Acids and Bases

Acids and bases change the color of compounds called indicators.

Hydrangeas

Properties of Acids and Bases

How many foods can you think of that are sour? Chances are that almost all the foods you thought of, like those in **Figure 1a,** owe their sour taste to an acid. Sour milk contains *lactic acid.* Vinegar, which can be produced by fermenting juices, contains *acetic acid. Phosphoric acid* gives a tart flavor to many carbonated beverages. Most fruits contain some kind of acid. Lemons, oranges, grapefruits, and other citrus fruits contain *citric acid.* Apples contain *malic acid,* and grape juice contains *tartaric acid*.

Many substances known as bases are commonly found in household products, such as those in **Figure 1b.** Household ammonia is an ammonia-water solution that is useful for all types of general cleaning. Sodium hydroxide, NaOH, known by the common name *lye,* is present in some commercial cleaners. Milk of magnesia is a suspension in water of magnesium hydroxide, $Mg(OH)_2$, which is not very water-soluble. It is used as an antacid to relieve discomfort caused by excess hydrochloric acid in the stomach. Aluminum hydroxide, $Al(OH)_3$, and sodium hydrogen carbonate, $NaHCO_3$, are also bases commonly found in antacids.

Benzoic acid, $HC_7H_5O_2$
Sorbic acid, $HC_6H_7O_2$
Phosphoric acid, H_3PO_4
Carbonic acid, H_2CO_3

Citric acid, $H_3C_6H_5O_7$
Ascorbic acid, $H_2C_6H_6O_6$

$NH_3(aq)$

NaOH

$NaHCO_3$

$Al(OH)_3$

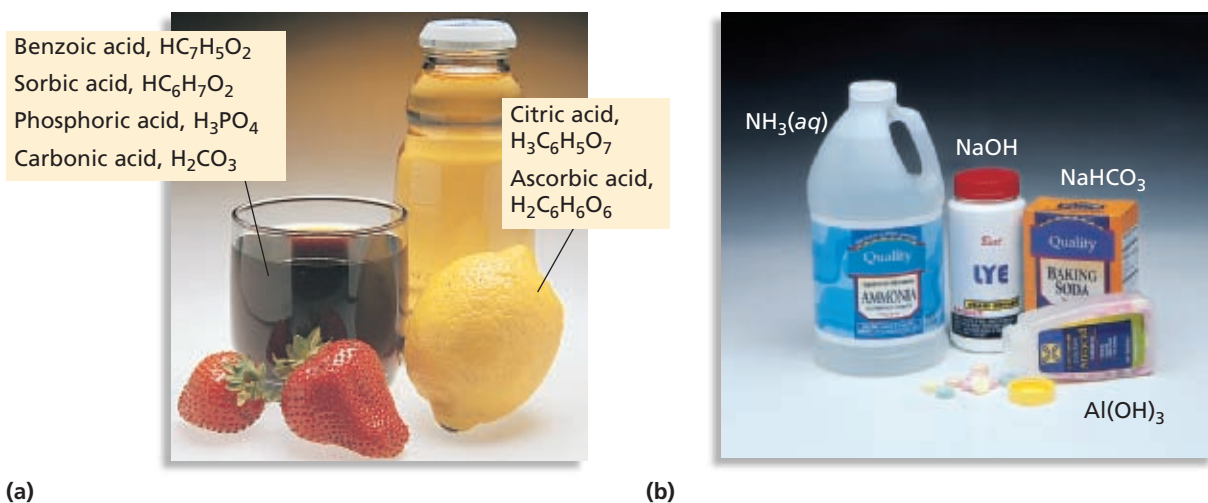**(a)**   **(b)**

FIGURE 1   (a) Fruits and fruit juices contain acids such as citric acid and ascorbic acid. Carbonated beverages contain benzoic acid, phosphoric acid, and carbonic acid. (b) Many household cleaners contain bases such as ammonia and sodium hydroxide. Antacids contain bases such as aluminum hydroxide.

Acids

Acids were first recognized as a distinct class of compounds because of the common properties of their aqueous solutions. These properties are listed below.

1. *Aqueous solutions of acids have a sour taste.* Taste, however, should NEVER be used as a test to evaluate any chemical substance. Many acids, especially in concentrated solutions, are corrosive; that is, they destroy body tissue and clothing. Many are also poisons.
2. *Acids change the color of acid-base indicators.* When pH paper is used as an indicator, the paper turns certain colors in acidic solution. This reaction is demonstrated in **Figure 2.**
3. *Some acids react with active metals and release hydrogen gas, H_2.* Recall that metals can be ordered in terms of an activity series. Metals above hydrogen in the series undergo single-displacement reactions with certain acids. Hydrogen gas is formed as a product, as shown by the reaction of barium with sulfuric acid.

$$Ba(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2(g)$$

4. *Acids react with bases to produce salts and water.* When chemically equivalent amounts of acids and bases react, the three properties just described disappear because the acid is "neutralized." The reaction products are water and an ionic compound called a *salt.*
5. *Acids conduct electric current.* Some acids completely separate into ions in water and are strong electrolytes. Other acids are weak electrolytes.

Acid Nomenclature

A **binary acid** *is an acid that contains only two different elements: hydrogen and one of the more electronegative elements.* Many common inorganic acids are binary acids. The hydrogen halides—HF, HCl, HBr, and HI—are all binary acids.

The procedure used to name binary acids is illustrated by the examples given in **Table 1.** In pure form, each compound listed in the table is a gas. Aqueous solutions of these compounds are known by the acid names. From the table you can see that naming binary compounds can be summarized as follows.

TABLE 1 *Names of Binary Acids*

Formula	Acid name	Molecule name
HF	hydrofluoric acid	hydrogen fluoride
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
HI	hydriodic acid	hydrogen iodide
H_2S	hydrosulfuric acid	hydrogen sulfide
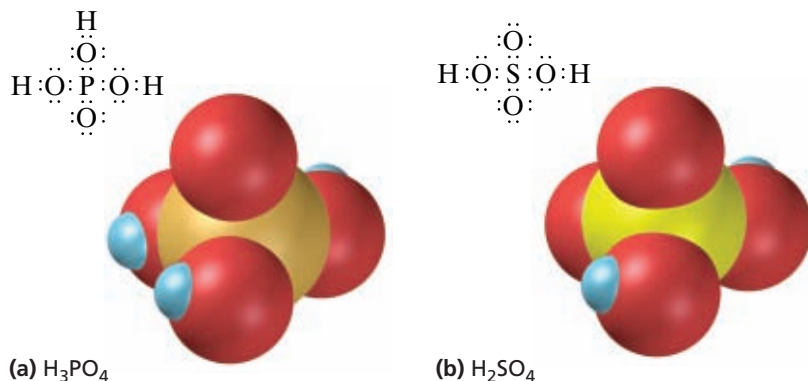
FIGURE 3   Structures of (a) phosphoric acid and (b) sulfuric acid

(a) H_3PO_4 **(b)** H_2SO_4

Binary Acid Nomenclature

1. The name of a binary acid begins with the prefix *hydro-*.
2. The root of the name of the second element follows this prefix.
3. The name then ends with the suffix *-ic*.

An **oxyacid** *is an acid that is a compound of hydrogen, oxygen, and a third element, usually a nonmetal.* Nitric acid, HNO_3, is an oxyacid. The structures of two other oxyacids are shown in **Figure 3.** Oxyacids are one class of ternary acids, which are acids that contain three different elements. Usually, the elements in an oxyacid formula are written as one or more hydrogen atoms followed by a polyatomic anion. But as you can see from the structures, the H atoms are bonded to O atoms. The names of oxyacids follow a pattern, and the names of their anions are based on the names of the acids. Some common oxyacids and their anions are given in **Table 2.**

TABLE 2   *Names of Common Oxyacids and Oxyanions*

Formula	Acid name	Anion
CH_3COOH	acetic acid	CH_3COO^-, acetate
H_2CO_3	carbonic acid	CO_3^{2-}, carbonate
$HClO$	hypochlorous acid	ClO^-, hypochlorite
$HClO_2$	chlorous acid	ClO_2^-, chlorite
$HClO_3$	chloric acid	ClO_3^-, chlorate
$HClO_4$	perchloric acid	ClO_4^-, perchlorate
HIO_3	iodic acid	IO_3^-, iodate
HNO_2	nitrous acid	NO_2^-, nitrite
HNO_3	nitric acid	NO_3^-, nitrate
H_3PO_3	phosphorous acid	PO_3^{3-}, phosphite
H_3PO_4	phosphoric acid	PO_4^{3-}, phosphate
H_2SO_3	sulfurous acid	SO_3^{2-}, sulfite
H_2SO_4	sulfuric acid	SO_4^{2-}, sulfate

Some Common Industrial Acids

The properties of acids make them important chemicals both in the laboratory and in industry. Sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, and acetic acid are all common industrial acids.

Sulfuric Acid

Sulfuric acid is the most commonly produced industrial chemical in the world. More than 37 million metric tons of it are made each year in the United States alone. Sulfuric acid is used in large quantities in petroleum refining and metallurgy as well as in the manufacture of fertilizer. It is also essential to a vast number of industrial processes, including the production of metals, paper, paint, dyes, detergents, and many chemical raw materials. Sulfuric acid is the acid used in automobile batteries.

Because it attracts water, concentrated sulfuric acid is an effective dehydrating (water-removing) agent. It can be used to remove water from gases with which it does not react. Sugar and certain other organic compounds are also dehydrated by sulfuric acid. Skin contains organic compounds that are attacked by concentrated sulfuric acid, which can cause serious burns.

Nitric Acid

Pure nitric acid is a volatile, unstable liquid. Dissolving the acid in water makes the acid more stable. Solutions of nitric acid are widely used in industry. Nitric acid also stains proteins yellow. The feather in **Figure 4** was stained by nitric acid. The acid has a suffocating odor, stains skin, and can cause serious burns. It is used in making explosives, many of which are nitrogen-containing compounds. It is also used to make rubber,
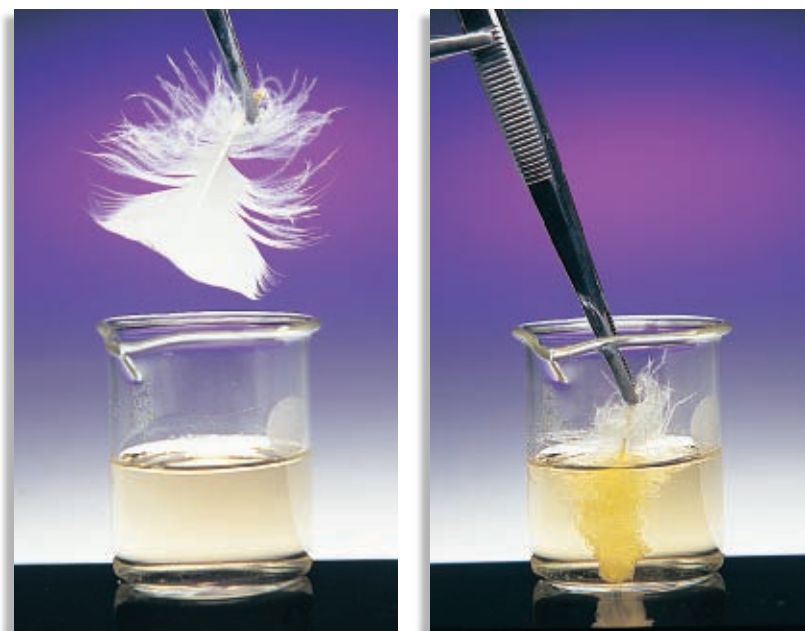
FIGURE 4   Concentrated nitric acid stains a feather yellow.

plastics, dyes, and pharmaceuticals. Initially, nitric acid solutions are colorless; however, upon standing, they gradually become yellow because of slight decomposition to brown nitrogen dioxide gas.

Phosphoric Acid

Phosphorus, along with nitrogen and potassium, is an essential element for plants and animals. The bulk of phosphoric acid produced each year is used directly for manufacturing fertilizers and animal feed. Dilute phosphoric acid has a pleasant but sour taste and is not toxic. It is used as a flavoring agent in beverages and as a cleaning agent for dairy equipment. Phosphoric acid is also important in the manufacture of detergents and ceramics.

Hydrochloric Acid

The stomach produces HCl to aid in digestion. Industrially, hydrochloric acid is important for "pickling" iron and steel. Pickling is the immersion of metals in acid solutions to remove surface impurities. This acid is also used in industry as a general cleaning agent, in food processing, in the activation of oil wells, in the recovery of magnesium from sea water, and in the production of other chemicals.

Concentrated solutions of hydrochloric acid, commonly referred to as *muriatic acid,* can be found in hardware stores. It is used to maintain the correct acidity in swimming pools and to clean masonry.

Acetic Acid

Pure acetic acid is a clear, colorless, and pungent-smelling liquid known as *glacial acetic acid.* This name is derived from the fact that pure acetic acid has a freezing point of 17°C. It can form crystals in a cold room. The fermentation of certain plants produces vinegars containing acetic acid. White vinegar contains 4% to 8% acetic acid.

Acetic acid is important industrially in synthesizing chemicals used in the manufacture of plastics. It is a raw material in the production of food supplements—for example, lysine, an essential amino acid. Acetic acid is also used as a fungicide.

Bases

How do bases differ from acids? You can answer this question by comparing the following properties of bases with those of acids.

1. *Aqueous solutions of bases taste bitter.* You may have noticed this fact if you have ever gotten soap, a basic substance, in your mouth. As with acids, taste should NEVER be used to test a substance to see if it is a base. Many bases are caustic; they attack the skin and tissues, causing severe burns.
2. *Bases change the color of acid-base indicators.* As **Figure 5** shows, an indicator will be a different color in a basic solution than it would be in an acidic solution.
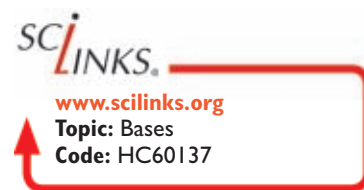

FIGURE 5 pH paper turns blue in the presence of this solution of sodium hydroxide.

QuickLAB

Household Acids and Bases

Question

Which of the household substances are acids, and which are bases?

Procedure

Record all your results in a data table.

1. To make an acid-base indicator, extract juice from red cabbage. First, cut up some red cabbage and place it in a large beaker. Add enough water so that the beaker is half full. Then, bring the mixture to a boil. Let it cool, and then pour off and save the cabbage juice. This solution is an acid-base indicator.

2. Assemble foods, beverages, and cleaning products to be tested.

3. If the substance being tested is a liquid, pour about 5 mL into a small beaker. If it is a solid, place a small amount into a beaker, and moisten it with about 5 mL of water.

4. Add a drop or two of the red cabbage juice to the solution being tested, and note the color. The solution will turn red if it is acidic and green if it is basic.

Discussion

1. Are the cleaning products acids, bases, or neither?

2. What are acid/base characteristics of foods and beverages?

3. Did you find consumer warning labels on basic or acidic products?

Materials

- **dishwashing liquid, dishwasher detergent, laundry detergent, laundry stain remover, fabric softener, and bleach**
- **mayonnaise, baking powder, baking soda, white vinegar, cider vinegar, lemon juice, soft drinks, mineral water, and milk**
- **fresh red cabbage**
- **hot plate**
- **beaker, 500 mL or larger**
- **beakers, 50 mL**
- **spatula**
- **tap water**
- **tongs**

Red cabbage, which contains an anthocyanin pigment, can be made into an acid-base indicator.

3. *Dilute aqueous solutions of bases feel slippery.* You encounter this property of aqueous bases whenever you wash with soap.

4. *Bases react with acids to produce salts and water.* The properties of a base disappear with the addition of an equivalent amount of an acid. It could also be said that "neutralization" of the base occurs when these two substances react to produce a salt and water.

5. *Bases conduct electric current.* Like acids, bases form ions in aqueous solutions and are thus electrolytes.
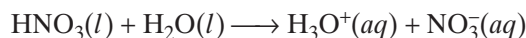
Arrhenius Acids and Bases

Svante Arrhenius, a Swedish chemist who lived from 1859 to 1927, understood that aqueous solutions of acids and bases conducted electric current. Arrhenius therefore theorized that acids and bases must produce ions in solution. *An **Arrhenius acid** is a chemical compound that increases the concentration of hydrogen ions, H^+, in aqueous solution.* In other words, an acid will ionize in solution, increasing the number of hydrogen ions present. *An **Arrhenius base** is a substance that increases the concentration of hydroxide ions, OH^-, in aqueous solution.* Some bases are ionic hydroxides. These bases dissociate in solution to release hydroxide ions into the solution. Other bases are substances that react with water to remove a hydrogen ion, leaving hydroxide ions in the solution.

Aqueous Solutions of Acids

The acids described by Arrhenius are molecular compounds with ionizable hydrogen atoms. Their water solutions are known as *aqueous acids*. All aqueous acids are electrolytes.

Because acid molecules are sufficiently polar, water molecules attract one or more of their hydrogen ions. Negatively charged anions are left behind. As explained in Chapter 13, the hydrogen ion in aqueous solution is best represented as H_3O^+, the hydronium ion. The ionization of an HNO_3 molecule is shown by the following equation. **Figure 6** also shows how the hydronium ion forms when nitric acid reacts with water.

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

Similarly, ionization of a hydrogen chloride molecule in hydrochloric acid can be represented in the following way.

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

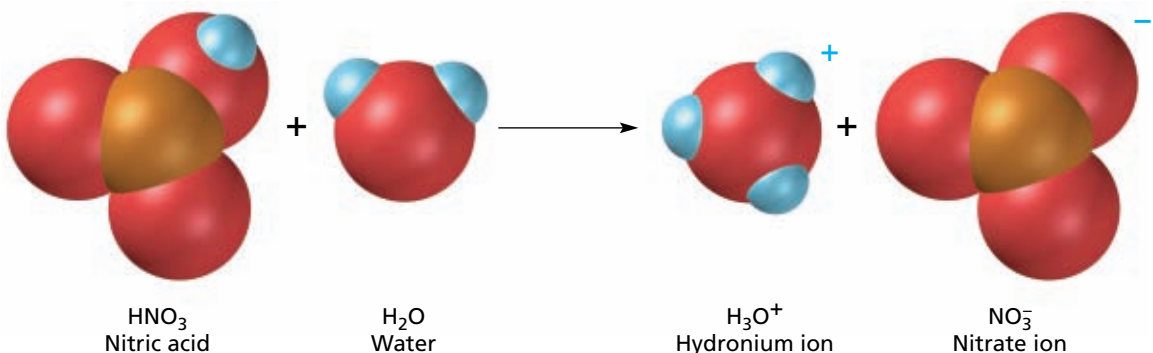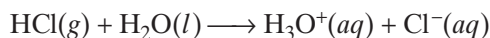| HNO_3 | H_2O | H_3O^+ | NO_3^- |
| Nitric acid | Water | Hydronium ion | Nitrate ion |

FIGURE 6 Arrhenius's observations form the basis of a definition of acids. Arrhenius acids, such as the nitric acid shown here, produce hydronium ions in aqueous solution.
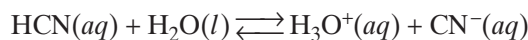
TABLE 3 *Common Aqueous Acids*

| Strong acids	Weak acids		
$HI + H_2O \longrightarrow H_3O^+ + I^-$	$HSO_4^- + H_2O$	$\rightleftharpoons H_3O^+ + SO_4^{2-}$	
$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$	$H_3PO_4 + H_2O$	$\rightleftharpoons H_3O^+ + H_2PO_4^-$	
$HBr + H_2O \longrightarrow H_3O^+ + Br^-$	$HF + H_2O$	$\rightleftharpoons H_3O^+ + F^-$	
$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$	$CH_3COOH + H_2O$	$\rightleftharpoons H_3O^+ + CH_3COO^-$	
$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$	$H_2CO_3 + H_2O$	$\rightleftharpoons H_3O^+ + HCO_3^-$	
$HClO_3 + H_2O \longrightarrow H_3O^+ + ClO_3^-$	$H_2S + H_2O$	$\rightleftharpoons H_3O^+ + HS^-$	
	$HCN + H_2O$	$\rightleftharpoons H_3O^+ + CN^-$	
	$HCO_3^- + H_2O$	$\rightleftharpoons H_3O^+ + CO_3^{2-}$	

Strength of Acids

A **strong acid** *is one that ionizes completely in aqueous solution.* A strong acid is a strong electrolyte. Perchloric acid, $HClO_4$, hydrochloric acid, HCl, and nitric acid, HNO_3, are examples of strong acids. In water, 100% of the acid molecules are ionized. The strength of an acid depends on the polarity of the bond between hydrogen and the element to which it is bonded and the ease with which that bond can be broken. Acid strength increases with increasing polarity and decreasing bond energy.

An acid that releases few hydrogen ions in aqueous solution is a **weak acid.** The aqueous solution of a weak acid contains hydronium ions, anions, and dissolved acid molecules. Hydrocyanic acid is an example of a weak acid. In aqueous solution, both the ionization of HCN and the reverse reaction occur simultaneously. In a 1 M solution of HCN there will be only two H^+ ions and two CN^- ions out of 100,000 molecules. The other 99,998 molecules remain as HCN.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Common aqueous acids are listed in **Table 3.** Each strong acid ionizes completely in aqueous solution to give up one hydrogen ion per molecule. Notice that the number of hydrogen atoms in the formula does not indicate acid strength. Molecules with multiple hydrogen atoms may not readily give up each hydrogen. The fact that phosphoric acid has three hydrogen atoms per molecule does not mean that it is a strong acid. None of these ionize completely in solution, so phosphoric acid is weak.

Organic acids, which contain the acidic carboxyl group —COOH, are generally weak acids. For example, acetic acid, CH_3COOH, ionizes slightly in water to give hydronium ions and acetate ions, CH_3COO^-.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
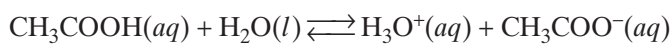
A molecule of acetic acid contains four hydrogen atoms. However, only one of the hydrogen atoms is ionizable. The hydrogen atom in the

carboxyl group in acetic acid is the one that is "acidic" and forms the hydronium ion. This acidic hydrogen can be seen in the structural diagram in **Figure 7.**
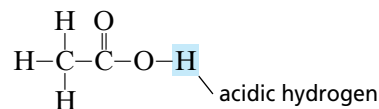
FIGURE 7 Acetic acid contains four hydrogen atoms, but only one of them is "acidic" and forms the hydronium ion in solution.

Aqueous Solutions of Bases

Most bases are ionic compounds containing metal cations and the hydroxide anion, OH^-. Because these bases are ionic, they dissociate when dissolved in water. When a base completely dissociates in water to yield aqueous OH^- ions, the solution is referred to as strongly basic. Sodium hydroxide, NaOH, is a common laboratory base. It is water-soluble and dissociates as shown by the equation below.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

You will remember from Chapter 5 that Group 1 elements are the alkali metals. This group gets its name from the fact that the hydroxides of Li, Na, K, Rb, and Cs all form alkaline (basic) solutions.

Not all bases are ionic compounds. A base commonly used in household cleaners is ammonia, NH_3, which is molecular. Ammonia is a base because it produces hydroxide ions when it reacts with water molecules, as shown in the equation below.

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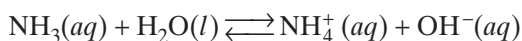
Strength of Bases

As with acids, the strength of a base also depends on the extent to which the base dissociates, or adds hydroxide ions to the solution. For example, potassium hydroxide, KOH, is a strong base because it completely dissociates into its ions in dilute aqueous solutions.

$$KOH(s) \xrightarrow{H_2O} K^+(aq) + OH^-(aq)$$
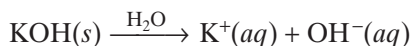
Strong bases are strong electrolytes, just as strong acids are strong electrolytes. **Table 4** lists some strong bases.

extension

Chemistry in Action

Go to **go.hrw.com** for a full-length article on drain cleaners.

Keyword: HC6ACDX

TABLE 4 *Common Aqueous Bases*	
Strong bases	**Weak bases**
$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$	
$NaOH \longrightarrow Na^+ + OH^-$	
$KOH \longrightarrow K^+ + OH^-$	
$RbOH \longrightarrow Rb^+ + OH^-$	
$CsOH \longrightarrow Cs^+ + OH^-$	

Na$^+$(aq) + OH$^-$(aq)

Chloride ion, Cl$^-$

Sodium ion, Na$^+$

Cu(OH)$_2$(s)

Chloride ion, Cl$^-$

Copper(II) ion, Cu^{2+}

Water molecule, H$_2$O

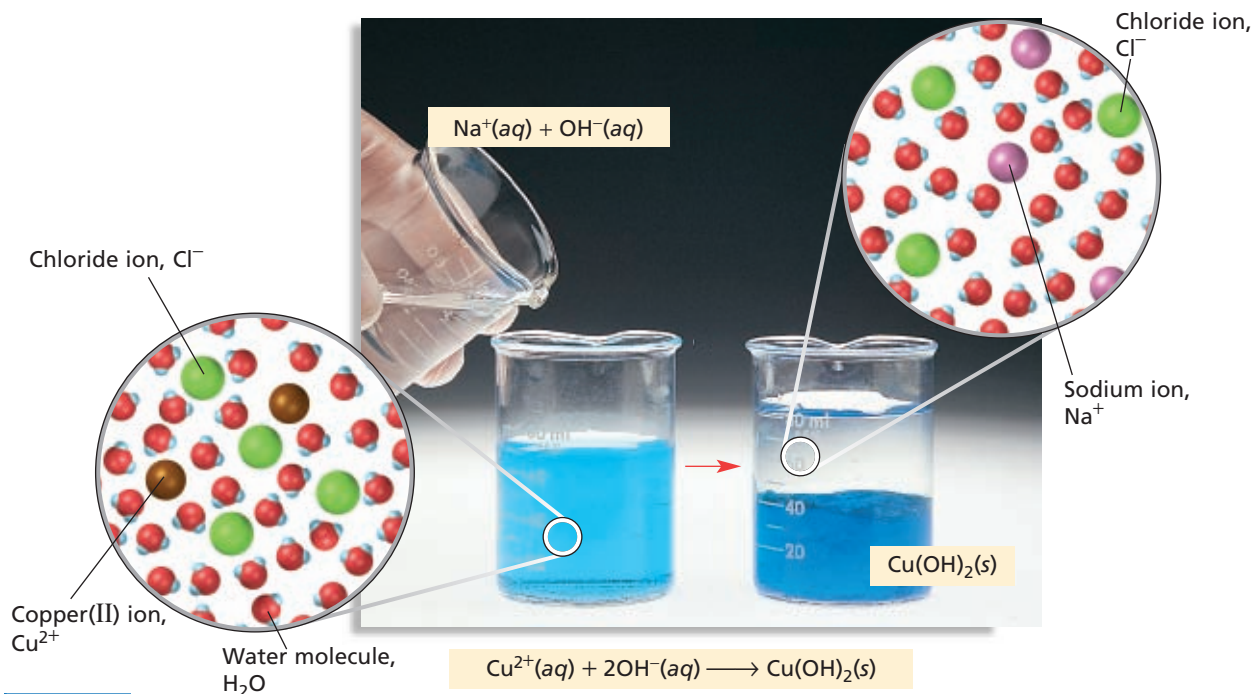Cu^{2+}(aq) + 2OH$^-$(aq) $\longrightarrow$ Cu(OH)$_2$(s)

FIGURE 8 The hydroxides of most *d*-block metals are nearly insoluble in water, as is shown by the gelatinous precipitate, copper(II) hydroxide, Cu(OH)$_2$, in the beaker on the right.

Bases that are not very soluble do not produce a large number of hydroxide ions when added to water. Some metal hydroxides, such as Cu(OH)$_2$, are not very soluble in water, as seen in **Figure 8.** They cannot produce strongly alkaline solutions. The alkalinity of aqueous solutions depends on the concentration of OH$^-$ ions in solution. It is unrelated to the number of hydroxide ions in the undissolved compound.

Now consider ammonia, which is highly soluble but is a weak electrolyte. The concentration of OH$^-$ ions in an ammonia solution is relatively low. Ammonia is therefore a *weak base*. Many organic compounds that contain nitrogen atoms are also weak bases. For example, codeine, C$_{18}$H$_{21}$NO$_3$, a pain reliever and common cough suppressant found in prescription cough medicine, is a weak base.

SECTION REVIEW

1. **a.** What are five general properties of aqueous acids?
   b. Name some common substances that have one or more of these properties.

2. Name the following acids: a. HBrO b. HBrO$_3$.

3. **a.** What are five general properties of aqueous bases?
   b. Name some common substances that have one or more of these properties.

4. **a.** Why are strong acids also strong electrolytes?
   b. Is every strong electrolyte also a strong acid?

Critical Thinking

5. **RELATING IDEAS** A classmate states, "All compounds containing H atoms are acids, and all compounds containing OH groups are bases." Do you agree? Give examples.
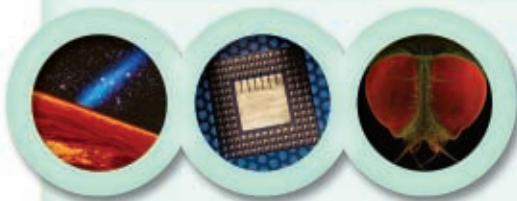
Acid Water—A Hidden Menace

Many people are unaware of the pH of the tap water in their home until they are confronted with such phenomena as a blue ring materializing around a porcelain sink drain, a water heater suddenly giving out, or tropical fish that keep dying. Each of these events could be due to acidic water. Acidic water can also cause the amount of lead in the water to rise.

The possibility of lead poisoning from home water supplies is a concern. Many older homes still have lead pipes in their plumbing, while most modern homes use copper piping. Copper pipe joints, however, are often sealed with lead-containing solder. Highly acidic water can leach out both the lead from the solder joints and copper from the pipes themselves, which turns the sink drain blue. In addition, people who are in the habit of filling their tea kettles and coffee pots in the morning without letting the tap run awhile first could be adding copper and lead ions to their tea or coffee.

Lead poisoning is of particular concern in young children. The absorption rate of lead in the intestinal tract of a child is much higher than in that of an adult, and lead poisoning can permanently impair a child's rapidly growing nervous system. The good news is that lead poisoning and other effects of acidic water in the home can be easily prevented by following these tips:

1. Monitor the pH of your water on a regular basis, especially if you have well water. This can easily be done with pH test kits (see photograph) that are sold in hardware or pet stores—many tropical fish are intolerant of water with a pH that is either too high (basic) or too low (acidic). The pH of municipal water supplies is already regulated, but regularly checking your water's pH yourself is a good idea.

2. In the morning, let your water tap run for about half a minute before you fill your kettle or drink the water. If the water is acidic, the first flush of water will have the highest concentration of lead and copper ions.

3. Install an alkali-injection pump, a low-cost, low-maintenance solution that can save your plumbing and lessen the risk of lead poisoning from your own water supply. The pump injects a small amount of an alkali (usually potassium carbonate or sodium carbonate) into your water-pressure tank each time your well's pump starts. This effectively neutralizes the acidity of your water.

Questions

1. What is the source of lead contamination in water in the home?

2. Does the use of copper water pipes ensure that your household water is free from lead?

3. Why does lead poisoning affect children more severely than it affects adults?

◄ The pH of your home's water supply can be easily monitored using a test kit, such as the one shown here.

