{3.00 \times 10^{-5}} = 3.33 \times 10^{-10} M$$

Verify your results.

Multiplying the values for $[H_3O^+]$ and $[OH^-]$ gives the known K_w and confirms that the concentration of hydroxide ion in the solution is 3.33×10^{-10} M.

PRACTICE

- Calculate the hydronium ion concentration in an aqueous solution that has a hydroxide ion concentration of 7.24×10^{-4} M.
- **2** What is $[OH^-]$ in a 0.450 M solution of HNO₃?
- What is $[H_3O^+]$ in a solution of NaOH whose concentration is 3.75×10^{-2} M?
- 4 Calculate the hydroxide ion concentration of a 0.200 M solution of HClO₄.
- 5 If 1.2×10^{-4} moles of magnesium hydroxide, Mg(OH)₂, are dissolved in 1.0 L of aqueous solution, what are [OH⁻] and [H₃O⁺]?

PRACTICE HINT

Remember that $[H_3O^+]$ is equivalent to the concentration of the acid itself only if the acid is a strong acid. The same is true for $[OH^-]$ and strong bases.





neutral

describes an aqueous solution that contains equal concentrations of hydronium ions and hydroxide ions

pН

a value used to express the acidity or alkalinity of a solution; it is defined as the logarithm of the reciprocal of the concentration of hydronium ions; a pH of 7 is neutral, a pH of less than 7 is acidic, and a pH of greater than 7 is basic

The Meaning of pH

You have probably seen commercials in which products, such as that pictured in Figure 11 on the next page, are described as "pH balanced." Perhaps you know that pH has to do with how basic or acidic something is. You may have learned that the pH of pure water is 7 and that acid rain has a lower pH. But what does pH actually mean?

pH and Acidity

When acidity and basicity are exactly balanced such that the numbers of H_3O^+ and OH^- ions are equal, we say that the solution is **neutral.** Pure water is neutral because it contains equal amounts of the two ions.

Two of the solutions listed in Table 5 are neutral: both have a hydronium ion concentration of 1.00×10^{-7} M. The other solutions are either acidic or basic, depending on whether a strong acid or a strong base was dissolved in water. The solution listed last in Table 5 was made by dissolving 0.100 mol of NaOH in 1.00 L of water, so it has a hydroxide ion concentration of 0.100 M. Its hydronium ion concentration can be calculated using K_w , as shown below.

$$[H_3O^+] = \frac{[H_3O^+][OH^-]}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.100} = 1.00 \times 10^{-13}$$

Notice that the hydronium ion concentrations in the listed solutions span a very wide range-in fact a trillionfold range. You can see that working with $[H_3O^+]$ can involve awkward negative exponents. In part to avoid this inconvenience, scientists adopted the suggestion, made by the Danish chemist Søren Sørensen in 1909, to focus not on the value of $[H_3O^+]$ but on the power of 10 that arises when $[H_3O^+]$ is expressed in scientific notation. Sørensen proposed using the negative of the power of 10 (that is, the negative logarithm) of $[H_3O^+]$ as the index of basicity and acidity. He called this measure the **pH**. The letters p and H represent power of hydrogen. Keep in mind that because pH is a negative logarithmic scale, a lower pH reflects a higher hydronium ion concentration.

Table 5pH Values at Specified $[H_3O^+]$				
Solution	[H ₃ O ⁺] (M)	рН		
1.00 L of H ₂ O	1.00×10^{-7}	7.00		
0.100 mol HCl in 1.00 L of H_2O	1.00×10^{-1}	1.00		
0.0100 mol HCl in 1.00 L of H_2O	1.00×10^{-2}	2.00		
0.100 mol NaCl in 1.00 L of H_2O	1.00×10^{-7}	7.00		
0.0100 mol NaOH in 1.00 L of H_2O	1.00×10^{-12}	12.00		
0.100 mol NaOH in 1.00 L of H_2O	1.00×10^{-13}	13.00		

Calculating pH from [H₃O⁺]

Based on Sørensen's definition, pH can be calculated by the following mathematical equation:

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

Because of the negative sign, as the hydronium ion concentration increases, the pH will *decrease*. A solution of pH 0 is very acidic. A solution of pH 14 is very alkaline. A solution of pH 7 is neutral.

The equation above may be rearranged to calculate the hydronium ion concentration from the pH. In that form, the equation is as follows:

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

When the pH is a whole number, you can do this calculation in your head. For example, if a solution has a pH of 3, its $[H_3O^+]$ is 10^{-3} M, or 0.001 M.

Because pH is related to powers of 10, a change in one pH unit corresponds to a tenfold change in the concentrations of the hydroxide and hydronium ions. Therefore, a solution whose pH is 2.0 has a $[H_3O^+]$ that is ten times greater than a solution whose pH is 3.0 and 100 times greater than a solution whose pH is 4.0.



Figure 11

Soap manufacturers sometimes make claims about the pH of their products.



Using Logarithms in pH Calculations

It is easy to find the pH or the $[H_3O^+]$ of a solution by using a scientific calculator. Because calculators differ, check your manual to find out which keys are used for log and antilog functions and how to use these functions.

1. Calculating pH from [H_3O^+]

(see Sample Problem B for an example)

Use the definition of pH:

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

- Take the logarithm of the hydronium ion concentration.
- Change the sign (+/–).
- The result is the pH.

2. Calculating [H₃O⁺] from pH (see Sample Problem C for an example)

If you rearrange $pH = -log [H_3O^+]$ to solve for $[H_3O^+]$, the equation becomes

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

- Change the sign of the pH (+/-)
- Raise 10 to the negative pH power (take the antilog).
- The result is $[H_3O^+]$.

SAMPLE PROBLEM B

Calculating pH for an Acidic or Basic Solution

What is the pH of (a) a 0.000 10 M solution of HNO₃, a strong acid, and (b) a 0.0136 M solution of KOH, a strong base?

Gather information.

(a) Concentration of HNO₃ solution = 0.000 10 M = 1.0×10^{-4} M; pH = ? (b) Concentration of KOH solution = 0.0136 M = 1.36×10^{-2} M; pH = ? $K_w = 1.00 \times 10^{-14}$

2 Plan your work.

Because HNO₃ and KOH are strong electrolytes, their aqueous solutions are completely ionized.

(a) Therefore, for HNO₃ solution, $[H_3O^+] = 1.0 \times 10^{-4} \text{ M}.$

(b) Therefore, for KOH solution, $[OH^{-}] = 1.36 \times 10^{-2} \text{ M}.$

The equation relating pH to $[H_3O^+]$ is pH = $-\log [H_3O^+]$. This equation alone is adequate for (a). For (b), you must first use K_w to calculate $[H_3O^+]$ from $[OH^-]$.

3 Plan your work.

Using a scientific calculator and following the instructions under item 1 of **Skills Toolkit 1**, one calculates for (a)

$$pH = -log [H_3O^+] = -log (1.0 \times 10^{-4}) = -(-4.00) = 4.00$$

For (b),
$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1.36 \times 10^{-2}} = 7.35 \times 10^{-13}$$
 and then

$$pH = -log [H_3O^+] = -log (7.35 \times 10^{-13}) = -(-12.13) = 12.13.$$

4 Verify your results.

Because the solution in (a) is acidic, a pH between 0 and 7 is expected, so the calculated value of 4.00 is reasonable. The solution in (b) will be basic; therefore, a pH between 7 and 14 is expected. Therefore, the answer pH = 12.13 is reasonable.

PRACTICE

- Calculate pH if $[H_3O^+] = 5.0 \times 10^{-3}$ M.
- 2 What is the pH of a 0.2 M solution of a strong acid?
- **5** Calculate pH if $[OH^{-}] = 2.0 \times 10^{-3}$ M.
 - What is the pH of a solution that contains 0.35 mol/L of the strong base NaOH?

PRACTICE HINT

Because it is easy to make calculator errors when dealing with logarithms, always check to see that answers to pH problems are reasonable. For example, negative pH values and pH values greater than 14 are unlikely.



SAMPLE PROBLEM C

Calculating $[H_3O^+]$ and $[OH^-]$ from pH

What are the concentrations of the hydronium and hydroxide ions in a sample of rain that has a pH of 5.05?

Gather information.

pH = 5.05 $K_w = 1.00 \times 10^{-14}$ $[H_3O^+] = ?$ $[OH^-] = ?$

2 Plan your work.

Because you know the rain's pH, the equation $[H_3O^+] = 10^{-pH}$ can be used to find the hydronium ion concentration.

Then the equation $[H_3O^+][OH^-] = K_w$ can be rearranged and used to find $[OH^-]$.

3 Calculate.

Using a scientific calculator and following the instruction under item 2 of **Skills Toolkit 1**, one finds

$$[H_3O^+] = 10^{-pH} = 10^{-5.05} = 8.9 \times 10^{-6} M_{\odot}$$

Next,
$$[OH^{-}] = \frac{K_w}{[H_3O^{+}]} = \frac{1.00 \times 10^{-14}}{8.9 \times 10^{-6}} = 1.1 \times 10^{-9} M.$$

The concentrations of the hydronium and hydroxide ions are 8.9×10^{-6} M and 1.1×10^{-9} M, respectively.

Verify your results.

