CHAPTER 13

Properties of Liquids

Bushkill Falls and Bridesmaid Falls (lower level) at Delaware Water Gap, Pennsylvania.

Chapter Outline

Planet Earth, that magnificient blue sphere we enjoy viewing from space, is spectacular. Over 75% of Earth is covered with water. We are born from it, drink it, bathe in it, cook with it, enjoy its beauty in waterfalls and rainbows, and stand in awe of the majesty of icebergs. Water supports and enhances life.

In chemistry, water provides the medium for numerous reactions. The shape of the water molecule is the basis for hydrogen bonds. These bonds determine the unique properties and reactions of water. The tiny water molecule holds the answers to many of the mysteries of chemical reactions.

13.1 What Is a Liquid?

In the last chapter, we found that gases contain particles that are far apart, in rapid random motion, and essentially independent of each other. The kinetic-molecular theory, along with the ideal gas law, summarizes the behavior of most gases at relatively high temperatures and low pressures.

Solids are obviously very different from gases. Solids contain particles that are very close together; solids have a high density, compress negligibly, and maintain their shape regardless of container. These characteristics indicate large attractive forces between particles. The model for solids is very different from the one for gases.

Liquids, on the other hand, lie somewhere between the extremes of gases and solids. Liquids contain particles that are close together; liquids are essentially incompressible, and have definite volume. These properties are very similar to those of solids. But liquids also take the shape of their containers; this is closer to the model of a gas.

Although liquids and solids show similar properties, they differ tremendously from gases (see Figure 13.1). No simple mathematical relationship, like the ideal gas law, works well for liquids or solids. Instead, these models are directly related to the forces of attraction between molecules. With these general statements in mind, let's consider some specific properties of liquids.

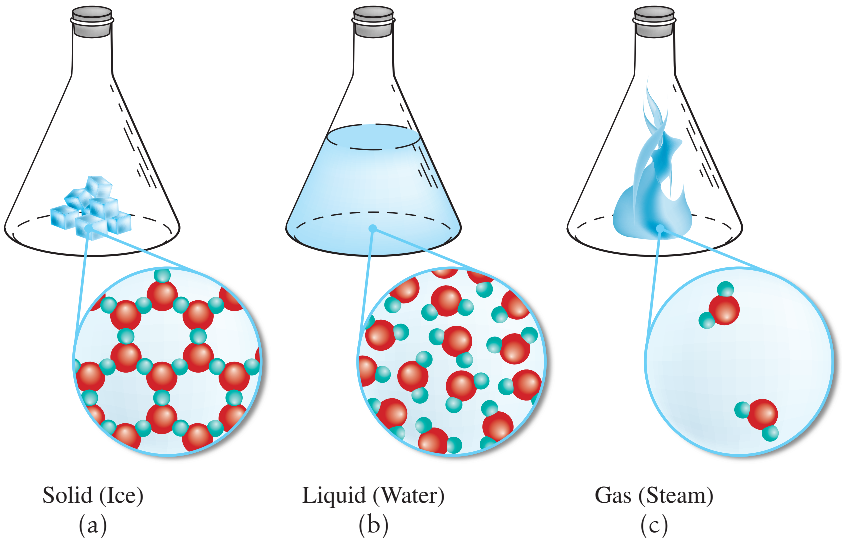


Figure 13.1
The three states of matter. (a) Solid—water molecules are held together rigidly and are very close to each other. (b) Liquid—water molecules are close together but are free to move around and slide over each other. (c) Gas—water molecules are far apart and move freely and randomly.

13.2 Evaporation

When beakers of water, ethyl ether, and ethyl alcohol (all liquids at room temperature) are allowed to stand uncovered, their volumes gradually decrease. The process by which this change takes place is called *evaporation*.

Attractive forces exist between molecules in the liquid state. Not all of these molecules, however, have the same kinetic energy. Molecules that have greater-than-average kinetic energy can overcome the attractive forces and break away from the surface of the liquid to become a gas (see Figure 13.2). **Evaporation,** or **vaporization,** is the escape of molecules from the liquid state to the gas or vapor state.

evaporation
vaporization

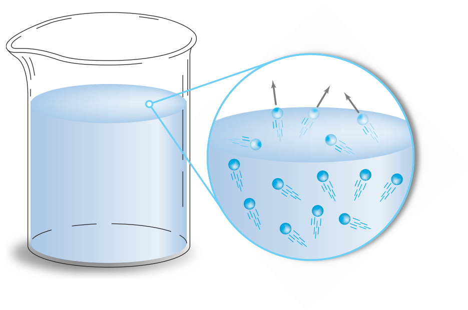


Figure 13.2
The high-energy molecules escape from the surface of a liquid in a process known as evaporation.

In evaporation, molecules of greater-than-average kinetic energy escape from a liquid, leaving it cooler than it was before they escaped. For this reason, evaporation of perspiration is one way the human body cools itself and keeps its temperature constant. When volatile liquids such as ethyl chloride (C_2H_5Cl) are sprayed on the skin, they evaporate rapidly, cooling the area by removing heat. The numbing effect of the low temperature produced by evaporation of ethyl chloride allows it to be used as a local anesthetic for minor surgery.

Solids such as iodine, camphor, naphthalene (moth balls), and, to a small extent, even ice will go directly from the solid to the gaseous state, bypassing the liquid state. This change is a form of evaporation and is called **sublimation:**

sublimation

$$\text{liquid} \xrightarrow{\text{evaporation}} \text{vapor}$$

$$\text{solid} \xrightarrow{\text{sublimation}} \text{vapor}$$

13.3 Vapor Pressure

When a liquid vaporizes in a closed system like that shown in Figure 13.3b, some of the molecules in the vapor or gaseous state strike the surface and return to the liquid state by the process of **condensation.** The rate of condensation increases until it's equal to the rate of vaporization. At this point, the space above the liquid is said to be saturated with vapor, and an equilibrium, or steady state, exists between the liquid and the vapor. The equilibrium equation is

condensation

$$\text{liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{vapor}$$

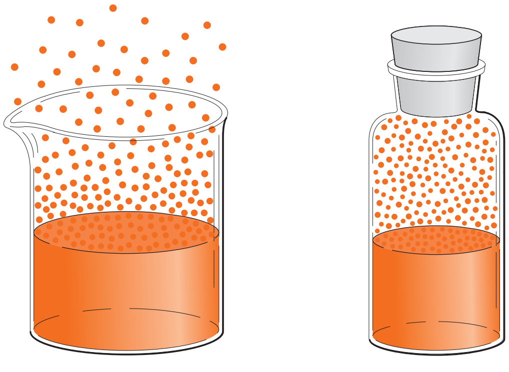
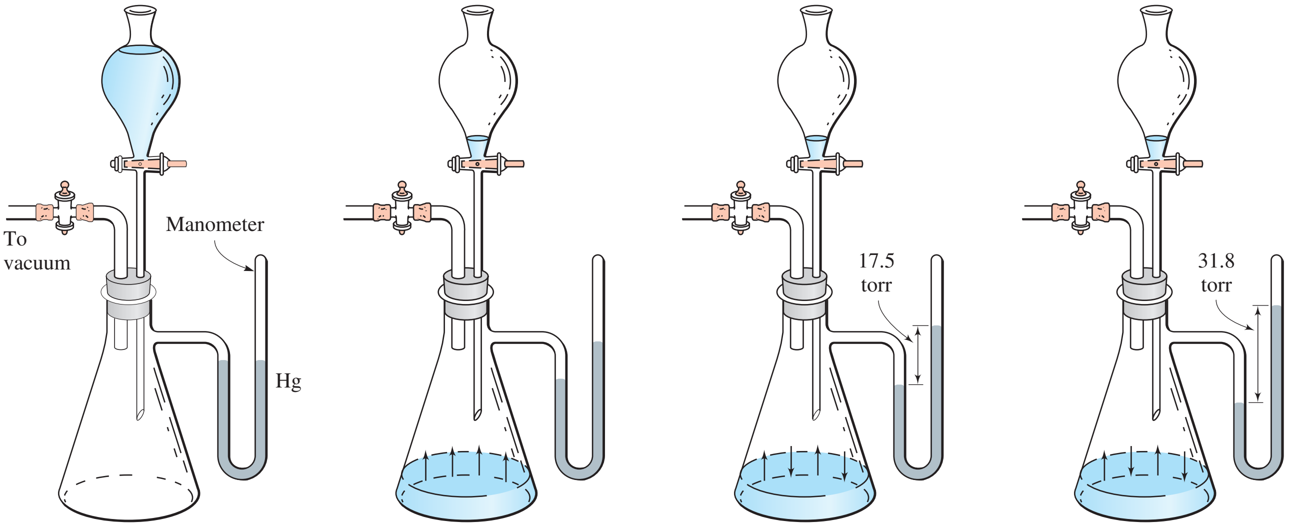


Figure 13.3
(a) Molecules in an open beaker evaporate from the liquid and disperse into the atmosphere. Evaporation will continue until all the liquid is gone. (b) Molecules leaving the liquid are confined to a limited space. With time, the concentration in the vapor phase will increase until an equilibrium between liquid and vapor is established.

This equilibrium is dynamic; both processes—vaporization and condensation—are taking place, even though we cannot see or measure a change. The number of molecules leaving the liquid in a given time interval is equal to the number of molecules returning to the liquid.

vapor pressure

At equilibrium, the molecules in the vapor exert a pressure like any other gas. The pressure exerted by a vapor in equilibrium with its liquid is known as the **vapor pressure** of the liquid. The vapor pressure may be thought of as a measure of the "escaping" tendency of molecules to go from the liquid to the vapor state. The vapor pressure of a liquid is independent of the amount of liquid and vapor present, but it increases as the temperature rises. Figure 13.4 illustrates a liquid–vapor equilibrium and the measurement of vapor pressure.



(a) Evacuated flask

(b) Water added at 20°C

(c) Water–vapor equilibrium at 20° C

(d) Water–vapor equilibrium at 30° C

Figure 13.4
Measurement of the vapor pressure of water at 20°C and 30°C. (a) The system is evacuated. The mercury manometer attached to the flask shows equal pressure in both legs. (b) Water has been added to the flask and begins to evaporate, exerting pressure as indicated by the manometer. (c) When equilibrium is established, the pressure inside the flask remains constant at 17.5 torr. (d) The temperature is changed to 30°C, and equilibrium is reestablished with the vapor pressure at 31.8 torr.

Table 13.1 Vapor Pressure of Water, Ethyl Alcohol, and Ethyl Ether at Various Temperatures

	Vapor pressure (torr)		
Temperature (°C)	Water	Ethyl alcohol	Ethyl ether*
0	4.6	12.2	185.3
10	9.2	23.6	291.7
20	17.5	43.9	442.2
30	31.8	78.8	647.3
40	55.3	135.3	921.3
50	92.5	222.2	1276.8
60	152.9	352.7	1729.0
70	233.7	542.5	2296.0
80	355.1	812.6	2993.6
90	525.8	1187.1	3841.0
100	760.0	1693.3	4859.4
110	1074.6	2361.3	6070.1

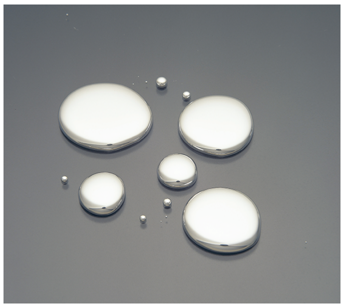
*Note that the vapor pressure of ethyl ether at temperatures of 40°C and higher exceeds standard pressure, 760 torr, which indicates that the substance has a low boiling point and should therefore be stored in a cool place in a tightly sealed container.