SCiLINKS.

www.scilinks.org
Topic: Acid Water
Code: HC60011

Acid-Base Theories

- Define and recognize *Brønsted-Lowry acids* and *bases.*

- Define a *Lewis acid* and a *Lewis base.*

- Name compounds that are acids under the Lewis definition but are not acids under the Brønsted-Lowry definition.

For most uses, scientists found the Arrhenius definition of acids and bases to be adequate. However, as scientists further investigated acid-base behavior, they found that some substances acted as acids or bases when they were not in a water solution. Because the Arrhenius definition requires that the substances be aqueous, the definitions of acids and bases had to be revised.
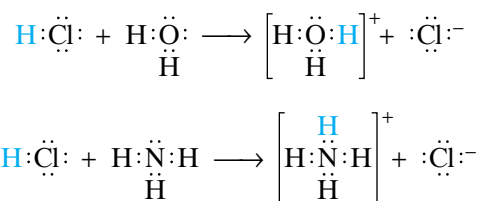
Brønsted-Lowry Acids and Bases

In 1923, the Danish chemist J. N. Brønsted and the English chemist T. M. Lowry independently expanded the Arrhenius acid definition. *A* **Brønsted-Lowry acid** *is a molecule or ion that is a proton donor.* Because H^+ is a proton, all acids as defined by Arrhenius donate protons to water and are Brønsted-Lowry acids as well. Substances other than molecules, such as certain ions, can also donate protons. Such substances are not Arrhenius acids but are included in the category of Brønsted-Lowry acids.

Hydrogen chloride acts as a Brønsted-Lowry acid when it reacts with ammonia. The HCl transfers protons to NH_3 much as it does in water.

$$HCl + NH_3 \longrightarrow NH_4^+ + Cl^-$$

A proton is transferred from the hydrogen chloride molecule, HCl, to the ammonia molecule, NH_3. The ammonium ion, NH_4^+, is formed. Electron-dot formulas show the similarity of this reaction to the reaction of HCl with water.

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

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

In both reactions, hydrogen chloride is a Brønsted-Lowry acid.

Water can also act as a Brønsted-Lowry acid. Consider, for example, the following reaction, in which the water molecule donates a proton to the ammonia molecule.
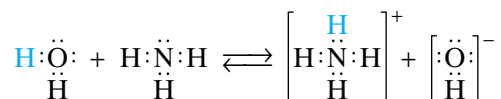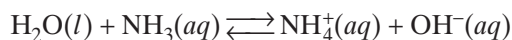
$$H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$H{:}\ddot{\underset{\underset{H}{|}}{O}}{:} \ + \ H{:}\overset{..}{N}{:}H \ \rightleftharpoons \ \left[H{:}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}{:}H \right]^+ + \ \left[{:}\ddot{\underset{\underset{H}{|}}{O}}{:} \right]^-$$

A **Brønsted-Lowry base** *is a molecule or ion that is a proton acceptor.* In the reaction between hydrochloric acid and ammonia, ammonia accepts a proton from the hydrochloric acid. It is a Brønsted-Lowry base. The Arrhenius hydroxide bases, such as NaOH, are not, strictly speaking, Brønsted-Lowry bases. Instead, it is the OH^- ion produced in solution that is the Brønsted-Lowry base. It is the species that can accept a proton.

In a **Brønsted-Lowry acid-base reaction,** *protons are transferred from one reactant (the acid) to another (the base).* **Figure 9** shows the reaction between the Brønsted-Lowry acid HCl and the Brønsted-Lowry base NH_3.
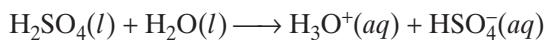
Monoprotic and Polyprotic Acids

An acid that can donate only one proton (hydrogen ion) per molecule is known as a **monoprotic acid.** Perchloric acid, $HClO_4$, hydrochloric acid, HCl, and nitric acid, HNO_3, are all monoprotic. The following equation shows how a molecule of the monoprotic acid HCl donates a proton to a water molecule. The HCl ionizes to form H_3O^+ ions and Cl^- ions. The Cl^- has no hydrogens to lose, so HCl has only one ionization step.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
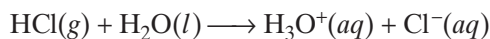
A **polyprotic acid** *is an acid that can donate more than one proton per molecule.* Sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4, are examples of polyprotic acids. The ionization of a polyprotic acid occurs in stages. The acid loses its hydrogen ions one at a time. Sulfuric acid

ionizes in two stages. In its first ionization, sulfuric acid is a strong acid. It is completely converted to hydrogen sulfate ions, HSO_4^-.

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

The hydrogen sulfate ion is itself a weak acid. It establishes the following equilibrium in solution.

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$
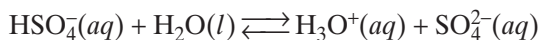
All stages of ionization of a polyprotic acid occur in the same solution. Sulfuric acid solutions therefore contain H_3O^+, HSO_4^-, and SO_4^{2-} ions. Note that in sulfuric acid solutions, there are many more hydrogen sulfate and hydronium ions than there are sulfate ions.

Sulfuric acid is the type of polyprotic acid that *can donate two protons per molecule, and it is therefore known as a* **diprotic acid.** Ionizations of a monoprotic acid and a diprotic acid are shown in **Figure 10.**

Phosphoric acid is the type of polyprotic acid known as a **triprotic acid**—*an acid able to donate three protons per molecule.* The equations for these reactions are shown below.
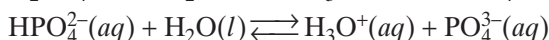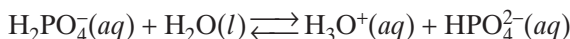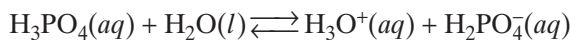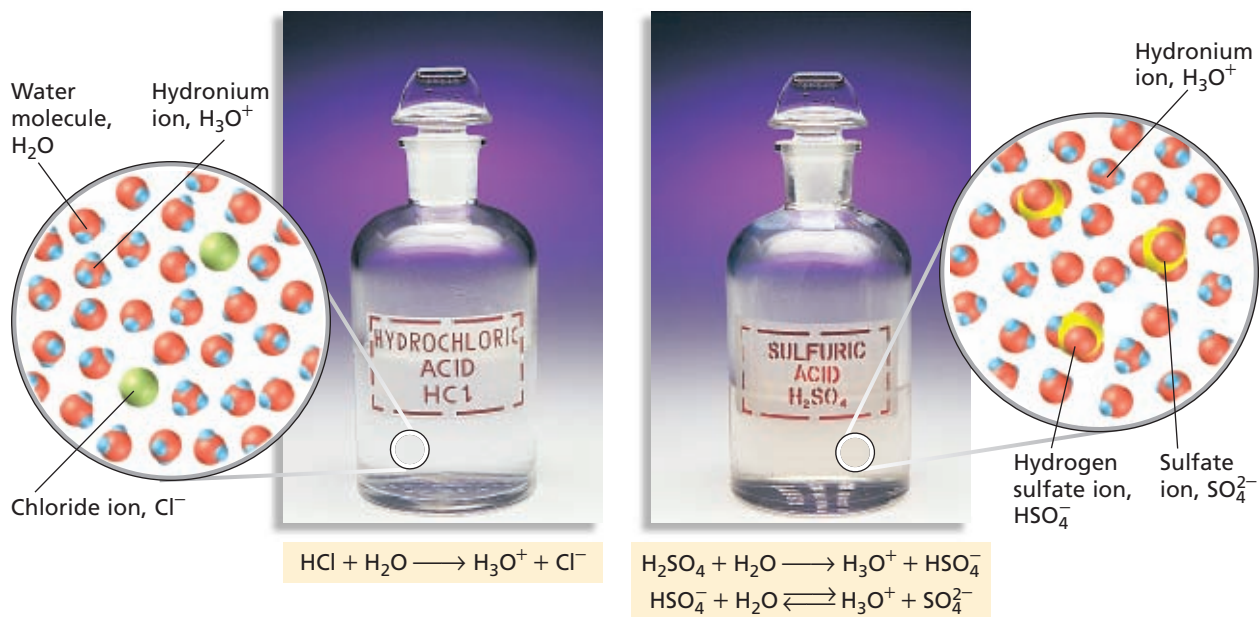
$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

FIGURE 10 Hydrochloric acid, HCl, is a strong monoprotic acid. A dilute HCl solution contains hydronium ions and chloride ions. Sulfuric acid, H_2SO_4, is a strong diprotic acid. A dilute H_2SO_4 solution contains hydrogen sulfate ions from the first ionization, sulfate ions from the second ionization, and hydronium ions from both ionizations.

Water molecule, H_2O

Hydronium ion, H_3O^+

Chloride ion, Cl^-

Hydronium ion, H_3O^+

Hydrogen sulfate ion, HSO_4^-

Sulfate ion, SO_4^{2-}

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

A solution of phosphoric acid contains H_3O^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. As with most polyprotic acids, the concentration of ions formed in the first ionization is the greatest. There are lesser concentrations of the respective ions from each succeeding ionization. Phosphoric acid is a weak acid in each step of its ionization.

Lewis Acids and Bases

The Arrhenius and Brønsted-Lowry definitions describe most acids and bases. Both definitions assume that the acid contains or produces hydrogen ions. A third acid classification, based on bonding and structure, includes, as acids, substances that do not contain hydrogen at all. This definition of acids was introduced in 1923 by G. N. Lewis, the American chemist whose name was given to electron-dot structures. Lewis's definition emphasizes the role of electron pairs in acid-base reactions. *A **Lewis acid** is an atom, ion, or molecule that accepts an electron pair to form a covalent bond.*

The Lewis definition is the broadest of the three acid definitions you have read about so far. It applies to any species that can accept an electron pair to form a covalent bond with another species. A bare proton (hydrogen ion) is a Lewis acid in reactions in which it forms a covalent bond, as shown below.

$$H^+(aq) + :NH_3(aq) \longrightarrow [H-NH_3]^+(aq) \text{ or } [NH_4]^+(aq)$$

The formula for a Lewis acid need not include hydrogen. Even a silver ion can be a Lewis acid, accepting electron pairs from ammonia to form covalent bonds.

$$Ag^+(aq) + 2:NH_3(aq) \longrightarrow [H_3N-Ag-NH_3]^+(aq) \text{ or } [Ag(NH_3)_2]^+$$

Any compound in which the central atom has three valence electrons and forms three covalent bonds can react as a Lewis acid. It does so by accepting a pair of electrons to form a fourth covalent bond, completing an electron octet. Boron trifluoride, for example, is an excellent Lewis acid. It forms a fourth covalent bond with many molecules and ions. Its reaction with a fluoride ion is shown below.
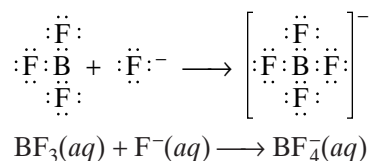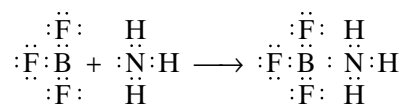
$$BF_3(aq) + F^-(aq) \longrightarrow BF_4^-(aq)$$

TABLE 5 *Acid-Base Definitions*		
Type	**Acid**	**Base**
Arrhenius	H^+ or H_3O^+ producer	OH^- producer
Brønsted-Lowry	proton (H^+) donor	proton (H^+) acceptor
Lewis	electron-pair acceptor	electron-pair donor

The Lewis definition of acids can apply to species in any phase. For example, boron trifluoride is a Lewis acid in the gas-phase combination with ammonia.

$$
\begin{array}{ccc}
:\!\overset{..}{F}\!: \quad H & & :\!\overset{..}{F}\!: \quad H \\
:\!\overset{..}{F}\!:\!B \;+\; :N\!:\!H \longrightarrow & & :\!\overset{..}{F}\!:\!B \;:\; N\!:\!H \\
:\!\overset{..}{F}\!: \quad H & & :\!\overset{..}{F}\!: \quad H
\end{array}
$$

*A **Lewis base** is an atom, ion, or molecule that donates an electron pair to form a covalent bond.* An anion is a Lewis base in a reaction in which it forms a covalent bond by donating an electron pair. In the example of boron trifluoride reacting with the fluoride anion, F^- donates an electron pair to boron trifluoride. F^- acts as a Lewis base.

$$
BF_3(aq) + \;:\!\overset{..}{\underset{..}{F}}\!:^-(aq) \longrightarrow BF_4^-(aq)
$$
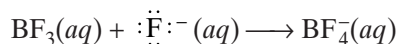
*A **Lewis acid-base reaction** is the formation of one or more covalent bonds between an electron-pair donor and an electron-pair acceptor.*

Note that although the three acid-base definitions differ, many compounds may be categorized as acids or bases according to all three descriptions. For example, ammonia is an Arrhenius base because OH^- ions are created when ammonia is in solution, it is a Brønsted-Lowry base because it accepts a proton in an acid-base reaction, and it is a Lewis base in all reactions in which it donates its lone pair to form a covalent bond. A comparison of the three acid-base definitions is given in **Table 5.**

SECTION REVIEW

1. Label each reactant in the reaction below as a proton donor or a proton acceptor and as acidic or basic.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$
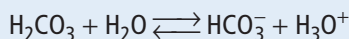
2. For the reaction below, label each reactant as an electron pair acceptor or electron pair donor and as a Lewis acid or a Lewis base.

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$
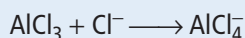
Critical Thinking

3. **ANALYZING INFORMATION** For the following three reactions, identify the reactants that are Arrhenius bases, Brønsted-Lowry bases, and/or Lewis bases. State which type(s) of bases each reactant is. Explain your answers.

a. $NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$

b. $HF(aq) + H_2O(l) \longrightarrow F^-(aq) + H_3O^+(aq)$

c. $H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$

Acid-Base Reactions

OBJECTIVES

● Describe a conjugate acid, a conjugate base, and an amphoteric compound.

● Explain the process of neutralization.

● Define *acid rain,* give examples of compounds that can cause acid rain, and describe effects of acid rain.

In the previous sections, you learned about three acid-base theories: Arrhenius, Brønsted-Lowry, and Lewis. The Brønsted-Lowry theory is especially useful for describing acid-base reactions that take place in aqueous solutions. This section will use the Brønsted-Lowry description to explore reactions between acids and bases.
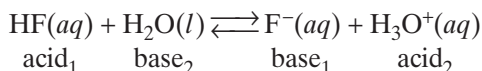
Conjugate Acids and Bases

The Brønsted-Lowry definitions of acids and bases provide a basis for studying proton-transfer reactions. Suppose that a Brønsted-Lowry acid gives up a proton; the remaining ion or molecule can re-accept that proton and can act as a base. Such a base is known as a conjugate base. Thus, *the species that remains after a Brønsted-Lowry acid has given up a proton is the* **conjugate base** *of that acid.* For example, the fluoride ion is the conjugate base of hydrofluoric acid.

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$
$$\text{acid} \qquad\qquad\qquad \text{conjugate base}$$
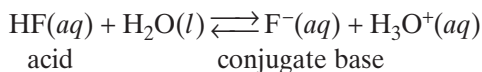
In this reaction, the water molecule is a Brønsted-Lowry base. It accepts a proton from HF to form H_3O^+, which is an acid. The hydronium ion is the conjugate acid of water. *The species that is formed when a Brønsted-Lowry base gains a proton is the* **conjugate acid** *of that base.*

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$
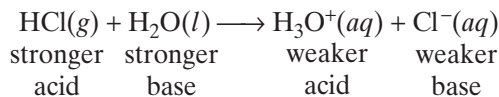$$\qquad\quad \text{base} \qquad\qquad\qquad \text{conjugate acid}$$
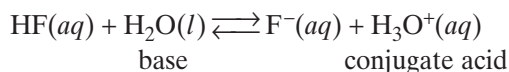
In general, Brønsted-Lowry acid-base reactions are equilibrium systems meaning that both the forward and reverse reactions occur. They involve two acid-base pairs, known as conjugate acid-base pairs.

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$
$$\text{acid}_1 \quad \text{base}_2 \qquad \text{base}_1 \quad \text{acid}_2$$

The subscripts designate the two conjugate acid-base pairs: (1) HF and F^- and (2) H_3O^+ and H_2O. In every conjugate acid-base pair, the acid has one more proton than its conjugate base.
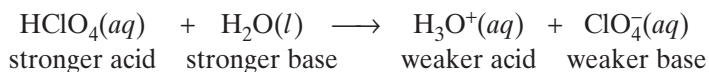
Strength of Conjugate Acids and Bases

The extent of the reaction between a Brønsted-Lowry acid and base depends on the relative strengths of the acids and bases involved. Consider the following example. Hydrochloric acid is a strong acid. It gives up protons readily. Therefore, the Cl^- ion has little tendency to attract and retain a proton. Consequently, the Cl^- ion is an extremely weak base.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
stronger stronger   weaker   weaker
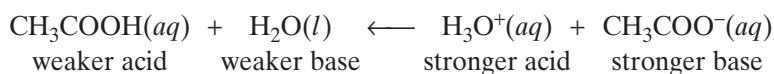acid   base   acid   base

This observation leads to an important conclusion: *the stronger an acid is, the weaker its conjugate base; the stronger a base is, the weaker its conjugate acid.*

This concept allows strengths of different acids and bases to be compared to predict the outcome of a reaction. As an example, consider the reaction of perchloric acid, $HClO_4$, and water.

$$HClO_4(aq) \quad + \quad H_2O(l) \quad \longrightarrow \quad H_3O^+(aq) \quad + \quad ClO_4^-(aq)$$
stronger acid   stronger base   weaker acid   weaker base

The hydronium ion is too weak an acid to compete successfully with perchloric acid in donating a proton; $HClO_4$ is the stronger acid. In this reaction, the perchlorate ion, ClO_4^-, and H_2O are both bases. Because $HClO_4$ is a very strong acid, ClO_4^- is an extremely weak base. Therefore, H_2O competes more strongly than ClO_4^- to acquire a proton. The reaction proceeds such that the stronger acid reacts with the stronger base to produce the weaker acid and base.

Now consider a comparable reaction between water and acetic acid.

$$CH_3COOH(aq) \quad + \quad H_2O(l) \quad \longleftarrow \quad H_3O^+(aq) \quad + \quad CH_3COO^-(aq)$$
weaker acid   weaker base   stronger acid   stronger base

The H_3O^+ ion concentration in this solution is much lower than it was in the $HClO_4$ solution because acetic acid is a weak acid. The CH_3COOH molecule does not compete successfully with the H_3O^+ ion in donating protons to a base. The acetate ion, CH_3COO^-, is a stronger base than H_2O. Therefore, the H_2O molecule does not compete successfully with the CH_3COO^- ion in accepting a proton. The H_3O^+ ion is the stronger acid, and the CH_3COO^- ion is the stronger base. Thus, the reverse reaction (to the left) is more favorable.

Note that in the reactions for both perchloric acid and acetic acid, the favored direction is toward the weaker acid and the weaker base. This observation leads to a second important general conclusion: *proton-transfer reactions favor the production of the weaker acid and the weaker base.* For an acid-base reaction to form products completely, the reactants must be much stronger as acids and bases than the products.

By comparing many different acids and bases, a table of relative strengths, such as **Table 6,** can be assembled. Note that a very strong acid, such as $HClO_4$, has a very weak conjugate base, ClO_4^-. The

TABLE 6 *Relative Strengths of Acids and Bases*

	Conjugate acid	Formula	Conjugate base	Formula	
	hydriodic acid*	HI	iodide ion	I^-	
	perchloric acid*	$HClO_4$	perchlorate ion	ClO_4^-	
	hydrobromic acid*	HBr	bromide ion	Br^-	
	hydrochloric acid*	HCl	chloride ion	Cl^-	
	sulfuric acid*	H_2SO_4	hydrogen sulfate ion	HSO_4^-	
	chloric acid*	$HClO_3$	chlorate ion	ClO_3^-	
	nitric acid*	HNO_3	nitrate ion	NO_3^-	
	hydronium ion	H_3O^+	water	H_2O	
	chlorous acid	$HClO_2$	chlorite ion	ClO_2^-	
	hydrogen sulfate ion	HSO_4^-	sulfate ion	SO_4^{2-}	
	phosphoric acid	H_3PO_4	dihydrogen phosphate ion	$H_2PO_4^-$	
	hydrofluoric acid	HF	fluoride ion	F^-	
	acetic acid	CH_3COOH	acetate ion	CH_3COO^-	
	carbonic acid	H_2CO_3	hydrogen carbonate ion	HCO_3^-	
	hydrosulfuric acid	H_2S	hydrosulfide ion	HS^-	
	dihydrogen phosphate ion	$H_2PO_4^-$	hydrogen phosphate ion	HPO_4^{2-}	
	hypochlorous acid	HClO	hypochlorite ion	ClO^-	
	ammonium ion	NH_4^+	ammonia	NH_3	
	hydrogen carbonate ion	HCO_3^-	carbonate ion	CO_3^{2-}	
	hydrogen phosphate ion	HPO_4^{2-}	phosphate ion	PO_4^{3-}	
	water	H_2O	hydroxide ion	OH^-	
	ammonia	NH_3	amide ion†	NH_2^-	
	hydrogen	H_2	hydride ion†	H^-	

Increasing acid strength (left margin, pointing up)

Increasing base strength (right margin, pointing down)
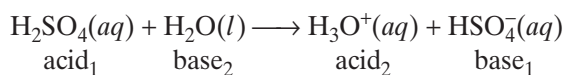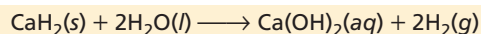
* Strong acids
† Strong bases

strongest base listed in the table, the hydride ion, H^-, has the weakest conjugate acid, H_2. In aqueous solutions, all of the strong acids are 100% ionized, forming hydronium ions along with their anion. The acids below hydronium ion in **Table 6** do not ionize 100% in water. Water is a very weak acid, but it will react as an acid if a very strong base, such as hydride ion, is present. Such a reaction is illustrated in **Figure 11.**

Amphoteric Compounds

You have probably noticed that water can be either an acid or a base. *Any species that can react as either an acid or a base is described as* **amphoteric.** For example, consider the first ionization of sulfuric acid, in which water acts as a base.

FIGURE 11 Calcium hydride, CaH_2, reacts vigorously with water to produce hydrogen gas.

$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$

$$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$
$$\text{acid}_1 \qquad \text{base}_2 \qquad \text{acid}_2 \qquad \text{base}_1$$

However, water acts as an acid in the following reaction.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$\text{base}_1 \qquad \text{acid}_2 \qquad \text{acid}_1 \qquad \text{base}_2$$

Thus, water can act as either an acid or a base and is amphoteric. Such a substance acts as either an acid or a base depending on the strength of the acid or base with which it is reacting. For example, if water reacts with a compound that is a stronger acid than water, water acts as a base. If water reacts with a molecule that is a weaker acid than water, water will act as an acid and the other molecule will act as a base.
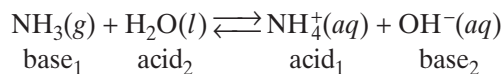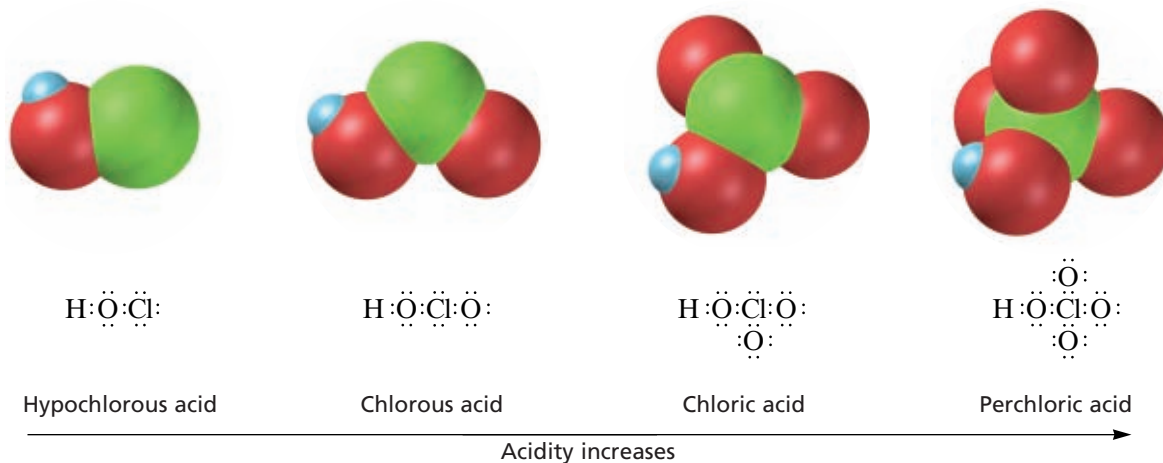
FIGURE 12 Each oxyacid of chlorine contains one chlorine atom and one hydrogen atom. They differ in the number of oxygen atoms they contain. The effect of the changing O—H bond polarity can be seen in the increasing acid strength from hypochlorous acid to perchloric acid.

Hypochlorous acid

Chlorous acid

Chloric acid

Perchloric acid

Acidity increases

–OH in a Molecule

Molecular compounds containing −OH groups can be acidic or ampho-teric. The covalently bonded −OH group in an acid is referred to as a *hydroxyl group*. For the compound to be acidic, a water molecule must be able to attract a hydrogen atom from a hydroxyl group. This occurs more easily when the O−H bond is very polar. Any feature of a mole-cule that increases the polarity of the O−H bond increases the acidity of a molecular compound. The small, more-electronegative atoms of nonmetals at the upper right in the periodic table form compounds with acidic hydroxyl groups. All oxyacids are molecular electrolytes that con-tain one or more of these O−H bonds. Such compounds include chloric and perchloric acids.

Figure 12 shows the electron-dot formulas of the four oxyacids of chlorine. Notice that all of the oxygen atoms are bonded to the chlorine atom. Each hydrogen atom is bonded to an oxygen atom. Aqueous solu-tions of these molecules are acids because the O−H bonds are broken as the hydrogen is pulled away by water molecules.

The behavior of a compound is affected by the number of oxygen atoms bonded to the atom connected to the −OH group. The larger the number of such oxygen atoms is, the more acidic the compound is. The electronegative oxygen atoms draw electron density away from the O−H bond and make it more polar. For example, chromium forms three different compounds containing −OH groups, as shown below.
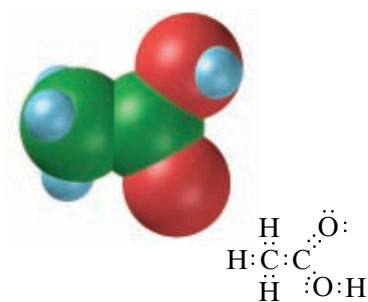
basic	*amphoteric*	*acidic*
$Cr(OH)_2$	$Cr(OH)_3$	H_2CrO_4
chromium(II) hydroxide	chromium(III) hydroxide	chromic acid

Notice that as the number of oxygen atoms increases, so does the acid-ity of the compound.
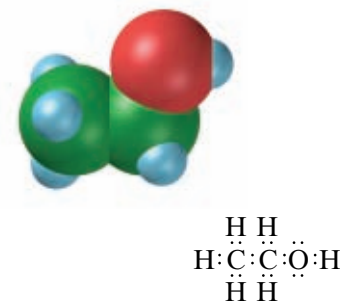
Consider also the compounds shown in **Figure 13.** In acetic acid, but not in ethanol, a second oxygen atom is bonded to the carbon atom connected to the −OH group. That explains why acetic acid is acidic but ethanol is not, even though the same elements form each compound.

(a) CH_3COOH
Acetic acid

(b) C_2H_5OH
Ethanol

FIGURE 13 (a) Acetic acid is acidic. The second oxygen atom on the carbon draws electron density away from the −OH group, making the O−H bond more polar. (b) Ethanol is essentially neutral. It has no second oxygen atom, so the O—H bond is less polar than in acetic acid, and is a much weaker acid.

Neutralization Reactions

There are many common examples of acidic compounds reacting with basic compounds, each neutralizing the other. Sodium bicarbonate, $NaHCO_3$, and tartaric acid, $H_2C_4H_4O_6$, are two components in baking powder. When water is added, the two compounds produce carbon dioxide. The escaping carbon dioxide causes foods, such as biscuits, to rise. Another example is an antacid soothing an overly acidic stomach by neutralizing the stomach acid.
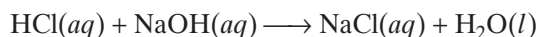
Strong Acid-Strong Base Neutralization

An acid-base reaction occurs in aqueous solution between hydrochloric acid, a strong acid that completely ionizes to produce H_3O^+, and sodium hydroxide, a strong base that completely dissociates to produce OH^-. The formula equation for this reaction is written as follows.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

In an aqueous solution containing 1 mol of sodium hydroxide, NaOH dissociates as represented by the following equation.

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

A solution containing 1 mol of hydrochloric acid ionizes as represented by the following equation.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
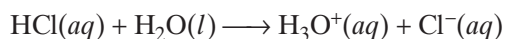
If the two solutions are mixed, as in **Figure 14,** a reaction occurs between the aqueous H_3O^+ and OH^- ions. Notice that sodium chloride, NaCl, and water are produced. The overall ionic equation is shown below.

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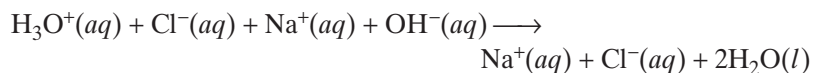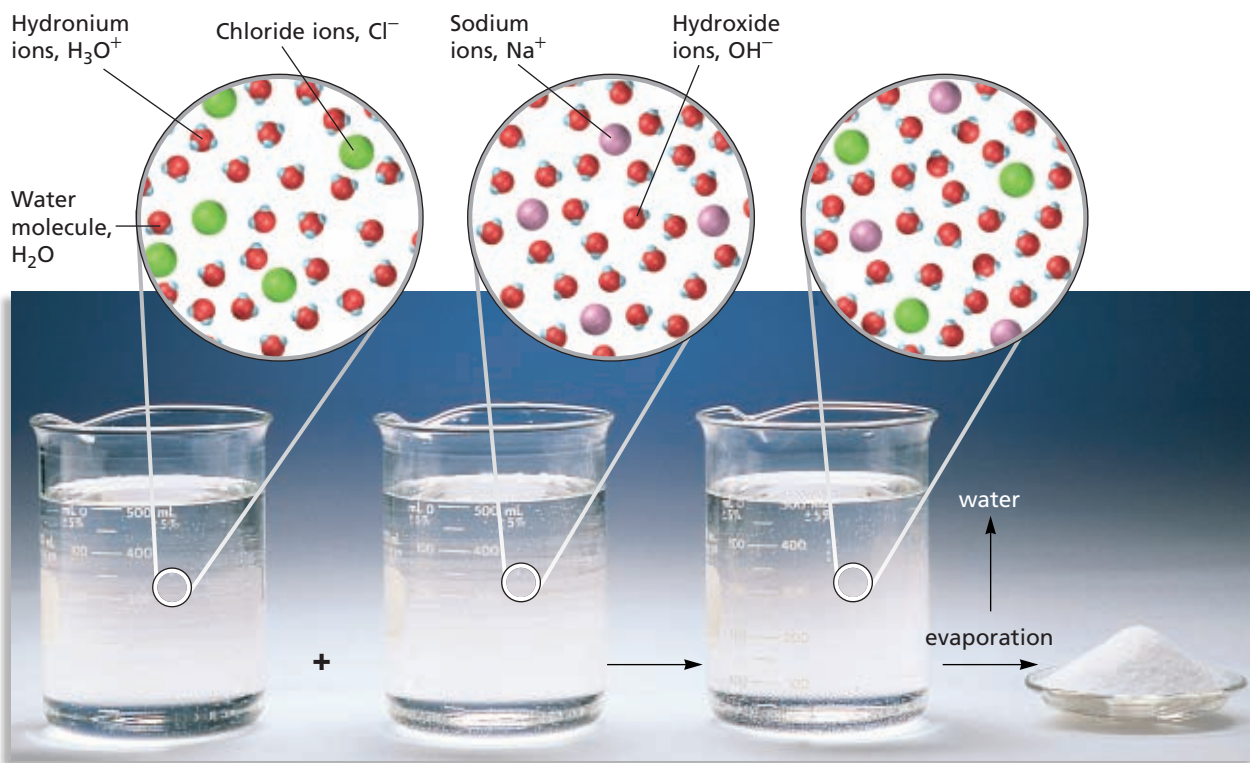$$Na^+(aq) + Cl^-(aq) + 2H_2O(l)$$

FIGURE 14 When aqueous hydrochloric acid, HCl, reacts with aqueous sodium hydroxide, NaOH, the reaction produces aqueous sodium chloride, NaCl. Ions that are present in each solution are represented by the models.