The rain's pH is mildly acidic, so the hydronium ion concentration should be more than 1.0×10^{-7} M, and the hydroxide concentration should be less than 1.0×10^{-7} M. Thus, the answers are reasonable.

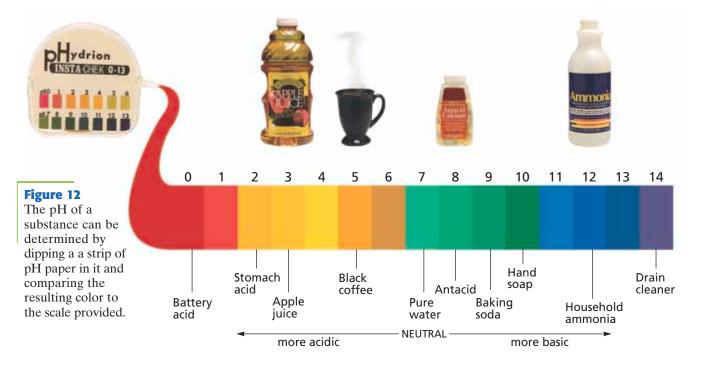
PRACTICE

- What is the hydronium ion concentration in a fruit juice that has a pH of 3.3?
- 2 A commercial window-cleaning liquid has a pH of 11.7. What is the hydroxide ion concentration?
- If the pH of a solution is 8.1, what is [H₃O⁺] in the solution? What is [OH⁻] in the solution?
- A Normal human blood has a hydroxide ion concentration that ranges from 1.7×10^{-7} M to 3.5×10^{-7} M, but diabetics often have readings outside this range. A patient's blood has a pH of 7.67. Is there cause for concern?

PRACTICE HINT

For further verification, you could recalculate the pH from the found concentrations by using the methods in Sample Problems B and C.





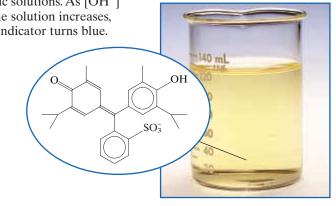
Measuring pH

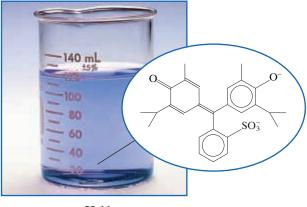
Measuring pH is an operation that is carried out frequently, for a variety of reasons, in chemical laboratories. There are two ways to measure pH. The first method, which uses indicators, is quick and convenient but does not give very precise results. The second method, which uses a pH meter, is very precise but is more complicated and expensive.

Indicators

Certain dyes, known as **indicators,** turn different colors in solutions of different pH. The pH paper pictured in **Figure 12** contains a variety of indicators and can develop a rainbow of colors, each of which corresponds to a particular pH value.

Thymol blue is an example of an indicator. It is yellow in solutions whose pH is between 3 and 8 but blue in solutions whose pH is 10 or higher. **Figure 13** shows the structure of the organic ion responsible for the yellow color—it is a weak acid. The blue form is the conjugate base.





pH 11

indicator

a compound that can reversibly change color depending on the pH of the solution or other chemical change

Figure 13

The indicator thymol blue is yellow in neutral and acidic solutions. As [OH⁻] in the solution increases, the indicator turns blue. Dozens of indicator dyes are available. Some indicators, such as litmus, are natural products, but most are synthetic. Each indicator has its own colors and its individual range of pH over which it changes shade. By suitably blending several indicators, chemists have prepared "universal indicators," which turn different colors throughout the entire pH range. One such universal indicator is incorporated into the "pH paper" shown in **Figure 12.** By matching the color the paper develops to a standard chart, one can easily measure the solution's approximate pH.

pH Meters

The pH of a solution is being measured by a pH meter in **Figure 14.** A pH meter is an electronic instrument equipped with a probe that can be dipped into a solution of unknown pH. The probe has two electrodes, one of which is sensitive to the hydronium ion. An electrical voltage develops between the two electrodes, and the circuitry measures this voltage very precisely. The instrument converts the measurement into a pH reading, which is displayed on the meter's screen.

After calibration with standard solutions of known pH, a pH meter can measure pH with a precision of 0.01 pH units, which is much greater that the precision of measurements with indicators.



Figure 14 A pH meter is a

A pH meter is an electrochemical instrument that can measure pH accurately.

2 Section Review

UNDERSTANDING KEY IDEAS

- **1.** Describe the relationship between hydronium and hydroxide ion concentrations in an aqueous solution.
- **2.** What does pH measure? How is pH defined?
- **3.** What is a *neutral* solution? What is its pH?
- **4.** Write equations linking the terms K_w , pH, $[H_3O^+]$, and $[OH^-]$.
- **5.** The pH of pancreatic juice is 7.9. Is pancreatic juice acidic or basic?
- **6.** What methods are used to measure pH? Briefly describe how each method works.

PRACTICE PROBLEMS

The hydronium ion concentration in a solution is 3.16 × 10⁻³ mol/L. What is [OH⁻]? What is the pH?

- **8.** The pH of vinegar is 2.9. Calculate the concentrations of H_3O^+ and OH.
- **9.** If 5.3 g of the strong base NaOH is dissolved in water to form 1500 mL of solution, what are the pH, $[H_3O^+]$, and $[OH^-]$?
- **10.** The $[OH^{-}]$ of a fruit juice is 3.2×10^{-11} M. What is the pH?
- **11.** What amount in moles of a strong acid such as HBr must be dissolved in 1.00 L of water to prepare a solution whose pH is 2.00?
- 12. What volume of solution is needed to dissolve 1.0 mol of a strong base such as KOH to make a solution whose pH is 12.5?

CRITICAL THINKING

- **13.** Why is "deionized water" *not* an entirely accurate description of pure water?
- **14.** Can pH be negative? Why or why not?
- **15.** Why would pH paper be unsuitable for measuring blood pH?

SECTION



Neutralization and Titrations

Predict the product of an acid-base reaction.

concentration of an acid or base solution.

Describe the conditions at the equivalence point in a titration.

Explain how you would select an indicator for an acid-base titration.

Describe the procedure for carrying out a titration to determine the

The solution of strong acid in the beaker on the left in Figure 15 contains

a high H_3O^+ concentration: high enough to react with and dissolve metals. The solution of strong base on the right is concentrated enough in OH⁻

to free a grease-clogged drain. Yet when these acidic and basic solutions

are mixed in equal amounts, the solution formed has little effect on metal

or grease. What has occurred? Because the relationship $[H_3O^+][OH^-] =$

 1.0×10^{-14} must always be true, high concentrations of H₃O⁺(aq) and

 $OH^{-}(aq)$ cannot coexist. Most of these ions have reacted with each other

OBJECTIVES

Neutralization

Key Terms

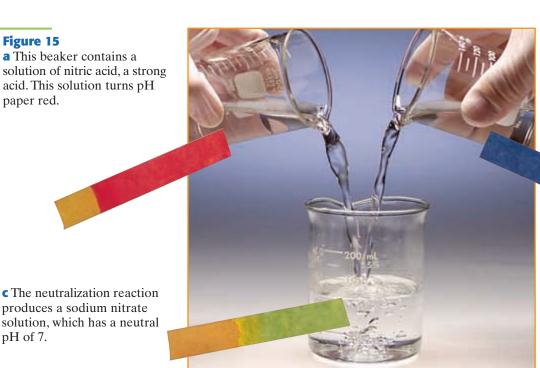
- neutralization reaction
- equivalence point
- titration
- titrant
- standard solution
- transition range
- end point

Figure 15

paper red.

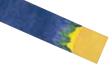
neutralization reaction

the reaction of the ions that characterize acids (hydronium ions) and the ions that characterize bases (hydroxide and a salt



in a process known as a **neutralization reaction**.

b This beaker contains a solution of sodium hydroxide, a strong base. This solution turns pH paper blue.



c The neutralization reaction produces a sodium nitrate solution, which has a neutral pH of 7.

ions) to form water molecules

a This beaker contains a

All Neutralizations Are the Same Reaction

When solutions of a strong acid and a strong base, having exactly equal amounts of $H_3O^+(aq)$ and $OH^-(aq)$ ions, are mixed, almost all of the hydronium and hydroxide ions react to form water. The reaction is described by the equation below.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

This same reaction happens regardless of the identities of the strong acid and strong base.

Suppose, as in **Figure 16**, that the acid was hydrochloric acid, HCl, and the base was sodium hydroxide, NaOH. When these solutions are mixed, the result will be a solution of only water and the spectator ions sodium and chloride. This is just a solution of sodium chloride. You can prepare the same solution by dissolving common salt, NaCl(s), in water.

You may sometimes see this reaction described as follows:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Arrhenius might have said "an acid plus a base produces a salt plus water." This representation can be misleading because the only reactants are $H_3O^+(aq)$ and $OH^-(aq)$ ions and the only product is H_2O .

Figure 16

After hydrochloric acid neutralizes a solution of sodium hydroxide, the only solutes remaining are Na⁺(*aq*) and Cl⁻(*aq*). When the water is evaporated, a small amount of sodium chloride crystals, which will be just like the ones shown, will be left.