When equal volumes of water, ethyl ether, and ethyl alcohol are placed in beakers and allowed to evaporate at the same temperature, we observe that the ether evaporates faster than the alcohol, which evaporates faster than the water. This order of evaporation is consistent with the fact that ether has a higher vapor pressure at any particular temperature than ethyl alcohol or water. One reason for this higher vapor pressure is that the attraction is less between ether molecules than between alcohol or water molecules. The vapor pressures of these three compounds at various temperatures are compared in Table 13.1.

volatile

Substances that evaporate readily are said to be **volatile.** A volatile liquid has a relatively high vapor pressure at room temperature. Ethyl ether is a very volatile liquid; water is not too volatile; and mercury, which has a vapor pressure of 0.0012 torr at 20°C, is essentially a nonvolatile liquid. Most substances that are normally in a solid state are nonvolatile (solids that sublime are exceptions).

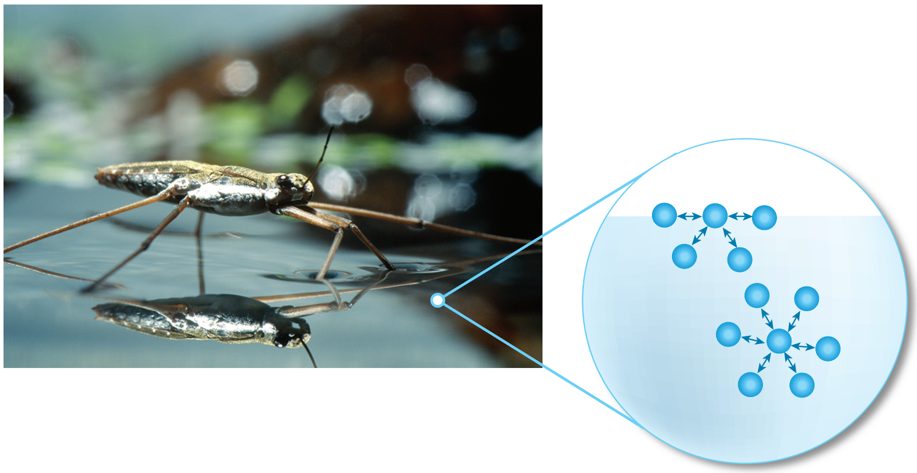
13.4 Surface Tension



Mercury droplets.

surface tension

Have you ever observed water and mercury in the form of small drops? These liquids form drops because liquids have *surface tension.* A droplet of liquid that is not falling or under the influence of gravity (as on the space shuttle) will form a sphere. Spheres minimize the ratio of surface area to volume. The molecules within the liquid are attracted to the surrounding liquid molecules, but at the liquid's surface, the attraction is nearly all inward. This pulls the surface into a spherical shape. The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid. Substances with large attractive forces between molecules have high surface tensions. The effect of surface tension in water is illustrated by floating a needle on the surface of still water.



A water strider skims the surface of the water as a result of surface tension. At the molecular level the surface tension results from the net attraction of the water molecules toward the liquid below. In the interior of the water, the forces are balanced in all directions.

Other examples include a water strider walking across a calm pond and water beading on a freshly waxed car. Surface tension is temperature dependent, decreasing with increasing temperature.

capillary action

Liquids also exhibit a phenomenon called **capillary action,** the spontaneous rising of a liquid in a narrow tube. This action results from the *cohesive forces* within the liquid and the *adhesive forces* between the liquid and the walls of the container. If the forces between the liquid and the container are greater than those within the liquid itself, the liquid will climb the walls of the container. For example, consider the California sequoia, a tree that reaches over 200 feet in height. Although water rises only 33 feet in a glass tube (under atmospheric pressure), capillary action causes water to rise from the sequoia's roots to all its parts.

meniscus

The meniscus in liquids is further evidence of cohesive and adhesive forces. When a liquid is placed in a glass cylinder, the surface of the liquid shows a curve called the **meniscus** (see Figure 13.5). The concave shape of water's meniscus shows that the adhesive forces between the glass and water are stronger than the cohesive forces within the water. In a nonpolar substance such as mercury, the meniscus is convex, indicating that the cohesive forces within mercury are greater than the adhesive forces between the glass wall and the mercury.

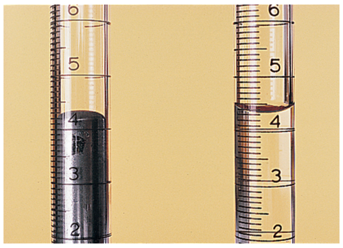


Figure 13.5
The meniscus of mercury (left) and water (right). The meniscus is the characteristic curve of the surface of a liquid in a narrow tube.

13.5 Boiling Point

The boiling temperature of a liquid is related to its vapor pressure. We've seen that vapor pressure increases as temperature increases. When the internal or vapor pressure of a liquid becomes equal to the external pressure, the liquid boils. (By external pressure we mean the pressure of the atmosphere above the liquid.) The boiling temperature of a pure liquid remains constant as long as the external pressure does not vary.

The boiling point (bp) of water is 100°C at 1 atm pressure. Table 13.1 shows that the vapor pressure of water at 100°C is 760 torr. The significant fact here is that the boiling point is the temperature at which the vapor pressure of the water or other liquid is equal to standard, or atmospheric, pressure at sea level. **Boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure above the liquid.

boiling point

We can readily see that a liquid has an infinite number of boiling points. When we give the boiling point of a liquid, we should also state the pressure. When we express the boiling point without stating the pressure, we mean it to be the **normal boiling point** at standard pressure (760 torr). Using Table 13.1 again, we see that the normal boiling point of ethyl ether is between 30°C and 40°C, and for ethyl alcohol it is between 70°C and 80°C because for each compound 760 torr lies within these stated temperature ranges. At the normal boiling point, 1 g of a liquid changing to a vapor (gas) absorbs an amount of energy equal to its heat of vaporization (see Table 13.2).

normal boiling point

The boiling point at various pressures can be evaluated by plotting the data of Table 13.1 on the graph in Figure 13.6, where temperature is plotted horizontally along the *x*-axis and vapor pressure is plotted vertically along the *y*-axis.

Table 13.2 Physical Properties of Ethyl Chloride, Ethyl Ether, Ethyl Alcohol, and Water

Substance	Boiling point (°C)	Melting point (°C)	Heat of vaporization J/g (cal/g)	Heat of fusion J/g (cal/g)
Ethyl chloride	12.3	−139	387 (92.5)	—
Ethyl ether	34.6	−116	351 (83.9)	—
Ethyl alcohol	78.4	−112	855 (204.3)	104 (24.9)
Water	100.0	0	2259 (540)	335 (80)

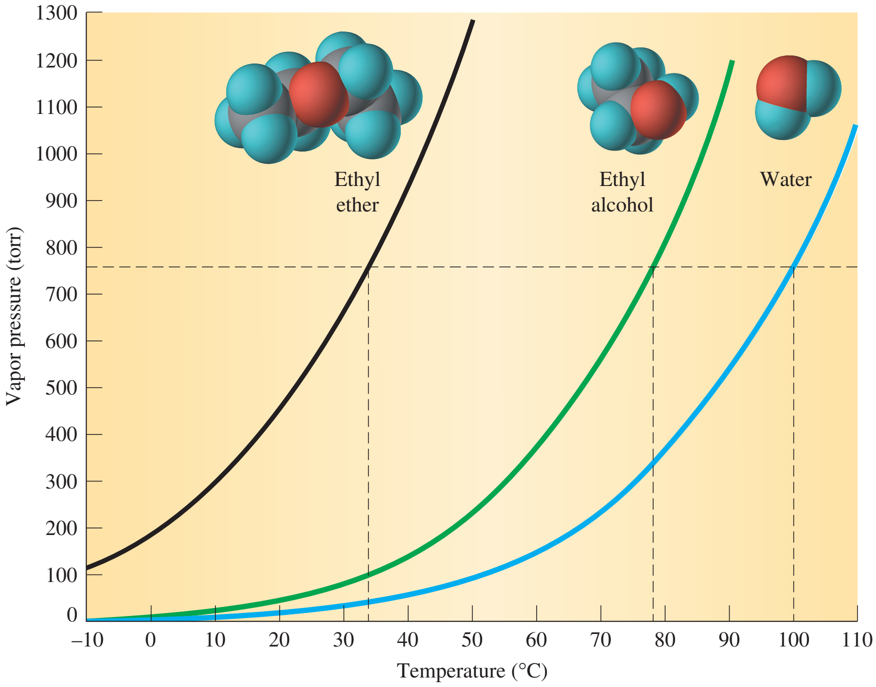


Figure 13.6
Vapor pressure–temperature curves for ethyl ether, ethyl alcohol, and water.

vapor pressure curves

The resulting curves are known as **vapor pressure curves.** Any point on these curves represents a vapor–liquid equilibrium at a particular temperature and pressure. We can find the boiling point at any pressure by tracing a horizontal line from the designated pressure to a point on the vapor pressure curve. From this point, we draw a vertical line to obtain the boiling point on the temperature axis. Three such points are shown in Figure 13.6; they represent the normal boiling points of the three compounds at 760 torr. By reversing this process, you can ascertain at what pressure a substance will boil at a specific temperature. The boiling point is one of the most commonly used physical properties for characterizing and identifying substances.

Practice 13.1

Use the graph in Figure 13.6 to determine the boiling points of ethyl ether, ethyl alcohol, and water at 600 torr.

Practice 13.2

The average atmospheric pressure in Denver is 0.83 atm. What is the boiling point of water in Denver?

13.6 Freezing Point or Melting Point

freezing or melting point

As heat is removed from a liquid, the liquid becomes colder and colder, until a temperature is reached at which it begins to solidify. A liquid changing into a solid is said to be *freezing,* or *solidifying.* When a solid is heated continuously, a temperature is reached at which the solid begins to liquefy. A solid that is changing into a liquid is said to be *melting.* The temperature at which the solid phase of a substance is in equilibrium with its liquid phase is known as the **freezing point** or **melting point** of that substance. The equilibrium equation is

$$\text{solid} \xrightleftharpoons[\text{freezing}]{\text{melting}} \text{liquid}$$

When a solid is slowly and carefully heated so that a solid–liquid equilibrium is achieved and then maintained, the temperature will remain constant as long as both phases are present. The energy is used solely to change the solid to the liquid. The melting point is another physical property that is commonly used for characterizing substances.