Hydronium ions, H_3O^+

Chloride ions, Cl^-

Water molecule, H_2O

Sodium ions, Na^+

Hydroxide ions, OH^-

water

evaporation

Because they appear on both sides of the overall ionic equation, Na^+ and Cl^- are spectator ions. The only participants in the reaction are the hydronium ion and the hydroxide ion, as shown in the following net ionic equation.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$
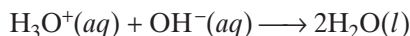
There are equal numbers of H_3O^+ and OH^- ions in this reaction, and they are fully converted to water. In aqueous solutions, **neutralization** *is the reaction of hydronium ions and hydroxide ions to form water molecules.*

Notice that water is not the only product of a neutralization. A salt is also produced. *A* **salt** *is an ionic compound composed of a cation from a base and an anion from an acid.*

Acid Rain

Many industrial processes produce gases such as NO, NO_2, CO_2, SO_2, and SO_3. These compounds can dissolve in atmospheric water to produce acidic solutions that fall to the ground in the form of rain or snow. For example, sulfur from the burning of oil and coal forms sulfur dioxide, SO_2. The SO_2 is then converted to SO_3, sulfur trioxide, which reacts with water in the atmosphere to produce sulfuric acid, as shown below.

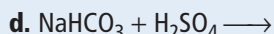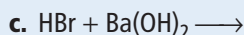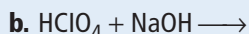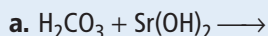$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$
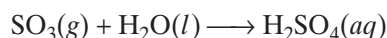
Rainwater is normally slightly acidic, but sometimes rain is very acidic and is called *acid rain*. **Figure 15** shows a forest that was damaged by severe acid rain. Acid rain can erode statues and affect ecosystems, such as water environments and forests. In the 1970s, scientists found that acid rain was causing the fish populations in some lakes and streams to decline. When fish are completely eliminated from lakes and streams because of acid rain, the biodiversity of the ecosystem decreases. Because of amendments to the Clean Air Act in 1990, a limit was set on the amount of SO_2 that power plants are permitted to emit. This limit has decreased but not eliminated acid rain in the United States.

FIGURE 15 Acid precipitation causes extensive environmental damage.

SECTION REVIEW

1. Complete and balance the equations for the following acid-base reactions:
   a. $H_2CO_3 + Sr(OH)_2 \longrightarrow$
   b. $HClO_4 + NaOH \longrightarrow$
   c. $HBr + Ba(OH)_2 \longrightarrow$
   d. $NaHCO_3 + H_2SO_4 \longrightarrow$

2. Consider the equation for acetic acid plus water.
   $$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$$
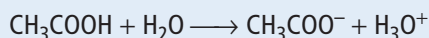
   a. Refer to **Table 6** to compare the strengths of the two acids in the equation. Do the same for the two bases.

   b. Determine which direction—forward or reverse—is favored in the reaction.

Critical Thinking

3. **INFERRING RELATIONSHIPS** Explain how the presence of several oxygen atoms in a compound containing an –OH group can make the compound acidic.

Properties of Acids and Bases

Vocabulary

binary acid
oxyacid
Arrhenius acid
Arrhenius base
strong acid
weak acid

- Acids have a sour taste and react with active metals. Acids change the colors of acid-base indicators, react with bases to produce salts and water, and conduct electricity in aqueous solutions.
- Bases have a bitter taste, feel slippery to the skin in dilute aqueous solutions, change the colors of acid-base indicators, react with acids to produce salts and water, and conduct electricity in aqueous solution.
- An Arrhenius acid contains hydrogen and ionizes in aqueous solution to form hydrogen ions. An Arrhenius base produces hydroxide ions in aqueous solution.
- The strength of an Arrhenius acid or base is determined by the extent to which the acid or base ionizes or dissociates in aqueous solutions.

Acid-Base Theories

Vocabulary

Brønsted-Lowry acid
Brønsted-Lowry base
Brønsted-Lowry acid-
  base reaction
monoprotic acid
polyprotic acid
diprotic acid
triprotic acid
Lewis acid
Lewis base
Lewis acid-base
  reaction

- A Brønsted-Lowry acid is a proton donor. A Brønsted-Lowry base is a proton acceptor.
- A Lewis acid is an electron-pair acceptor. A Lewis base is an electron-pair donor.
- Acids are described as monoprotic, diprotic, or triprotic depending on whether they can donate one, two, or three protons per molecule, respectively, in aqueous solutions. Polyprotic acids include both diprotic and triprotic acids.

Acid-Base Reactions

Vocabulary

conjugate base
conjugate acid
amphoteric
neutralization
salt

- In every Brønsted-Lowry acid-base reaction, there are two conjugate acid-base pairs.
- A strong acid has a weak conjugate base; a strong base has a weak conjugate acid.
- Proton-transfer reactions favor the production of the weaker acid and weaker base.
- The acidic or basic behavior of a molecule containing $-OH$ groups depends on the electronegativity of other atoms in the molecule and on the number of oxygen atoms bonded to the atom that is connected to the $-OH$ group.
- A neutralization reaction produces water and an ionic compound called a *salt*.
- Acid rain can create severe ecological problems.

Properties of Acids and Bases

SECTION 1 REVIEW

1. Compare the general properties of acids with the general properties of bases.
2. a. Distinguish between binary acids and oxyacids in terms of their component elements and the systems used in naming them.
   b. Give three examples of each type of acid.
3. Identify and describe the characteristic properties of five common acids used in industry. Give some examples of the typical uses of each.
4. Although HCl(*aq*) exhibits properties of an Arrhenius acid, pure HCl gas and HCl dissolved in a nonpolar solvent exhibit none of the properties of an Arrhenius acid. Explain why.
5. a. What distinguishes strong acids from weak acids?
   b. Give two examples each of strong acids and weak acids.
6. H_3PO_4, which contains three hydrogen atoms per molecule, is a weak acid, whereas HCl, which contains only one hydrogen atom per molecule, is a strong acid. Explain why.
7. a. What determines the strength of an Arrhenius base?
   b. Give one example each of an aqueous solution of a strong base and an aqueous solution of a weak base.

PRACTICE PROBLEMS

8. Name each of the following binary acids:
   a. HCl
   b. H_2S
9. Name each of the following oxyacids:
   a. HNO_3 c. $HClO_3$
   b. H_2SO_3 d. HNO_2
10. Write formulas for the following binary acids:
    a. hydrofluoric acid
    b. hydriodic acid
11. Write formulas for the following oxyacids:
    a. perbromic acid
    b. chlorous acid
    c. phosphoric acid
    d. hypochlorous acid

Acid-Base Theories

SECTION 2 REVIEW

12. Distinguish between a monoprotic, a diprotic, and a triprotic acid. Give an example of each.
13. Which of the three acid definitions is the broadest? Explain.

PRACTICE PROBLEMS

14. a. Write the balanced equations that describe the two-step ionization of sulfuric acid in a dilute aqueous solution.
    b. How do the degrees of ionization in the two steps compare?
15. Dilute HCl(*aq*) and KOH(*aq*) are mixed in chemically equivalent quantities. Write the following:
    a. formula equation for the reaction
    b. overall ionic equation
    c. net ionic equation
16. Repeat item 15, but mix H_3PO_4(*aq*) and NaOH(*aq*).
17. Write the formula equation and net ionic equation for each of the following reactions:
    a. $Zn(s) + HCl(aq) \longrightarrow$
    b. $Al(s) + H_2SO_4(aq) \longrightarrow$
18. Write the formula equation and net ionic equation for the reaction between Ca(*s*) and HCl(*aq*).

Acid-Base Reactions

SECTION 3 REVIEW

19. Define and give an equation to illustrate each of the following substances:
    a. a conjugate base
    b. a conjugate acid
20. a. What is the relationship between the strength of an acid and the strength of its conjugate base?
    b. What is the relationship between the strength of a base and the strength of its conjugate acid?

21. a. What trend is there in the favored direction of proton-transfer reactions?

b. What determines the extent to which a proton-transfer reaction occurs?

22. a. What is meant by the term *amphoteric?*

b. Give an example of a substance or ion that has amphoteric characteristics.

23. For each reaction listed, identify the proton donor or acid and the proton acceptor or base. Label each conjugate acid-base pair.

a. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons$
$$H_3O^+(aq) + CH_3COO^-(aq)$$

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

c. $HNO_3 + SO_4^{2-} \longrightarrow HSO_4^- + NO_3^-$

24. Using the information given in **Table 6,** determine the following relative to HF, H_2S, HNO_3, and CH_3COOH:

a. strongest acid

b. weakest acid

c. strongest conjugate base among the four conjugate bases produced by the acids listed

d. weakest conjugate base among the four conjugate bases produced by the acids listed

25. Explain why the conjugate base of a strong acid is a weak base and the conjugate acid of a strong base is a weak acid.

PRACTICE PROBLEMS

26. Complete the following neutralization reactions. Balance each reaction, and then write the overall ionic and net ionic equation for each.

a. $HCl(aq) + NaOH(aq) \longrightarrow$

b. $HNO_3(aq) + KOH(aq) \longrightarrow$

c. $Ca(OH)_2(aq) + HNO_3(aq) \longrightarrow$

d. $Mg(OH)_2(aq) + HCl(aq) \longrightarrow$

27. Write the formula equation, the overall ionic equation, and the net ionic equation for the neutralization reaction involving aqueous solutions of H_3PO_4 and $Mg(OH)_2$. Assume that the solutions are sufficiently dilute so that no precipitates form.

28. Write the balanced chemical equation for each of the following reactions between water and the non-metallic oxide to form an acid.

a. $CO_2(g) + H_2O(l) \longrightarrow$

b. $SO_3(g) + H_2O(l) \longrightarrow$

c. $N_2O_5(g) + H_2O(l) \longrightarrow$

29. Write the formula equation, the overall ionic equation, and the net ionic equation for a neutralization reaction that would form each of the following salts.

a. $RbClO_4$ c. $CaCl_2$

b. $BaSO_4$ d. K_2SO_4

30. Zinc reacts with 100.0 mL of 6.00 M cold, aqueous sulfuric acid through single replacement.

a. How many grams of zinc sulfate can be produced?

b. How many liters of hydrogen gas could be released at STP?

31. A 211 g sample of barium carbonate, $BaCO_3$, reacts with a solution of nitric acid to give barium nitrate, carbon dioxide and water. If the acid is present in excess, what mass and volume of dry carbon dioxide gas at STP will be produced?

32. A seashell that is composed largely of calcium carbonate reacts with a solution of HCl. As a result, 1500 mL of dry CO_2 gas at STP is produced. The other products are $CaCl_2$ and H_2O.

a. How many grams of $CaCO_3$ are consumed in the reaction?

b. What volume of 2.00 M HCl solution is used in this reaction?

33. *Acid precipitation* is the term generally used to describe rain or snow that is more acidic than it normally is. One cause of acid precipitation is the formation of sulfuric and nitric acids from various sulfur and nitrogen oxides produced in volcanic eruptions, forest fires, and thunderstorms. In a typical volcanic eruption, for example, 3.50×10^8 kg SO_2 may be produced. If this amount of SO_2 were converted to H_2SO_4 according to the two-step process given below, how many kilograms of H_2SO_4 would be produced from such an eruption?

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

MIXED REVIEW

34. Suppose that dilute $HNO_3(aq)$ and $LiOH(aq)$ are mixed in chemically equivalent quantities. Write the following for the resulting reaction:
 a. formula equation
 b. overall ionic equation
 c. net ionic equation

35. Write the balanced chemical equation for the reaction between hydrochloric acid and magnesium metal.

36. Write equations for the three-step ionization of phosphoric acid, H_3PO_4. Compare the degree of ionization for the three steps.

37. Name or give the molecular formula for each of the following acids:
 a. HF
 b. acetic acid
 c. phosphorous acid
 d. $HClO_4$
 e. H_3PO_4
 f. hydrobromic acid
 g. HClO
 h. H_2CO_3
 i. sulfuric acid

CRITICAL THINKING

38. Analyzing Conclusions 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 to exhibit acidic behavior, a substance must contain oxygen. However, today that inference is known to be incorrect. Provide evidence to refute Lavoisier's conclusion.

USING THE HANDBOOK

39. Group 16 of the *Elements Handbook* contains a section covering the acid-base chemistry of oxides. Review this material, and answer the following questions:
 a. What types of compounds form acidic oxides?
 b. What is an acid anhydride?
 c. What are three examples of compounds that are classified as acid anhydrides?
 d. What types of compounds form basic oxides? Why are they basic oxides?

40. a. Look at Table 7A in the *Elements Handbook*. What periodic trends regarding the acid-base character of oxides do you notice?
 b. How is the nature of the product affected by the concentrations of the reactants?

RESEARCH & WRITING

41. Explain how sulfuric acid production serves as a measure of a country's economy. Write a report on your findings.

42. Performance Conduct library research to find out about the buffering of solutions. Include information on why solutions are buffered and what kinds of materials used as buffers. Write a brief report on your findings.

43. Obtain some pH paper from your teacher. Determine whether the soil around your house is acidic or basic. Find one type of plant that would grow well in the type of soil around your home and one that would not grow well.

ALTERNATIVE ASSESSMENT

44. Antacids are designed to neutralize excess hydrochloric acid secreted by the stomach during digestion. Carbonates, bicarbonates, and hydroxides are the active ingredients in the most widely used antacids. These ingredients act to drive the neutralization reactions. Examine the labels of several common antacids, and identify the active ingredients.

45. Design an experiment that compares three brands of antacids in terms of the speed of symptom relief and amount of acid neutralized.

Many chemical reactions that occur in water solutions are reactions involving ions. Soluble ionic compounds dissociate into ions when they dissolve, and some molecular compounds, including acids, ionize when they dissolve. An ionic equation represents the species actually present more accurately than an equation that uses full formulas.

Problem-Solving *TIPS*

- All dissolved substances in ionic reactions are dissociated into ions. Therefore, soluble ionic compounds are shown as the separated ions in the full ionic equation. Strong acids and bases are also shown as the separated ions in the full ionic equation because they are 100% ionized.

- Ions that do not take part in the reaction are called *spectator ions*. In other words, spectator ions stay in solution and will be labeled "(aq)" on both sides of the equation. Eliminating spectator ions reduces the "clutter" of the full ionic equation and produces a net ionic equation that shows only the species that actually react.
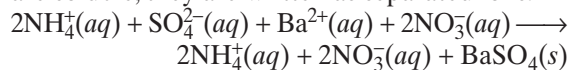
SAMPLE 1

Write the net ionic equation for the reaction of aqueous ammonium sulfate and aqueous barium nitrate to produce a precipitate of barium sulfate. The balanced formula equation is
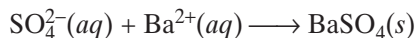
$$(NH_4)_2SO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow 2NH_4NO_3(aq) + BaSO_4(s)$$
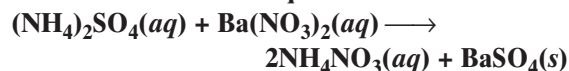
Rewrite the equation in full ionic form; because ammonium sulfate and barium nitrate are soluble, they are written as separated ions:

$$2NH_4^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \longrightarrow 2NH_4^+(aq) + 2NO_3^-(aq) + BaSO_4(s)$$

Eliminating spectator ions, NH_4^+ and NO_3^-, yields the net ionic equation:

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4(s)$$

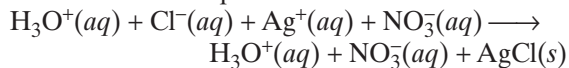### SAMPLE 2

Write full and net ionic equations for the reaction that occurs when hydrochloric acid solution is combined with silver nitrate solution.

Hydrochloric acid is a strong acid, so it is completely ionized in solution. Silver nitrate is a soluble ionic compound, so its ions are separated in solution. Although most chlorides are soluble, silver chloride is not, so silver chloride will precipitate. The balanced formula equation is

$$HCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + HNO_3(aq)$$

The full ionic equation is
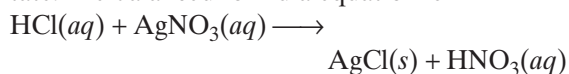
$$H_3O^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow H_3O^+(aq) + NO_3^-(aq) + AgCl(s)$$

Eliminate spectator ions to obtain the net ionic equation:

$$Cl^-(aq) + Ag^+(aq) \longrightarrow AgCl(s)$$
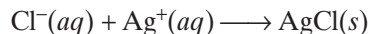
PRACTICE PROBLEMS

1. Aqueous copper(II) sulfate reacts with aqueous sodium sulfide to produce a black precipitate of copper(II) sulfide. Write the formula equation, the full ionic equation, and the net ionic equation for this reaction.

2. Write full and net ionic equations for the reaction that occurs when a solution of cadmium chloride, $CdCl_2$, is mixed with a solution of sodium carbonate, Na_2CO_3. Cadmium carbonate is insoluble.

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

1. Which of the following is *not* a characteristic of an acid?
   A. An acid changes the color of an indicator.
   B. An acid has a bitter taste.
   C. An acid ionizes in water.
   D. An acid produces hydronium ions in water.

2. When an acid reacts with an active metal,
   A. the hydronium ion concentration increases.
   B. the metal forms anions.
   C. hydrogen gas is produced.
   D. carbon dioxide gas is produced.

3. Which of the following is a Brønsted-Lowry base?
   A. an electron pair donor
   B. an electron pair acceptor
   C. a proton donor
   D. a proton acceptor

4. Which acid is the most commonly produced industrial chemical?
   A. hydrochloric acid
   B. acetic acid
   C. nitric acid
   D. sulfuric acid

5. Which of the following is a conjugate pair?
   A. H^+ and OH^-
   B. NH_2^- and NH_4^+
   C. HCl and Cl^-
   D. H_2SO_4 and SO_4^{2-}

6. What is the formula for acetic acid?
   A. CH_3COOH
   B. HNO_3
   C. $HClO_4$
   D. HCN

7. Which of the following species is the conjugate acid of another species in the list?
   A. PO_4^{3-}
   B. H_3PO_4
   C. H_2O
   D. $H_2PO_4^-$

8. Identify the salt that forms when a solution of H_2SO_4 is titrated with a solution of $Ca(OH)_2$.
   A. calcium sulfate
   B. calcium hydroxide
   C. calcium oxide
   D. calcium phosphate

9. Which of the following statements is true for the reaction below?
   $$HF(aq) + HPO_4^{2-}(aq) \rightleftharpoons F^-(aq) + H_2PO_4^-(aq)$$
   A. HF is the base.
   B. HPO_4^{2-} is the acid.
   C. F^- is the conjugate base.
   D. $H_2PO_4^-$ is the conjugate base.

SHORT ANSWER

10. How does a strong acid differ from a weak acid? Give one example of each.

11. Identify the conjugate acid-base pairs in the following reaction:
    $$HClO_2(aq) + NH_3(aq) \rightleftharpoons ClO_2^-(aq) + NH_4^+(aq)$$

EXTENDED RESPONSE

12. Phosphoric acid, H_3PO_4, has three hydrogen atoms and is classified as a triprotic acid. Acetic acid, CH_3COOH, has four hydrogen atoms and is classified as a monoprotic acid. Explain the difference, and justify your explanation by drawing the Lewis structure for both acids.

13. Write the full equation, ionic equation, and net ionic equation for the neutralization reaction between ammonia and sulfuric acid. Identify the spectator ion(s).

Test TIP Double check (with a calculator, if permitted) all mathematical computations involved in answering a question.

INQUIRY LAB

MICRO LAB

Is It an Acid or a Base?

OBJECTIVES

- *Design* an experiment to solve a chemical problem.
- *Relate* observations of chemical properties to identify unknowns.
- *Infer* a conclusion from experimental data.
- *Apply* acid-base concepts.

MATERIALS

- 24-well microplate or 24 small test tubes
- labeled pipets containing solutions numbered 1–8
- toothpicks

  For other supplies, check with your teacher.

BACKGROUND

When scientists uncover a problem that they need to solve, they think carefully about the problem and then use their knowledge and experience to develop a plan for solving it. In this experiment, you will be given a set of eight colorless solutions. Four of them are acidic solutions (dilute hydrochloric acid), and four are basic solutions (dilute sodium hydroxide). The concentrations of both the acidic and the basic solutions are 0.1 M, 0.2 M, 0.4 M, and 0.8 M. Phenolphthalein has been added to the acidic solutions.

First, write a procedure to determine which solutions are acidic and which are basic. Then, carry out your procedure. Next, develop and carry out procedure that allows you to list the acidic and basic solutions in order from lowest to highest concentration. As you plan your procedures, consider the properties of acids and bases that are discussed in Chapter 14. Predict what will happen to a solution of each type and concentration when you do each test. Then, compare your predictions with what actually happens. You will have limited amounts of the unknown solutions to work with, so use them carefully. Ask your teacher what additional supplies (if any) will be available to you.

SAFETY

For review of safety, please see **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. Make two data tables in your lab notebook. For Data Table 1, make two columns, one labeled "Acids" and the other labeled "Bases."

FIGURE A   After adding phenolphthalein indicator, you can more easily determine which solution is acidic and which solution is basic.

You will record the numbers of the unknown solutions in the proper column as you identify them.

For Data Table 2, make three columns, with the headings "Concentration," "HCl," and "NaOH." Record the concentration of each solution as you test it, and then record the concentrations of HCl and NaOH present in the solution.

2. In your lab notebook, write the steps that you will use to determine which solutions are acids and which solutions are bases. Figure A shows one test that you can use to make this determination.

3. Ask your teacher to approve your plan and to give you any additional supplies that you will need.

PROCEDURE

1. Carry out your plan for determining which solutions are acids and which are bases. As you perform your tests, avoid letting the tips of the storage pipets come into contact with other chemicals. Squeeze drops out of the pipets onto the 24-well plate, and then use these drops for your tests. Record all observations in your lab notebook, and then record your results in your first data table.

2. In your lab notebook, write your procedure for determining the concentrations of the solutions. Ask your teacher to approve your plan, and request any additional supplies that you will need.

3. Carry out your procedure for determining the concentrations of the solutions. Record all observations in your lab notebook, and record your results in the second data table.

CLEANUP AND DISPOSAL

4. Clean all equipment and your lab station. Return equipment to its proper place. Dispose of chemicals and solutions in the containers designated by your teacher. Do not pour any chemicals down the drain or in the trash unless your teacher directs you to do so. Wash your hands thoroughly before you leave the lab and after all work is finished.

CONCLUSIONS

1. Analyzing Conclusions: List the numbers of the solutions and their concentrations.

2. Analyzing Conclusions: Describe the test results that led you to identify some solutions as acids and others as bases. Explain how you determined the concentrations of the unknown solutions.

EXTENSIONS

1. Evaluating Methods: Compare your results with those of another lab group. Do you think that your teacher gave both groups the same set of solutions? (For example, is your solution 1 the same as the other group's solution 1?) Explain your reasoning.

2. Applying Conclusions: Imagine that you are helping clean out the school's chemical storeroom. You find a spill of a clear liquid coming from a large, unlabeled reagent bottle. What tests would you do to quickly determine if the substance is acidic or basic?

Acid-Base Titration and pH

Many of the foods we eat, such as tomatoes, are acidic.

Heirloom Tomatoes

Aqueous Solutions and the Concept of pH

Hydronium Ions and Hydroxide Ions

You have already seen that acids and bases form hydronium ions and hydroxide ions, respectively, in aqueous solutions. However, these ions formed from the solute are not the only such ions present in an aqueous solution. Hydronium ions and hydroxide ions are also provided by the solvent, water.

Self-Ionization of Water

Careful electrical conductivity experiments have shown that pure water is an extremely weak electrolyte. Water undergoes self-ionization, as shown in the model in **Figure 1.** *In the* **self-ionization of water,** *two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton.* The following equilibrium takes place.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
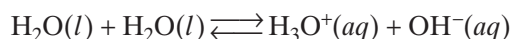
Conductivity measurements show that concentrations of H_3O^+ and OH^- in pure water are each only 1.0×10^{-7} mol/L of water at 25°C.

There is a standard notation to represent concentration in moles per liter. The formula of the particular ion or molecule is enclosed in brackets, [ ]. For example, the symbol $[H_3O^+]$ means "hydronium ion concentration in moles per liter," or "molar hydronium ion concentration." In water at 25°C, $[H_3O^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M.

The mathematical product of $[H_3O^+]$ and $[OH^-]$ remains constant in water and dilute aqueous solutions at constant temperature. This

OBJECTIVES

- Describe the self-ionization of water.

- Define *pH*, and give the pH of a neutral solution at 25°C.

- Explain and use the pH scale.

- Given $[H_3O^+]$ or $[OH^-]$, find pH.

- Given pH, find $[H_3O^+]$ or $[OH^-]$.

FIGURE 1   Water undergoes self-ionization to a slight extent. A proton is transferred from one water molecule to another. A hydronium ion, H_3O^+, and a hydroxide ion, OH^-, are produced.
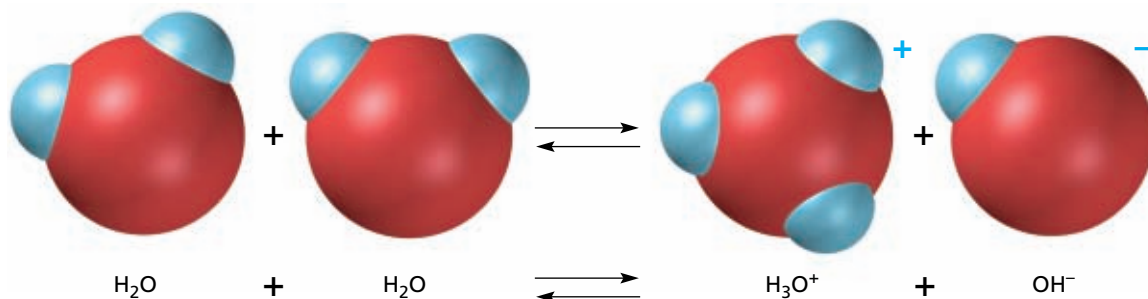

H_2O + H_2O ⇌ H_3O^+ + OH^-

TABLE 1 K_w at Selected Temperatures	
Temperature (°C)	K_w
0	1.2×10^{-15}
10	3.0×10^{-15}
25	1.0×10^{-14}
50	5.3×10^{-14}

constant mathematical product is called the *ionization constant of water,* K_w, and is expressed by the following equation.

$$K_w = [H_3O^+][OH^-]$$

For example, in water and dilute aqueous solutions at 25°C, the following relationship is valid.

$$K_w = [H_3O^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

The ionization of water increases as temperature increases. Therefore, the ion product, K_w, also increases as temperature increases, as shown in **Table 1.** However, at any given temperature K_w is always a constant value. The value 1.0×10^{-14} is assumed to be constant within the ordinary range of room temperatures. In this chapter, you can assume that these conditions are present unless otherwise stated.

Neutral, Acidic, and Basic Solutions

Because the hydronium ion and hydroxide ion concentrations are the same in pure water, it is *neutral.* In fact, any solution in which $[H_3O^+] = [OH^-]$ is neutral. Recall from Chapter 14 that acids increase the concentration of H_3O^+ in aqueous solutions, as shown in **Figure 2a.** Solutions in which the $[H_3O^+]$ is greater than the $[OH^-]$ are *acidic.* Bases increase the concentration of OH^- in aqueous solutions, as shown in **Figure 2b.** In *basic* solutions, the $[OH^-]$ is greater than the $[H_3O^+]$.

As stated earlier, the $[H_3O^+]$ and the $[OH^-]$ of a neutral solution at 25°C both equal 1.0×10^{-7} M. Therefore, if the $[H_3O^+]$ is increased to greater than 1.0×10^{-7} M, the solution becomes acidic. A solution containing 1.0×10^{-5} mol H_3O^+ ion/L at 25°C is acidic because 1.0×10^{-5} is greater than 1.0×10^{-7}. If the $[OH^-]$ is increased to greater than 1.0×10^{-7} M, the solution becomes basic. A solution containing 1.0×10^{-4} mol OH^- ions/L at 25°C is basic because 1.0×10^{-4} is greater than 1.0×10^{-7}.

FIGURE 2 (a) Addition of dry ice, carbon dioxide, to water increases the $[H_3O^+]$, which is shown by the color change of the indicator bromthymol blue to yellow. The white mist is formed by condensation of water vapor because the dry ice is cold. (b) Addition of sodium peroxide to water increases the $[OH^-]$, which is shown by the color change of the indicator phenolphthalein to pink.