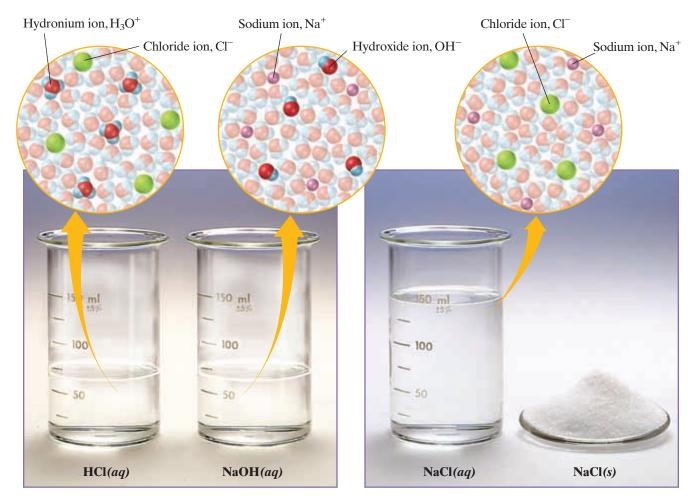


Figure 17

a A titration is done by using a buret, as shown here, to deliver a measured volume of titrant into a solution of unknown concentration.



b When reading the liquid level in a buret, you must read the level at the bottom of the meniscus. Here, the reading is 0.42 mL.





equivalence point

the point at which the two solutions used in a titration are present in chemically equivalent amounts

titration

a method to determine the concentration of a substance in solution by adding a solution of known volume and concentration until the reaction is completed, which is usually indicated by a change in color

titrant

a solution of known concentration that is used to titrate a solution of unknown concentration

standard solution

a solution of known concentration

Titrations

If an acidic solution is added gradually to a basic solution, at some point the neutralization reaction ends because the hydroxide ions become used up. Likewise, if a basic solution is added to an acid, eventually all of the hydronium ions will be used up. The point at which a neutralization reaction is complete is known as the **equivalence point.**

When a solution of a strong base is added to a solution of a strong acid, the equivalence point occurs when the amount of added hydroxide ions equals the amount of hydronium ions originally present. As you have learned, at 25°C this is the point at which both $H_3O^+(aq)$ and $OH^-(aq)$ ions have concentrations of 1.0×10^{-7} M, and the pH is 7.

The gradual addition of one solution to another to reach an equivalence point is called a **titration**. The purpose of a titration is to determine the concentration of an acid or a base. In addition to the two solutions, the equipment needed to carry out a titration usually includes two burets, a titration flask, and a suitable indicator. **Skills Toolkit 2,** later in this section, will describe how this equipment is used to perform a titration.

If an acid is to be titrated with a base, one buret is used to measure the volume of the acid solution dispensed into the titration flask. The second buret is used to deliver and measure the volume of the alkaline solution, as shown in **Figure 17.** The solution added in this way is called the **titrant.** Titrations can just as easily be carried out the other way around. That is, acid titrant may be added to a basic solution in the flask.

To find the concentration of the solution being titrated, you must, of course, already know the concentration of the titrant. A solution whose concentration is already known is called a **standard solution**. The concentration of a standard solution has usually been determined by reacting the solution with a precisely weighed mass of a solid acid or base.

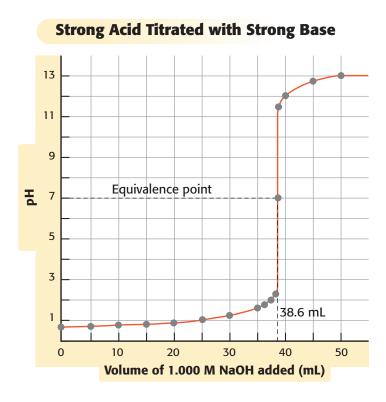


Figure 18

This graph of pH versus the volume of 1.000 M NaOH added to an HCl solution indicates that the equivalence point occurred after 38.6 mL of titrant was added.

The Equivalence Point

As titrant is added to the flask containing the solution of unknown concentration, pH is measured. A distinctively shaped graph, called a *titration curve*, results when pH is plotted against titrant volume. **Figure 18** shows a typical example. Because the curve is steep at the equivalence point, it is easy to locate the exact volume that corresponds to a pH of 7.00.

A titration is exact only if the equivalence point can be accurately detected. A pH meter can be used to monitor the pH during the titration, and indicators are also commonly used to detect the equivalence point.

Carrying Out a Titration

Skills Toolkit 2, on the next two pages, has step-by-step instructions to help you carry out an acid-base titration. Study and understand all of the steps *before* you start to perform a titration experiment. If your attention alternates between book and buret, you're likely to make mistakes. Experience helps, and your second titration should be much better than your first.

With each addition of titrant, the indicator will begin to change color but then will go back to its original color as you swirl the flask. The color will fade ever more slowly as the end point gets near. Immediately slow down to a drop-by-drop flow rate. Otherwise, you may miss the end point.

If you do miss the end point by adding too much titrant, however, you do not have to start all over. You can "back-titrate" by adding more unknown solution to the flask until the indicator turns back to its original color. Measure the volume of unknown solution that you added, then slowly add titrant again until the equivalence point is reached. You can then use the total volumes of unknown and titrant in your calculations.

Performing a Titration

The following procedure is used to determine the unknown concentration of an acid solution by titrating the solution with a standardized base solution.

Decide which buret will be used for the acid and which will be used for the base. Label each buret to avoid confusion. Rinse the acid buret three times with the acid to be used in the titration. Use the base solution to rinse the other buret in a similar manner.



Fill the acid buret with the acid solution to a point above the 0 mL mark.



Release some acid into a waste flask to lower the volume into the calibrated portion of the buret.





Record the volume of the acid in the buret to the nearest 0.01 mL as your starting point.



5 Release a volume of acid (determined by your lab procedure) into a clean Erlenmeyer flask.



6 Record the new volume reading, and subtract the starting volume to find the volume of acid added.



Add three drops of an appropriate indicator (phenolphthalein in this case) to the flask.



Fill the other buret with standardized base solution to a point above the 0 mL mark. Record the concentration of the standardized solution.

Release some base from the buret into a waste flask so that the top of the liquid is in the calibrated portion of the buret.



10 Record the volume of the base to the nearest 0.01 mL as your starting point.



Place the flask containing the acid under the base buret. Notice that the tip of the buret extends into the mouth of the flask.



13 Near the end point, add base drop by drop.



14 The end point is reached when a very light pink color remains after 30 s of swirling.





12 Slowly release base from the buret into the flask while constantly swirling the flask. The pink color should fade with swirling.



15 Record the new volume, and determine the volume of base added.

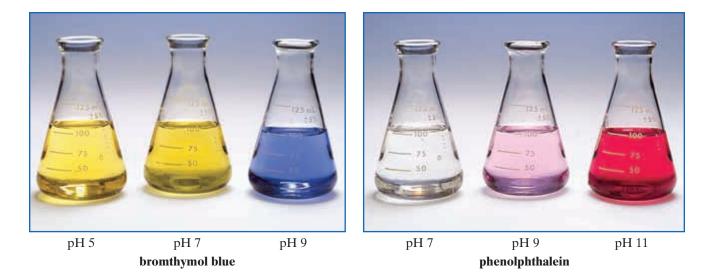


Figure 19

Bromthymol blue changes color between a pH of 6.0 and 7.6, as in the neutralization of a strong acid and a strong base. Phenolphthalein changes color between a pH of 8.0 and 9.6, as in the neutralization of a weak acid with a strong base.

transition range

the pH range through which an indicator changes color

end point

the point in a titration at which a marked color change takes place

Selecting a Suitable Indicator

All indicators have a **transition range.** In this range, the indicator is partly in its acidic form and partly in its basic form. Thus, the indicator's color is intermediate between those of its acid and base colors. **Figure 19** illustrates the transition range for two typical indicators, bromthymol blue and phenolphthalein.

The instant at which the indicator changes color is the **end point** of the titration. If an appropriate indicator is chosen, the end point and the equivalence point will be the same. In order to determine the concentration of the titrated solution, you must determine the titrant volume at which the indicator changes color.

In titrations of a strong acid by a strong base, the equivalence point occurs at pH 7, and bromthymol blue would be an appropriate indicator, as **Table 6** confirms. However, when a weak acid is titrated by a strong base, the equivalence point is at a pH greater than 7 and thymol blue or phenolphthalein would be a better choice. On the other hand, methyl orange could be the best choice if your titration uses a weak base and a strong acid, because the equivalence point might be at pH 4.

Indicator name	Acid color	Transition range (pH)	Base color
Thymol blue	red	1.2–2.8	yellow
Methyl orange	red	3.1–4.4	orange
Litmus	red	5.0-8.0	blue
Bromthymol blue	yellow	6.0–7.6	blue
Thymol blue	yellow	8.0–9.6	blue
Phenolphthalein	colorless	8.0–9.6	red
Alizarin yellow	yellow	10.1–12.0	red

Table 6 Transition Ranges of Some Indicators

Titration Calculations: From Volume to Amount in Moles

The goal of a titration is to determine either the original concentration of the solution in the titration flask or the original amount of acid or base.