The most common example of a solid–liquid equilibrium is ice and water. In a well-stirred system of ice and water, the temperature remains at 0°C as long as both phases are present. The melting point changes only slightly with pressure unless the pressure change is very large.

13.7 Changes of State

The majority of solids undergo two changes of state upon heating. A solid changes to a liquid at its melting point, and a liquid changes to a gas at its boiling point. This warming process can be represented by a graph called a *heating*

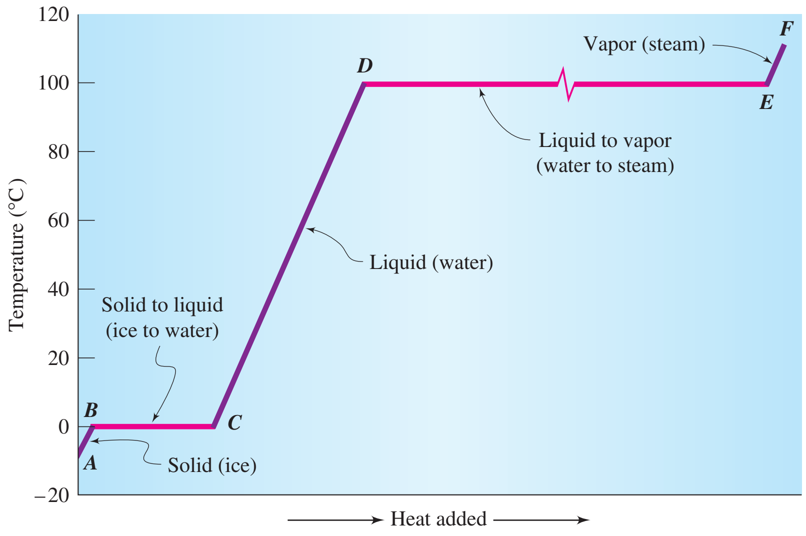


Figure 13.7
Heating curve for a pure substance—the absorption of heat by a substance from the solid state to the vapor state. Using water as an example, the *AB* interval represents the ice phase; *BC* interval, the melting of ice to water; *CD* interval, the elevation of the temperature of water from 0°C to 100°C; *DE* interval, the boiling of water to steam; and *EF* interval, the heating of steam.

curve (Figure 13.7). This figure shows ice being heated at a constant rate. As energy flows into the ice, the vibrations within the crystal increase and the temperature rises ($A \longrightarrow B$). Eventually, the molecules begin to break free from the crystal and melting occurs ($B \longrightarrow C$). During the melting process all energy goes into breaking down the crystal structure; the temperature remains constant.

The energy required to change exactly one gram of a solid at its melting point into a liquid is called the **heat of fusion.** When the solid has completely melted, the temperature once again rises ($C \longrightarrow D$); the energy input is increasing the molecular motion within the water. At 100°C, the water reaches its boiling point; the temperature remains constant while the added energy is used to vaporize the water to steam ($D \longrightarrow E$). The **heat of vaporization** is the energy required to change exactly one gram of liquid to vapor at its normal boiling point. The attractive forces between the liquid molecules are overcome during vaporization. Beyond this temperature all the water exists as steam and is being heated further ($E \longrightarrow F$).

heat of fusion

heat of vaporization

Example 13.1

How many joules of energy are needed to change 10.0 g of ice at 0.00°C to water at 20.0°C?

SOLUTION

Ice will absorb 335 J/g (heat of fusion) in going from a solid at 0°C to a liquid at 0°C. An additional 4.184 J/g°C (specific heat of water) is needed to raise the temperature of the water by 1°C.

Joules needed to melt the ice:

$$(10.0\,\cancel{\text{g}})\left(\frac{335\text{ J}}{1\,\cancel{\text{g}}}\right) = 3.35 \times 10^3\text{ J}$$

Joules needed to heat the water from 0.00°C to 20.0°C [(mass) (sp ht)(Δt)]:

$$(10.0\,\cancel{\text{g}})\left(\frac{4.184\text{ J}}{1\,\cancel{\text{g}}\cancel{^\circ\text{C}}}\right)(20.0\cancel{^\circ\text{C}}) = 837\text{ J}$$

Thus, 3350 J + 837 J = 4.19×10^3 J are needed.

Example 13.2 How many kilojoules of energy are needed to change 20.0 g of water at 20.°C to steam at 100.°C?

SOLUTION The specific heat of water is 4.184 J/g°C, so the kilojoules needed to heat the water from 20.°C to 100.°C are:

$$(\text{mass})\ (\text{sp ht})\ (\Delta t) = \text{energy}$$

$$(20.0\ \cancel{g})\left(\frac{4.184\ \cancel{J}}{1\ \cancel{g}\cancel{°C}}\right)\left(\frac{1\ \text{kJ}}{1000\ \cancel{J}}\right)(100. - 20.0)\ \cancel{°C} = 6.7\ \text{kJ}$$

Heat of vaporization of water is 2.26 kJ/g, so kilojoules needed to change water at 100.°C to steam at 100.°C are:

$$(20.0\ \cancel{g})\left(\frac{2.26\ \text{kJ}}{1\ \cancel{g}}\right) = 45.2\ \text{kJ}$$

Thus, 6.7 kJ + 45.2 kJ = 51.9 kJ are needed.

Practice 13.3

How many kilojoules of energy are required to change 50.0 g of ethyl alcohol from 60.0°C to vapor at 78.4°C? The specific heat of ethyl alcohol is 2.138 J/g°C.

13.8 The Hydrogen Bond

Table 13.3 compares the physical properties of H_2O, H_2S, H_2Se, and H_2Te. From this comparison, it is apparent that four physical properties of water—melting point, boiling point, heat of fusion, and heat of vaporization—are extremely high and do not fit the trend relative to the molar masses of the four compounds. For example, if the properties of water followed the progression shown by the other three compounds, we would expect the melting point of water to be below −85°C and the boiling point to be below −60°C.

Why does water exhibit these anomalies? Because liquid water molecules are held together more strongly than other molecules in the same family. The intermolecular force acting between water molecules is called a **hydrogen bond,** which acts like a very weak bond between two polar molecules.

hydrogen bond

Table 13.3 Physical Properties of Water and Other Hydrogen Compounds of Group 6A Elements

Formula	Color	Molar mass (g/mol)	Melting point (°C)	Boiling point, 1 atm (°C)	Heat of fusion J/g (cal/g)	Heat of vapor ization J/g (cal/g)
H_2O	Colorless	18.02	0.00	100.0	335 (80.0)	2.26×10^3(540)
H_2S	Colorless	34.09	−85.5	−60.3	69.9 (16.7)	548 (131)
H_2Se	Colorless	80.98	−65.7	−41.3	31 (7.4)	238 (57.0)
H_2Te	Colorless	129.6	−49	−2	—	179 (42.8)

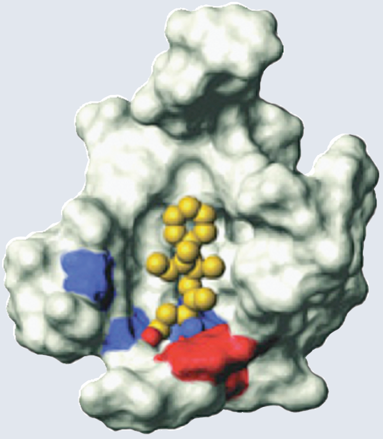
CHEMISTRY IN ACTION • How Sweet It Is!

Did you think artificial sweeteners were a product of the post–World War II chemical industry? Not so—many of them have been around a long time, and several of the important ones were discovered quite by accident. In 1878, Ira Remsen was working late in his laboratory and realized he was about to miss a dinner with friends. In his haste to leave the lab, he forgot to wash his hands. Later at dinner he broke a piece of bread and tasted it only to discover that it was very sweet. The sweet taste had to be the chemical he had been working with in the lab. Back at the lab, he isolated saccharin—the first of the artificial sweeteners.

In 1937, Michael Sveda was smoking a cigarette in his laboratory (a very dangerous practice to say the least!). He touched the cigarette to his lips and was surprised by the exceedingly sweet taste. The chemical on his hands turned out to be cyclamate, which soon became a staple of the artificial sweetener industry.

In 1965, James Schlatter was researching antiulcer drugs for the pharmaceutical firm G. D. Searle. In the course of his work, he accidentally ingested a small amount of a preparation and found to his surprise that it had an extremely sweet taste. He had discovered aspartame, a molecule consisting of two amino acids joined together. Since only very small quantities of aspartame are necessary to produce sweetness, it proved to be an excellent low-calorie artificial sweetener. More than 50 different molecules have a sweet taste, and it is difficult a find a single binding site that could interact with all of them.

Our taste receptors are composed of proteins that can form hydrogen bonds with other molecules. The proteins contain $-\mathrm{NH}$ and $-\mathrm{OH}$ groups (with hydrogen available to bond) as well as $\mathrm{C{=}O}$ groups (providing oxygen for hydrogen bonding). "Sweet molecules" also contain H-bonding groups including $-\mathrm{OH}$, $-\mathrm{NH_2}$, and O or N. These molecules not only must have the proper atoms to form hydrogen bonds, they must also contain a hydrophobic region (repels H_2O). A new model for binding to a sweetness receptor has been developed at Senomyx in La Jolla, California. The model shows four binding sites that can act independently. Small molecules bind to a pocket on a subunit as shown in the model. Large molecules (such as proteins) bind to a different site above one of the pockets.



Sweet bondage. Model shows how the sweetener aspartame binds to a site on the sweetness receptor's T1R3 subunit. Red and blue are hydrogen-bond donor and acceptor residues, respectively; aspartame is in gold, except for its carboyxlate (red) and ammonium (blue) groups. Model prepared with MOLMOL (*J. Mol. Graphics* 1996, 14, 51). Adapted from *J. Med. Chem.*

A hydrogen bond is formed between polar molecules that contain hydrogen covalently bonded to a small, highly electronegative atom such as fluorine, oxygen, or nitrogen ($\mathrm{F{-}H}$, $\mathrm{O{-}H}$, $\mathrm{N{-}H}$). A hydrogen bond is actually the dipole–dipole attraction between polar molecules containing these three types of polar bonds.

Compounds that have significant hydrogen-bonding ability are those that contain H covalently bonded to F, O, or N.

Because a hydrogen atom has only one electron, it forms only one covalent bond. When it is bonded to a strong electronegative atom such as oxygen, a hydrogen atom will also be attracted to an oxygen atom of another molecule, forming a dipole–dipole attraction (H bond) between the two molecules. Water has two types of bonds: covalent bonds that exist between hydrogen and oxygen atoms within a molecule and hydrogen bonds that exist between hydrogen and oxygen atoms in *different* water molecules.