(a)

(b)
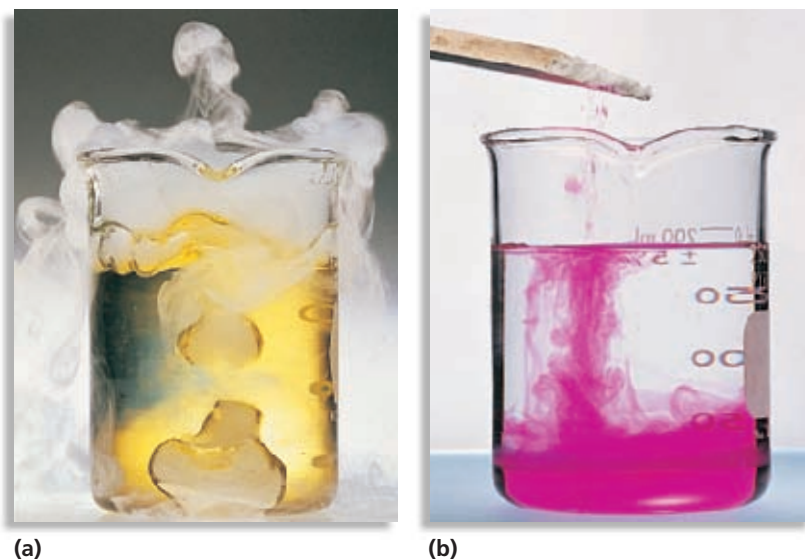
Calculating [H_3O^+] and [OH^-]

Recall that strong acids and bases are considered completely ionized or dissociated in weak aqueous solutions. A review of strong acids and bases is given in **Table 2.** Because NaOH is a strong base, 1 mol of it will yield 1 mol of OH^- in an aqueous solution.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$
$$\text{1 mol} \qquad\qquad \text{1 mol} \quad \text{1 mol}$$
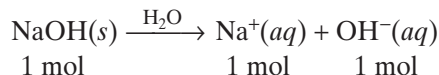
Therefore, a 1.0×10^{-2} M NaOH solution has an [OH^-] of 1.0×10^{-2} M, as shown by the following.

$$\frac{1.0 \times 10^{-2} \text{ mol NaOH}}{1 \text{ L solution}} \times \frac{1 \text{ mol } OH^-}{1 \text{ mol NaOH}} = \frac{1.0 \times 10^{-2} \text{ mol } OH^-}{1 \text{ L solution}}$$
$$= 1.0 \times 10^{-2} \text{ M } OH^-$$

Notice that the [OH^-] is greater than 1.0×10^{-7} M. This solution is basic.
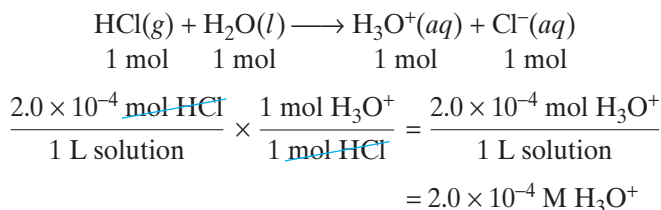
Because the K_w of an aqueous solution is a relatively constant 1.0×10^{-14} at ordinary room temperatures, the concentration of either ion can be determined if the concentration of the other ion is known. The [H_3O^+] of this solution is calculated as follows.

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

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \text{ M}$$

The [OH^-], 1.0×10^{-2} M, is greater than the [H_3O^+], 1.0×10^{-12} M, as is true for all basic solutions.

Now consider a 2.0×10^{-4} M HCl solution. Because HCl is a strong acid, the [H_3O^+] is 2.0×10^{-4} M, as shown by the following.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$\text{1 mol} \quad \text{1 mol} \qquad\qquad \text{1 mol} \quad \text{1 mol}$$

$$\frac{2.0 \times 10^{-4} \text{ mol HCl}}{1 \text{ L solution}} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol HCl}} = \frac{2.0 \times 10^{-4} \text{ mol } H_3O^+}{1 \text{ L solution}}$$
$$= 2.0 \times 10^{-4} \text{ M } H_3O^+$$

Notice that the [H_3O^+] is greater than 1.0×10^{-7} M. This solution is acidic. The [OH^-] of this solution is calculated as follows.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$
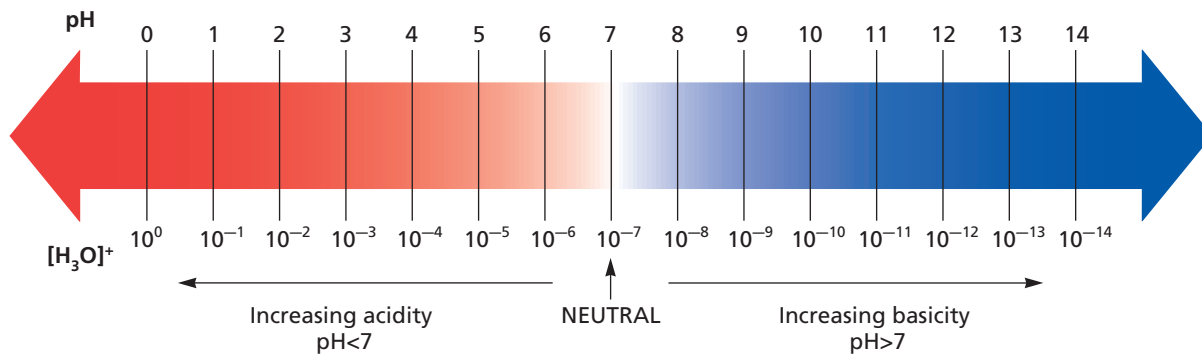
$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-4}} = 5.0 \times 10^{-10} \text{ M}$$

The [H_3O^+] is greater than the [OH^-] for all acidic solutions.

You may have realized that in order for K_w to remain constant, an increase in either the [H_3O^+] or the [OH^-] in an aqueous solution causes a decrease in the concentration of the other ion. Sample Problem A also shows calculation of the [H_3O^+] and [OH^-] of an acidic solution.

TABLE 2 Common Strong Acids and Bases	
Strong Acids	Strong Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
$HClO_3$	CsOH
HNO_3	$Ca(OH)_2$
H_2SO_4	$Sr(OH)_2$
	$Ba(OH)_2$

A 1.0×10^{-4} M solution of HNO_3 has been prepared for a laboratory experiment.
a. Calculate the $[H_3O^+]$ of this solution.   b. Calculate the $[OH^-]$.

SOLUTION

1   ANALYZE   **Given:** Concentration of the solution $= 1.0 \times 10^{-4}$ M HNO_3
Unknown: a. $[H_3O^+]$ **b.** $[OH^-]$

2   PLAN HNO_3 is a strong acid, which means that it is essentially 100% ionized in dilute solutions. One molecule of acid produces one hydronium ion. The concentration of the hydronium ions thus equals the concentration of the acid. Because the ion product, $[H_3O^+][OH^-]$, is a constant, $[OH^-]$ can easily be determined by using the value for $[H_3O^+]$.

a. $$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \qquad \text{(assuming 100\% ionization)}$$
$$\quad 1 \text{ mol} \qquad 1 \text{ mol} \qquad\quad 1 \text{ mol} \qquad\quad 1 \text{ mol}$$

$$\text{molarity of } HNO_3 = \frac{\text{mol } HNO_3}{1 \text{ L solution}}$$

$$\frac{\text{mol } HNO_3}{\text{L solution}} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol } HNO_3} = \frac{\text{mol } H_3O^+}{\text{L solution}} = \text{molarity of } H_3O^+$$

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

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

3   COMPUTE   a. $$\frac{1.0 \times 10^{-4} \text{ mol } HNO_3}{1 \text{ L solution}} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol } HNO_3} = \frac{1.0 \times 10^{-4} \text{ mol } H_3O^+}{1 \text{ L solution}} = 1.0 \times 10^{-4} \text{ M } H_3O^+$$

b. $$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ M}$$

4   EVALUATE   Because the $[H_3O^+]$, 1.0×10^{-4}, is greater than 1.0×10^{-7}, the $[OH^-]$ must be less than 1.0×10^{-7}. The answers are correctly expressed to two significant digits.

PRACTICE   *Answers in Appendix E*

1. Determine the hydronium and hydroxide ion concentrations in a solution that is 1×10^{-4} M HCl.

2. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0×10^{-3} M HNO_3.

3. Determine the hydronium and hydroxide ion concentrations in a solution that is 3.0×10^{-2} M NaOH.

4. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0×10^{-4} M $Ca(OH)_2$.

extension
Go to **go.hrw.com** for more practice problems that ask you to calculate concentration of hydronium and hydroxide ions.

Keyword: HC6ABTX

| pH | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |

$[H_3O]^+$ 10^0 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12} 10^{-13} 10^{-14}

Increasing acidity
pH<7

NEUTRAL

Increasing basicity
pH>7

FIGURE 3 As the concentration of hydronium ions increases, the solution becomes more acidic and the pH decreases. As the concentration of hydronium ions decreases, the solution becomes more basic and the pH increases.

The pH Scale

Expressing acidity or basicity in terms of the concentration of H_3O^+ or OH^- can be cumbersome because the values tend to be very small. A more convenient quantity, called pH, also indicates the hydronium ion concentration of a solution. The letters *pH* stand for the French words *pouvoir hydrogène,* meaning "hydrogen power." *The* **pH** *of a solution is defined as the negative of the common logarithm of the hydronium ion concentration,* $[H_3O^+]$. The pH is expressed by the following equation.

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

The common logarithm of a number is the power to which 10 must be raised to equal the number. A neutral solution at 25°C has a $[H_3O^+]$ of 1×10^{-7} M. The logarithm of 1×10^{-7} is −7.0. The pH is determined as follows.

$$pH = -\log [H_3O^+] = -\log (1 \times 10^{-7}) = -(-7.0) = 7.0$$

The relationship between pH and $[H_3O^+]$ is shown on the scale in **Figure 3.**

Likewise, *the* **pOH** *of a solution is defined as the negative of the common logarithm of the hydroxide ion concentration,* $[OH^-]$.

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

A neutral solution at 25°C has a $[OH^-]$ of 1×10^{-7} M. Therefore, the pOH is 7.0.

Remember that the values of $[H_3O^+]$ and $[OH^-]$ are related by K_w. The negative logarithm of K_w at 25°C, 1×10^{-14}, is 14.0. You may have noticed that the sum of the pH and the pOH of a neutral solution at 25°C is also equal to 14.0. The following relationship is true at 25°C.

$$pH + pOH = 14.0$$

At 25°C the range of pH values of aqueous solutions generally falls between 0 and 14, as shown in **Table 3.**

TABLE 3 Approximate pH Range of Some Common Materials (at 25°C)

Material	pH	Material	pH
Gastric juice	1.0–3.0	Bread	5.0–6.0
Lemons	1.8–2.4	Rainwater	5.5–5.8
Vinegar	2.4–3.4	Potatoes	5.6–6.0
Soft drinks	2.0–4.0	Milk	6.3–6.6
Apples	2.9–3.3	Saliva	6.5–7.5
Grapefruit	2.9–3.4	Pure water	7.0
Oranges	3.0–4.0	Blood	7.3–7.5
Cherries	3.2–4.7	Eggs	7.6–8.0
Tomatoes	4.0–4.4	Sea water	8.0–8.5
Bananas	4.5–5.7	Milk of magnesia	10.5

Suppose the $[H_3O^+]$ in a solution is greater than the $[OH^-]$, as is true for acidic solutions. For example, the pH of an acidic solution at 25°C with a $[H_3O^+]$ of 1×10^{-6} M is 6.0.

$$pH = -\log [H_3O^+] = -\log (1 \times 10^{-6}) = -(-6.0) = 6.0$$

The pH of this solution is less than 7. This is the case for all acidic solutions at 25°C. The following calculation shows that the pOH is greater than 7.0, as is true for all acidic solutions at 25°C.

$$pOH = 14.0 - pH = 14.0 - 6.0 = 8.0$$

Similar calculations show that the pH of a basic solution at 25°C is more than 7.0 and the pOH is less than 7.0. These and other relationships are listed in **Table 4.** Remember that as the temperature changes, the exact values will change because the value of K_w changes. However, the relationship $pH + pOH = pK_w$ will remain the same.

TABLE 4 [H₃O⁺], [OH⁻], pH, and pOH of Solutions

Solution	General condition	At 25°C
Neutral	$[H_3O^+] = [OH^-]$ $pH = pOH$	$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ M $pH = pOH = 7.0$
Acidic	$[H_3O^+] > [OH^-]$ $pH < pOH$	$[H_3O^+] > 1 \times 10^{-7}$ M $[OH^-] < 1 \times 10^{-7}$ M $pH < 7.0$ $pOH > 7.0$
Basic	$[H_3O^+] < [OH^-]$ $pH > pOH$	$[H_3O^+] < 1 \times 10^{-7}$ M $[OH^-] > 1 \times 10^{-7}$ M $pH > 7.0$ $pOH < 7.0$

Calculations Involving pH

If either the $[H_3O^+]$ or pH of a solution is known, the other can be calculated. Significant figures involving pH must be handled carefully. Because pH represents a logarithm, the number to the *left of the decimal* only locates the decimal point. It is not included when counting significant figures. So there must be as many significant figures to the *right of the decimal* as there are in the number whose logarithm was found. For example, a $[H_3O^+]$ value of 1×10^{-7} has *one* significant figure. Therefore, the pH, or –log, of this value must have one digit to the right of the decimal. Thus, pH = 7.0 has the correct number of significant figures.

Calculating pH from $[H_3O^+]$

You have already seen the simplest pH problems. In these problems, the $[H_3O^+]$ of the solution is an integral power of 10, such as 1 M or 0.01 M. The pH of this type of solution is the exponent of the hydronium ion concentration with the sign changed. For example, the pH of a solution in which $[H_3O^+]$ is 1×10^{-5} M is 5.0.

SAMPLE PROBLEM B   *For more help, go to the Math Tutor at the end of this chapter.*

What is the pH of a 1.0×10^{-3} M NaOH solution?

SOLUTION

1 ANALYZE   **Given:** Identity and concentration of solution = 1.0×10^{-3} M NaOH
Unknown: pH of solution

2 PLAN   concentration of base $\longrightarrow$ concentration of OH^- $\longrightarrow$ concentration of H_3O^+ $\longrightarrow$ pH

NaOH is completely dissociated when it is dissolved in water. A 1.0×10^{-3} M NaOH solution therefore produces a $[OH^-]$ equal to 1.0×10^{-3} M. The ion product of $[H_3O^+]$ and $[OH^-]$ is a constant, 1.0×10^{-14}. By substitution, the $[H_3O^+]$ can be determined. The pH can then be calculated.

3 COMPUTE

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

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11} \text{ M}$$

$$pH = -\log\,[H_3O^+] = -\log\,(1.0 \times 10^{-11}) = 11.00$$

4 EVALUATE   The answer correctly indicates that NaOH forms a solution with pH > 7, which is basic.

PRACTICE   *Answers in Appendix E*

1. Determine the pH of the following solutions:
   a. 1×10^{-3} M HCl
   b. 1.0×10^{-5} M HNO_3
   c. 1×10^{-4} M NaOH
   d. 1.0×10^{-2} M KOH

Using a Calculator to Calculate pH from $[H_3O^+]$

Most problems involve hydronium ion concentrations that are not equal to integral powers of 10. These problems require a calculator. Most scientific calculators have a "log" key. Consult the instructions for your particular calculator.

An estimate of pH can be used to check your calculations. For example, suppose the $[H_3O^+]$ of a solution is 3.4×10^{-5} M. Because 3.4×10^{-5} lies between 1×10^{-4} and 1×10^{-5}, the pH of the solution must be between 4 and 5. Sample Problem C continues the actual calculation of the pH value for a solution with $[H_3O^+] = 3.4 \times 10^{-5}$ M.

SAMPLE PROBLEM C   *For more help, go to the Math Tutor at the end of this chapter.*

What is the pH of a solution if the $[H_3O^+]$ is 3.4×10^{-5} M?

SOLUTION

1 ANALYZE   **Given:** $[H_3O^+] = 3.4 \times 10^{-5}$ M
Unknown: pH of solution

2 PLAN

$$[H_3O^+] \longrightarrow pH$$
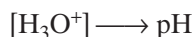
The only difference between this problem and previous pH problems is that you will determine the logarithm of 3.4×10^{-5} using your calculator. You can convert numbers to logarithms on most calculators by using the "log" key.

3 COMPUTE

$$pH = -\log [H_3O^+]$$
$$= -\log (3.4 \times 10^{-5})$$
$$= 4.47$$

On most calculators, this problem is entered in the following steps.

$$\boxed{3} \quad \boxed{.} \quad \boxed{4} \quad \boxed{EE} \quad \boxed{5} \quad \boxed{+/-} \quad \boxed{LOG} \quad \boxed{+/-}$$

4 EVALUATE   The pH of a 1×10^{-5} M H_3O^+ solution is 5.0. A solution that has a greater concentration of hydronium ions will be more acidic and will have a pH less than 5. Because the concentration has two significant figures, the pH will have two figures following the decimal point.

PRACTICE   *Answers in Appendix E*

1. What is the pH of a solution if the $[H_3O^+]$ is 6.7×10^{-4} M?

2. What is the pH of a solution with a hydronium ion concentration of 2.5×10^{-2} M?

3. Determine the pH of a 2.5×10^{-6} M HNO_3 solution.

4. Determine the pH of a 2.0×10^{-2} M $Sr(OH)_2$ solution.

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

You have now learned to calculate the pH of a solution, given its [H_3O^+]. Suppose that you are given the pH of a solution instead. How can you determine its hydronium ion concentration?

You already know the following equation.

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

Remember that the base of common logarithms is 10. Therefore, the antilog of a common logarithm is 10 raised to that number.

$$\log[H_3O^+] = -pH$$
$$[H_3O^+] = \text{antilog}(-pH)$$
$$[H_3O^+] = 10^{-pH}$$

The simplest cases are those in which pH values are integers. The exponent of 10 that gives the [H_3O^+] is the negative of the pH. For an aqueous solution that has a pH of 2, for example, the [H_3O^+] is equal to 1×10^{-2} M. Likewise, when the pH is 0, the [H_3O^+] is 1 M because $10^0 = 1$. Sample Problem D shows how to convert a pH value that is a positive integer. Sample Problem E shows how to use a calculator to convert a pH that is not an integral number.

SAMPLE PROBLEM D   *For more help, go to the* **Math Tutor** *at the end of this chapter.*

Determine the hydronium ion concentration of an aqueous solution that has a pH of 4.0.

SOLUTION

1 *ANALYZE*   **Given:** $pH = 4.0$
Unknown: [H_3O^+]

2 *PLAN* $$pH \longrightarrow [H_3O^+]$$

This problem requires that you rearrange the pH equation and solve for the [H_3O^+]. Because 4.0 has one digit to the right of the decimal, the answer must have one significant figure.

$$pH = -\log[H_3O^+]$$
$$\log[H_3O^+] = -pH$$
$$[H_3O^+] = \text{antilog}(-pH)$$
$$[H_3O^+] = 1 \times 10^{-pH}$$

3 *COMPUTE* $$[H_3O^+] = 1 \times 10^{-pH}$$
$$[H_3O^+] = 1 \times 10^{-4} \text{ M}$$

4 *EVALUATE*   A solution with a pH of 4.0 is acidic. The answer, 1×10^{-4} M, is greater than 1.0×10^{-7} M, which is correct for an acidic solution.

The pH of a solution is measured and determined to be 7.52.
a. What is the hydronium ion concentration?   **c. Is the solution acidic or basic?**
b. What is the hydroxide ion concentration?

SOLUTION

1 *ANALYZE*

Given: pH of the solution = 7.52
Unknown: a. $[H_3O^+]$ **b.** $[OH^-]$ **c.** Is the solution acidic or basic?

2 *PLAN*
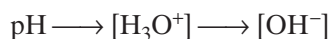
$$pH \longrightarrow [H_3O^+] \longrightarrow [OH^-]$$

This problem is very similar to previous pH problems. You will need to substitute values into the $pH = -\log [H_3O^+]$ equation and use a calculator. Once the $[H_3O^+]$ is determined, the ion-product constant $[H_3O^+] [OH^-] = 1.0 \times 10^{-14}$ may be used to calculate $[OH^-]$.

3 *COMPUTE*

a. $pH = -\log [H_3O^+]$
$\log [H_3O^+] = -pH$
$[H_3O^+] = $ antilog $(-pH) = $ antilog $(-7.52) = 1.0 \times 10^{-7.52} = 3.0 \times 10^{-8}$ M H_3O^+

On most calculators, this is entered in one of the following two ways.

[7] [.] [5] [2] [+/-] [2nd] [10^x]   *or*   [7] [.] [5] [2] [+/-] [2nd] [LOG]

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

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

$$= \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7} \text{ M OH}^-$$

c. A pH of 7.52 is slightly greater than a pH of 7. This means that the solution is slightly basic.

4 *EVALUATE*

Because the solution is slightly basic, a hydroxide ion concentration slightly larger than 10^{-7} M is predicted. A hydronium ion concentration slightly less than 10^{-7} M is also predicted. The answers agree with these predictions.

PRACTICE   *Answers in Appendix E*

1. The pH of a solution is determined to be 5.0. What is the hydronium ion concentration of this solution?

2. The pH of a solution is determined to be 12.0. What is the hydronium ion concentration of this solution?

3. The pH of an aqueous solution is measured as 1.50. Calculate the $[H_3O^+]$ and the $[OH^-]$.

4. The pH of an aqueous solution is 3.67. Determine $[H_3O^+]$.

extension
Go to **go.hrw.com** for more practice problems that ask you to calculate hydronium ion concentration.

Keyword: HC6ABTX

TABLE 5 *Relationship of [H_3O^+] to [OH^-] and pH (at 25°C)*

Solution	[H_3O^+]	[OH^-]	pH
1.0×10^{-2} M KOH	1.0×10^{-12}	1.0×10^{-2}	12.00
1.0×10^{-2} M NH_3	2.4×10^{-11}	4.2×10^{-4}	10.63
Pure H_2O	1.0×10^{-7}	1.0×10^{-7}	7.00
1.0×10^{-3} M HCl	1.0×10^{-3}	1.0×10^{-11}	3.00
1.0×10^{-1} M CH_3COOH	1.3×10^{-3}	7.5×10^{-12}	2.87

pH Calculations and the Strength of Acids and Bases

So far, we have discussed the pH of solutions that contain only strong acids or strong bases. We must also consider weak acids and weak bases. **Table 5** lists the [H_3O^+], the [OH^-], and the pH for several solutions.

KOH, the solute in the first solution listed, is a soluble ionic compound and a strong base. The molarity of a KOH solution directly indicates the [OH^-], and the [H_3O^+] can be calculated. Once the [H_3O^+] is known, the pH can be calculated as in Sample Problem C. If the pH of this solution is measured experimentally, it will be the same as this calculated value. Methods for experimentally determining the pH of solutions will be presented in Section 2. Hydrochloric acid, HCl, is a strong acid, and similar calculations can be made for solutions that contain HCl.

Solutions of weak acids, such as acetic acid, CH_3COOH, present a different problem. The [H_3O^+] cannot be calculated directly from the molar concentration because not all of the acetic acid molecules are ionized. The same problem occurs for weak bases such as ammonia, NH_3. The pH of these solutions must be measured experimentally. The [H_3O^+] and [OH^-] can then be calculated from the measured pH values.

SECTION REVIEW

1. What is the concentration of hydronium and hydroxide ions in pure water at 25°C?

2. Why does the pH scale generally range from 0 to 14 in aqueous solutions?

3. Why does a pH of 7 represent a neutral solution at 25°C?

4. A solution contains 4.5×10^{-3} M HCl. Determine the following for the solution:
   a. [H_3O^+]   b. [OH^-]   c. pH

5. A $Ca(OH)_2$ solution has a pH of 8.0. Determine the following for the solution:
   a. [H_3O^+]   b. [OH^-]   c. [$Ca(OH)_2$]

Critical Thinking

6. **PREDICTING OUTCOMES** Arrange the following solutions in order from lowest to highest pH: 0.10 M HCl, 0.10 M H_2SO_4, and 0.10 M HF.

Liming Streams

In 1987, Dr. Ken Simmons tested some rainbow trout in the waters of north-central Massachusetts' Whetstone Brook. He placed the trout in cages in the brook so that their behavior and survival could be monitored. Three days later, they were dead. Acid rain had lowered the pH level of the water to a point at which the trout simply could not survive.

Acid rain begins with the fossil fuels that we burn to power our cars and factories. Those fuels release combustion products that contain sulfur and nitrogen that combine with the water vapor in the atmosphere and turn the vapor acidic. The pH level of normal rainwater is about 5.5, but levels as low as 4.3 have been recorded.

Acid rain lowers the brook's pH level, which significantly affects most of the organisms living in the brook. Some fish, such as the rainbow trout, simply die. Other species, such as Whetstone's brown trout, will not spawn in acidic waters.

In 1987, brown trout did not spawn in Whetstone Brook. The pH level of the brook averaged 5.97 that year. The population of all the trout dropped significantly. In 1989, Dr. Simmons and other researchers instituted an experiment to decrease the acidity of the stream. They created a system to continuously add calcium carbonate, or limestone, in measured amounts to part of the brook. The limestone, which was ground into a powder, immediately reacted with the acid, which raised the pH level of the water.

The experiment lasted three years and managed to raise the average pH level of the stream from 5.97 to 6.54, which met the scientists' goal.

▲ Biologists studied trout to determine the effectiveness of liming Whetstone Brook to raise the pH.

At the same time, the concentration of aluminum ion, which is toxic to trout, in the limed area decreased, while it increased in untreated parts of the brook.

The success of the project was most convincingly demonstrated by the stream's residents. The population of brook trout increased; the mortality rate of brown trout decreased, and for the first time in years, fish actually began to move into the stream from its source, the Millers River. In 1991, Dr. Simmons again tested rainbow trout in the waters of the Whetstone. This time, they all survived.

"We clearly don't view it as a solution," says Dr. Simmons. "It's a band-aid approach, but we need data to make intelligent management decisions as to how useful or harmful liming could be. And I think that is the key thing this study has shown. It has provided us with information that we can use."

Questions

1. Describe two possible benefits of adding measured amounts of $CaCO_3$, a base, to an acidified stream.

2. What elements are responsible for acid rain? How do they get into rainwater?

Determining pH and Titrations

Indicators and pH Meters

An approximate value for the pH of a solution can be obtained using acid-base indicators. **Acid-base indicators** *are compounds whose colors are sensitive to pH.* In other words, the color of an indicator changes as the pH of a solution changes.

Indicators change colors because they are either weak acids or weak bases. In solution, a weak-acid indicator (H*In*) can be represented by the equation below, which is modeled in **Figure 4.**

$$HIn \rightleftharpoons H^+ + In^-$$
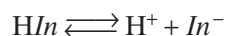
(*In*⁻ is the symbol of the anion part of the indicator.) Because the reaction is reversible, both H*In* and *In*⁻ are present. The colors displayed result from the fact that H*In* and *In*⁻ are different colors.

In acidic solutions, any *In*⁻ ions that are present act as Brønsted bases and accept protons from the acid. The indicator is then present in largely nonionized form, H*In*. The indicator has its acid-indicating color, as shown for litmus in **Figure 4.**

In basic solutions, the OH⁻ ions from the base combine with the H⁺ ions produced by the indicator. The indicator molecules further ionize to offset the loss of H⁺ ions. The indicator is thus present largely in the form of its anion, *In*⁻. The solution now displays the base-indicating color, which for litmus is blue.

In basic solution →
← In acidic solution

Nonionized form   Ionized form
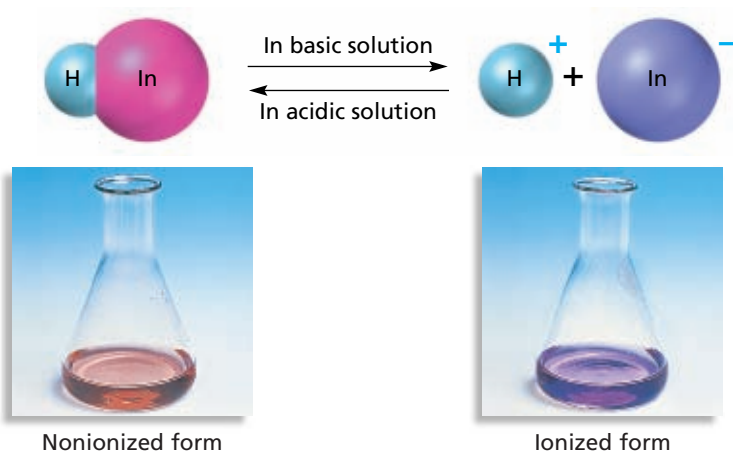
FIGURE 4 Basic solutions shift the equilibrium of litmus to the right. The ionized form, *In*⁻, then predominates, and the litmus turns blue. Acidic solutions shift the equilibrium of the indicator litmus to the left. The nonionized form, H*In*, predominates, and the litmus turns red.
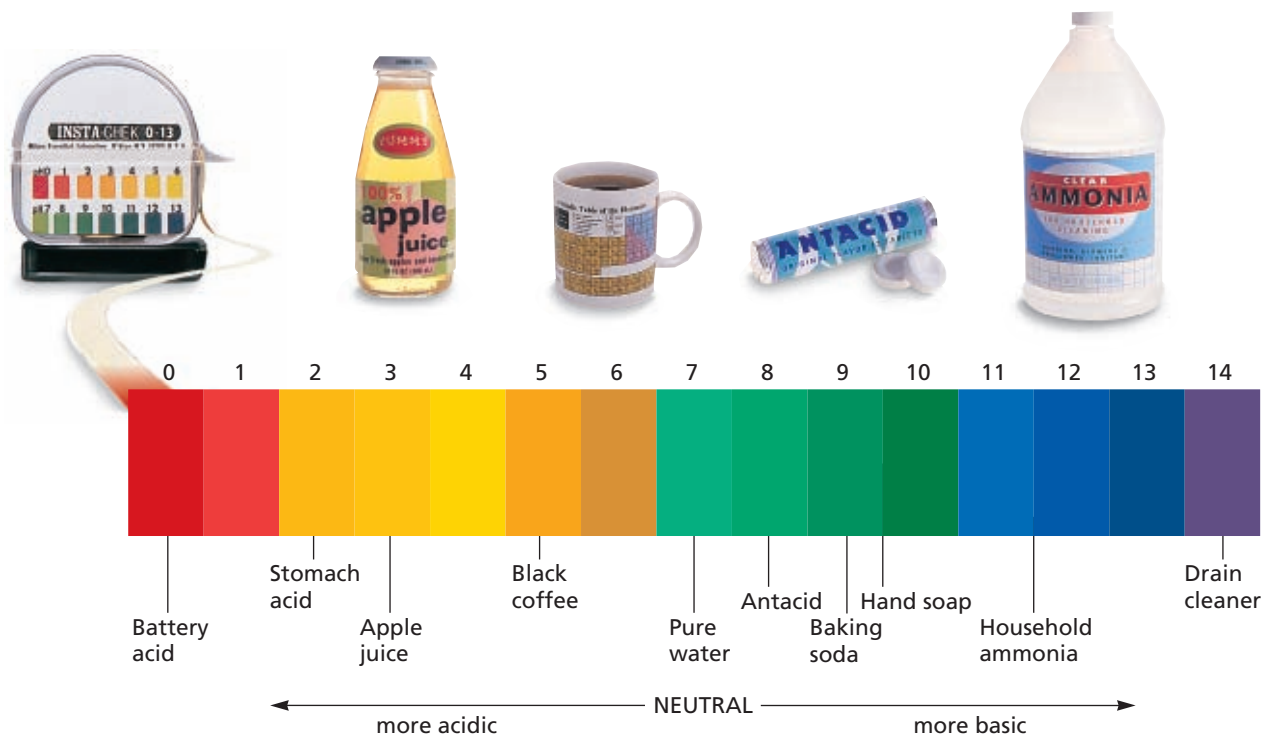
FIGURE 5 The pH of a solution can be determined by comparing the color it turns pH paper with the scale of the paper. The colors of pH paper at various pH values are shown, as are the pH values for some common materials.

FIGURE 6 A pH meter precisely measures the pH of a solution.

Indicators come in many different colors. The exact pH range over which an indicator changes color also varies. *The pH range over which an indicator changes color is called its* **transition interval. Table 6** gives the color changes and transition intervals for a number of common acid-base indicators.