Recall the simple equation, given below, that relates the amount n (in moles) of a solute to the concentration and volume.

$$n = cV$$

Here *c* is the concentration (in moles per liter) and *V* is the volume (in liters) of the solution. At the equivalence point in a titration of a strong acid by a strong base, the amount of hydroxide ion added equals the initial amount of hydronium ion. This relationship may be represented as $n_{\rm H_3O^+} = n_{\rm OH^-}$. If each of these amounts is replaced by the corresponding product of concentration and volume, the following equation is the result.

$$(c_{\rm H_3O^+})(V_{\rm H_3O^+}) = (c_{\rm OH^-})(V_{\rm OH^-})$$

This relationship is the one that you will need for most titration calculations. The equation applies whether the titrant is an acid or a base.

SAMPLE PROBLEM D

Calculating Concentration from Titration Data

A student titrates 40.00 mL of an HCl solution of unknown concentration with a 0.5500 M NaOH solution. The volume of base solution needed to reach the equivalence point is 24.64 mL. What is the concentration of the HCl solution in moles per liter?

1 Gather information.

$V_{\rm H_3O^+} = 40.00 \text{ mL} = 0.040 \text{ 00 L}$	$V_{\rm OH^-} = 24.64 \text{ mL} = 0.024 \text{ 64 L}$
$c_{\rm OH^{-}} = 0.5500 \text{ mol/L}$	$c_{\rm H_3O^+} = ?$

2 Plan your work.

The general equation $(c_{H_3O^+})(V_{H_3O^+}) = (c_{OH^-})(V_{OH^-})$ can be rearranged into the following equation:

$$c_{\rm H_3O^+} = \frac{(c_{\rm OH^-})(V_{\rm OH^-})}{V_{\rm H_3O^+}}$$

3 Calculate.

$$c_{\rm H_3O^+} = \frac{(c_{\rm OH^-})(V_{\rm OH^-})}{V_{\rm H_3O^+}} = \frac{(0.5500 \text{ mol/L})(0.024 \text{ 64 L})}{0.040 \text{ 00 L}} = 0.3388 \text{ mol/L}$$

Verify your results.

Amounts of hydronium and hydroxide ions should be the same.

 $n_{\rm H_3O^+} = c_{\rm H_3O^+}V_{\rm H_3O^+} = (0.3388 \text{ mol/L})(0.040 \text{ 00 L}) = 0.013 \text{ 55 mol}$ $n_{\rm OH^-} = c_{\rm OH^-}V_{\rm OH^-} = (0.5500 \text{ mol/L})(0.024 \text{ 64 L}) = 0.013 \text{ 55 mol}$

Practice problems on next page

PRACTICE HINT

If you get confused, remember to keep track of amounts of acid and base. The rest is just a matter of converting molarity to moles by multiplying molarity by volume.

PRACTICE



If 20.6 mL of 0.010 M aqueous HCl is required to titrate 30.0 mL of an aqueous solution of NaOH to the equivalence point, what is the molarity of the NaOH solution?

- In the titration of 35.0 mL of drain cleaner that contains NaOH, 50.08 mL of 0.409 M HCl must be added to reach the equivalence point. What is the concentration of the base in the cleaner?
- Titrating a sludge sample of unknown origin required 41.55 mL of 0.1125 M NaOH. How many moles of H₃O⁺ did the sample contain?
- Neutralizing 5.00 L of an acid rain sample required 11.3 mL of 0.0102 M KOH. Calculate the hydronium ion concentration in the rain sample.



UNDERSTANDING KEY IDEAS

- **1.** What are the reactants and the product common to all neutralization reactions?
- **2.** Define *equivalence point*. How does the equivalence point differ from the *end point* of a titration?
- **3.** What are standard solutions, and how are they standardized?
- **4.** How would you choose an indicator for titrating a strong acid with a strong base?
- **5.** What titration data are needed to calculate an unknown acid concentration?
- **6.** What are the roles of the two burets in a titration experiment?
- **7.** At the equivalence point of a titration, what is present in the solution?

PRACTICE PROBLEMS

8. If 29.5 mL of 0.150 M HCl neutralizes 25.0 mL of a basic solution, what was [OH⁻] in the basic solution?

- **9.** What volume of 0.250 M nitric acid is needed to neutralize 17.35 mL of 0.195 M KOH solution?
- **10.** In a titration of 30.00 mL of 0.0987 M HBr solution with a strong base of unknown concentration, the pH reached 7 after the addition of 37.43 mL of titrant. What was the concentration of the base?
- 11. If it took 72 mL of 0.55 NaOH titrant to neutralize 220 mL of an acidic solution, what was the hydronium ion concentration in the acidic solution?
- 12. In a titration of a sample of 0.31 M HNO₃, it took 75 mL of a 0.24 M KOH solution to reach a pH of 7. What was the volume of the sample?

CRITICAL THINKING

- **13.** What indicator would you choose for the titration of acetic acid with potassium hydroxide?
- **14.** Why is the steepness of a titration curve helpful in locating the equivalence point?
- **15.** Explain why the titration of a strong acid with a weak base ends at a pH lower than 7.

S E C T I O N



Equilibria of Weak Acids and Bases

Key Terms

- acid-ionization constant, K_a
- buffer solution

OBJECTIVES

- **Write** an equilibrium equation that shows how a weak acid is in equilibrium with its conjugate base.
- **Calculate** *K*_{*a*} from the hydronium ion concentration of a weak acid solution.
- **Describe** the components of a buffer solution, and explain how a buffer solution resists changes in pH.

Weak Acids and Bases

Consider the reaction represented by the following equation, in which one arrow is longer than the other:

$$A(aq) + B(aq) \xrightarrow{\frown} C(aq) + D(aq)$$

Chemists use this notation to indicate that the forward reaction is *favored*. In other words, when the reaction has reached equilibrium, there will be more products than reactants.

Some Acids are Better Proton Donors Than Others

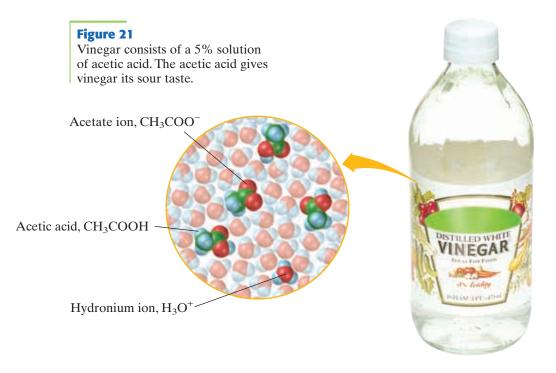
Some aspects of formic acid, HCOOH, are illustrated in **Figure 20**. Formic acid is a typical Brønsted-Lowry acid, able to donate a proton to a base, such as the acetate ion, CH_3COO^- . Thus, in a solution prepared by dissolving formic acid and sodium acetate in water, a reaction will occur.





Figure 20

The name *formic acid* comes from *formica*, the Latin word for "ant." Formic acid was first isolated by distillation from ants in 1670. A molecular model of formic acid is shown.



The reaction will produce the conjugate base of the formic acid, the formate ion, $HCOO^-$, and the conjugate acid of the acetate ion, acetic acid, CH_3COOH , as shown below.

$$\begin{array}{c} \text{HCOOH}(aq) + \text{CH}_3\text{COO}^-(aq) \xrightarrow{} \text{HCOO}^-(aq) + \text{CH}_3\text{COOH}(aq) \\ \text{acid} \\ \end{array}$$

Acetic acid is the active ingredient in vinegar, as shown in **Figure 21.** The unequal arrows in the equation above indicate that if you dissolved equal amounts of all four substances in water, the concentrations of HCOO⁻ and CH₃COOH would be greater than the concentrations of HCOOH and CH₃COO⁻ at equilibrium. If you think of this as a contest between the two acids to see which is better able to donate protons, formic acid would be the winner. HCOOH is more willing to lose a proton than CH₃COOH is. Therefore, formic acid is considered a *stronger* acid than acetic acid is.

Some Bases Accept Protons More Readily Than Others

Now look at the same reaction from the standpoint of the two bases:

$$\begin{array}{c} \text{HCOOH}(aq) + \text{CH}_{3}\text{COO}^{-}(aq) \xrightarrow{} \text{HCOO}^{-}(aq) + \text{CH}_{3}\text{COOH}(aq) \\ \text{base} \qquad \text{base} \end{array}$$

Both bases can accept protons, but the acetate ion, CH_3COO^- , has been more successful in accepting protons than the formate ion, $HCOO^-$, has. The formate ion is a weaker base than the acetate ion is. At equilibrium, there is more formate ion than acetate ion in solution.