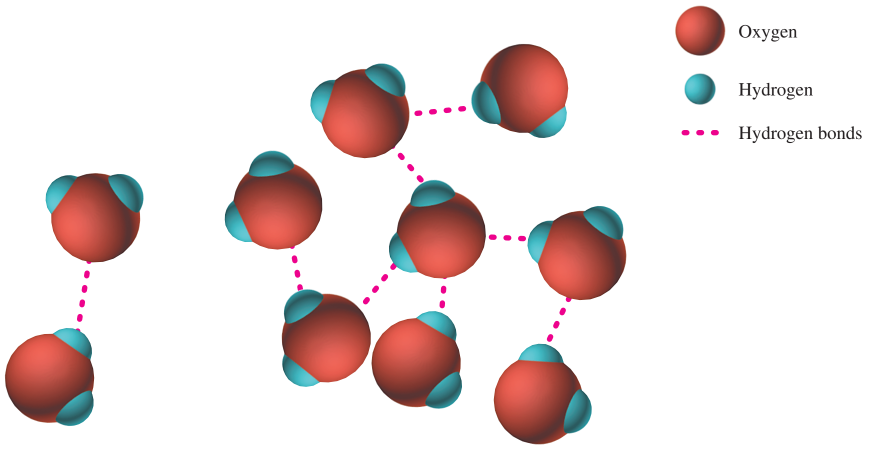
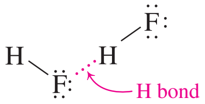


Figure 13.8
Hydrogen bonding. Water in the liquid and solid states exists as aggregates in which the water molecules are linked together by hydrogen bonds.

Hydrogen bonds are *intermolecular* bonds; that is, they are formed between atoms in different molecules. They are somewhat ionic in character because they are formed by electrostatic attraction. Hydrogen bonds are much weaker than the ionic or covalent bonds that unite atoms to form compounds. Despite their weakness, they are of great chemical importance.

The oxygen atom in water can form two hydrogen bonds—one through each of the unbonded pairs of electrons. Figure 13.8 shows two water molecules linked by a hydrogen bond and eight water molecules linked by hydrogen bonds. A dash (—) is used for the covalent bond and a dotted line (····) for the hydrogen bond. In water each molecule is linked to others through hydrogen bonds to form a three-dimensional aggregate of water molecules. This intermolecular hydrogen bonding effectively gives water the properties of a much larger, heavier molecule, explaining in part its relatively high melting point, boiling point, heat of fusion, and heat of vaporization. As water is heated and energy absorbed, hydrogen bonds are continually being broken until at 100°C, with the absorption of an additional 2.26 kJ/g, water separates into individual molecules, going into the gaseous state. Sulfur, selenium, and tellurium are not sufficiently electronegative for their hydrogen compounds to behave like water. The lack of hydrogen bonding is one reason H_2S is a gas, not a liquid, at room temperature.

Fluorine, the most electronegative element, forms the strongest hydrogen bonds. This bonding is strong enough to link hydrogen fluoride molecules together as *dimers,* H_2F_2, or as larger $(HF)_n$ molecular units. The dimer structure may be represented in this way:

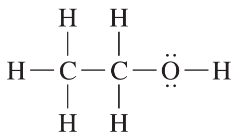


Hydrogen bonding can occur between two different atoms that are capable of forming H bonds. Thus, we may have an O····H—N or O—H····N linkage in which the hydrogen atom forming the H bond is between an oxygen and a nitrogen atom. This form of H bond exists in certain types of protein molecules and many biologically active substances.

Example 13.3

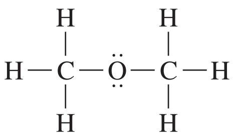
Would you expect hydrogen bonding to occur between molecules of these substances?

(a)



ethyl alcohol

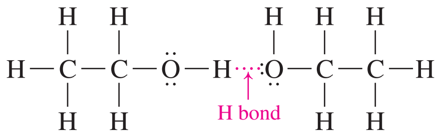
(b)



dimethyl ether

SOLUTION

(a) Hydrogen bonding should occur in ethyl alcohol because one hydrogen atom is bonded to an oxygen atom:



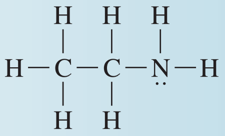
(b) There is no hydrogen bonding in dimethyl ether because all the hydrogen atoms are bonded only to carbon atoms.

Both ethyl alcohol and dimethyl ether have the same molar mass (46.07 g/mol). Although both compounds have the same molecular formula, C_2H_6O, ethyl alcohol has a much higher boiling point (78.4°C) than dimethyl ether (−23.7°C) because of hydrogen bonding between the alcohol molecules.

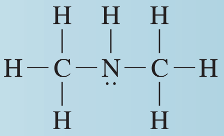
Practice 13.4

Would you expect hydrogen bonding to occur between molecules of these substances?

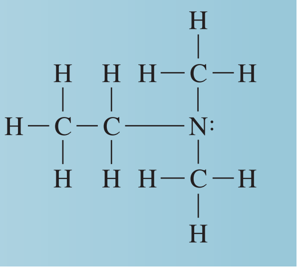
(a)



(b)



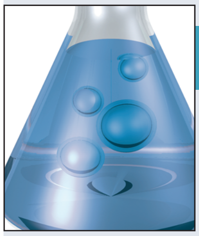
(c)



13.9 Hydrates

When certain solutions containing ionic compounds are allowed to evaporate, some water molecules remain as part of the crystalline compound that is left after evaporation is complete. Solids that contain water molecules as part of their crystalline structure are known as **hydrates.** Water in a hydrate is known as **water of hydration** or **water of crystallization.**

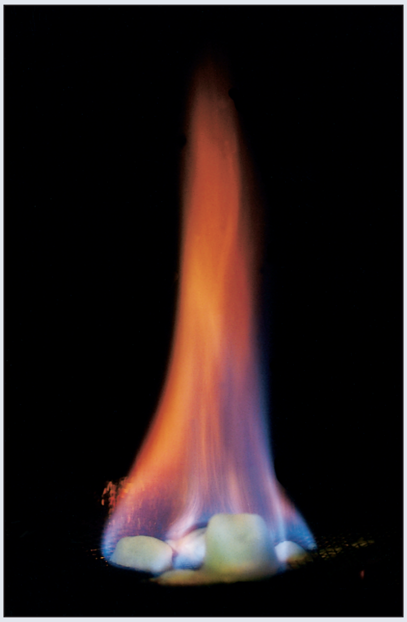
hydrate
water of hydration
water of crystallization



CHEMISTRY IN ACTION • Hot Ice—It's a Gas!

Ice could well become the most abundant source of energy in the 21st century. This particular type of ice has unusual properties. Even its existence has been the subject of debate since 1810, when Humphrey Davy synthesized the first hydrate of chlorine. Chemists have long debated whether water could crystallize around a gas to form an unusual state of matter known as a gas hydrate. The material looks just like a chunk of ice left from a winter storm, gray and ugly. But unlike ice, this gas hydrate ice pops and sizzles and a lit match causes it to burst into flames. Left alone, it melts quickly into a puddle of water.

Just what is gas hydrate ice and how does it form? It turns out that gas hydrates form when water and some gases (like propane, ethane, or methane) are present at high pressure and low temperature. These conditions occur in nature at the bottom of the ocean and under permafrost in the Arctic north. Oil companies struggle with hydrate ice since it plugs pipelines and damages oil rigs in oil fields in the Arctic. A gas hydrate is a gas molecule trapped inside the crystal lattice of water molecules. The most common gas is methane produced from the decomposition of organic matter. Sonar mapping has revealed large gas hydrate deposits in polar regions such as Alaska and Siberia and off the southeastern coast of the United States.



Nuggets of gas hydrate burn as they revert to water (or ice) and gas.

Scientists think that gas hydrates trap huge amounts of natural gas. One cubic meter of methane hydrate can contain the amount of gas that would fill 164 m^3 at room temperature and pressure. If this gas could be brought to the surface economically, it could supply 1000 years of fuel for the United States. As prices increase for energy sources, the costs for liberating gas hydrates become more feasible. At this point, most American research is focused on figuring out how to recover the gas cost-effectively from the hydrates and on transporting the methane to customers. But one day in the not too distant future we could be heating our homes and running our cars by mining gas hydrates from ice!

Formulas for hydrates are expressed by first writing the usual anhydrous (without water) formula for the compound and then adding a dot followed by the number of water molecules present. An example is $BaCl_2 \cdot 2\,H_2O$. This formula tells us that each formula unit of this compound contains one barium ion, two chloride ions, and two water molecules. A crystal of the compound contains many of these units in its crystalline lattice.

In naming hydrates, we first name the compound exclusive of the water and then add the term *hydrate,* with the proper prefix representing the number of water molecules in the formula. For example, $BaCl_2 \cdot 2\,H_2O$ is called *barium chloride dihydrate*. Hydrates are true compounds and follow the law of definite composition. The molar mass of $BaCl_2 \cdot 2\,H_2O$ is 244.2 g/mol; it contains 56.22% barium, 29.03% chlorine, and 14.76% water.

Water molecules in hydrates are bonded by electrostatic forces between polar water molecules and the positive or negative ions of the compound. These forces are not as strong as covalent or ionic chemical bonds. As a result, water of crystallization can be removed by moderate heating of the compound. A partially dehydrated or completely anhydrous compound may result. When $BaCl_2 \cdot 2\,H_2O$ is heated, it loses its water at about 100°C:

$$BaCl_2 \cdot 2\,H_2O(s) \xrightarrow{100^\circ C} BaCl_2(s) + 2\,H_2O(g)$$

(a) (b)

Figure 13.9
(a) When these blue crystals of $CuSO_4 \cdot 5\,H_2O$ are dissolved in water, a blue solution forms. (b) The anhydrous crystals of $CuSO_4$ are pale green. When water is added, they immediately change color to blue $CuSO_4 \cdot 5\,H_2O$ crystals.

When a solution of copper(II) sulfate ($CuSO_4$) is allowed to evaporate, beautiful blue crystals containing 5 moles water per 1 mole $CuSO_4$ are formed (Figure 13.9a). The formula for this hydrate is $CuSO_4 \cdot 5\,H_2O$; it is called copper(II) sulfate pentahydrate. When $CuSO_4 \cdot 5\,H_2O$ is heated, water is lost, and a pale green-white powder, anhydrous $CuSO_4$, is formed:

$$CuSO_4 \cdot 5\,H_2O(s) \xrightarrow{250°C} CuSO_4(s) + 5\,H_2O(g)$$

When water is added to anhydrous copper(II) sulfate, the foregoing reaction is reversed, and the compound turns blue again (Figure 13.9b). Because of this outstanding color change, anhydrous copper(II) sulfate has been used as an indicator to detect small amounts of water. The formation of the hydrate is noticeably exothermic.

The formula for plaster of paris is $(CaSO_4)_2 \cdot H_2O$. When mixed with the proper quantity of water, plaster of paris forms a dihydrate and sets to a hard mass. It is therefore useful for making patterns for the production of art objects, molds, and surgical casts. The chemical reaction is

$$(CaSO_4)_2 \cdot H_2O(s) + 3\,H_2O(l) \longrightarrow 2\,CaSO_4 \cdot 2\,H_2O(s)$$

Table 13.4 lists a number of common hydrates.