Different indicators change color at different pH values. The color depends on the relative amounts of H*In* and *In*⁻ at a given pH. Methyl red changes from red to yellow between pH 4.4 and 6.2. At pH 4.4, the indicator exists mostly as H*In* molecules, which appear red in the solution. Above pH 6.2, the indicator exists mostly as *In*⁻ ions, which appear yellow. A similar situation exists with other indicators. Phenol red at 6.4 or below is yellow as H*In*. Above 8.0, it is in the *In*⁻ form, which is red. In the transition interval, significant amounts of both forms are present, so the color is due to the mixture of H*In* and *In*⁻.

Universal indicators are made by mixing several different indicators. Paper soaked in universal indicator solution is called pH paper. This paper can turn almost any color of the rainbow and provides a fairly accurate way of distinguishing the pH of solutions, as shown in **Figure 5.**

If a more precise value for the pH of a solution is needed, a pH meter, shown in **Figure 6,** should be used. *A* **pH meter** *determines the pH of a solution by measuring the voltage between the two electrodes that are placed in the solution.* The voltage changes as the hydronium ion concentration in the solution changes.

TABLE 6 Color Ranges of Various Indicators Used in Titrations

Titration type	Indicator	Acid color	Transition color	Base color
Strong acid/ strong base	methyl red (4.4–6.2)			
	bromthymol blue (6.2–7.6)			
Strong acid/ weak base	methyl orange (3.1–4.4)			
	bromphenol blue (3.0–4.6)			
Weak acid/ strong base	phenolphthalein (8.0–10.0)			
	phenol red (6.4–8.0)			

QuickLAB

Wear safety goggles and an apron.

Testing the pH of Rainwater

Question

Do you have acid precipitation in your area?

Procedure

Record all of your results in a data table.

1. Each time it rains, set out five clean jars to collect the rainwater. If the rain continues for more than 24 hours, put out new containers at the end of each 24-hour period until the rain stops. (The same procedure can be used with snow if the snow is allowed to melt before measurements are taken. You may need to use larger containers if a heavy snowfall is expected.)

2. After the rain stops or at the end of each 24-hour period, use a thin, plastic ruler to measure the depth of the water to the nearest 0.1 cm with a thin plastic ruler. Using the pH paper, test the water to determine its pH to the nearest 0.2 to 0.3.

3. Record the following information:
   a. the date and time the collection started
   b. the date and time the collection ended
   c. the location where the collection was made (town and state)
   d. the amount of rainfall in centimeters
   e. the pH of the rainwater

4. Find the average pH of each collection that you have made for each rainfall, and record it in the data table.

5. Collect samples on at least five different days. The more samples you collect, the more informative your data will be.

6. For comparison, determine the pH of pure water by testing five samples of distilled water with pH paper. Record your results in a separate data table, and then calculate an average pH for distilled water.

Discussion

1. What is the pH of distilled water?

2. What is the pH of normal rainwater? How do you explain any differences between the pH readings?

3. What are the drawbacks of using a ruler to measure the depth of collected water? How could you increase the precision of your measurement?

4. Does the amount of rainfall or the time of day the sample is taken have an effect on its pH? Try to explain any variability among samples.

5. What conclusion can you draw from this investigation? Explain how your data support your conclusion.
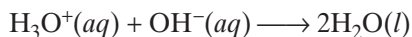
Materials

- rainwater
- distilled water
- 500 mL jars
- thin, transparent metric ruler (± 0.1 cm)
- pH test paper: narrow range, ± 0.2–0.3, or pH meter

Titration

As you know, neutralization reactions occur between acids and bases. The OH⁻ ion acquires a proton from the H₃O⁺ ion, forming two molecules of water. The following equation summarizes this reaction.

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

This equation shows that one mol of hydronium ions and one mol of hydroxide ions are chemically equivalent amounts. They combine in a one-to-one mole ratio. Neutralization occurs when hydronium ions and hydroxide ions are supplied in equal numbers by reactants, as shown in **Figure 7.**

One liter of a 0.10 M HCl solution contains 0.10 mol of hydronium ions. Now suppose that 0.10 mol of solid NaOH is added to 1 L of 0.10 M HCl solution. The NaOH dissolves and supplies 0.10 mol of hydroxide ions to the solution. HCl and NaOH are present in chemically equivalent amounts. Hydronium and hydroxide ions, which are present in equal numbers, combine until the product $[H_3O^+] [OH^-]$ returns to the value of 1×10^{-14}. NaCl, the salt produced in the reaction, is the product of this neutralization of a strong acid and a strong base. The resulting solution is neutral.

Because acids and bases react, the progressive addition of an acid to a base (or a base to an acid) can be used to compare the concentrations of the acid and the base. **Titration** *is the controlled addition and measurement of the amount of a solution of known concentration required to react completely with a measured amount of a solution of unknown concentration.* Titration provides a sensitive means of determining the chemically equivalent amounts of acid and base.
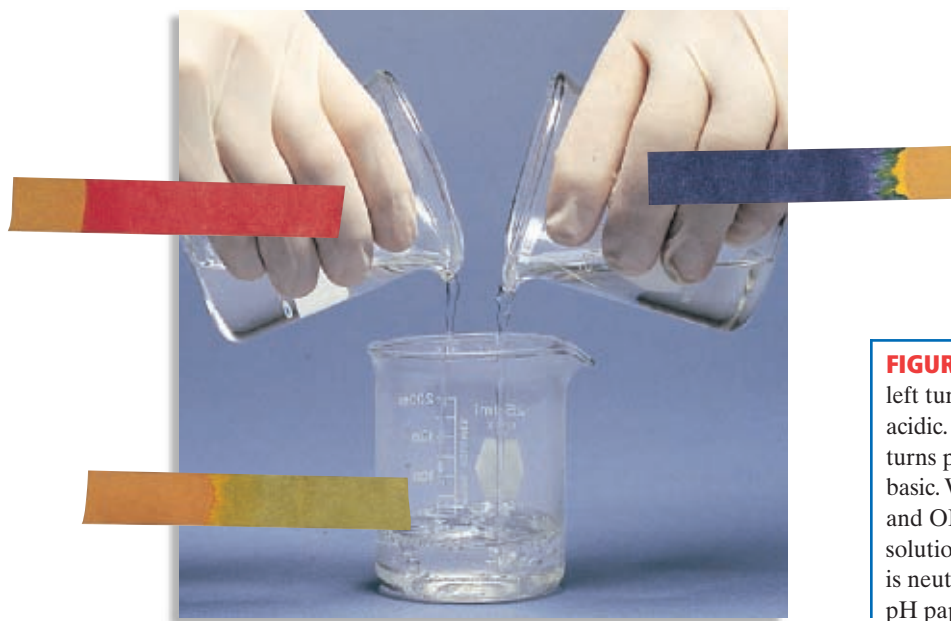

FIGURE 7 The solution on the left turns pH paper red because it is acidic. The solution on the right turns pH paper blue because it is basic. When equal numbers of H₃O⁺ and OH⁻ from the acidic and basic solutions react, the resulting solution is neutral. The neutral solution turns pH paper green.

Equivalence Point

The point at which the two solutions used in a titration are present in chemically equivalent amounts is the **equivalence point.** Indicators and pH meters can be used to determine the equivalence point. The pH will change rapidly as the equivalence point is approached. If an indicator is used, it must change color over a range that includes the pH of the equivalence point, as shown in **Figure 8.** *The point in a titration at which an indicator changes color is called the* **end point** *of the indicator.*

Some indicators, such as litmus, change color at about pH 7. However, the color-change interval for litmus is broad, pH 5.5–8.0. This broad range makes it difficult to determine an accurate pH. Bromthymol blue is better because it has a smaller transition interval, pH 6.2–7.6 (see **Table 6**). Indicators that undergo transition at about pH 7 are used to determine the equivalence point of strong-acid/strong-base titrations because the neutralization of strong acids with strong bases produces a salt solution with a pH of 7.

Indicators that change color at pH lower than 7 are useful in determining the equivalence point of strong-acid/weak-base titrations. Methyl orange is an example of this type. The equivalence point of a strong-acid/weak-base titration is acidic because the salt formed is itself a weak acid. Thus the salt solution has a pH lower than 7 at the equivalence point.

Indicators that change color at pH higher than 7 are useful in determining the equivalence point of weak-acid/strong-base titrations. Phenolphthalein is an example. These reactions produce salt solutions whose pH is greater than 7. This occurs because the salt formed is a weak base.

You may be wondering what type of indicator is used to determine the equivalence point of weak-acid/weak-base titrations. The surprising answer is "none at all." The pH at the equivalence point of a weak-acid/weak-base titration could be acidic, basic, or neutral, depending on
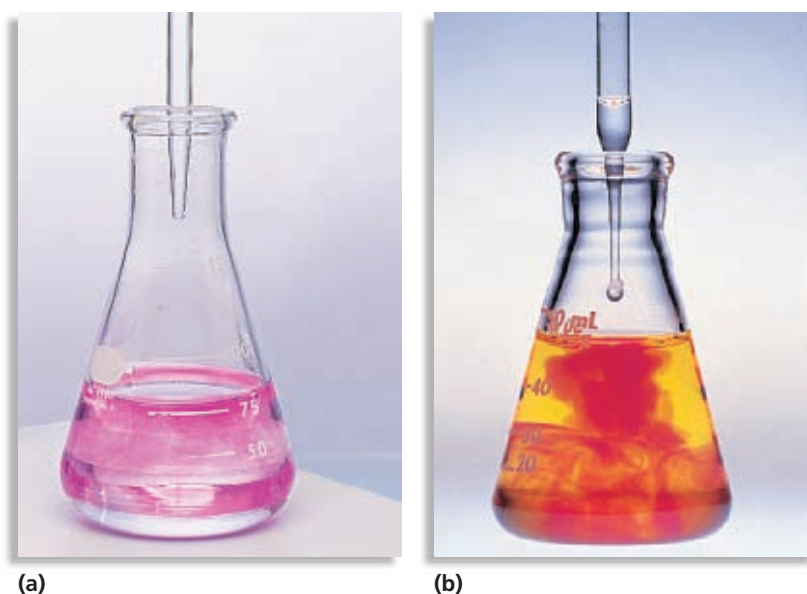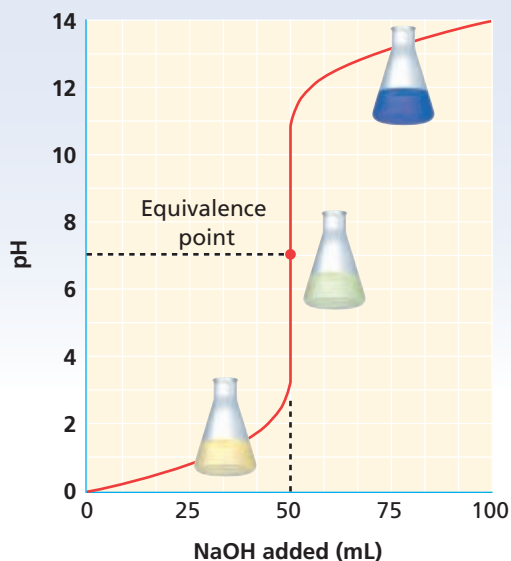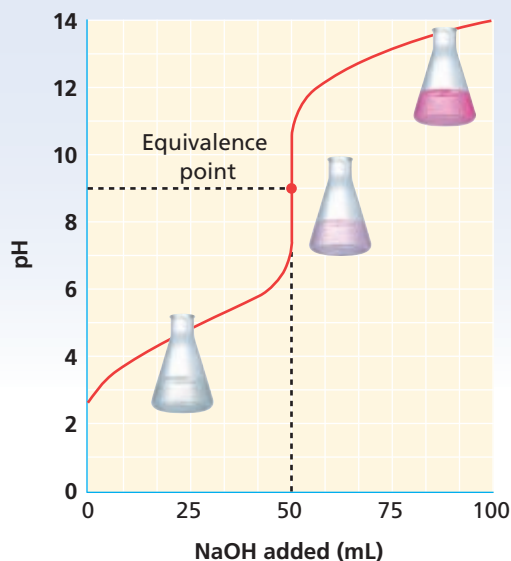

FIGURE 8 Indicators change color at the end point of a titration. Phenolphthalein (a) turns pink and methyl red (b) turns red at the end point of these titrations with a base.

(a)   (b)

Strong Acid Titrated with Strong Base

(a)

Weak Acid Titrated with Strong Base

(b)

the relative acid-base strengths. Since the pH value does not change dramatically as the equivalence point is approached, it is not practical to carry out weak-acid/weak-base titrations.

In a titration, successive additions of an aqueous base are made to a measured volume of an aqueous acid. As base is added, the pH changes from a lower numerical value to a higher one. The change in pH occurs slowly at first, then rapidly through the equivalence point, and then slowly again as the solution becomes more basic. Near the equivalence point, one drop can cause a pH change of 3 to 5 pH units! Typical pH curves for strong-acid/strong-base and weak-acid/strong-base titrations are shown in **Figure 9.**

FIGURE 9 (a) When a strong acid, such as 50.0 mL of 1.00 M HCl, is titrated with a strong base, such as 1.00 M NaOH, the equivalence point occurs at pH 7.00. (b) When a weak acid, such as 50.0 mL of 1.00 M CH_3COOH, is titrated with a strong base, such as 1.00 M NaOH, the initial pH is higher and the equivalence point occurs at a pH above 7.00.

Molarity and Titration

Figure 10 shows the proper method of carrying out a titration. If the concentration of one solution is known precisely, the concentration of the other solution in a titration can be calculated from the chemically equivalent volumes. *The solution that contains the precisely known concentration of a solute is known as a* **standard solution.** It is often called simply the "known" solution.

To be certain of the concentration of the known solution, that solution must first be compared with a solution of a primary standard. *A* **primary standard** *is a highly purified solid compound used to check the concentration of the known solution in a titration.* The known solution is prepared first to give approximately the desired concentration. The known solution concentration is then determined precisely by titrating a carefully measured quantity of the primary standard.

SCLINKS.

www.scilinks.org
**Topic:** Titration/Indicators
Code: HC61533

FIGURE 10 Following is the proper method for carrying out an acid-base titration. To be sure you have an accurate value, you should repeat the titration until you have three results that agree within 0.05 mL. A standardized base solution is used in this procedure to determine the unknown concentration of an acid.


First set up two clean burets as shown. Decide which buret to use for the acid and which to use for the base. Rinse the acid buret three times with the acid that will be used in the titration. Then, rinse the base buret three times with the base solution to be used.

Fill the first buret to a point above the 0 mL calibration mark with the acid of unknown concentration.
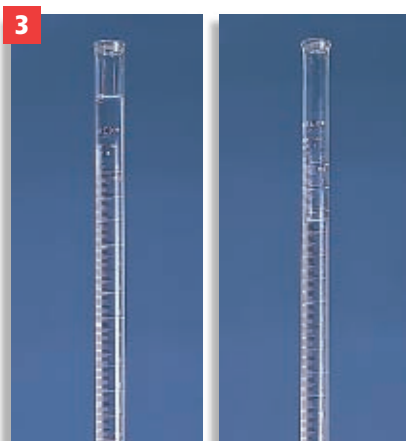
Release some acid from the buret to remove any air bubbles from the tip and to lower the volume to the calibrated portion of the buret.
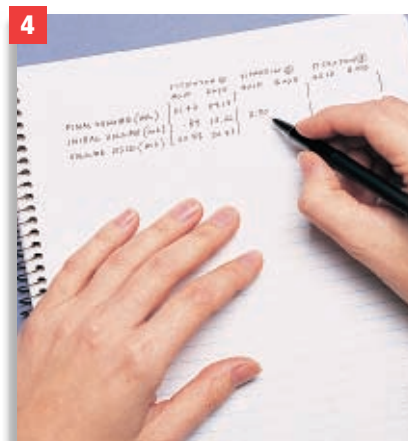
Record the volume of the acid in the buret to the nearest 0.01 mL as the initial volume. Remember to read the volume at the bottom of the meniscus.

Allow approximately the volume of acid that was determined by your teacher or lab procedure to flow into a clean Erlenmeyer flask.

Subtract the initial volume reading on the buret from the final reading. This is the exact volume of the acid released into the flask. Record it to the nearest 0.01 mL.

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

Fill the other buret with the standard base solution to a point above the calibration mark. The concentration of the standard base is known to a certain degree of precision because the base was previously titrated with an exact mass of solid acid, which is the primary standard.
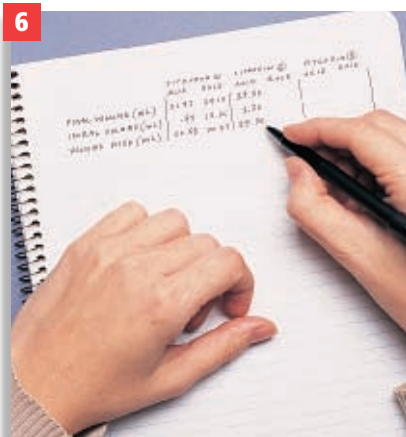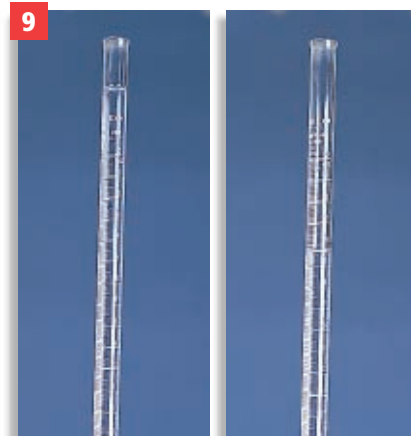

Release some base from the buret to remove any air bubbles and to lower the volume to the calibrated portion of the buret.

Record the volume of the base to the nearest 0.01 mL as your initial volume. Remember to read the volume at the bottom of the meniscus.

Place the Erlenmeyer flask under the base buret as shown. Notice that the tip of the buret extends into the mouth of the flask.

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

The titration is nearing the end point when the pink color stays for longer periods of time. At this point, add base drop by drop.

The equivalence point is reached when a very light pink color remains after 30 seconds of swirling.


Subtract the initial volume reading on the buret from the final reading. This is the exact volume of the base released into the flask. Record it to the nearest 0.01 mL.

The known solution can be used to determine the molarity of another solution by titration. Suppose 20.0 mL of 5.00×10^{-3} M NaOH is required to reach the end point in the titration of 10.0 mL of HCl of unknown concentration. How can these titration data be used to determine the molarity of the acidic solution?

Begin with the balanced neutralization reaction equation. From the equation, determine the chemically equivalent amounts of HCl and NaOH.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
$$\text{1 mol} \qquad \text{1 mol} \qquad \qquad \text{1 mol} \qquad \text{1 mol}$$
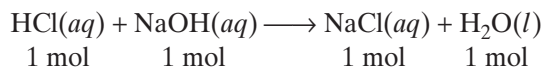
Calculate the number of moles of NaOH used in the titration.

$$\frac{5.00 \times 10^{-3} \text{ mol NaOH}}{1 \, \cancel{L}} \times \frac{1 \, \cancel{L}}{1000 \, \cancel{mL}} \times 20.0 \, \cancel{mL} = 1.00 \times 10^{-4} \text{ mol NaOH used}$$

Because 1 mol of NaOH is needed to neutralize 1 mol of HCl, the amount of HCl in the titration must be 1.00×10^{-4} mol. This is confirmed by the following equation.

$$1.00 \times 10^{-4} \, \cancel{\text{mol NaOH}} \times \frac{1 \text{ mol HCl}}{1 \, \cancel{\text{mol NaOH}}} = 1.00 \times 10^{-4} \text{ mol HCl}$$

This amount of acid must be in the 10.0 mL of the HCl solution used for the titration. The molarity of the HCl solution can now be calculated.

$$\frac{1.00 \times 10^{-4} \text{ mol HCl}}{10.0 \, \cancel{mL}} \times \frac{1000 \, \cancel{mL}}{1 \text{ L}} = \frac{1.00 \times 10^{-2} \text{ mol HCl}}{1 \text{ L}}$$
$$= 1.00 \times 10^{-2} \text{ M HCl}$$

Sample Problem F illustrates the following four steps.
1. Start with the balanced equation for the neutralization reaction, and determine the chemically equivalent amounts of the acid and base.
2. Determine the moles of acid (or base) from the known solution used during the titration.
3. Determine the moles of solute of the unknown solution used during the titration.
4. Determine the molarity of the unknown solution.

SAMPLE PROBLEM F

In a titration, 27.4 mL of 0.0154 M Ba(OH)$_2$ is added to a 20.0 mL sample of HCl solution of unknown concentration until the equivalence point is reached. What is the molarity of the acid solution?

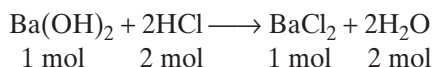### SOLUTION

1 ANALYZE

Given: volume and concentration of known solution = 27.4 mL of 0.0154 M Ba(OH)$_2$
volume of unknown HCl solution = 20.0 mL

Unknown: molarity of acid solution

2 PLAN

1. balanced neutralization equation $\longrightarrow$ chemically equivalent amounts

$$Ba(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O$$
$$\text{1 mol} \qquad \text{2 mol} \qquad \text{1 mol} \quad \text{2 mol}$$

2. volume of known basic solution used (mL) $\longrightarrow$ amount of base used (mol)

$$\frac{\text{mol Ba(OH)}_2}{\text{1 L}} \times \text{mL of Ba(OH)}_2 \text{ solution} \times \frac{\text{1 L}}{\text{1000 mL}} = \text{mol Ba(OH)}_2$$

3. moles of base used, mole ratio $\longrightarrow$ moles of acid used from unknown solution

$$\text{mol Ba(OH)}_2 \times \frac{\text{2 mol HCl}}{\text{1 mol Ba(OH)}_2} \text{ in known solution} = \text{mol HCl in unknown solution}$$

4. volume of unknown, moles of solute in unknown $\longrightarrow$ molarity of unknown

$$\frac{\text{amount of solute in unknown solution (mol)}}{\text{volume of unknown solution (mL)}} \times \frac{\text{1000 mL}}{\text{1 L}} = \text{molarity of unknown solution}$$

3 COMPUTE

1. The mole ratio from the equation is 1 mol Ba(OH)$_2$ for every 2 mol HCl.

2. $\dfrac{0.0154 \text{ mol Ba(OH)}_2}{1 \text{ L}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}} \times 27.4 \text{ mL} = 4.22 \times 10^{-4} \text{ mol Ba(OH)}_2$

3. $4.22 \times 10^{-4} \text{ mol Ba(OH)}_2 \times \dfrac{2 \text{ mol HCl}}{1 \text{ mol Ba(OH)}_2} = 8.44 \times 10^{-4} \text{ mol HCl}$

4. $\dfrac{8.44 \times 10^{-4} \text{ mol HCl}}{20.0 \text{ mL}} \times \dfrac{1000 \text{ mL}}{1 \text{ L}} = \dfrac{4.22 \times 10^{-2} \text{ mol HCl}}{1 \text{ L}} = 4.22 \times 10^{-2} \text{ M HCl}$

PRACTICE   *Answers in Appendix E*

1. A 15.5 mL sample of 0.215 M KOH solution required 21.2 mL of aqueous acetic acid solution in a titration experiment. Calculate the molarity of the acetic acid solution.

2. By titration, 17.6 mL of aqueous H$_2$SO$_4$ neutralized 27.4 mL of 0.0165 M LiOH solution. What was the molarity of the aqueous acid solution?

SECTION REVIEW

1. Name an appropriate indicator for titrating the following:

   a. a strong acid and a weak base

   b. a strong base and a weak acid

2. If 20.0 mL of 0.0100 M aqueous HCl is required to neutralize 30.0 mL of an aqueous solution of NaOH, determine the molarity of the NaOH solution.

3. Suppose that 20.0 mL of 0.010 M Ca(OH)$_2$ is required to neutralize 12.0 mL of aqueous HCl solution. What is the molarity of the HCl solution?

Critical Thinking

4. **PREDICTING OUTCOMES** Sketch the titration curve for 50.0 mL of 0.10 M NH$_3$ that is titrated with 0.10 M HCl.

Aqueous Solutions and the Concept of pH

Vocabulary

self-ionization of water

pH

pOH

- Pure water undergoes self-ionization to give 1.0×10^{-7} M H_3O^+ and 1.0×10^{-7} M OH^- at 25°C.
- $pH = -\log[H_3O^+]$; $pOH = -\log[OH^-]$; at 25°C, $pH + pOH = 14.0$.
- At 25°C, acids have a pH of less than 7, bases have a pH of greater than 7, and neutral solutions have a pH of 7.
- If a solution contains a strong acid or a strong base, the $[H_3O^+]$, $[OH^-]$, and pH can be calculated from the molarity of the solution. If a solution contains a weak acid or a weak base, the $[H_3O^+]$ and the $[OH^-]$ must be calculated from an experimentally measured pH.

Determining pH and Titrations

Vocabulary

acid-base indicators

transition interval

pH meter

titration

equivalence point

end point

standard solution

primary standard

- The pH of a solution can be measured using either a pH meter or acid-base indicators.
- Titration uses a solution of known concentration to determine the concentration of a solution of unknown concentration.
- To determine the end point of a titration, one should choose indicators that change color over ranges that include the pH of the equivalence point.
- When the molarity and volume of a known solution used in a titration are known, then the molarity of a given volume of an unknown solution can be found.

Aqueous Solutions and the Concept of pH

SECTION 1 REVIEW

1. Why is pure water a very weak electric conductor?

2. What does it mean when the formula of a particular ion or molecule is enclosed in brackets?

3. a. What is the $[H_3O^+]$ of pure water at 25°C?
   b. Is this true at all temperatures? Why or why not?

4. a. What is always true about the $[H_3O^+]$ value of acidic solutions?
   b. What is true about the $[H_3O^+]$ value of acidic solutions at 25°C?

5. a. Describe what is meant by the pH of a solution.
   b. Write the equation for determining pH.
   c. Explain and illustrate what is meant by the common logarithm of a number.

6. Identify each of the following solutions that are at 25°C as acidic, basic, or neutral:
   a. $[H_3O^+] = 1.0 \times 10^{-7}$ M
   b. $[H_3O^+] = 1.0 \times 10^{-10}$ M
   c. $[OH^-] = 1.0 \times 10^{-7}$ M
   d. $[OH^-] = 1.0 \times 10^{-11}$ M
   e. $[H_3O^+] = [OH^-]$
   f. pH = 3.0
   g. pH = 13.0

7. Arrange the following common substances in order of increasing pH:
   a. eggs   f. potatoes
   b. apples   g. lemons
   c. tomatoes   h. milk of magnesia
   d. milk   i. sea water
   e. bananas

PRACTICE PROBLEMS

8. Calculate the $[H_3O^+]$ and $[OH^-]$ for each of the following. (Hint: See Sample Problem A.)
   a. 0.030 M HCl
   b. 1.0×10^{-4} M NaOH
   c. 5.0×10^{-3} M HNO_3
   d. 0.010 M $Ca(OH)_2$

9. Determine the pH of each of the following solutions. (Hint: See Sample Problem B.)
   a. 1.0×10^{-2} M HCl   c. 1.0×10^{-5} M HI
   b. 1.0×10^{-3} M HNO_3 d. 1.0×10^{-4} M HBr

10. Given the following $[OH^-]$ values, determine the pH of each solution.
    a. 1.0×10^{-6} M   c. 1.0×10^{-2} M
    b. 1.0×10^{-9} M   d. 1.0×10^{-7} M

11. Determine the pH of each solution.
    a. 1.0×10^{-2} M NaOH
    b. 1.0×10^{-3} M KOH
    c. 1.0×10^{-4} M LiOH

12. Determine the pH of solutions with each of the following $[H_3O^+]$. (Hint: See Sample Problem C.)
    a. 2.0×10^{-5} M
    b. 4.7×10^{-7} M
    c. 3.8×10^{-3} M

13. Given the following pH values, determine the $[H_3O^+]$ for each solution. (Hint: See Sample Problem D.)
    a. 3.0   c. 11.0
    b. 7.00   d. 5.0

14. Given the following pH values, determine the $[OH^-]$ for each solution.
    a. 7.00   c. 4.00
    b. 11.00   d. 6.00

15. Determine $[H_3O^+]$ for solutions with the following pH values. (Hint: See Sample Problem E.)
    a. 4.23
    b. 7.65
    c. 9.48

16. A nitric acid solution is found to have a pH of 2.70. Determine each of the following:
    a. $[H_3O^+]$
    b. $[OH^-]$
    c. the number of moles of HNO_3 required to prepare 5.50 L of this solution
    d. the mass of HNO_3 in the solution in part (c)
    e. the milliliters of concentrated acid needed to prepare the solution in part (c) (Concentrated nitric acid is 69.5% HNO_3 by mass and has a density of 1.42 g/mL.)

Determining pH and Titrations

SECTION 2 REVIEW

17. What is meant by the transition interval of an indicator?

18. Explain how changes in pH affect the color of an indicator.

19. a. Without using an indicator, how can you determine the equivalence point of a titration experiment or the pH of a solution?
b. What can be observed about the rate of change of the pH of a solution near the end point of a titration?

20. a. What is meant by the end point of a titration?
b. What is the role of an indicator in the titration process?
c. On what basis is an indicator selected for a particular titration experiment?

21. For each of the four possible types of acid-base titration combinations (strong-strong, strong-weak, etc.), indicate the approximate pH at the end point. Also name a suitable indicator for detecting that end point.

22. Use **Figures 9(a)** and **9(b)** to sketch the pH curve of a strong acid being titrated by a weak base.

23. An unknown solution is colorless when tested with phenolphthalein but causes the indicator phenol red to turn red. Use this information to find the approximate pH of this solution.

PRACTICE PROBLEMS

24. For each of the following acid-base titration combinations, determine the number of moles of the first substance listed that would be the chemically equivalent amount of the second substance.
a. NaOH with 1.0 mol HCl
b. HNO_3 with 0.75 mol KOH
c. $Ba(OH)_2$ with 0.20 mol HF
d. H_2SO_4 with 0.90 mol $Mg(OH)_2$

25. Suppose that 15.0 mL of 2.50×10^{-2} M aqueous H_2SO_4 is required to neutralize 10.0 mL of an aqueous solution of KOH. What is the molarity of the KOH solution? (Hint: See Sample Problem F.)

26. In a titration experiment, a 12.5 mL sample of 1.75×10^{-2} M $Ba(OH)_2$ just neutralized 14.5 mL of HNO_3 solution. Calculate the molarity of the HNO_3 solution.

MIXED REVIEW

27. a. What is the $[OH^-]$ of a 4.0×10^{-4} M solution of $Ca(OH)_2$?
b. What is the $[H_3O^+]$ of the solution?

28. Given the following $[H_3O^+]$ values, determine the pH of each solution.
a. 1.0×10^{-7} M   c. 1.0×10^{-12} M
b. 1.0×10^{-3} M   d. 1.0×10^{-5} M

29. What is the $[H_3O^+]$ for a solution that has a pH of 6.0?

30. Suppose that a 5.0×10^{-5} M solution of $Ba(OH)_2$ is prepared. What is the pH of the solution?

31. a. Calculate the pH of a solution that has an $[H_3O^+]$ of 8.4×10^{-11} M.
b. Calculate the $[H_3O^+]$ of a solution that has a pH of 2.50.

32. a. What is the concentration of OH^- in a 5.4×10^{-5} M solution of magnesium hydroxide, $Mg(OH)_2$?
b. Calculate the concentration of H_3O^+ for this solution.