In this example, formic acid is the stronger acid, but its conjugate base, the formate ion, is the weaker base. This example illustrates a general principle: *In an acid-base reaction, the conjugate base of the stronger acid is the weaker base, and the conjugate acid of the stronger base is the weaker acid.*

	Acid	Formula	K _a of acid	Conjugate base	Formula	
•	Hydronium ion	H_3O^-	5.53×10^1	water	H ₂ O	
	Hydrogen sulfate ion	HSO ₄	1.23×10^{-2}	sulfate ion	SO ₄ ²⁻	
	Phosphoric acid	H ₃ PO ₄	7.52×10^{-3}	dihydrogen phosphate ion	H ₂ PO ₄	
	Formic acid	НСООН	1.82×10^{-4}	formate ion	HCOO ⁻	
	Benzoic acid	C ₆ H ₅ COOH	6.46×10^{-5}	benzoate ion	C ₆ H ₅ COO ⁻	
2	Acetic acid	CH ₃ COOH	1.75×10^{-5}	acetate ion	CH ₃ COO ⁻	
	Carbonic acid	H ₂ CO ₃	4.30×10^{-7}	hydrogen carbonate ion	HCO ₃	and Gunder
Increasing	Dihydrogen phosphate ion	$H_2PO_4^-$	6.31×10^{-8}	monohydrogen phosphate ion	HPO ₄ ^{2–}	6 or on but
	Hypochlorous acid	HOCI	2.95×10^{-9}	hypochlorite ion	C10 ⁻	1
	Ammonium ion	NH_4^+	5.75×10^{-10}	ammonia	NH ₃	
	Hydrogen carbonate ion	HCO ₃	4.68×10^{-11}	carbonate ion	CO ₃ ^{2–}	
	Monohydrogen phosphate ion	HPO ₄ ^{2–}	4.47×10^{-13}	phosphate ion	PO ₄ ³⁻	
	Water	H ₂ O	1.81×10^{-16}	hydroxide ion	OH-	¥
	Conjugate acid	Formula	K _a of acid	Base	Formula	

Table 7 Relative Strengths of Acids and Bases

The Acid-Ionization Constant

The strengths of acids may be described in relative terms of *stronger* or *weaker*, but the strength of an acid may also be expressed quantitatively by its **acid-ionization constant**, K_{ar} . This is just the equilibrium constant, K_{eq} , that describes the ionization of an acid in water.

Consider the following equation, which describes the equilibrium established when acetic acid dissolves in water.

$$CH_3COOH(aq) + H_2O(l) \xleftarrow{} H_3O^+(aq) + CH_3COO^-(aq)$$

The equilibrium expression for this reaction is written as follows:

$$\frac{[\text{H}_{3}\text{O}^{+}][\text{CH}_{3}\text{COO}^{-}]}{[\text{CH}_{3}\text{COOH}]} = K_{a} = 1.75 \times 10^{-5}$$

Recall that only solutes appear in equilibrium expressions. When water is a solvent, it is omitted. Remember, too, that K_a is unitless.

Table 7 lists many acid-ionization constants. Note that the stronger the acid is, the weaker its conjugate base is. Accordingly, the stronger the base is, the weaker its conjugate acid is.

acid-ionization constant, *K_a*

the equilibrium constant for a reaction in which an acid donates a proton to water



Refer to the "Chemical Equilibrium" chapter for a discussion of equilibrium constants.

SAMPLE PROBLEM E

Calculating K_a of a Weak Acid

A vinegar sample is found to have 0.837 M CH₃COOH. Its hydronium ion concentration is found to be 3.86×10^{-3} mol/L. Calculate K_a for acetic acid.

1 Gather information.

 $[CH_3COOH] = 0.837 \text{ M}$ $[H_3O^+] = 3.86 \times 10^{-3} \text{ M}$ $K_a = ?$

2 Plan your work.

The equation for the equilibrium is

$$CH_3COOH(aq) + H_2O(l) \xleftarrow{} H_3O^+(aq) + CH_3COO^-(aq)$$

which establishes that the expression for K_a is

$$K_a = \frac{[\mathrm{H}_3\mathrm{O}^+][\mathrm{CH}_3\mathrm{COO}^-]}{[\mathrm{CH}_3\mathrm{COOH}]}$$

The equation also shows that hydronium and acetate ions are produced in equal amounts, so $[CH_3COO^-] = [H_3O^+]$. Hence, all of the necessary concentration data are known.

3 Calculate.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(3.86 \times 10^{-3})(3.86 \times 10^{-3})}{0.837} = 1.78 \times 10^{-5}$$

4 Verify your results.

The calculated acid-ionization constant is very close to the value listed in **Table 7**, so the answer seems reasonable.

PRACTICE

- **1** Calculate $[H_3O^+]$ of a 0.150 M acetic acid solution.
- 2 Find K_a if a 0.50 M solution of a weak acid has a hydronium ion concentration of 1.3×10^{-4} M.
- 3 A solution prepared by dissolving 1.0 mol of benzoic acid in water to form 1.0 L of solution has a pH of 2.1. Calculate the acid-ionization constant.

Use Table 7 to calculate the concentration of formate ion in 0.085 M formic acid.

PRACTICE HINT

Earlier in this chapter, a sample problem demonstrated how to calculate $[H_3O^+]$ from pH. In some K_a problems, you may need to perform this step first.

Table 8 Typical pH Values of Human Body Fluids			
Solution	рН	Solution	рН
Gastric juice	1.5	Blood	7.4
Urine	6.0	Tears	7.4
Saliva	6.5	Pancreatic juice	7.9
Milk	6.6	Bile	8.2



Buffer Solutions

You can see in **Table 8** that the pH of blood is 7.4. Keeping your blood pH between 7.35 and 7.45 is vital to your health. If your blood's pH goes outside this very narrow range, you will become ill. If your blood pH is lower than 7.35, you suffer *acidosis*. If your blood's pH rises above 7.45, symptoms of *alkalosis* appear. How does your body control the pH of blood within such narrow bounds? Your body relies on the properties of **buffer solutions** —solutions that resist changes in pH that would otherwise be caused by the addition of acids or bases. These solutions are said to be "buffered" against pH changes.

A Buffer Has Two Ingredients

A buffer solution, often simply called a *buffer*, is a solution that contains approximately equal amounts of a weak acid and its conjugate base.

Imagine preparing two solutions. In the first, you dissolve one mole of sodium acetate in one liter of water. Sodium acetate is a strong electrolyte and ionizes completely in solution.

 $CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$

For the second solution, you prepare one mole of acetic acid in one liter of water. Acetic acid is a weak acid that ionizes very little in water. The following equilibrium equation describes the solution:

 $CH_3COOH(aq) + H_2O(l) \xleftarrow{} H_3O^+(aq) + CH_3COO^-(aq)$

As the unequal arrows suggest, this equilibrium favors the reactants on the left side. About 99.6% of the acetic acid is un-ionized. Its pH is 2.4.

Now mix the two solutions. Both contain the acetate ion, so the common ion effect comes into play. Recall that Le Châtelier's principle predicts that the equilibrium will adjust to reduce the stress imposed by the increase in the $CH_3COO^-(aq)$ concentration. It does this by shifting even more heavily toward the left. In fact, now 99.996% of the acetic acid is unionized. The pH has doubled to 4.8.

The mixture is a buffer solution. It contains nearly equal amounts of the weak acid acetic acid, $CH_3COOH(aq)$, and its conjugate base, the acetate ion, $CH_3COO^-(aq)$. It is not necessary that the acid and its conjugate base be present in equal amounts to act as a buffer, but there must be a substantial concentration of each.

buffer solution

a solution made from a weak acid and its conjugate base that neutralizes small amounts of acids or bases added to it



Refer to the "Chemical Equilibrium" chapter for a discussion of Le Châtelier's principle.

Figure 22

The left-hand beaker in each photo contains a neutral solution. The right-hand beaker in each photo contains the same solution plus hydrochloric acid.



a When a small amount of HCl is added to an unbuffered solution, the solution's pH drops significantly.



b When the same amount of HCl is added to a buffered solution, the pH of the solution does not change very much.

Buffer Solutions Stabilize pH

How do buffer solutions prevent large changes in pH when small amounts of acid or base are added, as demonstrated in **Figure 22?** Le Châtelier's principle can help us understand the effect. If HX is a weak acid and X^- is its conjugate base, then in a buffer solution composed of the two, the following equilibrium is established:

$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$$

If a base is added to the buffer solution, the base will react with the H_3O^+ and remove some of this ion from solution. According to Le Châtelier's principle, the equilibrium will adjust by shifting to the right to make more H_3O^+ , preventing too great a pH change. It is a similar story if an acid is added. The tendency for $[H_3O^+]$ to increase is countered by a shift of the equilibrium to the left and the formation of more HX molecules.

The greater the concentrations of the two buffer components, the greater the ability of the buffer to resist changes in pH. The efficiency of the buffer is greatest when the concentrations of the two components are equal, but this condition is not necessary for the buffer to work.

The equilibrium-constant expression for the reaction above is simply $[H_3O^+][X^-]/[HX] = K_a$. From this expression, it is easy to see that when the concentration of each member of the conjugate pair is equal, $[H_3O^+] = K_a$. Thus the pH of such a buffer solution is $-\log(K_a)$.