Table 13.4 Selected Hydrates

Hydrate	Name	Hydrate	Name
$CaCl_2 \cdot 2\,H_2O$	calcium chloride dihydrate	$Na_2CO_3 \cdot 10\,H_2O$	sodium carbonate decahydrate
$Ba(OH)_2 \cdot 8\,H_2O$	barium hydroxide octahydrate	$(NH_4)_2C_2O_4 \cdot H_2O$	ammonium oxalate monohydrate
$MgSO_4 \cdot 7\,H_2O$	magnesium sulfate heptahydrate	$NaC_2H_3O_2 \cdot 3\,H_2O$	sodium acetate trihydrate
$SnCl_2 \cdot 2\,H_2O$	tin(II) chloride dihydrate	$Na_2B_4O_7 \cdot 10\,H_2O$	sodium tetraborate decahydrate
$CoCl_2 \cdot 6\,H_2O$	cobalt(II) chloride hexahydrate	$Na_2S_2O_3 \cdot 5\,H_2O$	sodium thiosulfate pentahydrate

Practice 13.5

Write formulas for

(a) beryllium carbonate tetrahydrate
(b) cadmium permanganate hexahydrate
(c) chromium(III) nitrate nonahydrate
(d) platinum(IV) oxide trihydrate

Practice 13.6

Calculate the percent water in Epsom salts, $MgSO_4 \cdot 7\,H_2O$.

13.10 Water, a Unique Liquid

Water is our most common natural resource. It covers about 75% of Earth's surface. Not only is it found in the oceans and seas, in lakes, rivers, streams, and glacial ice deposits, it is always present in the atmosphere and in cloud formations.

About 97% of Earth's water is in the oceans. This *saline* water contains vast amounts of dissolved minerals. More than 70 elements have been detected in the mineral content of seawater. Only four of these—chlorine, sodium, magnesium, and bromine—are now commercially obtained from the sea. The world's *fresh* water comprises the other 3%, of which about two-thirds is locked up in polar ice caps and glaciers. The remaining fresh water is found in groundwater, lakes, rivers and the atmosphere.

Water is an essential constituent of all living matter. It is the most abundant compound in the human body, making up about 70% of total body mass. About 92% of blood plasma is water; about 80% of muscle tissue is water; and about 60% of a red blood cell is water. Water is more important than food in the sense that we can survive much longer without food than without water.

Physical Properties of Water

Water is a colorless, odorless, tasteless liquid with a melting point of 0°C and a boiling point of 100°C at 1 atm. The heat of fusion of water is 335 J/g (80 cal/g). The heat of vaporization of water is 2.26 kJ/g (540 cal/g). The values for water for both the heat of fusion and the heat of vaporization are high compared with those for other substances; this indicates strong attractive forces between the molecules.

Ice and water exist together in equilibrium at 0°C, as shown in Figure 13.10. When ice at 0°C melts, it absorbs 335 J/g in changing into a liquid; the temperature remains at 0°C. To refreeze the water, 335 J/g must be removed from the liquid at 0°C.

In Figure 13.10, both boiling water and steam are shown to have a temperature of 100°C. It takes 418 J to heat 1 g of water from 0°C to 100°C, but water at its boiling point absorbs 2.26 kJ/g in changing to steam. Although boiling water and steam are both at the same temperature, steam contains considerably more heat per gram and can cause more severe burns than hot water.

The maximum density of water is 1.000 g/mL at 4°C. Water has the unusual property of contracting in volume as it is cooled to 4°C and then expanding when cooled from 4°C to 0°C. Therefore, 1 g of water occupies a volume greater than 1 mL at all temperatures except 4°C. Although most liquids

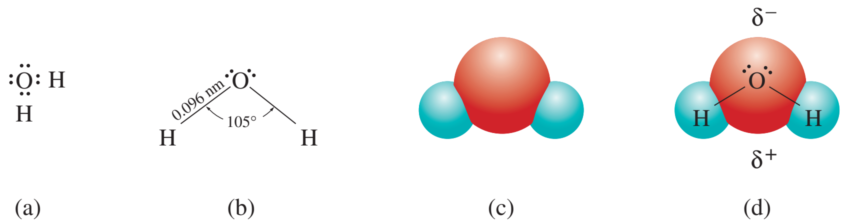
Figure 13.10
Water equilibrium systems. In the beaker on the left, ice and water are in equilibrium at 0°C; in the beaker on the right, boiling water and steam are in equilibrium at 100°C.

contract in volume all the way down to the point at which they solidify, a large increase (about 9%) in volume occurs when water changes from a liquid at 0°C to a solid (ice) at 0°C. The density of ice at 0°C is 0.917 g/mL, which means that ice, being less dense than water, will float in water.

Structure of the Water Molecule

A single water molecule consists of two hydrogen atoms and one oxygen atom. Each hydrogen atom is bonded to the oxygen atom by a single covalent bond. This bond is formed by the overlap of the 1*s* orbital of hydrogen with an unpaired 2*p* orbital of oxygen. The average distance between the two nuclei is known as the *bond length*. The O—H bond length in water is 0.096 nm. The water molecule is nonlinear and has a bent structure with an angle of about 105° between the two bonds (see Figure 13.11).

Oxygen is the second most electronegative element. As a result, the two covalent OH bonds in water are polar. If the three atoms in a water molecule were aligned in a linear structure, such as $\mathrm{H} \!+\!\!\!\longrightarrow \mathrm{O} \longleftarrow\!\!\!+\! \mathrm{H}$, the two polar



(a) (b) (c) (d)

Figure 13.11
Diagrams of a water molecule: (a) electron distribution, (b) bond angle and O—H bond length, (c) molecular orbital structure, and (d) dipole representation.

bonds would be acting in equal and opposite directions and the molecule would be nonpolar. However, water is a highly polar molecule. It therefore does not have a linear structure. When atoms are bonded in a nonlinear fashion, the angle formed by the bonds is called the *bond angle*. In water the HOH bond angle is 105°. The two polar covalent bonds and the bent structure result in a partial negative charge on the oxygen atom and a partial positive charge on each hydrogen atom. The polar nature of water is responsible for many of its properties, including its behavior as a solvent.

Formation of Water

Water is very stable to heat; it decomposes to the extent of only about 1% at temperatures up to 2000°C. Pure water is a nonconductor of electricity. But when a small amount of sulfuric acid or sodium hydroxide is added, the solution is readily decomposed into hydrogen and oxygen by an electric current. Two volumes of hydrogen are produced for each volume of oxygen:

$$2\,H_2O(l) \xrightarrow[H_2SO_4 \text{ or NaOH}]{\text{electrical energy}} 2\,H_2(g) + O_2(g)$$

Water is formed when hydrogen burns in air. Pure hydrogen burns very smoothly in air, but mixtures of hydrogen and air or oxygen explode when ignited. The reaction is strongly exothermic:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) + 484\text{ kJ}$$

Water is produced by a variety of other reactions, especially by (1) acid–base neutralizations, (2) combustion of hydrogen-containing materials, and (3) metabolic oxidation in living cells:

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

2. $\underset{\text{acetylene}}{2\,C_2H_2(g)} + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 2\,H_2O(g) + 1212\text{ kJ}$

$\underset{\text{methane}}{CH_4(g)} + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) + 803\text{ kJ}$

3. $\underset{\text{glucose}}{C_6H_{12}O_6(aq)} + 6\,O_2(g) \xrightarrow{\text{enzymes}} 6\,CO_2(g) + 6\,H_2O(l) + 2519\text{ kJ}$

The combustion of acetylene shown in (2) is strongly exothermic and is capable of producing very high temperatures. It is used in oxygen–acetylene torches to cut and weld steel and other metals. Methane is known as natural gas and is commonly used as fuel for heating and cooking. The reaction of glucose with oxygen shown in (3) is the reverse of photosynthesis. It is the overall reaction by which living cells obtain needed energy by metabolizing glucose to carbon dioxide and water.

Sodium reacts vigorously with water to produce hydrogen gas and sodium hydroxide.

Reactions of Water with Metals and Nonmetals

The reactions of metals with water at different temperatures show that these elements vary greatly in their reactivity. Metals such as sodium, potassium, and calcium react with cold water to produce hydrogen and a metal hydroxide. A small piece of sodium added to water melts from the heat produced by the reaction, forming a silvery metal ball, which rapidly flits back and forth on the surface of the water. Caution must be used when experimenting with this reaction, because the hydrogen produced is frequently ignited by the sparking of the sodium, and it will explode, spattering sodium. Potassium reacts even more vigorously than sodium. Calcium sinks in water and liberates a gentle stream of hydrogen. The equations for these reactions are

$$2\,\mathrm{Na}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2}(g) + 2\,\mathrm{NaOH}(aq)$$
$$2\,\mathrm{K}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2}(g) + 2\,\mathrm{KOH}(aq)$$
$$\mathrm{Ca}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2}(g) + \mathrm{Ca(OH)_2}(aq)$$

Zinc, aluminum, and iron do not react with cold water but will react with steam at high temperatures, forming hydrogen and a metallic oxide. The equations are

$$\mathrm{Zn}(s) + \mathrm{H_2O}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{ZnO}(s)$$
$$2\,\mathrm{Al}(s) + 3\,\mathrm{H_2O}(g) \longrightarrow 3\,\mathrm{H_2}(g) + \mathrm{Al_2O_3}(s)$$
$$3\,\mathrm{Fe}(s) + 4\,\mathrm{H_2O}(g) \longrightarrow 4\,\mathrm{H_2}(g) + \mathrm{Fe_3O_4}(s)$$

Copper, silver, and mercury are examples of metals that do not react with cold water or steam to produce hydrogen. We conclude that sodium, potassium, and calcium are chemically more reactive than zinc, aluminum, and iron, which are more reactive than copper, silver, and mercury.

Certain nonmetals react with water under various conditions. For example, fluorine reacts violently with cold water, producing hydrogen fluoride and free oxygen. The reactions of chlorine and bromine are much milder, producing what is commonly known as "chlorine water" and "bromine water," respectively. Chlorine water contains HCl, $HOCl$, and dissolved Cl_2; the free chlorine gives it a yellow-green color. Bromine water contains HBr, $HOBr$, and dissolved Br_2; the free bromine gives it a reddish-brown color. The equations for these reactions are

$$2\,\mathrm{F_2}(g) + 2\,\mathrm{H_2O}(l) \longrightarrow 4\,\mathrm{HF}(aq) + \mathrm{O_2}(g)$$
$$\mathrm{Cl_2}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{HCl}(aq) + \mathrm{HOCl}(aq)$$
$$\mathrm{Br_2}(l) + \mathrm{H_2O}(l) \longrightarrow \mathrm{HBr}(aq) + \mathrm{HOBr}(aq)$$

Reactions of Water with Metal and Nonmetal Oxides

Metal oxides that react with water to form hydroxides are known as **basic anhydrides.** Examples are

basic anhydride

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \underset{\text{calcium hydroxide}}{\mathrm{Ca(OH)_2}(aq)}$$

$$\mathrm{Na_2O}(s) + \mathrm{H_2O}(l) \longrightarrow \underset{\text{sodium hydroxide}}{2\,\mathrm{NaOH}(aq)}$$

Certain metal oxides, such as CuO and Al_2O_3, do not form solutions containing OH^- ions because the oxides are insoluble in water.