33. a. Calculate the molarity of H_3O^+ in a solution that has a pH of 8.90.
b. Calculate the concentration of OH^- for this solution.

34. What is the pH of a solution in which $[OH^-]$ equals 6.9×10^{-10} M?

35. In a titration, 25.9 mL of 3.4×10^{-3} M $Ba(OH)_2$ neutralized 16.6 mL of HCl solution. What is the molarity of the HCl solution?

36. Find the molarity of a $Ca(OH)_2$ solution given that 428 mL of the solution is neutralized in a titration by 115 mL of 6.7×10^{-3} M HNO_3.

37. Suppose that 10.1 mL of HNO_3 is neutralized by 71.4 mL of a 4.2×10^{-3} M solution of KOH in a titration. Calculate the concentration of the HNO_3 solution.

CRITICAL THINKING

38. Interpreting Graphics The following titration curve resulted from the titration of an unknown acid with 0.10 M NaOH. Analyze the curve. Make inferences related to the type of acidic solution titrated.

Titration of an Unknown Acid
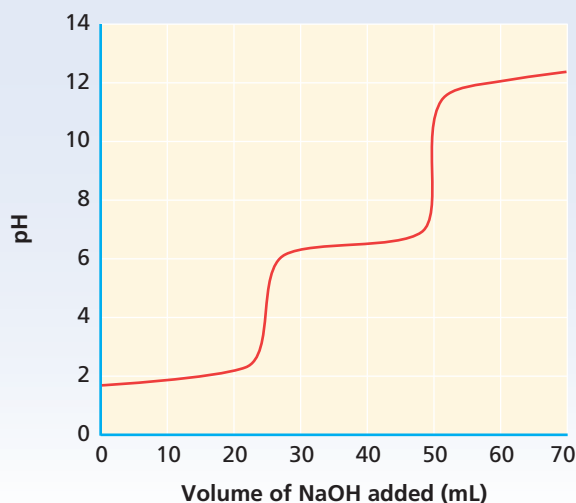
USING THE HANDBOOK

39. The normal pH of blood is about 7.4. When the pH shifts above or below that level, the results are acidosis or alkalosis. Review the section on blood pH in Group 14 of the *Elements Handbook,* and answer the following.
   a. What chemical species keep H_3O^+ in blood at the appropriate pH?
   b. What condition results when there is an excess of CO_2 in the blood?
   c. What is hyperventilation and how does it affect blood pH?

RESEARCH & WRITING

40. Examine the labels of at least five brands of shampoo. Note what is written there, if anything, regarding the pH of the shampoo. Do library research to find out why such pH ranges are chosen and why other ranges might be harmful to hair or eyes.

41. Acid rain is an environmental issue that crosses state and national boundaries. Conduct library research on this topic and write a brief report. Include a description of the areas in the United States affected by acid rain, and the geographical source of the sulfur and nitrogen oxides that are responsible for acid rain in each region.

ALTERNATIVE ASSESSMENT

42. Performance Use pH paper to determine the approximate pH of various brands of orange juice, which contains citric acid.

43. Performance Design and conduct an experiment to extract possible acid-base indicators from sources such as red cabbage, berries, and flower petals. Use known acidic, basic, and neutral solutions to test the action of each indicator that you are able to isolate.

extension

Graphing Calculator
Acid-Base Titration
Go to **go.hrw.com** for a graphing calculator exercise that asks you to graph acid-base titration curves.

Keyword: HC6ABTX

Math Tutor USING LOGARITHMS AND pH

When you work with acids and bases, you often need to state the hydronium ion concentration, $[H_3O^+]$, of a solution. One simple way is to use the negative logarithm of $[H_3O^+]$. This quantity is called *pH*. For example, pure water has a $[H_3O^+]$ of 1.00×10^{-7} M. So, the pH of pure water is $-\log (1.00 \times 10^{-7} \text{ M}) = 7.00$. A solution of 0.1 M HCl has a pH of 1.00 or pH $= -\log(1 \times 10^{-1}) = 1.00$. The term *pOH* is also used for the negative logarithm of the hydroxide ion concentration, $[OH^-]$. The pOH of pure water is also 7.00.

Problem-Solving *TIPS*

- For pure water at 25°C, $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ M.
- The ionization constant of water, K_w, is the product of $[H_3O^+]$ and $[OH^-]$, so
  $$K_w = [H_3O^+][OH^-] = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) = 1.00 \times 10^{-14} \text{ at } 25°C.$$
- If you know either $[H_3O^+]$ or $[OH^-]$, you can determine the other concentration.
- In terms of pH and pOH, pH + pOH = 14.00 for an aqueous solution at 25°C.
- Because pH calculations involve scientific notation and changes in signs, you should always check to see if answers make sense.

SAMPLE 1

What is the pH of a 0.0046 M solution of KOH?

KOH is completely dissociated into equal numbers of $K^+(aq)$ and $OH^-(aq)$. The concentration of OH^- is the same as the concentration of dissolved KOH, 0.0046 M. So, $[OH^-] = 4.6 \times 10^{-3}$ M, and pOH $= -\log (4.6 \times 10^{-3} \text{ M}) = 2.34$.

For an aqueous solution at 25°C, pH + pOH = 14.00, so pH + 2.34 = 14.00.

Therefore, the pH of 0.0046 M KOH solution = 14.00 − 2.34 = 11.66.

SAMPLE 2

What is the hydronium ion concentration, $[H_3O^+]$, of a solution with a pH of 4.08? What is the pOH of the solution?

In this solution,
$$\log [H_3O^+] = -4.08$$
$$[H_3O^+] = \text{antilog} (-4.08) = 0.000 \, 083 \text{ M} = 8.3 \times 10^{-5} \text{ M}$$

The pOH of the solution is 14.00 − pH = 14.00 − 4.08 = 9.92.

PRACTICE PROBLEMS

1. What is the pH of a 0.000 85 M solution of nitric acid, HNO_3, which is a strong acid?

2. What is the hydroxide ion concentration of an aqueous solution that has a pH of 9.95?

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

1. Distilled water contains
   A. H_2O.
   B. H_3O^+.
   C. OH^-.
   D. All of the above

2. What is the pH of a 0.0010 M HNO_3?
   A. 1.0
   B. 3.0
   C. 4.0
   D. 5.0

3. Which of the following solutions would have a pH value greater than 7?
   A. $[OH^-] = 2.4 \times 10^{-2}$ M
   B. $[H_3O^+] = 1.53 \times 10^{-2}$ M
   C. 0.0001 M HCl
   D. $[OH^-] = 4.4 \times 10^{-9}$ M

4. If the pH of a solution of the strong base NaOH is known, which property of the solution can be calculated?
   A. molar concentration
   B. $[OH^-]$
   C. $[H_3O^+]$
   D. All of the above

5. A neutral aqueous solution
   A. has a 7.0 M H_3O^+ concentration.
   B. contains neither hydronium ions nor hydroxide ions.
   C. has an equal number of hydronium ions and hydroxide ions.
   D. None of the above

6. Identify the salt that forms when a solution of H_2SO_4 is titrated with a solution of $Ca(OH)_2$.
   A. calcium sulfate
   B. calcium hydroxide
   C. calcium oxide
   D. calcium phosphate

7. The pH of a solution is 6.32. What is the pOH?
   A. 6.32
   B. 4.8×10^{-7}
   C. 7.68
   D. 2.1×10^{-8}

8. The K_w value for water can be affected by
   A. dissolving a salt in the solution.
   B. changes in temperature.
   C. changes in the hydroxide ion concentration.
   D. the presence of a strong acid.

9. Which of the pH levels listed below is the most acidic?
   A. pH = 1
   B. pH = 5
   C. pH = 9
   D. pH = 13

SHORT ANSWER

10. A solution has a pH of 4.75. What is the hydronium ion concentration? Is the solution acidic or basic?

11. A weak acid that is used as an indicator is added to a strong acid solution before titration of the strong acid with a strong base. Why doesn't the weak acid affect the value calculated for the concentration of the acid?

EXTENDED RESPONSE

12. The hydroxide ion concentration in a solution is 1.6×10^{-11} M. What are the $[H_3O^+]$, the pH, and the pOH of the solution?

13. Write the balanced equation and the net ionic equation that represent the reaction that takes place when milk of magnesia (magnesium hydroxide) reacts with hydrochloric acid in your stomach.

Test TIP If you do not understand a question, try to reword it. But be careful not to change its meaning.

How Much Calcium Carbonate Is in an Eggshell?

OBJECTIVES

- *Determine* the amount of calcium carbonate present in an eggshell.

- *Relate* experimental titration measurements to a balanced chemical equation.

- *Infer* a conclusion from experimental data.

- *Apply* reaction stoichiometry concepts.

MATERIALS

- 1.00 M HCl
- 1.00 M NaOH
- 10 mL graduated cylinder
- 50 mL micro solution bottle or small Erlenmeyer flask
- 100 mL beaker
- balance
- desiccator (optional)
- distilled water
- drying oven
- eggshell
- forceps
- mortar and pestle
- phenolphthalein solution
- thin-stemmed pipets or medicine droppers, 3
- weighing paper

BACKGROUND

The calcium carbonate content of eggshells can be easily determined by means of an acid/base back-titration. In this experiment, a strong acid will react with calcium carbonate in eggshells. Then, the amount of unreacted acid will be determined by titration with a strong base.

SAFETY

For review of safety, please see **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. Wash an empty eggshell with distilled water and carefully peel all the membranes from its inside. Place *all* of the shell in a premassed beaker and dry the shell in the drying oven at 110°C for about 15 min.

2. Copy data and calculations tables from your teacher.

3. Put exactly 5.0 mL of water in the 10.0 mL graduated cylinder. Record this volume in your data table. Label the first pipet "Acid." To calibrate the pipet, fill it with water. **Do not use this pipet for the base solution.** Holding the pipet vertically, add 20 drops of water to the cylinder. Record the new volume of water in the graduated cylinder in the first data table under Trial 1.

4. Without emptying the graduated cylinder, add an additional 20 drops from the pipet. Record the new volume for Trial 2. Repeat this procedure once more for Trial 3.

5. Repeat Preparation steps 3 and 4 for the second pipet. Label this pipet "Base." **Do not use this pipet for the acid solution.**

6. Make sure that the three trials produce data that are similar to one another. If one is greatly different from the others, perform Preparation steps 3–5 again.

7. Remove the beaker containing the eggshell from the oven. Cool them in a desiccator. Record the mass of the entire eggshell in the second table. Place half of the shell into the clean mortar, and grind the shell into a very fine powder.

PROCEDURE

1. Measure the mass of a piece of weighing paper. Transfer about 0.1 g of ground eggshell to a piece of weighing paper, and measure the eggshell's mass as accurately as possible. Record the mass in the second data table. Place this eggshell sample into a clean, 50 mL micro solution bottle (or Erlenmeyer flask).

2. Fill the acid pipet with 1.00 M HCl acid solution, and then empty the pipet into an extra 100 mL beaker. Label the beaker "Waste." Fill the base pipet with the 1.00 M NaOH base solution, and then empty the pipet into the waste beaker.

3. Fill the acid pipet once more with 1.00 M HCl. Holding the acid pipet vertically, add exactly 150 drops of 1.00 M HCl to the bottle or flask that contains the eggshell. Swirl the flask gently for 3 to 4 min. Observe the reaction taking place. Wash down the sides of the flask with about 10 mL of distilled water. Using a third pipet, add two drops of phenolphthalein solution.

4. Fill the base pipet with the 1.00 M NaOH. Slowly add NaOH from the base pipet into the bottle or flask that contains the eggshell reaction mixture, counting and recording the drops added. Stop adding base when the mixture remains a faint pink color, even after it is swirled gently. **Be sure to add the base drop by drop, and be certain the drops end up in the reaction mixture and not on the walls of the bottle or flask.** Record in the second data table the number of drops of base used.

CLEANUP AND DISPOSAL

5. Clean all equipment and your lab station. Dispose of chemicals and solutions as directed by your teacher. Wash your hands thoroughly before you leave the lab.

ANALYSIS AND INTERPRETATION

1. Organizing Ideas: The calcium carbonate in the eggshell sample undergoes a double-displacement reaction with the HCl in step 3. Write a balanced chemical equation for this reaction. (Hint: The gas evolved was CO_2.)

2. Organizing Ideas: Write the balanced chemical equation for the acid/base neutralization of the excess unreacted HCl with the NaOH.

3. Organizing Data: Calculate the volume of each drop in milliliters. Then convert the number of drops of HCl into volume in milliliters. Record this volume in your data table. Repeat this step for the drops of NaOH.

4. Organizing Data: Using the relationship between the molarity and volume of acid and the molarity and volume of base needed to neutralize it, calculate the number of moles of the HCl solution that was neutralized by the NaOH, and record it in your table. (Hint: This relationship was discussed in Section 2.)

5. Analyzing Results: Calculate the number of moles of HCl that reacted with the $CaCO_3$ and record both in your table.

CONCLUSIONS

1. Organizing Data: Use the balanced equation for the reaction to calculate the number of moles of $CaCO_3$ that reacted with the HCl, and record this number in your table.

2. Organizing Data: Use the periodic table to calculate the molar mass of $CaCO_3$. Then, use the number of moles of $CaCO_3$ to calculate the mass of $CaCO_3$ in your eggshell sample. Record this mass in your data table. Using the mass of $CaCO_3$, calculate the percentage of $CaCO_3$ in your eggshell and record it in your data table.

Reaction Energy

Many chemical reactions give off or take in energy as heat.

Kilauea volcano erupting, Hawaii Island

Thermochemistry

Virtually every chemical reaction is accompanied by a change in energy. Chemical reactions usually absorb or release energy as heat. You learned in Chapter 10 that energy is also absorbed or released in physical changes, such as melting a solid or condensing a vapor. **Thermochemistry** *is the study of the transfers of energy as heat that accompany chemical reactions and physical changes.*

Heat and Temperature

The energy absorbed or released as heat in a chemical or physical change is measured in a **calorimeter.** In one kind of calorimeter, known quantities of reactants are sealed in a reaction chamber, which is immersed in a known quantity of water in an insulated vessel. Therefore, the energy given off (or absorbed) during the reaction is equal to the energy absorbed (or given off) by the known quantity of water. The amount of energy is determined from the temperature change of the known mass of surrounding water. The data collected from calorimetry experiments are temperature changes because energy cannot be measured directly; but temperature, which is affected by the transfer of energy as heat, is directly measurable. To see why this is so, let us look at the definitions of heat and temperature and at how temperature is measured.

Temperature *is a measure of the average kinetic energy of the particles in a sample of matter.* The greater the kinetic energy of the particles in a sample, the higher the temperature is and the hotter it feels. To assign a numerical value to temperature, it is necessary to define a temperature scale. For calculations in thermochemistry, we use the Celsius and Kelvin scales. Celsius and Kelvin temperatures are related by the following equation.

$$K = 273.15 + {}^\circ C$$

For most calculations in this book, 273.15 is rounded to 273.

The ability to measure temperature is thus based on energy transfer. The amount of energy transferred as heat is usually measured in joules. *A* **joule** *is the SI unit of heat as well as all other forms of energy*. The joule, abbreviated J, is derived from the units for force and length.

$$N \times m = \frac{kg \times m^2}{s^2}$$

FIGURE 1 The direction of energy transfer is determined by the temperature differences between the objects within a system. The energy is transferred as heat from the hotter brass bar to the cooler water. This energy transfer will continue until the bar and the water reach the same temperature.

Heat *can be thought of as the energy transferred between samples of matter because of a difference in their temperatures.* Energy transferred as heat always moves spontaneously from matter at a higher temperature to matter at a lower temperature, as shown in **Figure 1.** The temperature of the cool water in the beaker increases as energy flows into it. Likewise, the temperature of the hot brass bar decreases as energy flows away from it. When the temperature of the water equals the temperature of the brass bar, energy is no longer transferred as heat within the system.

Specific Heat

The quantity of energy transferred as heat during a temperature change depends on the nature of the material changing temperature, the mass of the material changing temperature, and the size of the temperature change. One gram of iron heated to 100.0°C and cooled to 50.0°C in a calorimeter transfers 22.5 J of energy to the surrounding water. But one gram of silver transfers 11.8 J of energy under the same conditions. The difference depends on the metals' differing capacities for absorbing this energy. A quantity called specific heat can be used to compare heat absorption capacities for different materials. **Specific heat** *is the amount of energy required to raise the temperature of one gram of a substance by one Celsius degree (1°C) or one kelvin (1 K)*(because the sizes of the degree divisions on both scales are equal). Values of specific heat can be given in units of joules per gram per Celsius degree, J/(g•°C), joules per gram per kelvin, J/(g•K), or calories per gram per Celsius degree, cal/(g•°C). **Table 1** gives the specific heats of some common substances. Notice the extremely high specific heat of water, one of the highest of most common substances.

Specific heat is usually measured under constant pressure conditions, so its symbol, c_p, contains a subscripted p as a reminder to the reader.

TABLE 1 Specific Heats of Some Common Substances at 298.15 K

Substance	Specific heat J/(g·K)
Water (*l*)	4.18
Water (*s*)	2.06
Water (*g*)	1.87
Ammonia (*g*)	2.09
Benzene (*l*)	1.74
Ethanol (*l*)	2.44
Ethanol (*g*)	1.42
Aluminum (*s*)	0.897
Calcium (*s*)	0.647
Carbon, graphite (*s*)	0.709
Copper (*s*)	0.385
Gold (*s*)	0.129
Iron (*s*)	0.449
Mercury (*l*)	0.140
Lead (*s*)	0.129

In the following mathematical equation, c_p is the specific heat at a given pressure, q is the energy lost or gained, m is the mass of the sample, and ΔT represents the difference between the initial and final temperatures.

$$c_p = \frac{q}{m \times \Delta T}$$

This equation can be rearranged to give an equation that can be used to find the quantity of energy gained or lost with a change in temperature.

$$q = c_p \times m \times \Delta T$$

SAMPLE PROBLEM A

A 4.0 g sample of glass was heated from 274 K to 314 K, a temperature increase of 40. K, and was found to have absorbed 32 J of energy as heat.

a. What is the specific heat of this type of glass?

b. How much energy will the same glass sample gain when it is heated from 314 K to 344 K?

SOLUTION

1 ANALYZE

Given: $m = 4.0$ g

$\Delta T = 40.$ K

$q = 32$ J

Unknown: c_p in J/(g·K)

2 *PLAN*   **a.** The specific heat, c_p, of the glass is calculated using the equation given for specific heat.

$$c_p = \frac{q}{m \times \Delta T}$$

b. The rearranged specific heat equation is used to find the energy gained when the glass was heated.

$$q = c_p \times m \times \Delta T$$

3 *COMPUTE*   **a.** $\dfrac{32 \text{ J}}{(4.0 \text{ g})(40. \text{ K})} = 0.20 \text{ J/(g·K)}$

b. $\dfrac{0.20 \text{ J}}{(\text{g·K})}(4.0 \text{ g})(344 \text{ K} - 314 \text{ K})$

$\dfrac{0.20 \text{ J}}{(\text{g·K})}(4.0 \text{ g})(30 \text{ K}) = 24 \text{ J}$

4 *EVALUATE*   The units combine or cancel correctly to give the specific heat in J/(g·K) and the energy in J.

PRACTICE   *Answers in Appendix E*

1. Determine the specific heat of a material if a 35 g sample absorbed 96 J as it was heated from 293 K to 313 K.

2. If 980 kJ of energy are added to 6.2 L of water at 291 K, what will the final temperature of the water be?


Enthalpy of Reaction

The energy absorbed as heat during a chemical reaction at constant pressure is represented by ΔH. The H is the symbol for a quantity called *enthalpy*. It is not practical to talk just about enthalpy as a quantity, because we have no way to directly measure the enthalpy of a system. Only *changes* in enthalpy can be measured. The Greek letter Δ ("delta") stands for "change in." Therefore, ΔH is read as "change in enthalpy." *An **enthalpy change** is the amount of energy absorbed by a system as heat during a process at constant pressure.* The enthalpy change is always the difference between the enthalpies of the products and the reactants. The following equation expresses an enthalpy change for a reaction.

$$\Delta H = H_{products} - H_{reactants}$$

*The **enthalpy of reaction** is the quantity of energy transferred as heat during a chemical reaction.* You can think of enthalpy of reaction as the difference between the stored energy of the reactants and the products. Enthalpy of reaction is sometimes called "heat of reaction."

If a mixture of hydrogen and oxygen is ignited, water will form and energy will be released explosively. The energy that is released comes from the reactants as they form products. Because energy is released, the reaction is *exothermic,* and the energy of the product, water, must be less than the energy of the reactants. The following chemical equation for this reaction indicates that when 2 mol of hydrogen gas at room temperature are burned, 1 mol of oxygen gas is consumed and 2 mol of water vapor are formed.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$
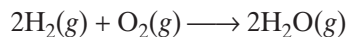
The equation does not tell you that energy is evolved as heat during the reaction. Experiments have shown that 483.6 kJ of energy are evolved when 2 mol of gaseous water are formed from its elements at 298.15 K.

Modifying the chemical equation to show the amount of energy as heat released during the reaction gives the following expression.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) + 483.6 \text{ kJ}$$
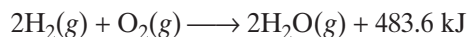
This expression is an example of a **thermochemical equation,** *an equation that includes the quantity of energy released or absorbed as heat during the reaction as written.* In any thermochemical equation, we must always interpret the coefficients as *numbers of moles* and never as *numbers of molecules.* The quantity of energy released as heat in this or any other reaction depends on the amounts of reactants and products. The quantity of energy as heat released during the formation of water from H_2 and O_2 is proportional to the quantity of water formed. Producing twice as much water vapor would require twice as many moles of reactants and would release 2×483.6 kJ of energy as heat, as shown in the following thermochemical equation (which is simply the previous thermochemical equation, multiplied by two).

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(g) + 967.2 \text{ kJ}$$
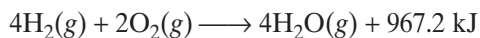
Producing one-half as much water would require one-half as many moles of reactants and would release only one-half as much energy, or $\frac{1}{2} \times 483.6$ kJ. The thermochemical equation for this reaction would be as follows.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) + 241.8 \text{ kJ}$$
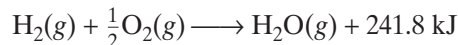
The situation is reversed in an *endothermic* reaction because products have a larger enthalpy than reactants. The decomposition of water vapor is endothermic; it is the reverse of the reaction that forms water vapor. The amount of energy as heat absorbed by water molecules to form hydrogen and oxygen equals the amount of energy as heat released when the elements combine to form the water. This is to be expected because the difference between the energy of reactants and products is unchanged. Enthalpy now appears on the reactant side of the thermochemical equation that follows, indicating that it is an endothermic reaction.

Exothermic Reaction Pathway

$$2H_2O(g) + 483.6 \text{ kJ} \longrightarrow 2H_2(g) + O_2(g)$$
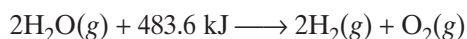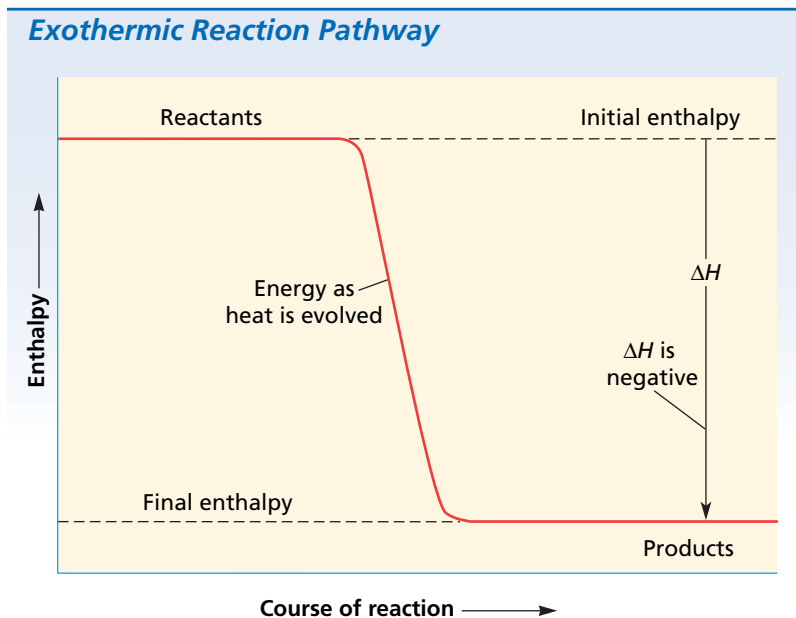
The physical states of reactants and products must always be included in thermochemical equations because they influence the overall amount of energy as heat gained or lost. For example, the energy needed for the decomposition of water would be greater than 483.6 kJ if we started with ice, because extra energy would be needed to melt the ice and to change the liquid into a vapor.

Thermochemical equations are usually written by designating the value of ΔH rather than writing the energy as a reactant or product. For an exothermic reaction, ΔH is always negative because the system loses energy. So, the thermochemical equation for the exothermic formation of 2 mol of gaseous water from its elements now has the following form.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \quad \Delta H = -483.6 \text{ kJ}$$

Figure 2 graphically shows the course of an exothermic reaction. The initial enthalpy of the reactants is greater than the final enthalpy of the products. This means energy as heat is evolved, or given off, during the reaction; this is described as a negative enthalpy change.

For an endothermic reaction, ΔH is always positive because the system gains energy. Thus, the endothermic decomposition of 2 mol of gaseous water has the following thermochemical equation.

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \quad \Delta H = +483.6 \text{ kJ}$$
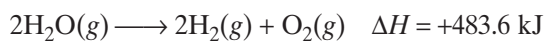
The course of an endothermic reaction is illustrated in **Figure 3.** Energy as heat is absorbed in this reaction, meaning that the initial enthalpy of

Endothermic Reaction Pathway
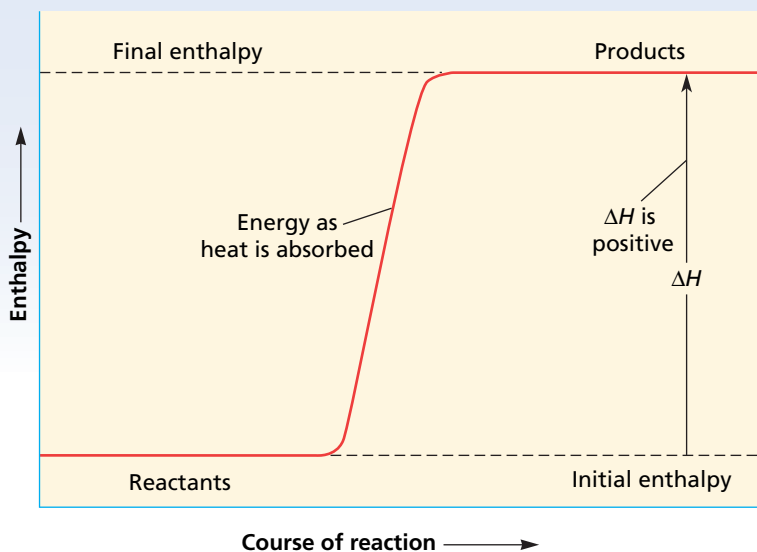
the reactants is lower than the final enthalpy of the products. In this case, ΔH is designated as positive.

Keep in mind the following when using thermochemical equations.

1. The coefficients in a balanced thermochemical equation represent the numbers of *moles* of reactants and products and never the numbers of *molecules*. This allows us to write these coefficients as fractions rather than whole numbers when necessary.
2. The physical state of the product or reactant involved in a reaction is an important factor and therefore must be included in the thermochemical equation.
3. The change in enthalpy represented by a thermochemical equation is directly proportional to the number of moles of substances undergoing a change. For example, if 2 mol of water are decomposed, twice as much enthalpy, 483.6 kJ, is needed than for the decomposition of 1 mol of water.
4. The value of the enthalpy change, ΔH, is usually not significantly influenced by changing temperature.

Enthalpy of Formation

The formation of water from hydrogen and oxygen is a composition reaction—the formation of a compound from its elements in their standard form. Thermochemical data are often recorded as the enthalpies of such composition reactions. *The* **molar enthalpy of formation** *is the enthalpy change that occurs when one mole of a compound is formed from its elements in their standard state at 25°C and 1 atm.*

To make comparisons meaningful, enthalpies of formation are given for the standard states of reactants and products—these are the states found at atmospheric pressure and, usually, room temperature (298.15 K). Thus, the standard state of water is liquid, not gas or solid. The standard state of iron is solid, not a molten liquid. To signify that a value represents measurements on substances in their standard states, a ^{0} sign is added to the enthalpy symbol, giving ΔH^0 for the standard enthalpy of a reaction. Adding a subscript f, as in ΔH^0_f, further indicates a standard enthalpy of formation.

Some standard enthalpies of formation are given in Appendix Table A-14. Each entry in the table is the enthalpy of formation for the synthesis of *one mole* of the compound listed from its elements in their standard states. The thermochemical equation to accompany each enthalpy of formation shows the formation of one mole of the compound from its elements in their standard states.

Stability and Enthalpy of Formation

If a large amount of energy as heat is released when a compound is formed, the compound has a large negative enthalpy of formation. Such compounds are very stable.

Elements in their standard states are *defined* as having $\Delta H^0_f = 0$. The ΔH^0_f of carbon dioxide is -393.5 kJ/mol of gas produced. Therefore, carbon dioxide is more stable than the elements from which it was formed. You can see in Appendix Table A-14 that the majority of the enthalpies of formation are negative.

Compounds with relatively positive values of enthalpies of formation, or only slightly negative values, are typically unstable. For example, hydrogen iodide, HI, is a colorless gas that decomposes somewhat when stored at room temperature. It has a relatively high positive enthalpy of formation of $+26.5$ kJ/mol. As it decomposes, violet iodine vapor, I_2, becomes visible throughout the container of the gas.

Compounds with a high positive enthalpy of formation are sometimes very unstable and may react or decompose violently. For example, ethyne (acetylene), C_2H_2 ($\Delta H^0_f = +226.7$ kJ/mol), reacts violently with oxygen and must be stored in cylinders as a solution in acetone. Mercury fulminate, $HgC_2N_2O_2$, has a very large enthalpy of formation of $+270$ kJ/mol. Its instability makes it useful as a detonator for explosives.