Buffers Are All Around

Now you understand what manufacturers of shampoos and antacids mean when they say that their products are buffered: the products have ingredients that resist pH changes. The pH of foods affects their taste and texture, so many packaged foods are buffered, too. Check ingredient labels for phosphates. The presence of phosphates probably means that the product contains the acid-base pair $H_2PO_4^-/HPO_4^{2-}$ to control the pH. The liquid portion of blood is an example of a buffer solution. To keep the blood's pH very close to 7.40, the body uses a buffer in which the weak acid H_2CO_3 , carbonic acid, is paired with its conjugate base, the hydrogen carbonate ion HCO_3^- . The equation below describes the equilibrium that is established.

$$H_2CO_3(aq) + H_2O(l) \xrightarrow{\longrightarrow} H_3O^+(aq) + HCO_3^-(aq)$$

There are many medical conditions that can disrupt the equilibrium of this system. Uncontrolled diabetes can cause acidosis, in which the equilibrium is displaced too far to the right. Alcoholic intoxication causes alkalosis, in which the equilibrium lies too far to the left. Hyperventilation removes CO_2 , which is also in equilibrium with H_2CO_3 . The equilibrium will shift to the left, causing alkalosis.



UNDERSTANDING KEY IDEAS

1. Identify the stronger acid and the stronger base in the reaction described by the following equation:

 $HOCl(aq) + NH_3(aq) \xrightarrow{\longleftarrow} NH_4^+(aq) + ClO^-(aq)$

- **2.** Write the acid-ionization constant expression for the weak acid H₂SO₃.
- **3.** The hydrogen sulfite ion, HSO₃, is a weak acid in aqueous solution. Write an equation showing the equilibrium established when hydrogen sulfite is dissolved in aqueous solution, using unequal arrows to show the equilibrium.
- **4.** What is a buffer solution?
- **5.** Give two examples of the practical uses of buffers.

PRACTICE PROBLEMS

6. Use **Table 7** to determine which direction is favored in the following reaction. Explain your answer.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

- **7.** A 0.105 M solution of HOCl has a pH of 4.19. What is the acid-ionization constant?
- **8.** A buffer solution, prepared from equal amounts of an acid and its conjugate base, has a pH of 10.1. What is the K_a of the acid?
- **9.** Calculate the K_a of nitrous acid, given that a 1.00 M solution of the acid contains 0.026 mol of NO₂ per liter of solution.

CRITICAL THINKING

- **10.** Ammonia is a weak base. A 0.0123 M solution of ammonia has a hydroxide ion concentration of 4.63×10^{-4} M. Calculate the K_a of NH₄⁺.
- **11.** What would be the value of the acidionization constant for an acid that was so strong that not a single molecule remained un-ionized?
- **12.** What would be a good acid-base pair from which to prepare a buffer solution whose pH is 10.3?
- **13.** If 99.0% of the weak acid HX stays un-ionized in 1.0 M aqueous solution, what is the K_a ?
- **14.** Write all three K_a expressions for H₃PO₄. Which will have the smallest value?
- **15.** Calculate K_{eq} for the following reaction:

 $H_2CO_3(aq) + CO_3^{2-}(aq) \xrightarrow{} 2HCO_3^{-}(aq)$



CONSUMER FOCUS

Antacids

The pH of gastric juice in the human stomach is 1.5. This strongly acidic environment activates digestive enzymes, such as pepsin, that work in the stomach.

Stomach acids and antacids

Acidity in the stomach is provided by 0.03 M hydrochloric acid, HCl(*aq*). Sometimes, a person's stomach generates too much acid. The discomfort known as *heartburn* results when the acid solution is forced into the esophagus. Heartburn can be temporarily relieved by taking an antacid to neutralize the excess stomach acid.

Although antacids contain other ingredients, all antacids contain a base that counteracts stomach acid. The base is either sodium hydrogen carbonate, NaHCO₃, calcium carbonate, CaCO₃, aluminum hydroxide, Al(OH)₃, or magnesium hydroxide, Mg(OH)₂.

Dangers of excess metals from antacids

In any antacid, the anion is the base that neutralizes the stomach acid. However, the cation in the antacid is also important. Antacids containing NaHCO₃ work fastest because NaHCO₃ is much more soluble than other antacid substances are. Overusing these antacids, however, can raise the level of positive ions in the body, just as salt does. Overuse can also seriously disrupt the acid-base balance in your blood.

Because of the risks associated with an excess of sodium, some antacid manufacturers have substituted calcium carbonate, $CaCO_3$, for NaHCO₃. But if calcium is taken in large amounts, it can promote kidney stones. Ingesting too much aluminum from antacid products, such as Al(OH)₃, can interfere with the body's absorption of phosphorus, which is needed for healthy



bones. Excess magnesium from antacids that contains $Mg(OH)_2$ may pose problems for people who have kidney disorders.

You should know the active ingredient in any antacid product before you ingest the product, and you should never use an antacid product for more than a few days without consulting a doctor. It is best to avoid the need for an antacid in the first place. You can minimize the production of excess stomach acid by following a healthy diet, avoiding stress, and limiting your consumption of

Questions

1. What class of compound is common to all antacids?

coffee, fatty foods, and chocolate.

2. Why should you pay attention to which ions an antacid contains?



CHAPTER HIGHLIGHTS

KEY TERMS

strong acid weak acid strong base weak base Brønsted-Lowry acid Brønsted-Lowry base conjugate acid conjugate base amphoteric

self-ionization constant of water, K_w neutral pH indicator

neutralization reaction equivalence point titration titrant standard solution transition range end point

acid-ionization constant, *K_a* buffer solution

KEY IDEAS

SECTION ONE What Are Acids and Bases?

- Acid solutions have distinctive properties attributable to the H_3O^+ ion.
- Bases have distinctive properties attributable to the OH⁻ ion.
- Brønsted and Lowry defined an acid as donating a proton, and a base as accepting a proton.
- Every acid has a conjugate base, and every base has a conjugate acid.
- An amphoteric species, such as water, can behave as an acid or a base.

SECTION TWO Acidity, Basicity, and pH

- In aqueous solutions, $[H_3O^+]$ and $[OH^-]$ are interrelated by K_w .
- pH, which is a quantitative measure of acidity and basicity, is the negative logarithm of $[H_3O^+]$.

SECTION THREE Neutralization and Titrations

- A neutralization reaction between an acid and a base produces water.
- In a titration, a solution of unknown concentration is neutralized by a standard solution of known concentration.
- An indicator has a transition range of pH, within which lies its end point pH.

SECTION FOUR Equilibria of Weak Acids and Bases

- The acid-ionization constant reflects the strength of a weak acid and the strength of the acid's conjugate base.
- K_a can be used to calculate [H₃O⁺] in a solution of a weak acid.
- Buffer solutions are mixtures of a weak acid and its conjugate base, and resist pH changes.

KEY SKILLS

Determining [OH⁻] using K_w Sample Problem A p. 541

Calculating pH for an Acidic or Basic Solution Skills Toolkit 1 p. 543 Sample Problem B p. 544 Per Calculating $[H_3O^+]$ and $[OH^-]$

from pH Skills Toolkit 1 p. 543 Sample Problem C p. 545 **Performing a Titration** Skills Toolkit 2 p. 552

Calculating Concentration from Titration Data Sample Problem D p. 555 **Calculating** *K_a* of a Weak Acid Sample Problem E p. 560



USING KEY TERMS

- **1.** How does a strong acid differ from a weak acid?
- 2. What kind of an electrolyte is a weak base?
- **3.** How does Brønsted and Lowry's definition of an acid differ from Arrhenius's definition of an acid? Explain which definition is broader.
- **4.** What is the conjugate acid of the base ammonia, NH₃?
- 5. Why is water considered amphoteric?
- **6.** What is the concentration of hydroxide ions in pure water?
- **7.** What is the value of K_w at 25°C?
- **8.** What is the pH of a neutral solution?
- **9.** Give the equation that relates pH to hydronium ion concentration.
- **10.** How does the strength of an acid relate to the concentration of the acid? How does the strength of an acid relate to the pH of an aqueous solution of the acid? How does the concentration of an acid solution relate to the solution's pH?
- **11.** What product do all neutralization reactions have in common?
- **12.** At what point in a titration are the amounts of hydronium ions and hydroxide ions equal?
- **13.** Group the following four terms into two pairs according to how the terms are related, and explain how they are related: *end point, standard solution, titrant,* and *transition range.*

- **14.** What is the equilibrium constant that is applied to a weak acid?
- **15.** How does the addition of a small amount of acid or base affect a buffered solution?

UNDERSTANDING KEY IDEAS

What Are Acids and Bases?

- **16.** Compare the properties of an acid with those of a base.
- **17.** What is a base according to Arrhenius? according to Brønsted and Lowry?
- **18.** Why are weak acids and weak bases poor electrical conductors?
- **19.** What is the difference between the strength and the concentration of an acid?
- **20.** Identify each of the following compounds as an acid or a base according to the Brønsted-Lowry classification. For each species, write the formula and the name of its conjugate.
 - a. CH₃COO⁻
 - **b.** HCN
 - c. HOOCCOOH
 - **d.** $C_6H_5NH_3^+$
- **21.** Write an equation for the reaction between hydrocyanic acid, HCN, and water. Label the acid, base, conjugate acid, and conjugate base.
- **22.** Write chemical equations that show how the hydrogen carbonate ion, HCO_3^- , acts as an amphoteric ion.

Acidity, Basicity, and pH

23. Explain the relationship between the self-ionization of water and K_w .

- **24.** Write an equation that shows the self-ionization of water.
- **25.** Three solutions have pHs of 3, 7, and 11. Which solution is basic? Which is acidic? Which is neutral?
- **26.** By what factor does $[OH^-]$ change when the pH increases by 3? by 2? by 1? by 0.5?
- **27.** Explain how you can calculate pH from $[H_3O^+]$ by using your calculator.
- **28.** Describe two methods of measuring pH, and explain the advantages and disadvantages of each method.