Practice 13.7

Copper does not react with water to produce hydrogen gas. However, hydrogen reacts with copper(II) oxide to produce water. Write a balanced equation for this reaction.

acid anhydride

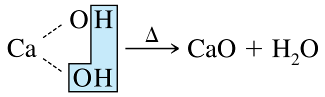
Nonmetal oxides that react with water to form acids are known as **acid anhydrides.** Examples are

$$CO_2(g) + H_2O(l) \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3(aq)}$$

$$SO_2(g) + H_2O(l) \rightleftharpoons \underset{\text{sulfurous acid}}{H_2SO_3(aq)}$$

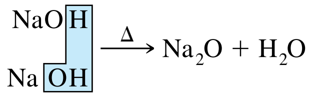
$$N_2O_5(s) + H_2O(l) \longrightarrow \underset{\text{nitric acid}}{2\,HNO_3(aq)}$$

The word *anhydrous* means "without water." An anhydride is a metal oxide or a nonmetal oxide derived from a base or an oxy-acid by the removal of water. To determine the formula of an anhydride, the elements of water are removed from an acid or base formula until all the hydrogen is removed. Sometimes more than one formula unit is needed to remove all the hydrogen as water. The formula of the anhydride then consists of the remaining metal or nonmetal and the remaining oxygen atoms. In calcium hydroxide, removal of water as indicated leaves CaO as the anhydride:



$$\mathrm{Ca}\begin{matrix}\mathrm{O}\boxed{\mathrm{H}}\\ \boxed{\mathrm{OH}}\end{matrix} \xrightarrow{\Delta} CaO + H_2O$$

In sodium hydroxide, H_2O cannot be removed from one formula unit, so two formula units of NaOH must be used, leaving Na_2O as the formula of the anhydride:



$$\begin{matrix}\mathrm{NaO}\boxed{\mathrm{H}}\\ \mathrm{Na}\boxed{\mathrm{OH}}\end{matrix} \xrightarrow{\Delta} Na_2O + H_2O$$

The removal of H_2O from H_2SO_4 gives the acid anhydride SO_3:

$$H_2SO_4 \xrightarrow{\Delta} SO_3 + H_2O$$

The foregoing are examples of typical reactions of water but are by no means a complete list of the known reactions of water.

13.11 Water Purification

Natural fresh waters are not pure, but contain dissolved minerals, suspended matter, and sometimes harmful bacteria. The water supplies of large cities are usually drawn from rivers or lakes. Such water is generally unsafe to drink without treatment. To make such water safe to drink, it is treated by some or all of the following processes (see Figure 13.12):

1. *Screening.* Removal of relatively large objects, such as trash, fish, and so on.
2. *Flocculation and sedimentation.* Chemicals, usually lime, CaO, and alum (aluminum sulfate), $Al_2(SO_4)_3$, are added to form a flocculent jellylike precipitate of aluminum hydroxide. This precipitate traps most of the fine suspended matter in the water and carries it to the bottom of the sedimentation basin.
3. *Sand filtration.* Water is drawn from the top of the sedimentation basin and passed downward through fine sand filters. Nearly all the remaining suspended matter and bacteria are removed by the sand filters.

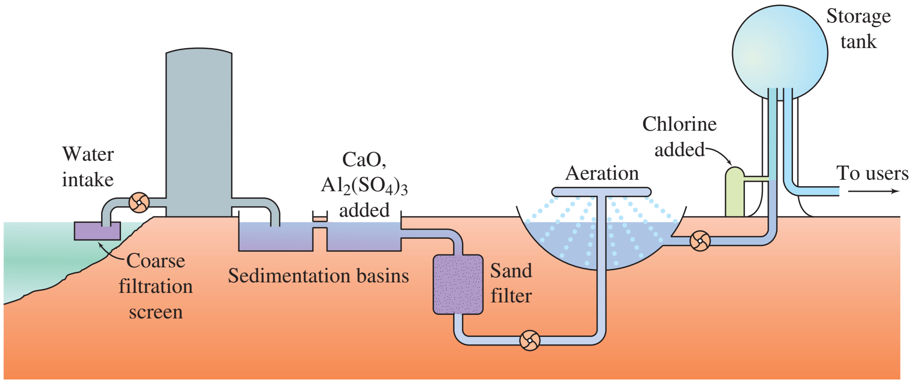


Figure 13.12 Typical municipal water-treatment plant.

4. *Aeration.* Water is drawn from the bottom of the sand filters and is aerated by spraying. The purpose of this process is to remove objectionable odors and tastes.
5. *Disinfection.* In the final stage chlorine gas is injected into the water to kill harmful bacteria before the water is distributed to the public. Ozone is also used to disinfect water. In emergencies, water may be disinfected by simply boiling it for a few minutes.

If the drinking water of children contains an optimum amount of fluoride ion, their teeth will be more resistant to decay.

Water that contains dissolved calcium and magnesium salts is called *hard water.* Ordinary soap does not lather well in hard water; the soap reacts with the calcium and magnesium ions to form an insoluble greasy scum. However, synthetic soaps, known as detergents, have excellent cleaning qualities and do not form precipitates with hard water. Hard water is also undesirable because it causes "scale" to form on the walls of water heaters, tea kettles, coffee pots, and steam irons, which greatly reduces their efficiency.

Many people today find that they want to further purify their drinking and cooking water. Often this is because of objectionable tastes in the municipal drinking water. People add filtration systems to appliances such as refrigerators and coffee pots or use home water filtration systems. People also buy bottled water for drinking and cooking.

Four techniques are used to "soften" hard water:

1. **Distillation** The water is boiled, and the steam formed is condensed into a liquid again, leaving the minerals behind in the distilling vessel. Figure 13.13 illustrates a simple laboratory distillation apparatus. Commercial stills are capable of producing hundreds of liters of distilled water per hour.
2. **Calcium and magnesium precipitation** Calcium and magnesium ions are precipitated from hard water by adding sodium carbonate and lime. Insoluble calcium carbonate and magnesium hydroxide are precipitated and are removed by filtration or sedimentation.
3. **Ion exchange** Hard water is effectively softened as it is passed through a bed or tank of zeolite—a complex sodium aluminum silicate. In this process, sodium ions replace objectionable calcium and magnesium ions, and the water is thereby softened:

   $$Na_2(\text{zeolite})(s) + Ca^{2+}(aq) \longrightarrow Ca(\text{zeolite})(s) + 2\,Na^{+}(aq)$$

   The zeolite is regenerated by back-flushing with concentrated sodium chloride solution, reversing the foregoing reaction.

Bottled water provides a convenient source of hydration for athletes.

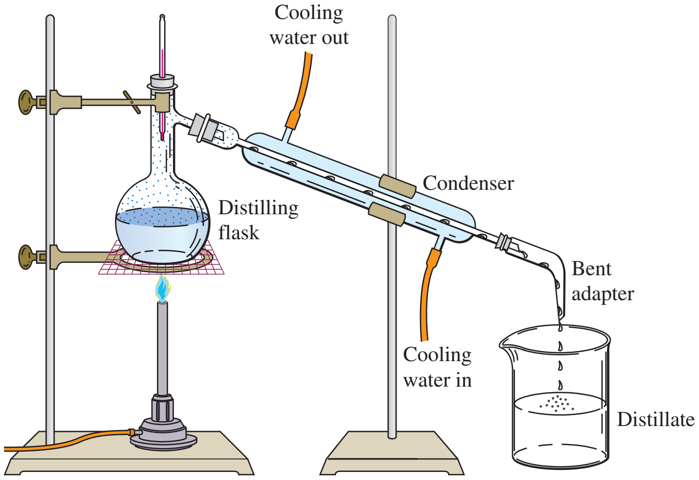


Figure 13.13
Simple laboratory setup for distilling liquids.

4. **Demineralization** Both cations and anions are removed by a two-stage ion-exchange system. Special synthetic organic resins are used in the ion-exchange beds. In the first stage metal cations are replaced by hydrogen ions. In the second stage anions are replaced by hydroxide ions. The hydrogen and hydroxide ions react, and essentially pure, mineral-free water leaves the second stage.

Our oceans are an enormous source of water, but seawater contains about 3.5 lb of salts per 100 lb of water. This 35,000 ppm of dissolved salts makes seawater unfit for agricultural and domestic uses. Water that contains less than 1000 ppm of salts is considered reasonably good for drinking, and safe drinking water is already being obtained from the sea in many parts of the world. Continuous research is being done in an effort to make usable water from our oceans more abundant and economical. See Figure 13.14.

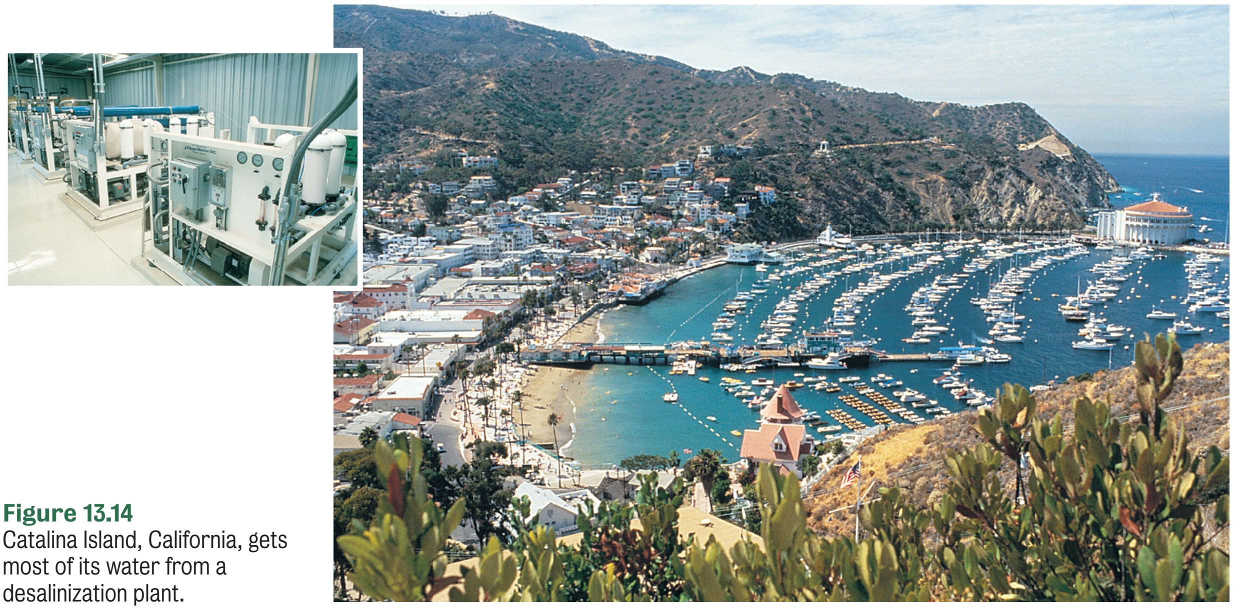


Figure 13.14
Catalina Island, California, gets most of its water from a desalinization plant.