Enthalpy of Combustion

Combustion reactions produce a considerable amount of energy in the form of light and heat when a substance is combined with oxygen. The enthalpy change that occurs during the complete combustion of one mole of a substance is call the **enthalpy of combustion** of the substance.
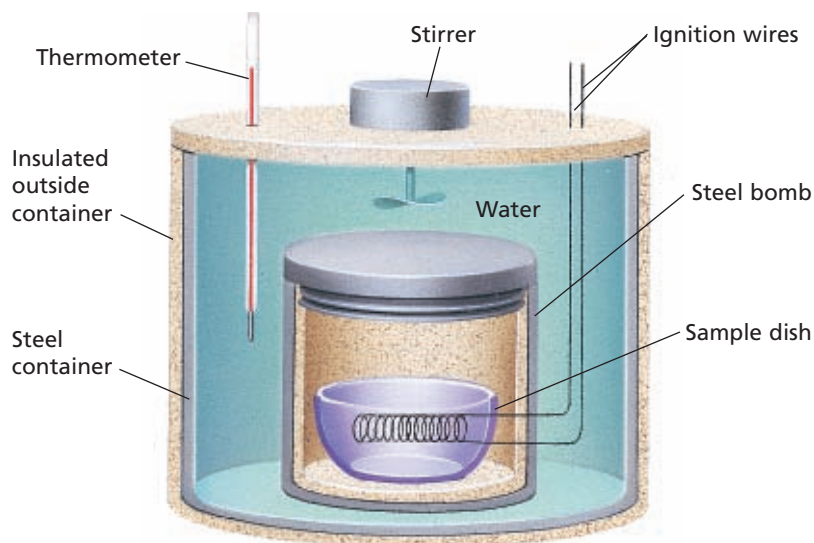
Thermometer

Stirrer

Ignition wires

Insulated outside container

Water

Steel bomb

Steel container

Sample dish

FIGURE 4 This is a diagram of a simple combustion calorimeter. A weighed sample is ignited by an electric spark and burned in the sample dish in an atmosphere of pure oxygen. The energy generated by the combustion reaction warms the steel bomb and the water surrounding it. The thermometer measures the initial and final temperatures of the water, and this temperature change is then used to calculate the energy evolved by the reaction as heat.

Enthalpy of combustion is defined in terms of *one mole of reactant,* whereas the enthalpy of formation is defined in terms of *one mole of product.* All substances are in their standard states. The general enthalpy notation, ΔH, applies to enthalpies of reaction, but the addition of a subscripted c, ΔH_c, refers specifically to enthalpy of combustion. A list of enthalpies of combustion can be found in Appendix Table A-5. A combustion calorimeter is a common instrument used to determine enthalpies of combustion. **Figure 4** shows a fixed-volume calorimeter. A similar apparatus under constant pressure is used to obtain enthalpy measurements.
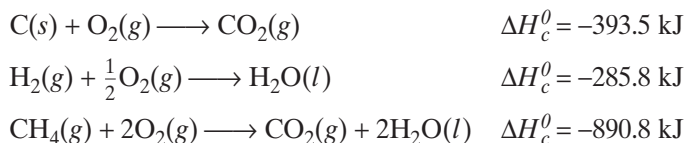
Calculating Enthalpies of Reaction

Thermochemical equations can be rearranged and added to give enthalpy changes for reactions not included in the data tables. The basis for calculating enthalpies of reaction is known as **Hess's law:** *The overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process.* The energy difference between reactants and products is independent of the route taken to get from one to the other. In fact, measured enthalpies of reaction can be combined to calculate enthalpies of reaction that are difficult or impossible to actually measure.

To demonstrate how to apply Hess's law, we will work through the calculation of the enthalpy of formation for the formation of methane gas, CH_4, from its elements, hydrogen gas and solid carbon (graphite), at 298.15 K (25°C).

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta H_f^0 = ?$$
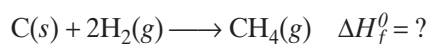
In order to calculate the change in enthalpy for this reaction, we can use the combustion reactions of the elements, carbon and hydrogen, and of methane.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H^0_c = -393.5 \text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad\qquad \Delta H^0_c = -285.8 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H^0_c = -890.8 \text{ kJ}$$

The general principles for combining thermochemical equations follow.

1. If a reaction is reversed, the sign of ΔH is also reversed.
2. Multiply the coefficients of the known equations so that when added together they give the desired thermochemical equation. Multiply the ΔH by the same factor as the corresponding equation.
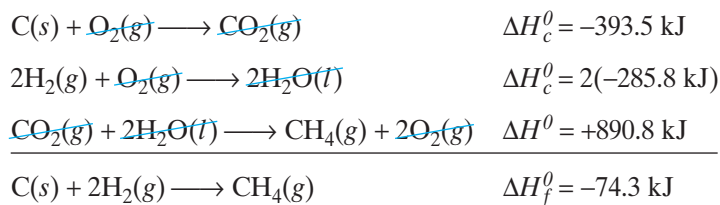
In this case, reverse the combustion equation for methane, and remember to change the sign of ΔH from negative to positive. This will change the exothermic reaction to an endothermic one.

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \quad \Delta H^0 = +890.8 \text{ kJ}$$
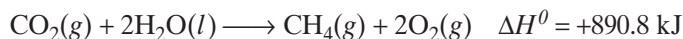
Now we notice that 2 moles of water are used as a reactant; therefore, 2 moles of water will be needed as a product. In the combustion reaction for hydrogen as it is written, it only produces one mole of water. We must multiply the coefficients of this combustion reaction and the value of ΔH by 2 in order to obtain the desired quantity of water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad \Delta H^0_c = 2(-285.8 \text{ kJ})$$
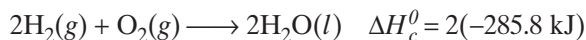
We are now ready to add the three equations together using Hess's law to give the enthalpy of formation for methane and the balanced equation.

$$C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \qquad\qquad \Delta H^0_c = -393.5 \text{ kJ}$$

$$2H_2(g) + \cancel{O_2(g)} \longrightarrow \cancel{2H_2O(l)} \qquad\qquad \Delta H^0_c = 2(-285.8 \text{ kJ})$$

$$\cancel{CO_2(g)} + \cancel{2H_2O(l)} \longrightarrow CH_4(g) + \cancel{2O_2(g)} \quad \Delta H^0 = +890.8 \text{ kJ}$$

$$\overline{C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad\qquad\qquad \Delta H^0_f = -74.3 \text{ kJ}}$$

Hess's law says that the enthalpy difference between reactants and products is independent of pathway. Therefore, any enthalpy of reaction may be calculated using enthalpies of formation for all the substances in the reaction of interest, without knowing anything else about how the reaction occurs. Mathematically, the overall equation for enthalpy change will be in the form of the equation shown below.
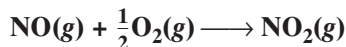
$$\Delta H^0 = \text{sum of } [(\Delta H^0_f \text{ of products}) \times (\text{mol of products})] - \text{sum of } [(\Delta H^0_f \text{ of reactants}) \times (\text{mol of reactants})]$$

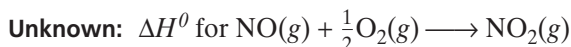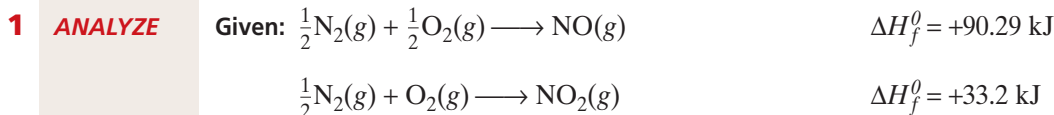An example using Hess's law is shown in **Sample Problem B.**

Calculate the enthalpy of reaction for the combustion of nitrogen monoxide gas, NO, to form nitrogen dioxide gas, NO_2, as given in the following thermochemical equation.

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

Use the enthalpy-of-formation data in Appendix Table A-14. Solve by combining the known thermochemical equations. Verify the result by using the general equation for finding enthalpies of reaction from enthalpies of formation.
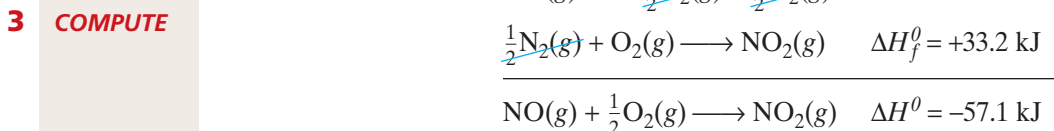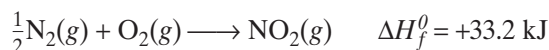
SOLUTION

1 ANALYZE

Given: $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ $\qquad\qquad\qquad$ $\Delta H_f^0 = +90.29$ kJ

$\qquad\qquad$ $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$ $\qquad\qquad\qquad$ $\Delta H_f^0 = +33.2$ kJ

Unknown: ΔH^0 for $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$

2 PLAN

ΔH can be found by adding the ΔHs of the component reactions as specified in Hess's law. The desired equation has $NO(g)$ and $\frac{1}{2}O_2(g)$ as reactants and $NO_2(g)$ as the product.

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$$
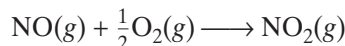
We need an equation with NO as a reactant. Reversing the first reaction for the formation of NO from its elements and the sign of ΔH yields the following thermochemical equation.

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = -90.29 \text{ kJ}$$
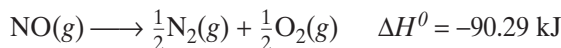
The other equation should have NO_2 as a product, so we can retain the second equation for the formation of NO_2 from its elements as it stands.

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^0 = +33.2 \text{ kJ}$$

3 COMPUTE

$$NO(g) \longrightarrow \cancel{\frac{1}{2}N_2(g)} + \frac{1}{2}O_2(g) \qquad \Delta H^0 = -90.29 \text{ kJ}$$
$$\cancel{\frac{1}{2}N_2(g)} + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^0 = +33.2 \text{ kJ}$$
$$\overline{NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \qquad \Delta H^0 = -57.1 \text{ kJ}}$$

Note the cancellation of the $\frac{1}{2}N_2(g)$ and the partial cancellation of the $O_2(g)$.

4 EVALUATE

The unnecessary reactants and products cancel to give the desired equation. The general relationship between the enthalpy of a reaction and the enthalpies of formation of the reactants and products is described in the following word equation.

$$\Delta H^0 = \text{sum of } [(\Delta H_f^0 \text{ of products}) \times (\text{mol of products})] -$$
$$\text{sum of } [(\Delta H_f^0 \text{ of reactants}) \times (\text{mol of reactants})]$$

To find the necessary sums, the ΔH_f^0 value for each reactant and each product must be multiplied by its respective coefficient in the desired equation. For the reaction of NO with O_2, applying this equation gives the following value for ΔH^0.
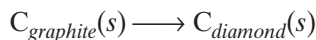
$$\Delta H^0 = \Delta H_f^0(NO_2) - [\Delta H_f^0(NO) + 0]$$
$$= +33.2 \text{ kJ/mol} - 90.29 \text{ kJ/mol} = -57.1 \text{ kJ}$$

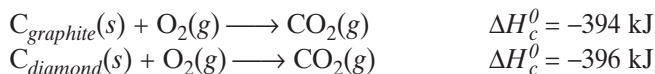Note that zero is the assigned value for the enthalpies of formation of elements in their standard states.

PRACTICE

Answers in Appendix E

1. Calculate the enthalpy of reaction for the combustion of methane gas, CH_4, to form $CO_2(g) + H_2O(l)$.

2. Carbon occurs in two distinct forms. It can be the soft, black material found in pencils and lock lubricants, called graphite, or it can be the hard, brilliant gem we know as diamond. Calculate ΔH^0 for the conversion of graphite to diamond for the following reaction.

$$C_{graphite}(s) \longrightarrow C_{diamond}(s)$$

The combustion reactions you will need follow.

$$C_{graphite}(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_c^0 = -394 \text{ kJ}$$
$$C_{diamond}(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_c^0 = -396 \text{ kJ}$$
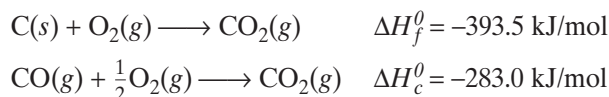
Determining Enthalpy of Formation

When carbon is burned in a limited supply of oxygen, carbon monoxide is produced. In this reaction, carbon is probably first oxidized to carbon dioxide. Then part of the carbon dioxide is reduced with carbon to give some carbon monoxide. Because these two reactions occur simultaneously and we get a mixture of CO and CO_2, it is not possible to directly measure the enthalpy of formation of $CO(g)$ from $C(s)$ and $O_2(g)$.

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H_f^0 = ?$$
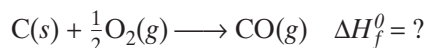
However, we do know the enthalpy of formation of carbon dioxide and the enthalpy of combustion of carbon monoxide.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_f^0 = -393.5 \text{ kJ/mol}$$
$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_c^0 = -283.0 \text{ kJ/mol}$$

We reverse the second equation because we need CO as a product. Adding gives the desired enthalpy of formation of carbon monoxide.
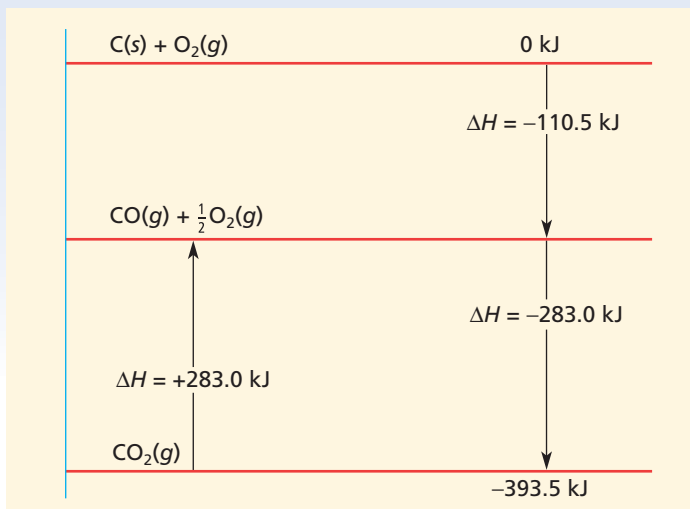
Enthalpies of Reaction

$C(s) + O_2(g)$ 0 kJ

$\Delta H = -110.5$ kJ

$CO(g) + \frac{1}{2}O_2(g)$

$\Delta H = -283.0$ kJ

$\Delta H = +283.0$ kJ

$CO_2(g)$

-393.5 kJ

FIGURE 5 This diagram shows the enthalpy of reaction for carbon dioxide, CO_2, and carbon monoxide, CO.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^0 = -393.5 \text{ kJ}$$
$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = +283.0 \text{ kJ}$$
$$\overline{C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H^0 = -110.5 \text{ kJ}}$$
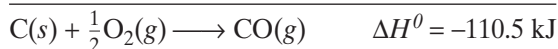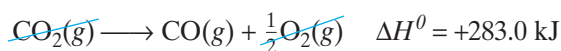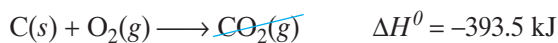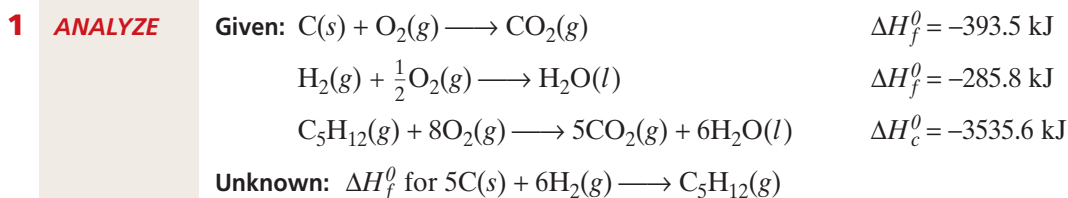
Figure 5 is a model for the process described in this section. If we plot the reactions based on their relative energy, you can see the relationship among the values obtained for the enthalpy of formation of carbon monoxide. The formation of CO_2 is plotted at a level corresponding to -393.5 kJ/mol. The diagram shows the reverse of the combustion reaction (+283.0 kJ/mol) is added to that level. From the diagram, you see the difference, which represents the formation of CO. This value is -110.5 kJ/mol.
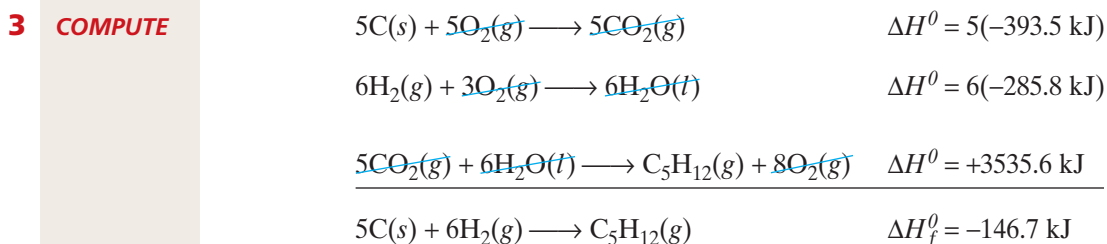

SAMPLE PROBLEM C

For more help, go to the Math Tutor at the end of this chapter.

Calculate the enthalpy of formation of pentane, C_5H_{12}, using the information on enthalpies of formation in Appendix Table A-14 and the information on enthalpies of combustion in Appendix Table A-5. Solve by combining the known thermochemical equations.

SOLUTION

1 ANALYZE

Given: $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^0 = -393.5$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f^0 = -285.8$ kJ

$C_5H_{12}(g) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l)$ $\Delta H_c^0 = -3535.6$ kJ

Unknown: ΔH_f^0 for $5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g)$

2 **PLAN** Combine the given equations according to Hess's law. We need C_5H_{12} as a product, so we reverse the equation for combustion of C_5H_{12} and the sign for ΔH_c^0. Multiply the equation for formation of CO_2 by 5 to give 5C as a reactant. Multiply the equation for formation of H_2O by 6 to give $6H_2$ as a reactant.
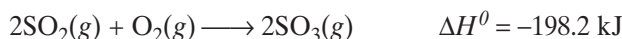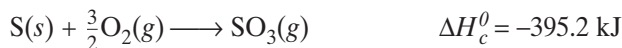
3 **COMPUTE**

$$5C(s) + 5O_2(g) \longrightarrow 5CO_2(g) \qquad\qquad \Delta H^0 = 5(-393.5 \text{ kJ})$$

$$6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(l) \qquad\qquad \Delta H^0 = 6(-285.8 \text{ kJ})$$

$$\underline{5CO_2(g) + 6H_2O(l) \longrightarrow C_5H_{12}(g) + 8O_2(g) \qquad \Delta H^0 = +3535.6 \text{ kJ}}$$

$$5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g) \qquad\qquad \Delta H_f^0 = -146.7 \text{ kJ}$$

4 **EVALUATE** The unnecessary reactants and products cancel to give the correct equation.

PRACTICE *Answers in Appendix E*

1. Calculate the enthalpy of formation of butane, C_4H_{10}, using the balanced chemical equation and information in Appendix Table A-5 and Table A-14. Write out the solution according to Hess's law.

2. Calculate the enthalpy of combustion of 1 mol of nitrogen, N_2, to form NO_2 using the balanced chemical equation and Appendix Table A-14.

3. Calculate the enthalpy of formation for sulfur dioxide, SO_2, from its elements, sulfur and oxygen. Use the balanced chemical equation and the following information.

$$S(s) + \tfrac{3}{2}O_2(g) \longrightarrow SO_3(g) \qquad \Delta H_c^0 = -395.2 \text{ kJ}$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H^0 = -198.2 \text{ kJ}$$

SECTION REVIEW

1. What is meant by enthalpy change?

2. What is meant by enthalpy of reaction?

3. Describe the relationship between a compound's stability and its enthalpy of formation.

4. What is the importance of Hess's law to thermodynamic calculations?

5. How much energy would be absorbed as heat by 75 g of iron when heated from 295 K to 301 K?

Critical Thinking

6. **INTEGRATING CONCEPTS** Isooctane (C_8H_{18}) is a major component of gasoline.

   a. Using the following thermodynamic data, calculate the change in enthalpy for the combustion of 1.0 mol of isooctane.

   $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \; \Delta H^0 = -241.8 \text{ kJ}$;
   $C(s) + O_2(g) \longrightarrow CO_2(g) \; \Delta H^0 = -393.5 \text{ kJ}$;
   $8C(s) + 9H_2(g) \longrightarrow C_8H_{18}(l) \; \Delta H^0 = -224.13 \text{ kJ}$.

   b. One gallon of isooctane has a mass of 2.6 kg. What is the change in enthalpy for the combustion of one gallon of this compound?

Chemistry in Action

Self-Heating Meals

Who would have thought that corrosion could be useful? The HeaterMeals Company did. This company uses the properties of saltwater corrosion to heat TV-type dinners, and now it is taking packaged foods to a new level of convenience.

HeaterMeals' products, as their name implies, come with a self-contained heat source. Each meal contains a package of food, a tray that holds a porous pouch containing Mg and Fe alloy, and a 2 oz pouch filled with salt water. When the salt water is poured into the tray with the porous pouch, it begins to vigorously corrode the metals. The sealed, pre-cooked food package is then placed on top of the tray and returned to its box, where the temperature of the food package is raised by 100°F, heating the meal in 14 min.

Corrosion, the process by which a metal reacts with air or water, is usually an undesirable event, such as when iron corrodes to form rust. With HeaterMeals, however, the corrosion process is speeded up to produce an exothermic reaction—with the excess energy as the desired result.

According to Drew McLandrich, of the HeaterMeals Company, the idea for using self-heating metallic alloy powders has been around since the

▲ This product uses supercorrosion to give you a hot meal.

1930s. "But," says McLandrich, "there really have been no significant uses of the product until the Desert Storm conflict, which led to the military's taking this technology and adopting it for field use so that soldiers could heat a meal-ready-to-eat."

"We've made about 80 million heaters for the military in the last 10 years. Lately we've been successfully marketing them to long-distance truck drivers. The product is in about 800 truck stops in 48 states."

The company has plans to develop other products using the controlled use of "supercorrosion." "A beverage could be heated," says McLandrich, "and we do have prototypes for a baby-bottle warmer. We're also working on making a portable hot cup of coffee or a hot cup of tea or cocoa."

Questions

1. How did the development of self-heating metallic alloy powders benefit the military?

2. If the temperature of 50.0 mL of water is raised from 25.0°C to 100.°C using the self-heating meal package, what is the change in the enthalpy of the magnesium reaction in this package?

Driving Force of Reactions

OBJECTIVES

● Explain the relationship between enthalpy change and the tendency of a reaction to occur.

● Explain the relationship between entropy change and the tendency of a reaction to occur.

● Discuss the concept of free energy, and explain how the value of this quantity is calculated and interpreted.

● Describe the use of free energy change to determine the tendency of a reaction to occur.

The change in energy of a reaction system is one of two factors that allow chemists to predict whether a reaction will occur spontaneously and to explain how it occurs. The randomness of the particles in a system is the second factor affecting whether a reaction will occur spontaneously.

Enthalpy and Reaction Tendency

The great majority of chemical reactions in nature are exothermic. As these reactions proceed, energy is liberated and the products have less energy than the original reactants. The products are also more resistant to change, more stable, than the original reactants. The tendency throughout nature is for a reaction to proceed in a direction that leads to a lower energy state.

We might think that endothermic reactions, in which energy is absorbed, cannot occur spontaneously because the products are at higher potential energy and are less stable than the original reactants. They would be expected to proceed only with the assistance of an outside influence, such as continued heating. However, some endothermic reactions *do* occur spontaneously. We conclude that something other than enthalpy change must help determine whether a reaction will occur.

Entropy and Reaction Tendency

A naturally occurring endothermic process is melting. An ice cube melts spontaneously at room temperature as energy is transferred from the warm air to the ice. The well-ordered arrangement of water molecules in the ice crystal is lost, and the less-ordered liquid phase of higher energy content is formed. A system that can go from one state to another without a decrease in enthalpy does so with an increase in entropy.

Look at the physical states of the reactants in the chemical equation for the decomposition of ammonium nitrate.

$$2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(l) + O_2(g)$$
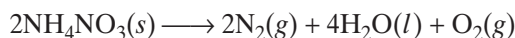
On the left side are 2 mol of solid ammonium nitrate. The right-hand side of the equation shows 3 mol of gaseous molecules plus 4 mol of a liquid. The arrangement of particles on the right-hand side of the equation is more random than the arrangement on the left side of the equation and hence is less ordered. **Figures 6a** and **6b** show the reactant and products of this decomposition reaction.

These examples illustrate that there is a tendency in nature to proceed in a direction that increases the randomness of a system. A random system is one that lacks a regular arrangement of its parts. This tendency toward randomness is called entropy. **Entropy,** *S,* can be defined in a simple qualitative way as *a measure of the degree of randomness of the particles, such as molecules, in a system.* To understand the concept of entropy, consider solids, liquids, and gases. In a solid, the particles are fixed in position in their small regions of space, but they are vibrating back and forth. Even so, we can determine with fair precision the location of the particles. The degree of randomness is low, so the entropy is low. When the solid melts, the particles are still very close together, but they can move about somewhat. The system is more random, and it is more difficult to describe the location of the particles. The entropy is higher. When the liquid evaporates, the particles are moving rapidly and are also much farther apart. Locating an individual particle is much more difficult, and the system is much more random. The entropy of the gas is still higher than that of the liquid. A general but not absolute rule is that the entropy of liquids is larger than that of solids and the entropy of gases is larger than that of liquids. But this rule must be used with caution. For example, the entropy of liquid mercury is much less than that of some solids.

The entropy of a pure crystalline solid is zero at absolute zero. As energy is added, the randomness of the molecular motion increases. Measurements of energy absorbed and calculations are used to determine the absolute entropy or standard molar entropy, and values are then recorded in tables. These molar values are reported as kJ/(mol•K). Entropy change, which can also be measured, is defined as the difference between the entropy of the products and the reactants. Therefore, an increase in entropy is represented by a positive value for ΔS, and a decrease in entropy is represented by a negative value for ΔS.

The process of forming a solution almost always involves an increase in entropy because there is an increase in randomness. This is true for mixing gases, dissolving a liquid in another liquid, and dissolving a solid in a liquid.

(a)
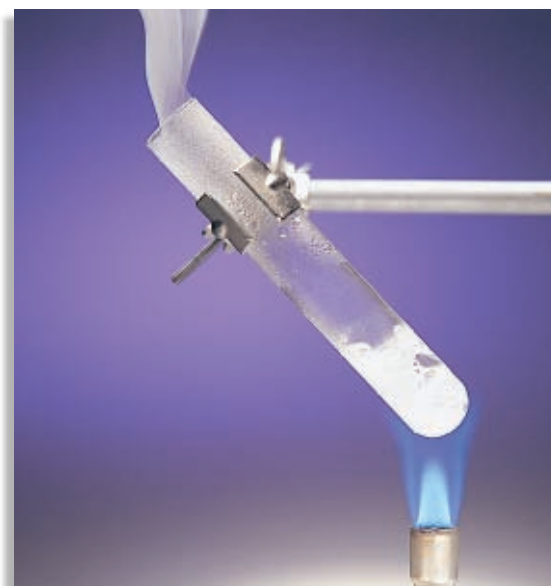
(b)

FIGURE 6 When ammonium nitrate, NH_4NO_3, decomposes, the entropy of the reaction system increases as (a) one solid reactant becomes (b) two gaseous products and one liquid product.
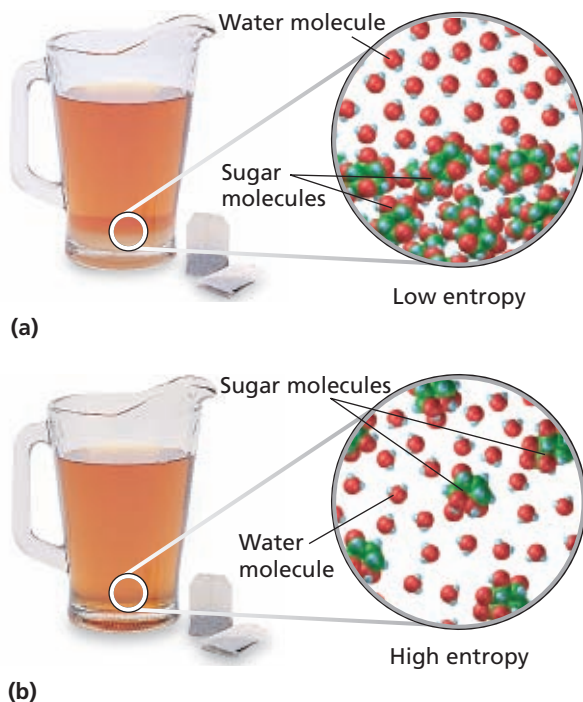
Water molecule

Sugar molecules

Low entropy

(a)

Sugar molecules

Water molecule

High entropy

(b)

FIGURE 7 When a solid dissolves in a liquid, the entropy of the system increases.

Figure 7 illustrates the entropy change that takes place when solid sugar is dissolved in tea (an aqueous solution). In the sugar-water system shown in **Figure 7a,** the solid sugar has just been added to the tea, but most of it has not yet dissolved. The entropy is low because the majority of the sugar molecules are in one region at the bottom of the pitcher and the majority of the water molecules can be found everywhere else in the pitcher. After the sugar dissolves in the tea, shown in **Figure 7b,** the sugar molecules are thoroughly mixed throughout the tea solution. Sugar molecules and water molecules might be found anywhere in the solution, so the entropy, the randomness, of the system increases. This would give ΔS a positive value for this solid-liquid system. You can imagine the same series of events happening for a system of gases mixing with each other or a system of liquids mixing. In each case, ΔS would have a positive value once the solution was formed.

Free Energy

Processes in nature are driven in two directions: toward least enthalpy and toward largest entropy. When these two oppose each other, the dominant factor determines the direction of change. As a way to predict which factor will dominate for a given system, a function has been defined to relate the enthalpy and entropy factors at a given temperature and constant pressure. *This combined enthalpy-entropy function is called the* **free energy,** *G, of the system;* it is also called *Gibbs free energy.* This function simultaneously assesses the tendencies for enthalpy and entropy to change. Natural processes proceed in the direction that lowers the free energy of a system.

Only the *change* in free energy can be measured. It can be defined in terms of changes in enthalpy and entropy. *At a constant pressure and temperature, the* **free-energy change,** *ΔG, of a system is defined as the difference between the change in enthalpy, ΔH, and the product of the Kelvin temperature and the entropy change, which is defined as TΔS.*

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Note that this expression is for substances in their standard states. The product $T\Delta S$ and the quantities ΔG and ΔH have the same units, usually kJ. The units of ΔS for use in this equation are usually kJ/K. If $\Delta G < 0$, the reaction is spontaneous.

ΔH and ΔS in the free-energy equation can have positive or negative values. This leads to four possible combinations of terms.

Table 2 on the next page shows that if ΔH is negative and ΔS is positive, then both terms on the right in the free energy equation are

negative. Both factors contribute to the process's being spontaneous. Therefore, ΔG will always be negative, and the reaction is definitely spontaneous. On the other hand, if ΔH is positive (endothermic process) and ΔS is negative (decrease in randomness), then the reaction as written is not spontaneous. When the enthalpy and entropy changes are operating in different directions, sometimes one will predominate and sometimes the other will predominate. There are reactions in which the enthalpy change is negative and the entropy change is negative. The enthalpy factor leads to a spontaneous process, but the negative entropy change opposes this. This is true in the following reaction. The entropy decreases because there is a decrease in moles of gas.

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$
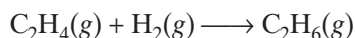
There is a fairly large decrease in entropy, $\Delta S^0 = -0.1207$ kJ/(mol•K). However, the reaction is strongly exothermic, with a $\Delta H^0 = -136.9$ kJ/mol. The reaction proceeds because the enthalpy term predominates.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -136.9 \text{ kJ/mol} - 298 \text{ K}[-0.1207 \text{ kJ/(mol•K)}]$$
$$= -100.9 \text{ kJ/mol}$$

We can contrast this with the common commercial process for the manufacture of syngas, a mixture of CO and H_2. (This gas mixture is the starting point for the synthesis of a number of large-volume commercial chemicals, such as methanol, CH_3OH.)