Neutralization and Titrations

- **29.** What is a neutralization reaction?
- **30.** Describe two precautions that should be taken to ensure an accurate titration.
- **31.** Explain what a titration curve is, and sketch its shape.
- **32.** How would you select an indicator for a particular acid-base titration?
- **33.** Would the pH at the equivalence point of a titration of a weak acid with a strong base be less than, equal to, or greater than 7.0?
- 34. Name an indicator you might use to titrate ammonia with hydrochloric acid.

Equilibria of Weak Acids and Bases

- **35.** The K_a of nitrous acid, HNO₂, is 6.76×10^{-4} . Write the equation describing the equilibrium established when HNO₂ reacts with NH₃. Use unequal arrows to indicate whether reactants or products are favored.
- **36. a.** What is the relationship between the strength of an acid and the strength of its conjugate base?
 - **b.** What is the realtionship between the strength of a base and the strenght of its conjugate acid?

- **37.** Propanoic acid, C_2H_5COOH , is a weak acid. Write the expression defining its acid-ionization constant.
- **38.** Place the following acids in order of increasing strength:
 - **a.** valeric acid, $K_a = 1.5 \times 10^{-5}$
 - **b.** glutaric acid, $K_a = 3.4 \times 10^{-4}$
 - **c.** hypobromous acid, $K_a = 2.5 \times 10^{-9}$
 - **d.** acetylsalicylic acid (aspirin),

 $K_a = 3.3 \times 10^{-4}$

39. What are the components of a buffer solution? Give an example.

PRACTICE PROBLEMS



Sample Problem A Determining [OH⁻] or $[H_3O^+]$ Using K_w

- **40.** If the hydronium ion concentration of a solution is 1.63×10^{-8} M, what is the hydroxide ion concentration?
- **41.** Calculate the hydronium ion concentration in a solution of 0.365 mol/L of NaOH.
- 42. How much HCl would you need to dissolve in 1.0 L of water so that $[OH^{-}] =$ $6.0 \times 10^{-12} \text{ M}?$
- 43. The hydronium ion concentration in a solution is 1.87×10^{-3} mol/L. What is [OH⁻]?
- 44. If 0.150 mol of KOH is dissolved in 500 mL of water, what are $[OH^{-}]$ and $[H_{3}O^{+}]$?
- **45.** If a solution contains twice the concentration of hydronium ions as hydroxide ions, what is the hydronium ion concentration?

Sample Problem B Calculating pH for an **Acidic or Basic Solution**

- **46.** Stomach acid contains HCl, whose concentration is about 0.03 mol/L. What is the pH of stomach acid?
- **47.** If $[OH^-]$ of an aqueous solution is 0.0134 mol/L, what is the pH?

- **48.** What is the pH of a 0.15 M solution of HClO₄, a strong acid?
- **49.** LiOH is a strong base. What is the pH of a 0.082 M LiOH solution?
- **50.** Find the pH of a solution consisting of 0.29 mol of HBr in 1.0 L of water.
- 51. What is the pH of aqueous solutions of the strong acid HNO₃, nitric acid, if the concentrations of the solutions are as follows:
 (a) 0.005 M, (b) 0.05 M, (c) 0.5 M, (d) 5 M?
- **52.** Find the pH of a solution prepared by dissolving 0.65 mol of the strong base NaOH in 1.0 L of water.
- 53. What is the pH of a solution prepared by dissolving 0.15 mol of the strong base Ba(OH)₂ in one liter of water? (Hint: How much hydroxide ion does barium hydroxide generate per mole in solution?)
- **54.** A solution has a hydronium ion concentration of 1.0×10^{-9} M. What is its pH?
- **55.** If a solution has a hydronium ion concentration of 6.7×10^{-1} M, what is its pH?
- **56.** What is the pH of a solution whose hydronium ion concentration is 2.2×10^{-12} M?
- **57.** What is the pH of a solution whose H_3O^+ concentration is 1.9×10^{-6} M?
- **58.** Calculate the pH of a 0.0316 M solution of the strong base RbOH.

Sample Problem C Calculating $[H_3O^+]$ and $[OH^-]$ from pH

- **59.** The pH of a solution is 9.5. What is [H₃O⁺]? What is [OH⁻]?
- **60.** A solution of a weak acid has a pH of 4.7. What is the hydronium ion concentration?
- 61. A 50 mL sample of apple juice has a pH of 3.2. What amount, in moles, of H₃O⁺ is present?
- **62.** Find $[H_3O^+]$ in a solution of pH 4.

- **63.** What is the hydroxide ion concentration in a solution of pH 8.72?
- **64.** Calculate the concentration of the H_3O^+ and OH^- ions in an aqueous solution of pH 5.0.
- **65.** A solution has a pH of 10.1. Calculate the hydronium ion concentration and the hydroxide ion concentration.
- **66.** What is the hydronium ion concentration in a solution of pH 5.5?
- **67.** If the pH of a solution is 4.3, what is the hydroxide ion concentration?
- **68.** What is the hydronium ion concentration in a solution whose pH is 10.0?
- **69.** The pH of a solution is 3.0. What is $[H_3O^+]$?
- **70.** What is $[H_3O^+]$ in a solution whose pH is 1.9?
- **71.** If a solution has a pH of 13.3, what is its hydronium ion concentration?

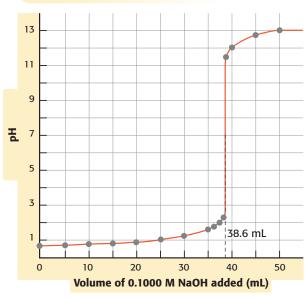
Skills Toolkit Performing a Titration

- **72.** To what volumetric mark should a buret be filled?
- **73.** Why is it important to slow down the drop rate of the buret near the end of a titration?
- **74.** What two buret readings need to be recorded in order to determine the volume of solution dispensed by the buret?

Sample Problem D Calculating Concentration from Titration Data

- **75.** What volume of 0.100 M NaOH is required to neutralize 25.00 mL of 0.110 M H₂SO₄?
- **76.** What volume of 0.100 M NaOH is required to neutralize 25.00 mL of 0.150 M HCl?
- **77.** If 35.40 mL of 1.000 M HCl is neutralized by 67.30 mL of NaOH, what is the molarity of the NaOH solution?
- **78.** If 50.00 mL of 1.000 M HI is neutralized by 35.41 mL of KOH, what is the molarity of the KOH solution?

- **79.** If 133.73 mL of a standard solution of KOH, of concentration 0.298 M, exactly neutralized 50.0 mL of an acidic solution, what was the acid concentration?
- 80. To standardize a hydrochloric acid solution, it was used as titrant with a solid sample of sodium hydrogen carbonate, NaHCO₃. The sample had a mass of 0.3967 g, and 41.77 mL of acid was required to reach the equivalence point. Calculate the concentration of the standard solution.



Strong Acid Titrated with Strong Base

- 81. The graph above shows a titration curve obtained during the titration of a 25.00 mL sample of an acid with 0.1000 M NaOH. Calculate the concentration of the acid.
- **82.** An HNO₃ solution has a pH of 3.06. What volume of 0.015 M LiOH will be required to titrate 65.0 mL of the HNO₃ solution to reach the equivalence point?

Sample Problem E Calculating *K_a* of a Weak Acid

83. The hydronium ion concentration in a 0.100 M solution of formic acid is 0.0043 M. Calculate K_a for formic acid.

- **84.** $[NO_2^-] = 9.1 \times 10^{-3}$ mol/L in a nitrous acid solution of concentration 0.123 mol/L. What is K_a for HNO₂?
- **85.** A solution of acetic acid had the following solute concentrations: $[CH_3COOH] =$ $0.035 \text{ M}, [H_3O^+] = 7.4 \times 10^{-4} \text{ M}, \text{ and}$ $[CH_3COO^-] = 7.4 \times 10^{-4} \text{ M}.$ Calculate the K_a of acetic acid based on these data.
- **86.** Hydrazoic acid, HN_3 , is a weak acid. A 0.01 M solution of hydrazoic acid contained a concentration of 0.0005 M of the N_3^- ion. Find the acid-ionization constant of hydrazoic acid.

MIXED REVIEW

- **87.** If 25 mL of 1.00 M HCl is mixed with 75 mL of 1.00 M NaOH, what are the final amounts and concentrations of all ions present?
- **88.** When 1.0 mol of a weak acid was dissolved in 10.0 L of water, the pH was found to be 3.90. What is K_a for the acid?
- **89.** At the end point of a titration of 25 mL of 0.300 M NaOH with 0.200 M HNO₃, what would the concentration of sodium nitrate in the titration flask be?
- 90. Make a table listing the ionic concentrations in solutions of the following pH values: 14.25, 14.00, 13.75, 13.25, 13.00, 7.25, 7.00, 6.75, 1.00, 0.75, 0.50, 0.25, 0.00, and -0.25.
- **91.** Write the equilibrium equation and the equilibrium constant expression for an ammonia–ammonium ion buffer solution.
- **92.** If 18.5 mL of a 0.0350 M H_2SO_4 solution neutralizes 12.5 mL of aqueous LiOH, what mass of LiOH was used to make 1.00 L of the LiOH solution?
- **93.** Use **Table 7** to calculate the pH of a buffer solution made from equal amounts of sodium monohydrogen phosphate and potassium dihydrogen phosphate.