Table 13.5 Classification of Water Pollutants

Type of pollutant	Examples
Oxygen-demanding wastes	Decomposable organic wastes from domestic sewage and industrial wastes of plant and animal origin
Infectious agents	Bacteria, viruses, and other organisms from domestic sewage, animal wastes, and animal process wastes
Plant nutrients	Principally compounds of nitrogen and phosphorus
Organic chemicals	Large numbers of chemicals synthesized by industry, pesticides, chlorinated organic compounds
Other minerals and chemicals	Inorganic chemicals from industrial operations, mining, oil field operations, and agriculture
Radioactive substances	Waste products from mining and processing radioactive materials, airborne radioactive fallout, increased use of radioactive materials in hospitals and research
Heat from industry	Large quantities of heated water returned to water bodies from power plants and manufacturing facilities after use for cooling
Sediment from land erosion	Solid matter washed into streams and oceans by erosion, rain, and water runoff

Our highly technical, industrial society has produced many new chemicals that add to our need for water purification. Many of the newer chemicals are not removed or destroyed by the usual water-treatment processes. For example, among the 66 organic compounds found in the drinking water of a major city on the Mississippi River, 3 are labeled slightly toxic, 17 moderately toxic, 15 very toxic, 1 extremely toxic, and 1 supertoxic. Two are known carcinogens (cancer-producing agents), 11 are suspect, and 3 are metabolized to carcinogens. The U.S. Public Health Service classifies water pollutants under eight broad categories. These categories are shown in Table 13.5.

The disposal of hazardous waste products adds to the water purification problem. These substances are unavoidable in the manufacture of many products we consider indispensable today. One common way to dispose of these wastes is to place them in toxic waste dumps. What has been found after many years of disposing of wastes in this manner is that toxic substances have seeped into the groundwater deposits. As a result, many people have become ill, and water wells have been closed until satisfactory methods of detoxifying this water are found. This problem is serious, because one-half the U.S. population gets its drinking water from groundwater. Cleaning up the thousands of industrial dumps and finding and implementing new and safe methods of disposing of wastes is ongoing and costly.

Chapter 13 Review

13.1 What Is a Liquid?

- Properties:
  - Particles are close together yet free to move.
  - Liquids are incompressible.
  - Liquids have definite volume but take the shape of the container.

13.2 Evaporation

KEY TERMS

Evaporation, or vaporization
Sublimation

- During evaporation, molecules of greater-than-average kinetic energy escape from the liquid.
- Sublimation is the evaporation of a solid directly to a gas.

13.3 Vapor Pressure

KEY TERMS

Condensation
Vapor pressure
Volatile

- Gaseous molecules return to the liquid state through condensation.
- At equilibrium the rate of evaporation equals the rate of condensation.
- The pressure exerted by the vapor in equilibrium with its liquid in a closed container is the vapor pressure of the liquid.
- A volatile substance evaporates readily.

13.4 Surface Tension

KEY TERMS

Surface tension
Capillary action
Meniscus

- The resistance of a liquid to an increase in its surface area is the surface tension of the liquid.
- Capillary action is caused by the cohesive forces within the liquid and adhesive forces between the liquid and the walls of the container:
  - If the forces between the liquid and the container are greater than those within the liquid, the liquid will climb the walls of the container.
- A meniscus is evidence of cohesive and adhesive forces:
  - It is concave if the adhesive forces are stronger than the cohesive forces.
  - It is convex if the cohesive forces are stronger than the adhesive forces.

13.5 Boiling Point

KEY TERMS

Boiling point
Normal boiling point
Vapor pressure curves

- The boiling point of a liquid is the temperature at which its vapor pressure equals the atmospheric pressure:
  - At 1 atm the boiling point is called the normal boiling point for a liquid.

13.6 Freezing Point or Melting Point

KEY TERM

Freezing point or melting point

- The temperature at which a solid is in equilibrium with its liquid phase is the freezing point or melting point.

13.7 Changes of State

KEY TERMS

Heat of fusion
Heat of vaporization

- A graph of the warming of a liquid is called a heating curve:
  - Horizontal lines on the heating curve represent changes of state:
    - The energy required to change 1 g of solid to liquid at its melting point is the heat of fusion.
    - The energy required to change 1 g of liquid to gas at its normal boiling point is the heat of vaporization.
    - The energy required to change the phase of a sample (at its melting or boiling point) is

$$\text{energy} = (\text{mass})(\text{heat of fusion (or vaporization)})$$

  - The energy required to heat molecules without a phase change is determined by

$$\text{energy} = (\text{mass})(\text{sp ht})(\Delta t)$$

13.8 The Hydrogen Bond

KEY TERM

Hydrogen bond

- A hydrogen bond is the dipole–dipole attraction between polar molecules containing any of these types of bonds: F—H, O—H, N—H.

13.9 Hydrates

KEY TERMS

Hydrate
Water of hydration or water crystallization

- Solids that contain water molecules as part of their crystalline structure are called hydrates.
- Formulas of hydrates are given by writing the formula for the anhydrous compound followed by a dot and then the number of water molecules present.
- Water molecules in hydrates are bonded by electrostatic forces, which are weaker than covalent or ionic bonds:
  - Water of hydration can be removed by heating the hydrate to form a partially dehydrated compound or the anhydrous compound.

13.10 Water, a Unique Liquid

KEY TERMS

Basic anhydride
Acid anhydride

- Water is our most common resource, covering 75% of the Earth's surface.
- Water is a colorless, odorless, tasteless liquid with a melting point of 0°C and boiling point of 100°C at 1 atm
- The water molecule consists of 2 H atoms and 1 O atom bonded together at a 105° bond angle, making the molecule polar.
- Water can be formed in a variety of ways including:
    - Burning hydrogen in air
    - Acid–base neutralizations
    - Combustion of hydrogen-containing materials
    - Metabolic oxidation in living cells
- Water undergoes reactions with many metals and nonmetals, depending on their reactivity.
- Water reacts with metal oxides (basic anhydrides) to form bases (hydroxides).
- Water reacts with nonmetal oxides (acid anhydrides) to form acids.

13.11 Water Purification

- Water can be purified at the commercial level by using some or all of the following processes: screening, flocculation and sedimentation, sand filtration, aeration, and disinfection.
- Water can be softened by one of the following techniques: distillation, calcium and magnesium precipitation, ion exchange, or demineralization.

Review Questions

All questions with blue numbers have answers in the appendix of the text.

1. Compare the potential energy of the three states of water shown in Figure 13.10.

2. In what state (solid, liquid, or gas) would H_2S, H_2Se, and H_2Te be at 0°C? (Table 13.3)

3. What property or properties of liquids are similar to solids?

4. What property or properties of liquids are similar to gases?

5. The temperature of the water in the beaker on the hotplate (Figure 13.10) reads 100°C. What is the pressure of the atmosphere?

6. Diagram a water molecule and point out the negative and positive ends of the dipole.

7. If the water molecule were linear, with all three atoms in a straight line rather than in the shape of a V, as shown in Figure 13.11, what effect would this have on the physical properties of water?

8. How do we specify 1, 2, 3, 4, 5, 6, 7, and 8 molecules of water in the formulas of hydrates? (Table 13.4)

9. Would the distillation setup in Figure 13.13 be satisfactory for separating salt and water? for separating ethyl alcohol and water? Explain.

10. If the liquid in the flask in Figure 13.13 is ethyl alcohol and the atmospheric pressure is 543 torr, what temperature will show on the thermometer? (Use Figure 13.6.)

11. If water were placed in both containers in Figure 13.3, would both have the same vapor pressure at the same temperature? Explain.

12. Why doesn't the vapor pressure of a liquid depend on the amount of liquid and vapor present?

13. In Figure 13.3, in which case, (a) or (b), will the atmosphere above the liquid reach a point of saturation?

14. Suppose a solution of ethyl ether and ethyl alcohol is placed in the closed bottle in Figure 13.3. (Use Figure 13.6 for information on the substances.)
(a) Are both substances present in the vapor?
(b) If the answer to part (a) is yes, which has more molecules in the vapor?

15. In Figure 13.4, if 50% more water is added in part (b), what equilibrium vapor pressure will be observed in (c)?

16. At approximately what temperature would each of the substances shown in Figure 13.6 boil when the pressure is 30 torr?

17. Use the graph in Figure 13.6 to find the following:
(a) boiling point of water at 500 torr
(b) normal boiling point of ethyl alcohol
(c) boiling point of ethyl ether at 0.50 atm

18. Consider Figure 13.7.
(a) Why is line *BC* horizontal? What is happening in this interval?
(b) What phases are present in the interval *BC*?
(c) When heating is continued after point *C*, another horizontal line, *DE*, is reached at a higher temperature. What does this line represent?

19. List six physical properties of water.

20. What condition is necessary for water to have its maximum density? What is its maximum density?

21. Account for the fact that an ice–water mixture remains at 0°C until all the ice is melted, even though heat is applied to it.

22. Which contains less energy: ice at 0°C or water at 0°C? Explain.

23. Why does ice float in water? Would ice float in ethyl alcohol ($d = 0.789$ g/mL)? Explain.

24. If water molecules were linear instead of bent, would the heat of vaporization be higher or lower? Explain.

25. The heat of vaporization for ethyl ether is 351 J/g and that for ethyl alcohol is 855 J/g. From this data, which of these compounds has hydrogen bonding? Explain.

26. Would there be more or less H bonding if water molecules were linear instead of bent? Explain.

27. In which condition are there fewer hydrogen bonds between molecules: water at 40°C or water at 80°C? Explain.

28. Which compound

$H_2NCH_2CH_2NH_2$ or $CH_3CH_2CH_2NH_2$

would you expect to have the higher boiling point? Explain. (Both compounds have similar molar masses.)

29. Explain why rubbing alcohol warmed to body temperature still feels cold when applied to your skin.

30. The vapor pressure at 20°C for the following substances is

methyl alcohol	96 torr
acetic acid	11.7 torr
benzene	74.7 torr
bromine	173 torr
water	17.5 torr
carbon tetrachloride	91 torr
mercury	0.0012 torr
toluene	23 torr

(a) Arrange these substances in order of increasing rate of evaporation.

(b) Which substance listed has the highest boiling point? the lowest?

31. Suggest a method whereby water could be made to boil at 50°C.

32. Explain why a higher temperature is obtained in a pressure cooker than in an ordinary cooking pot.

33. What is the relationship between vapor pressure and boiling point?

34. On the basis of the kinetic-molecular theory, explain why vapor pressure increases with temperature.

35. Why does water have such a relatively high boiling point?

36. The boiling point of ammonia, NH_3, is −33.4°C and that of sulfur dioxide, SO_2, is −10.0°C. Which has the higher vapor pressure at −40°C?

37. Explain what is occurring physically when a substance is boiling.

38. Explain why HF (bp = 19.4°C) has a higher boiling point than HCl (bp = −85°C), whereas F_2 (bp = −188°C) has a lower boiling point than Cl_2 (bp = −34°C).