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

This reaction is endothermic, with $\Delta H^0 = +206.1$ kJ/mol and $\Delta S^0 = +0.215$ kJ/(mol•K), at standard conditions. The resulting ΔG is positive at room temperature. This tells us that the reaction will not occur at room temperature even though the entropy change is favorable.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = +206.1 \text{ kJ/mol} - 298 \text{ K}[+0.215 \text{ kJ/(mol•K)}]$$
$$= +142.0 \text{ kJ/mol}$$

Chemistry in Action
Diamonds Are Forever?

Carbon occurs in different forms, two of which are graphite and diamond. Using thermodynamic data, the change in free energy for diamond converting to graphite under standard thermodynamic conditions is −3 kJ/mol. That is, since ΔG is negative for this reaction, diamond should spontaneously change to graphite at 25°C and 1 atm. So, why doesn't all of our diamond jewelry change to graphite? The reaction rate is too slow for this spontaneous change to be observed. Therefore, at 25°C and 1 atm, although diamonds are not "forever," they will last a very long time.

TABLE 2 Relating Enthalpy, Entropy, and Free-Energy Changes to Reaction Occurrence

ΔH	ΔS	ΔG
− value (exothermic)	+ value (more random)	always negative
− value (exothermic)	− value (less random)	negative at *lower* temperatures
+ value (endothermic)	+ value (more random)	negative at *higher* temperatures
+ value (endothermic)	− value (less random)	never negative

For the reaction $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$, at 298.15 K, $\Delta H^0 = 176$ kJ/mol and $\Delta S^0 = 0.285$ kJ/(mol·K). Calculate ΔG^0, and tell whether this reaction is spontaneous in the forward direction at 298.15 K.

SOLUTION

1 ANALYZE   **Given:** $\Delta H^0 = 176$ kJ/mol at 298.15 K
$\Delta S^0 = 0.285$ kJ/(mol·K) at 298.15 K
Unknown: ΔG^0 at 298.15 K

2 PLAN

$$\Delta S, \Delta H, T \rightarrow \Delta G$$

The value of ΔG can be calculated according to the following equation.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

3 COMPUTE

$$\Delta G^0 = 176 \text{ kJ/mol} - 298 \text{ K } [0.285 \text{ kJ/(mol·K)}]$$
$$= 176 \text{ kJ/mol} - 84.9 \text{ kJ/mol}$$
$$= 91 \text{ kJ/mol}$$

4 EVALUATE   The answer is reasonably close to an estimated value of 110, calculated as $200 - (300 \times 0.3)$. The positive value of ΔG shows that this reaction does not occur naturally at 298.15 K.

PRACTICE   *Answers in Appendix E*

1. For the vaporization reaction $Br_2(l) \longrightarrow Br_2(g)$, $\Delta H^0 = 31.0$ kJ/mol and $\Delta S^0 = 93.0$ J/(mol·K). At what temperature will this process be spontaneous?

extension
Go to **go.hrw.com** for more practice problems that ask you to determine spontaneity based on free-energy changes.

Keyword: HC6NRGX

SECTION REVIEW

1. What kind of enthalpy change favors a spontaneous reaction?

2. What is entropy, and how does it relate to spontaneity of reactions?

3. List several changes that result in an entropy increase.

4. Define *free energy*, and explain how its change is calculated.

5. Explain the relationship between free-energy change and spontaneity of reactions.

6. In the reaction in Sample Problem D, why does the entropy increase?

Critical Thinking

7. **APPLYING MODELS** Most biological enzymes become denatured when they are heated and lose their ability to catalyze reactions. This process (original enzyme $\longrightarrow$ denatured enzyme) is endothermic and spontaneous. Which structure, the original enzyme or the denatured enzyme, is more ordered? Explain your reasoning using thermodynamic concepts.

Thermochemistry

Vocabulary

thermochemistry
calorimeter
temperature
joule
heat
specific heat
enthalpy change
enthalpy of reaction
thermochemical equation
molar enthalpy of formation
enthalpy of combustion
Hess's law

- Thermochemistry is the study of the changes in energy that accompany chemical reactions and physical changes.
- A thermochemical equation is an equation that includes the quantity of energy released or absorbed as heat during the reaction as written.
- An enthalpy change is the amount of energy absorbed as heat by a system in a process carried out at constant pressure.
- The enthalpy of reaction is the enthalpy change that occurs during a chemical reaction.
- The enthalpy change is negative for exothermic reactions and positive for endothermic reactions.
- Compounds with highly negative enthalpies of formation tend to be stable; compounds with highly positive or only slightly negative enthalpies of formation tend to be unstable.
- The standard molar enthalpy of formation is the enthalpy change that occurs when one mole of a compound is formed from its elements in their standard states at 25°C and 1 atm.
- The enthalpy change that occurs in a combustion reaction is called the enthalpy of combustion.
- Enthalpies of reaction can be calculated by using enthalpies of formation of reactants and products.

Driving Force of Reactions

Vocabulary

entropy
free energy
free-energy change

- The tendency throughout nature is for a reaction to proceed in the direction that leads to a lower energy state.
- Entropy is a measure of the randomness of a system.
- Free-energy change combines the effects of entropy and enthalpy changes and temperature of a system, and it is a measure of the overall tendency toward natural change.
- A reaction is spontaneous if it is accompanied by a decrease in free energy. It is not spontaneous if there is an increase in free energy.

For more practice, go to the Problem Bank in Appendix D.

Thermochemistry

SECTION 1 REVIEW

1. How does the enthalpy of the products of a reaction system compare with the enthalpy of the reactants when the reaction is
   a. endothermic?
   b. exothermic?

2. a. Distinguish between enthalpies of reaction, formation, and combustion.
   b. On what basis are enthalpies of formation and combustion defined?

3. Write the equation that can be used to calculate the enthalpy of reaction from enthalpies of formation.

4. What factors affect the value of ΔH in a reaction system?

5. State Hess's law. How is it used?

6. Describe a combustion calorimeter. What information can it give?

PRACTICE PROBLEMS

7. How much energy is needed to raise the temperature of a 55 g sample of aluminum from 22.4°C to 94.6°C? Refer to **Table 1** for the specific heat of aluminum. (Hint: See Sample Problem A.)

8. If 3.5 kJ of energy are added to a 28.2 g sample of iron at 20°C, what is the final temperature of the iron in kelvins? Refer to **Table 1** for the specific heat of iron.

9. You need 70.2 J to raise the temperature of 34.0 g of ammonia, $NH_3(g)$, from 23.0°C to 24.0°C. Calculate the specific heat of ammonia.

10. Calculate c_p for indium metal, given that 1.0 mol In absorbs 53 J while increasing in temperature from 297.5 K to 299.5 K.

11. For each equation listed below, determine the ΔH and type of reaction (endothermic or exothermic).
    a. $C(s) + O_2(g) \longrightarrow CO_2(g) + 393.51$ kJ
    b. $CH_4(g) + 2O_2(g) \longrightarrow$
       $CO_2(g) + 2H_2O(l) + 890.31$ kJ
    c. $CaCO_3(s) + 176$ kJ $\longrightarrow CaO(s) + CO_2(g)$
    d. $H_2O(g) \longrightarrow H_2O(l) + 44.02$ kJ

12. Rewrite each equation below with the ΔH value included with either the reactants or the products, and identify the reaction as endothermic or exothermic.
    a. $H_2(g) + O_2(g) \longrightarrow H_2O(l)$;
       $\Delta H^0 = -285.83$ kJ
    b. $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$;
       $\Delta H^0 = -1200$ kJ
    c. $I_2(s) \longrightarrow I_2(g)$; $\Delta H^0 = +62.4$ kJ
    d. $3CO(g) + Fe_2O_3(s) \longrightarrow 2Fe(s) + 3CO_2(g)$;
       $\Delta H^0 = -24.7$ kJ

13. Use Appendix Table A-14 to write the reaction illustrating the formation of each of the following compounds from its elements. Write the ΔH as part of each equation, and indicate the ΔH for the reverse reaction.
    a. $CaCl_2(s)$
    b. $C_2H_2(g)$ (ethyne, or acetylene)
    c. $SO_2(g)$

14. The reaction $2Fe_2O_3(s) + 3C(s) \longrightarrow$ $4Fe(s) + 3CO_2(g)$ is involved in the smelting of iron. Use ΔH_f values given in Appendix Table A-14 to calculate the enthalpy change during the production of 1 mol of iron.

15. Use enthalpy-of-formation data given in Appendix Table A-14 to calculate the enthalpy of reaction for each of the following. Solve each by combining the known thermochemical equations. Verify each result by using the general equation for finding enthalpies of reaction from enthalpies of formation. (Hint: See Sample Problem B.)
    a. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
    b. $Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(g)$
    c. $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

16. For glucose, $C_6H_{12}O_6(s)$, $\Delta H_f = -1263$ kJ/mol. Calculate the enthalpy change when 1 mol of $C_6H_{12}O_6(s)$ combusts to form $CO_2(g)$ and $H_2O(l)$.

17. Calculate the standard enthalpies of reaction for combustion reactions in which ethane, C_2H_6, and benzene, C_6H_6, are the respective reactants and $CO_2(g)$ and $H_2O(l)$ are the products in each. Solve each by combining the known thermochemical equations using the ΔH_f values in

Appendix Table A-14. Verify the result by using the general equation for finding enthalpies of reaction from enthalpies of formation.

a. $C_2H_6(g) + O_2(g) \longrightarrow$

b. $C_6H_6(l) + O_2(g) \longrightarrow$

18. The enthalpy of formation of ethanol, C_2H_5OH, is −277.0 kJ/mol at 298.15 K. Calculate the enthalpy of combustion of one mole of ethanol, assuming that the products are $CO_2(g)$ and $H_2O(l)$. (Hint: See Sample Problem C.)

Driving Force of Reactions

SECTION 2 REVIEW

19. Would entropy increase or decrease for changes in state in which the reactant is a gas or liquid and the product is a solid? What sign would the entropy change have?

20. How does an increase in temperature affect the entropy of a system?

21. What combination of ΔH and ΔS values always produces a negative free-energy change?

22. Explain the relationship between temperature and the tendency for reactions to occur spontaneously.
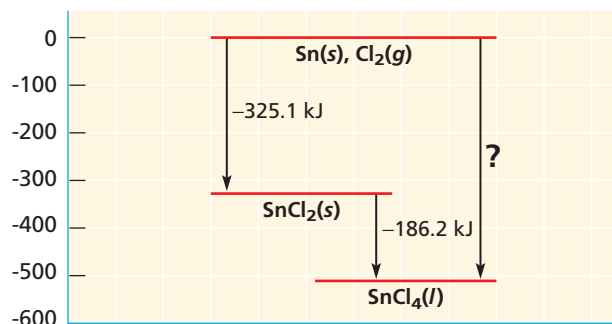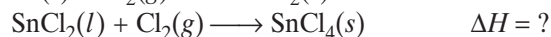
PRACTICE PROBLEMS

23. A reaction has ΔH = −356 kJ and ΔS = −36 J/K. Calculate ΔG at 25°C to confirm that the reaction is spontaneous.

24. A reaction has ΔH = 98 kJ and ΔS = 292 J/K. Investigate the spontaneity of the reaction at room temperature. Would increasing the temperature have any effect on the spontaneity of the reaction?

25. A reaction has ΔH = −76 kJ and ΔS = −117 J/K. Calculate ΔG for the reaction at 298.15 K. Is the reaction spontaneous?

26. The gas-phase reaction of H_2 with CO_2 to produce H_2O and CO has ΔH = 11 kJ and ΔS = 41 J/K. Is the reaction spontaneous at 298.15 K? What is ΔG?

27. Based on the following values, compute ΔG values for each reaction and predict whether the reaction will occur spontaneously. (Hint: See Sample Problem D.)

a. ΔH = +125 kJ, T = 293 K, ΔS = 0.0350 kJ/K

b. ΔH = −85.2 kJ, T = 127°C, ΔS = 0.125 kJ/K

c. ΔH = −275kJ, T = 773 K, ΔS = 0.450 kJ/K

28. The ΔS^0 for the reaction shown, at 298.15 K, is 0.003 00 kJ/(mol·K). Calculate the ΔG^0 for this reaction, and determine whether it will occur spontaneously at 298.15 K.

$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.51 \text{ kJ}$

MIXED REVIEW

29. When graphite reacts with hydrogen at 300 K, ΔH is −74.8 kJ and ΔS is −0.0809 kJ/K. Will this reaction occur spontaneously?

30. How might you change reaction conditions to induce an endothermic reaction that does not occur naturally?

31. The diagram below represents an interpretation of Hess's law for the following reaction.

$$Sn(s) + 2Cl_2(g) \longrightarrow SnCl_4(l)$$
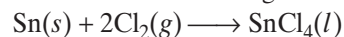
Use the diagram to determine ΔH for each step and the net reaction.

$Sn(s) + Cl_2(g) \longrightarrow SnCl_2(s)$ ΔH = ?

$SnCl_2(l) + Cl_2(g) \longrightarrow SnCl_4(s)$ ΔH = ?

$Sn(s) + 2Cl_2(g) \longrightarrow SnCl_4(l)$ ΔH = ?

**32.** The standard enthalpy of formation for sulfur dioxide gas is −296.8 kJ/mol. Calculate the amount of energy given off in kJ when 30.0 g of $SO_2(g)$ is formed from its elements.

33. The thermite reaction used in some welding applications has the following enthalpy and entropy changes at 298.15 K. Assuming ΔS and ΔH are constant, calculate ΔG at 448 K.
$Fe_2O_3 + 2Al(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$
$\Delta H^0 = -851.5$ kJ $\Delta S^0 = -38.5$ J/K

34. Rewrite each equation below with the ΔH value included in either the reactants or products, and identify the reaction as endothermic or exothermic.
a. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$;
  $\Delta H = -197.8$ kJ
b. $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$;
  $\Delta H = +114.2$ kJ
c. $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$;
  $\Delta H = -1411.0$ kJ

35. Calculate the change in enthalpy for the following reaction.
$$4FeO(s) + O_2(g) \longrightarrow 2Fe_2O_3(s)$$
Use the enthalpy-of-formation data listed in Appendix Table A-14.

36. The reaction to synthesize methanol (CH_3OH) industrially is
$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(g).$$
The $\Delta H^0_{reaction} = -90.7$ kJ and the $\Delta S^0_{reaction} = -220.8$ J/K. At what temperatures is the reaction nonspontaneous?

37. What is the main characteristic of a calorimeter in a bomb calorimeter experiment, and why is this characteristic essential?

CRITICAL THINKING

38. **Relating Ideas** Given the entropy change for the first two reactions below, calculate the entropy change for the third reaction below.
$S_8(s) + 8O_2(s) \longrightarrow 8SO_2(g)$ $\Delta S = 89$ J/K
$2SO_2(s) + O_2(s) \longrightarrow 2SO_3(g)$ $\Delta S = -188$ J/K
$S_8(s) + 12O_2(s) \longrightarrow 8SO_3(g)$ $\Delta S = ?$

39. **Interpreting Concepts** Look at the two pictures below. Which picture appears to have more order? Why? Are there any similarities between the amount of order the marbles have and the entropy of particles?

(a)　　　　　　　(b)
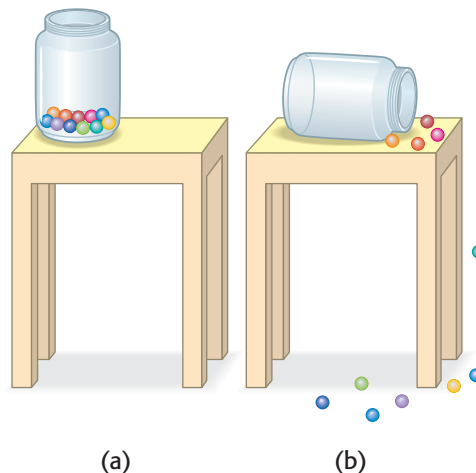
40. **Inferring Conclusions** A reaction is endothermic and has a $\Delta H = 8$ kJ. This reaction occurs spontaneously at 25°C. What must be true about the entropy change?

41. **Inferring Conclusions** If both ΔH and ΔS are negative, how does temperature affect spontaneity?

42. **Inferring Relationships** If the reaction $X \longrightarrow Y$ is spontaneous, what can be said about the reaction $Y \longrightarrow X$?

43. **Interpreting Concepts** Absolute enthalpy cannot be determined; only change in energy can be measured. However, absolute entropy can be determined. Explain why an absolute entropy can be determined.

RESEARCH & WRITING

44. Obtain information on alternative units of measure used to express values of energy as heat and other forms of energy. Also, find out how the quantities relate to SI units. Include information specifically on English units, such as the British thermal unit (BTU), and on typical BTU ratings of household appliances. Calculate how these ratings would be expressed in joules instead.

ALTERNATIVE ASSESSMENT

45. Performance Design a simple calorimeter investigation to determine the molar enthalpy of fusion of water. Use the following materials: a large plastic-foam cup with cover, a thermometer, a balance, water at room temperature, and an ice cube. Allow your teacher to review your design. Then carry out the investigation, and write a laboratory report including your calculations and a comparison of your quantitative results with known values. Try to account for any disagreements between the experimental and actual values.

46. Performance Design an experiment to measure the molar heat capacities of zinc and copper. If your teacher approves the design, obtain the materials needed and conduct the experiment. When you are finished, compare your experimental values with those from a chemical handbook or other reference source.

47. Performance Develop a procedure to measure the ΔH of the reaction shown below. If your teacher approves your procedure, test your procedure by measuring the ΔH value of the reaction. Determine the accuracy of your method by comparing your ΔH with the accepted ΔH value.

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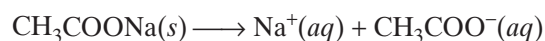
extension

Graphing Calculator
Free-Energy Changes
Go to **go.hrw.com** for a graphing calculator exercise that asks you to calculate and graph free-energy (ΔG) changes.

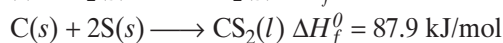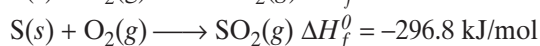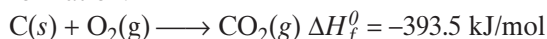**Keyword: HC6NRGX**

Math Tutor HESS'S LAW

You may have seen a popular comic strip in which a little boy takes a long, twisting path between the school-bus stop and home. No matter which path the boy takes, the result is always the same: He goes from the bus stop to the door of his house. Hess's law covers a similar situation in thermochemistry. No matter which or how many steps occur in the process of changing one or more substances into one or more other substances, the overall change in enthalpy is always the same. Hess's law can be used, for example, to predict the enthalpy change, ΔH^0, of a reaction without actually carrying out the reaction.
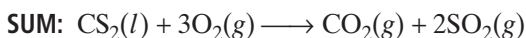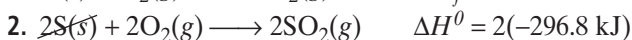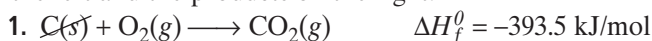
SAMPLE

Determine ΔH for the burning of carbon disulfide in oxygen.
$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \ \Delta H^0 = ?$$

Use the following information:
$$C(s) + O_2(g) \longrightarrow CO_2(g) \ \Delta H_f^0 = -393.5 \text{ kJ/mol}$$
$$S(s) + O_2(g) \longrightarrow SO_2(g) \ \Delta H_f^0 = -296.8 \text{ kJ/mol}$$
$$C(s) + 2S(s) \longrightarrow CS_2(l) \ \Delta H_f^0 = 87.9 \text{ kJ/mol}$$

Rearrange the given equations in a way that will put the reactants of the above equation on the left and the products on the right.

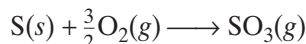**1.** $\cancel{C(s)} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^0 = -393.5 \text{ kJ/mol}$
2. $2\cancel{S(s)} + 2O_2(g) \longrightarrow 2SO_2(g)$ $\Delta H^0 = 2(-296.8 \text{ kJ})$
3. $CS_2(l) \longrightarrow \cancel{C(s)} + 2\cancel{S(s)}$ $\Delta H^0 = -87.9 \text{ kJ}$

SUM: $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$

Notice that equation 2 is double the original equation $S(s) + O_2(g) \longrightarrow SO_2(g)$. The reason for this is that $2SO_2$ are needed on the product side to match the $2SO_2$ in $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$. The third equation is the reverse of the original, putting CS_2 on the reactant side of the final equation. The sign of ΔH is likewise reversed. The value of ΔH^0 is the sum of the ΔH^0 values for the three added equations.

$$\Delta H^0 = -393.5 \text{ kJ} + 2(-296.8 \text{ kJ}) + (-87.9 \text{ kJ})$$
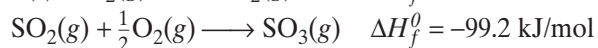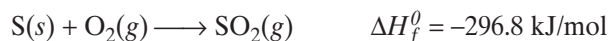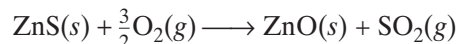$$\Delta H^0 = -1075.0 \text{ kJ}$$

PRACTICE PROBLEMS

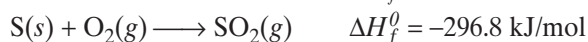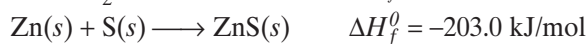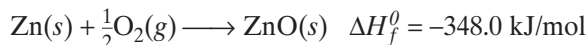**1.** Calculate ΔH^0 for the complete oxidation of sulfur to sulfur trioxide.
$$S(s) + \tfrac{3}{2}O_2(g) \longrightarrow SO_3(g)$$
Use the following information.
$$S(s) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H_f^0 = -296.8 \text{ kJ/mol}$$
$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H_f^0 = -99.2 \text{ kJ/mol}$$

2. Calculate ΔH^0 for the reaction in which zinc sulfide ore is roasted to obtain zinc oxide.
$$ZnS(s) + \tfrac{3}{2}O_2(g) \longrightarrow ZnO(s) + SO_2(g)$$
Use the following information.
$$Zn(s) + \tfrac{1}{2}O_2(g) \longrightarrow ZnO(s) \quad \Delta H_f^0 = -348.0 \text{ kJ/mol}$$
$$Zn(s) + S(s) \longrightarrow ZnS(s) \quad \Delta H_f^0 = -203.0 \text{ kJ/mol}$$
$$S(s) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H_f^0 = -296.8 \text{ kJ/mol}$$

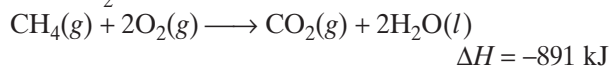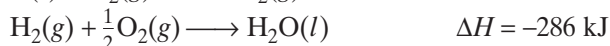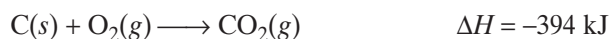**Answer the following items on a separate piece of paper.**

MULTIPLE CHOICE

1. Which of the following two conditions will favor a spontaneous reaction?
   A. an increase in entropy and a decrease in enthalpy
   B. an increase in entropy and an increase in enthalpy
   C. a decrease in entropy and a decrease in enthalpy
   D. a decrease in entropy and an increase in enthalpy

2. The gasification of coal is a method of producing methane by the following reaction.

   $$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = ?$$
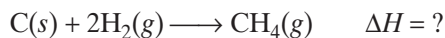
   Find ΔH by using the enthalpy changes in the following combustion reactions

   $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -394 \text{ kJ}$
   $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad\qquad \Delta H = -286 \text{ kJ}$
   $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
   $\qquad\qquad\qquad\qquad\qquad\qquad \Delta H = -891 \text{ kJ}$

   A. 75 kJ
   B. −75 kJ
   C. 1856 kJ
   D. −1856 kJ

3. Two metals of equal mass but different specific heats absorb the same amount of heat. Which metal undergoes the smaller change in temperature?
   A. The metal with the higher specific heat.
   B. The metal with the lower specific heat.
   C. Both undergo the same change in temperature.
   D. Cannot determine from the information given.

4. Which of the following processes has a negative ΔS?
   A. evaporating 1 mol of a liquid
   B. raising the temperature of 1 L of water from 295 K to 350 K
   C. freezing of 1 mol of a liquid
   D. None of the above

5. At a constant pressure, the following reaction is exothermic: $2NO_2(g) \longrightarrow N_2O_4(g)$. Which of the following statements is true about the reaction (as written)?
   A. The reaction is always spontaneous.
   B. The reaction is spontaneous at low temperatures, but not at high temperatures.
   C. The reaction is spontaneous at high temperatures, but not at low temperatures.
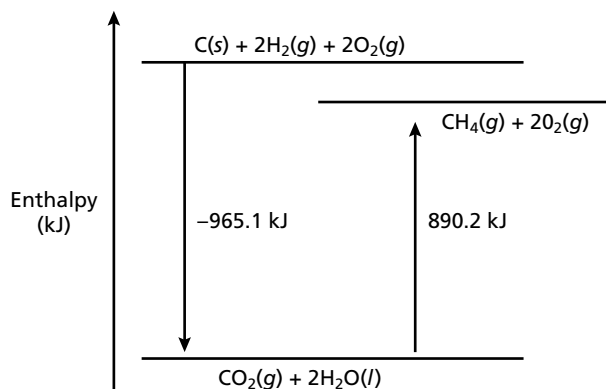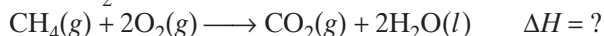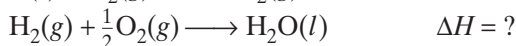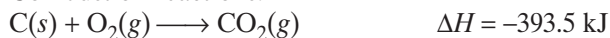   D. The reaction is never spontaneous.

SHORT ANSWER

6. For a reaction in which a diatomic molecule dissociates into atoms, what are the signs of ΔS and ΔH? Explain your answer. You may use the reaction $N_2(g) \longrightarrow 2N(g)$ as an example of such a reaction.

EXTENDED RESPONSE

7. For certain molecules, enthalpies of formation can be determined from combustion data. Using the diagram below, calculate the enthalpy of formation of methane gas, $CH_4(g)$, and the enthalpies for two of the combustion reactions listed below.

Combustion reactions:
$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -393.5 \text{ kJ}$
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad\qquad \Delta H = ?$
$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = ?$

Test TIP Always read the question before looking at the answer choices.

Calorimetry and Hess's Law

OBJECTIVES

- *Demonstrate* proficiency in the use of calorimeters and related equipment.

- *Relate* temperature changes to enthalpy changes.

- *Determine* enthalpies of reaction for several reactions.

- *Demonstrate* that enthalpies of reactions can be additive.

MATERIALS

- 4 g NaOH pellets
- 50 mL 1.0 M HCl acid solution
- 50 mL 1.0 M NaOH solution
- 100 mL 0.50 M HCl solution
- 100 mL graduated cylinder
- balance
- distilled water
- forceps
- glass stirring rod
- gloves
- plastic-foam cups (or calorimeter)
- spatula
- thermometer
- watch glass

BACKGROUND

Hess's law states that the overall enthalpy change in a reaction is equal to the sum of the enthalpy changes in the individual steps in the process. In this experiment, you will use a calorimeter to measure the energy released in three chemical reactions. From your experimental data, you will verify Hess's law.

SAFETY

For review of safety, please see **Safety in the Chemistry Laboratory** in the front of your book.

PREPARATION

1. Prepare a data table in which to record the total volumes of liquid, initial temperature, and final temperature of the three reactions you will carry out, as well as the mass of the empty watch glass and the watch glass plus NaOH pellets.

2. Gently insert the thermometer into the plastic foam cup held upside down. **Thermometers break easily, so be careful with them, and do not use them to stir a solution.**

PROCEDURE

Reaction 1: Dissolving NaOH

1. Pour 100 mL of distilled water into your calorimeter. Record the water temperature to the nearest 0.1°C.

2. Weigh a clean and dry watch glass to the nearest 0.01 g. Wearing gloves and using forceps, place about 2 g of NaOH pellets on the watch glass. Measure and record the mass of the watch glass and the pellets to the nearest 0.01 g. **It is important that this step be done quickly: NaOH absorbs moisture from the air.**

3. Immediately place the NaOH pellets in the calorimeter cup, and gently stir the solution with a stirring rod. **Do not stir with a thermometer.** Place the lid on the calorimeter. Watch the thermometer, and record the highest temperature in your data table.

4. Be sure to clean all equipment and rinse it with distilled water before continuing.

Reaction 2: NaOH and HCl in Solution

5. Pour 50 mL of 1.0 M HCl into your calorimeter. Record the temperature of the HCl solution to the nearest 0.1°C.

6. Pour 50 mL of 1.0 M NaOH into a graduated cylinder. **For this step only, rinse the thermometer, and measure the temperature of the NaOH solution in the graduated cylinder to the nearest 0.1°C. Record the temperature, and then replace the thermometer in the calorimeter.**

7. Pour the NaOH solution into the calorimeter cup, and stir gently. Place the lid on the calorimeter. Watch the thermometer and record the highest temperature.

8. Pour the solution in the container designated by your teacher. Clean and rinse all equipment before continuing with the procedure.

Reaction 3: Solid NaOH and HCl in Solution

9. Pour 100 mL of 0.50 M HCl into your calorimeter. Record the temperature of the HCl solution to the nearest 0.1°C.

10. Measure the mass of a clean and dry watch glass, and record the mass. Wear gloves, and using forceps, obtain approximately 2 g of NaOH pellets. Place them on the watch glass, and record the total mass. **As in step 2, it is important that this step be done quickly.**

11. Immediately place the NaOH pellets in the calorimeter, and gently stir the solution. Place the lid on the calorimeter. Watch the thermometer, and record the highest temperature. When finished with this reaction, pour the solution into the container designated by your teacher for disposal of basic solutions.

CLEANUP AND DISPOSAL

12. Check with your teacher for the proper disposal procedures. Always wash your hands thoroughly after cleaning up the lab area and equipment.

ANALYSIS AND INTERPRETATION

1. **Organizing Ideas:** Write a balanced chemical equation for each of the three reactions that you performed. (Hint: Be sure to include the physical states of matter for all substances.)

2. **Organizing Ideas:** Write the equation for the total reaction by adding two of the equations from item 1 and then canceling out substances that appear in the same form on both sides of the new equation.

3. **Organizing Data:** Calculate the change in temperature for each of the reactions.

4. **Organizing Data:** Assuming that the density of the water and the solutions is 1.00 g/mL, calculate the mass of liquid present for each of the reactions.

5. **Analyzing Results:** Using the calorimeter equation, calculate the energy as heat released by each reaction. (Hint: Use the specific heat of water in your calculations.)

$$c_{p,\,H_2O} = 4.184 \text{ J/g} \cdot {}^\circ C$$

$$\text{heat} = m \times \Delta t \times c_{p,\,H_2O}$$

6. **Organizing Data:** Calculate the moles of NaOH used in each of the reactions.

7. **Analyzing Results:** Calculate the ΔH value in kJ/mol of NaOH for each of the three reactions.

8. **Organizing Ideas:** Using your answer to Analysis and Interpretation item 2 and your knowledge of Hess's law, explain how the enthalpies for the three reactions should be mathematically related.