CRITICAL THINKING

- **94.** Why is a buret, rather than a graduated cylinder, used in titrations?
- **95.** A small volume of indicator solution is usually added to the titration flask right before the titration. As a result, the sample is diluted slightly. Does this matter? Why or why not?
- **96.** A student passes an end point in a titration. Is it possible to add an additional measured amount of the unknown and continue the titration? Explain how this process might work. How would the answer for the calculation of the molar concentration of the unknown differ from the answer the student would have gotten if the titration had been performed properly?

Indicator	Acid color	pH transition range	Base color	
Thymol red blue		1.2–2.8	yellow	
Bromphenol yellow blue		3.0-4.6	blue	
Bromcresol green	yellow	2.0–5.6	blue	
Bromthymol blueyellowPhenol redyellow		6.0–7.6	blue	
		6.6–8.0	red	
Alizarin yellow	yellow	10.1–12.0	red	

- **97.** Refer to the table above to answer the following questions:
 - **a.** Which indicator would be the best choice for a titration with an end point at a pH of 4.0?
 - **b.** Which indicators would work best for a titration of a weak base with a strong acid?
- **98.** Why does an indicator need to be a weak acid or a weak base?

- **99.** Explain the difference between *end point* and *equivalence point*. Why is it important that both occur at approximately the same pH in a titration?
- 100. Can you neutralize a strong acid solution by adding an equal volume of a weak base having the same molarity as the acid? Support your position.
- **101.** In the 18th century, Antoine Lavoisier experimented with oxides such as CO_2 and SO_2 . He observed that they formed acidic solutions. His observations led him to infer that for a substance to exhibit acidic behavior, it must contain oxygen. However, today that is known to be incorrect. Provide evidence to refute Lavoisier's conclusion.

ALTERNATIVE ASSESSMENT

- **102.** Design an experiment to test the neutralization effectiveness of various brands of antacid. Show your procedure, including all safety procedures and cautions, to your teacher for approval. If your teacher approves your plan, carry it out. After experimenting, write an advertisement for the antacid you judge to be the most effective. Cite data from your experiments as part of your advertising claims.
- **103.** Describe how you would prepare one or more buffer solutions, including which compounds to use. Predict the pH of each solution. If your teacher provides the needed materials, measure the pH to test your prediction.

CONCEPT MAPPING

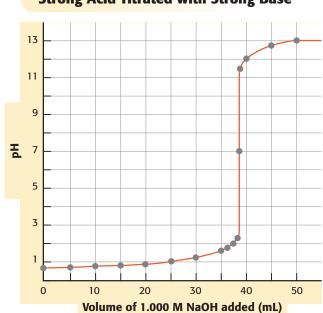


104. Use the following terms to create a concept map: *hydronium ions* (*H*₃*O*⁺), *hydroxide ions* (*OH*⁻), *neutralization reaction*, *pH*, and *titration*.

FOCUS ON GRAPHING

Study the graph below, and answer the questions that follow. For help in interpreting graphs, see Appendix B, "Study Skills for Chemistry."

- **105.** What variable is being measured along the *x*-axis?
- **106.** What is the pH at the beginning of the titration?
- **107.** What was the pH after 25 mL of titrant had been added?
- **108.** What volume of titrant was needed to reach a pH of 2.0?
- **109.** Where on the graph do you find the single most important data point?
- **110.** If the titration continued beyond what the graph shows, how would you expect the pH to change past the end of the graph?
- 111. Roughly sketch the titration curve (pH versus volume) that you would expect if you titrated a weak base with a strong acid. Mark the equivalence point.



Strong Acid Titrated with Strong Base

TECHNOLOGY AND LEARNING

112. Graphing Calculator

Graphing Titration Data

The graphing calculator can run a program that graphs data such as pH versus volume of base. Graphing the titration data will allow you to determine which combination of acid and base is represented by the shape of the graph.

Go to Appendix C. If you are using a TI-83 Plus, you can download the program and data and run the application as directed. Press the APPS key on your calculator, then choose the application CHEMAPPS. Press 5, then highlight ALL on the screen, press 1, then highlight LOAD and press 2 to load the data into your calculator. Quit the application, and then run the program TITRATN. For L_1 , press 2nd and LIST, and choose VOL1. For L_2 , press 2nd and LIST and choose PH1. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use.

- **a.** At what approximate volume does the pH change from acidic to basic?
- **b.** If the titrant was 0.24 M NaOH, and the volume of unknown was 230 mL, what was $[H_3O^+]$ in the unknown solution?

STANDARDIZED TEST PREP

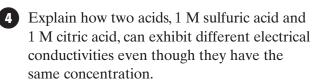


UNDERSTANDING CONCEPTS

Directions (1–3): For *each* question, write on a separate sheet of paper the letter of the correct answer.

- Which of the following solutions would have a pH value greater than 7?
 A. 0.0001 M HCl
 - **B.** $[H_30^+] = 1.3 \times 10^{-2} M$
 - **C.** $[OH^{-}] = 2.4 \times 10^{-2} M$
 - **D.** $[OH^{-}] = 4.4 \times 10^{-9} M$
- 2 What happens when a strong acid reacts with a metal?
 - **F.** The K_w value changes.
 - **G.** The metal forms anions.
 - **H.** Hydrogen gas is produced.
 - **I.** The hydronium ion concentration increases.
- **3** Which of the following is true of a neutral aqueous solution?
 - **A.** Its H_3O^+ ion concentration is 7.0 M.
 - **B.** It contains buffers that resist a change in pH.
 - **C.** It contains neither hydronium ions nor hydroxide ions.
 - **D.** It has an equal number of hydronium ions and hydroxide ions.

Directions (4–6): For *each* question, write a short response.



```
5 What are the concentrations of all the components of a benzoic acid solution if Ka is 6.5 \times 10^{-5}, pH is 2.96 and C<sub>6</sub>H<sub>5</sub>COOH has a concentration of 0.020 M?
```

6 What would be a suitable titrant (compound and concentration) with which to titrate 20.00 mL of a strong acid that has a concentration of about 0.015 M?

READING SKILLS

Directions (7–8): Read the passage below. Then answer the questions.

In 1987 Dr. Ken Simmons tested rainbow trout in the waters of Whetstone Brook in MA. He discovered that when the pH was 5.97, the trout did not spawn. Along with other scientists, he started an experiment to reduce the acidity of the stream by adding calcium carbonate, or limestone, in measured amounts. The calcium carbonate reacts with acid but is not toxic to the environment and does not risk raising the pH too much. The experiment caused the pH to rise to 6.54 over a three-year period. As a result the population of trout in the treated area increased and their health improved. According to Dr. Simmons, this is not a permanent solution, but rather a band-aid approach to the problem of stream acidification by acid rain.



Why is it important to use limestone to raise the pH rather than simply adding enough strong base to raise the pH to the desired value?

- **F.** Strong bases are not natural products.
- **G.** A strong base would cause a bad odor in the stream.
- **H.** Strong bases could make too great a change in pH.
- **I.** Calcium carbonate is much less expensive than strong bases.

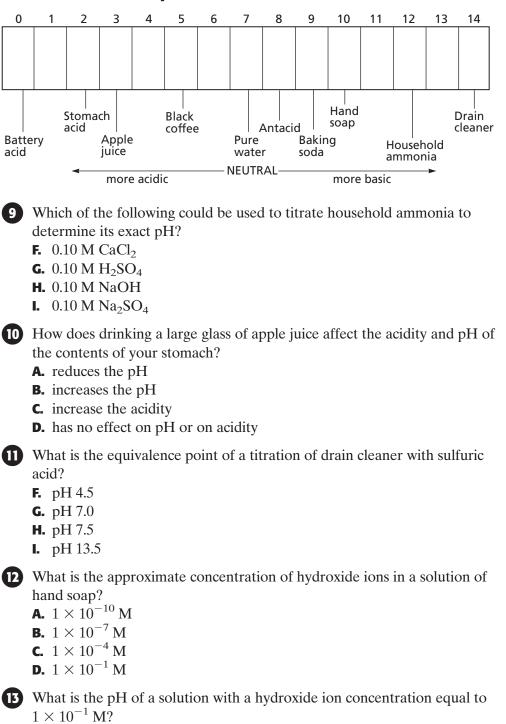
8 By approximately what factor did [OH⁻] change during this experiment?

А.	0.5	С.	3.8
В.	1.0	D.	12.0

INTERPRETING GRAPHICS

Directions (9–13): For *each* question below, record the correct answer on a separate sheet of paper.

The pH of common materials found around your home varies across the entire range shown on the chart below. Use this chart to answer questions 9 through 13.









If you are unsure of the correct answer to a multiple-choice question, start by crossing out answers that you know are wrong. Reducing the number of answer choices in this way may help you choose the correct answer.

CHAPTER

16 REACTION RATES