39. Why does a boiling liquid maintain a constant temperature when heat is continuously being added?

40. At what specific temperature will ethyl ether have a vapor pressure of 760 torr?

41. What water temperature would you theoretically expect to find at the bottom of a very deep lake? Explain.

42. Is the formation of hydrogen and oxygen from water an exothermic or an endothermic reaction? How do you know?

Paired Exercises

All exercises with blue numbers have answers in the appendix of the text.

1. Write the formulas for the anhydrides of these acids: $HClO_4$, H_2CO_3, H_3PO_4.

3. Write the formulas for the anhydrides of these bases: LiOH, NaOH, $Mg(OH)_2$.

5. Complete and balance these equations:

(a) $Ba(OH)_2 \xrightarrow{\Delta}$

(b) $CH_3OH + O_2 \xrightarrow{\Delta}$
methyl alcohol

(c) $Rb + H_2O \longrightarrow$

(d) $SnCl_2 \cdot 2\,H_2O \xrightarrow{\Delta}$

(e) $HNO_3 + NaOH \longrightarrow$

(f) $CO_2 + H_2O \longrightarrow$

2. Write the formulas for the anhydrides of these acids: H_2SO_3, H_2SO_4, HNO_3.

4. Write the formulas for the anhydrides of these bases: KOH, $Ba(OH)_2$, $Ca(OH)_2$.

6. Complete and balance these equations:

(a) $Li_2O + H_2O \longrightarrow$

(b) $KOH \xrightarrow{\Delta}$

(c) $Ba + H_2O \longrightarrow$

(d) $Cl_2 + H_2O$

(e) $SO_3 + H_2O \longrightarrow$

(f) $H_2SO_3 + KOH \longrightarrow$

7. Name these hydrates:
(a) $BaBr_2 \cdot 2\,H_2O$
(b) $AlCl_3 \cdot 6\,H_2O$
(c) $FePO_4 \cdot 4\,H_2O$

9. Distinguish between deionized water and
(a) hard water
(b) soft water

11. In which of the following substances would you expect to find hydrogen bonding? Explain your reasons.
(a) C_2H_6
(b) NH_3
(c) H_2O
(d) HI
(e) C_2H_5OH

13. For each of the compounds in Question 11 that forms hydrogen bonds, draw a diagram of the two molecules using a dotted line to indicate where the hydrogen bonding will occur.

15. Water spreads out on a glass plate. In this example, are adhesive forces or cohesive forces strongest? Explain.

17. How many moles of compound are in 100. g of $CoCl_2 \cdot 6\,H_2O$?

19. How many moles of water can be obtained from 100. g of $CoCl_2 \cdot 6\,H_2O$?

21. When a person purchases Epsom salts, $MgSO_4 \cdot 7\,H_2O$, what percent of the compound is water?

23. Sugar of lead, a hydrate of lead(II) acetate, $Pb(C_2H_3O_2)_2$, contains 14.2% H_2O. What is the empirical formula for the hydrate?

25. How many joules are needed to change 120. g of water at 20.°C to steam at 100.°C?

***27.** Suppose 100. g of ice at 0°C are added to 300. g of water at 25°C. Is this sufficient ice to lower the temperature of the system to 0°C and still have ice remaining? Show evidence for your answer.

***29.** If 75 g of ice at 0.0°C were added to 1.5 L of water at 75°C, what would be the final temperature of the mixture?

31. How many grams of water will react with the following?
(a) 1.00 g Na
(b) 1.00 g MgO
(c) 1.00 g N_2O_5

8. Name these hydrates:
(a) $MgNH_4PO_4 \cdot 6\,H_2O$
(b) $FeSO_4 \cdot 7\,H_2O$
(c) $SnCl_4 \cdot 5\,H_2O$

10. Distinguish between deionized water and
(a) distilled water
(b) natural water

12. In which of the following substances would you expect to find hydrogen bonding? Explain your reasons.
(a) HF
(b) CH_4
(c) H_2O_2
(d) CH_3OH
(e) H_2

14. For each of the compounds in Question 12 that forms hydrogen bonds, draw a diagram of the two molecules using a dotted line to indicate where the hydrogen bonding will occur.

16. Rainex is a product that causes water to “bead” instead of spread when sprayed on car windshields. When the water forms these droplets, are adhesive forces or cohesive forces strongest? Explain.

18. How many moles of compound are in 100. g of $FeI_2 \cdot 4\,H_2O$?

20. How many moles of water can be obtained from 100. g of $FeI_2 \cdot 4\,H_2O$?

22. Calculate the mass percent of water in the hydrate $Al_2(SO_4)_3 \cdot 18\,H_2O$.

24. A 25.0-g sample of a hydrate of $FePO_4$ was heated until no more water was driven off. The mass of anhydrous sample is 16.9 g. What is the empirical formula of the hydrate?

26. How many joules of energy must be removed from 126 g of water at 24°C to form ice at 0°C?

***28.** Suppose 35.0 g of steam at 100.°C are added to 300. g of water at 25°C. Is this sufficient steam to heat all the water to 100.°C and still have steam remaining? Show evidence for your answer.

***30.** If 9560 J of energy were absorbed by 500. g of ice at 0.0°C, what would be the final temperature?

32. How many grams of water will react with the following?
(a) 1.00 mol K
(b) 1.00 mol Ca
(c) 1.00 mol SO_3

Additional Exercises

All exercises with blue numbers have answers in the appendix of the text.

33. You walk out to your car just after a rain shower and notice that small droplets of water are scattered on the hood. How was it possible for the water to form those droplets?

34. Which causes a more severe burn: liquid water at 100°C or steam at 100°C? Why?

35. You have a shallow dish of alcohol set into a tray of water. If you blow across the tray, the alcohol evaporates, while the water cools significantly and eventually freezes. Explain why.

36. Regardless of how warm the outside temperature may be, we always feel cool when stepping out of a swimming pool, the ocean, or a shower. Why is this so?

37. Sketch a heating curve for a substance *X* whose melting point is 40°C and whose boiling point is 65°C.
  (a) Describe what you will observe as a 60.-g sample of *X* is warmed from 0°C to 100°C.
  (b) If the heat of fusion of *X* is 80. J/g, the heat of vaporization is 190. J/g, and if 3.5 J are required to warm 1 g of *X* each degree, how much energy will be needed to accomplish the change in (a)?

38. For the heating curve of water (see Figure 13.7), why doesn't the temperature increase when ice is melting into liquid water and liquid water is changing into steam?

39. Why does the vapor pressure of a liquid increase as the temperature is increased?

40. At the top of Mount Everest, which is just about 29,000 feet above sea level, the atmospheric pressure is about 270 torr. Use Figure 13.6 to determine the approximate boiling temperature of water on Mount Everest.

41. Explain how anhydrous copper(II) sulfate ($CuSO_4$) can act as an indicator for moisture.

42. Write formulas for magnesium sulfate heptahydrate and disodium hydrogen phosphate dodecahydrate.

43. How can soap make soft water from hard water? What objections are there to using soap for this purpose?

44. What substance is commonly used to destroy bacteria in water?

45. What chemical, other than chlorine or chlorine compounds, can be used to disinfect water for domestic use?

46. Some organic pollutants in water can be oxidized by dissolved molecular oxygen. What harmful effect can result from this depletion of oxygen in the water?

47. Why should you not drink liquids that are stored in ceramic containers, especially unglazed ones?

48. Write the chemical equation showing how magnesium ions are removed by a zeolite water softener.

49. Write an equation to show how hard water containing calcium chloride ($CaCl_2$) is softened by using sodium carbonate (Na_2CO_3).

50. Draw a heating curve and label the different phases and phase changes on the curve for solid H_2S at −95 °C and a pressure of 1 atm going to gaseous H_2S. (*Note:* For H_2S the melting point is −82.9°C and the boiling point is −59.6°C.)

51. How many calories are required to change 225 g of ice at 0°C to steam at 100.°C?

52. The molar heat of vaporization is the number of joules required to change 1 mol of a substance from liquid to vapor at its boiling point. What is the molar heat of vaporization of water?

*53. The specific heat of zinc is 0.096 cal/g°C. Determine the energy required to raise the temperature of 250. g of zinc from room temperature (20.0°C) to 150.°C.

54. How many joules of energy would be liberated by condensing 50.0 mol of steam at 100.0°C and allowing the liquid to cool to 30.0°C?

55. How many kilojoules of energy are needed to convert 100. g of ice at −10.0°C to water at 20.0°C? (The specific heat of ice at −10.0°C is 2.01 J/g°C.)

56. What mass of water must be decomposed to produce 25.0 L of oxygen at STP?

*57. Suppose 1.00 mol of water evaporates in 1.00 day. How many water molecules, on the average, leave the liquid each second?

58. Compare the volume occupied by 1.00 mol of liquid water at 0°C and 1.00 mol of water vapor at STP.

59. A mixture of 80.0 mL of hydrogen and 60.0 mL of oxygen is ignited by a spark to form water.
  (a) Does any gas remain unreacted? Which one, H_2 or O_2?
  (b) What volume of which gas (if any) remains unreacted? (Assume the same conditions before and after the reaction.)

60. A student (with slow reflexes) puts his hand in a stream of steam at 100.°C until 1.5 g of water has condensed. If the water then cools to room temperature (20.0°C), how many joules have been absorbed by the student's hand?

61. Determine which of the following molecules would hydrogen bond with other molecules like it. For those that do not hydrogen bond explain why. For those that hydrogen bond draw a diagram of two molecules using a dotted line to indicate where the hydrogen bonding will occur.
  (a) Br_2 (d) H_2O
  (b) $CH_3{-}O{-}H$ (e) H_2S
  (c) $CH_3{-}O{-}CH_3$

62. The heat of fusion of a substance is given in units of J/g. The specific heat of a substance is given in units of J/g °C. Why is a temperature factor not needed in the units for heat of fusion?

63. How many joules of energy are required to change 50.0 g Cu from 25.0°C to a liquid at its melting point, 1083 °C?
Specific heat of Cu = 0.385 J/g °C
Heat of fusion for Cu = 134 J/g

Challenge Exercises

All exercises with blue numbers have answers in the appendix of the text.

64. Why does a lake freeze from the top down? What significance does this have for life on Earth?

***65.** Suppose 150. g of ice at 0.0°C are added to 0.120 L of water at 45°C. If the mixture is stirred and allowed to cool to 0.0°C, how many grams of ice remain?

***66.** A quantity of sulfuric acid is added to 100. mL of water. The final volume of the solution is 122 mL and has a density of 1.26 g/mL. What mass of acid was added? Assume the density of the water is 1.00 g/mL.

Answers to Practice Exercises

13.1 28°C, 73°C, 93°C

13.2 approximately 95°C

13.3 44.8 kJ

13.4 (a) yes, (b) yes, (c) no

13.5 (a) $BeCO_3 \cdot 4\,H_2O$
(b) $Cd(MnO_4)_2 \cdot 6\,H_2O$
(c) $Cr(NO_3)_3 \cdot 9\,H_2O$
(d) $PtO_2 \cdot 3\,H_2O$

13.6 51.17% H_2O

13.7 $CuO + H_2 \longrightarrow Cu + H_2O$