Chapter 8

How Water Behaves

THE MAIN IDEA

Water is exceptional

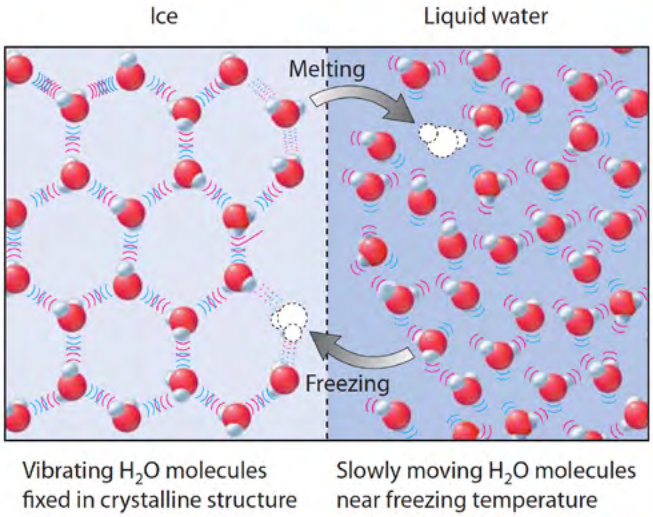
8.1 Open Structured Crystals
8.2 Melting and Freezing
8.3 The Stickiness of Water
8.4 Liquid and Gaseous Phases
8.5 Water's Specific Heat
8.6 Phase Changes and Energy

8.2 Melting and Freezing

As discussed in Section 2.7, *melting* occurs when a substance changes from solid to liquid, and *freezing* occurs when a substance changes from liquid to solid. When we view these processes from a molecular perspective, we see that melting and freezing occur simultaneously, as **Figure 8.6** illustrates.

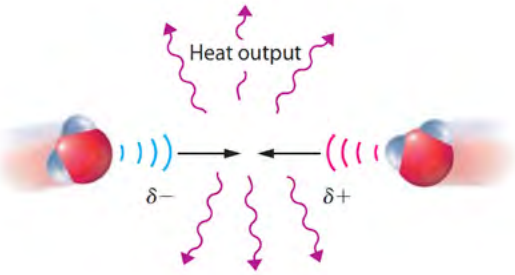
The temperature 0°C is both the melting temperature and the freezing temperature of water. At this temperature, water molecules in the liquid phase are moving slowly enough that they tend to clump together to form ice crystals—they freeze. At this same temperature, however, water molecules in ice are vibrating with great commotion, much more than they vibrate at colder temperatures. Many thus break loose from the crystalline structure to form liquid water—they melt. Thus, melting and freezing occur simultaneously.

For water, 0°C is the special temperature at which the rate of ice formation equals the rate of liquid water formation. In other words, it is the temperature at which the opposite processes of melting and freezing



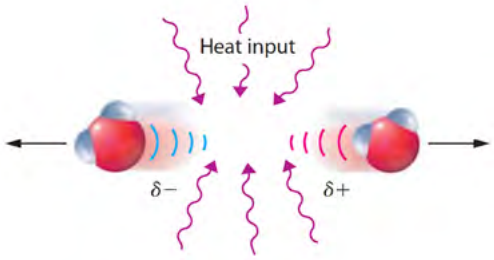
< Figure 8.6

At 0°C, ice crystals gain and lose water molecules simultaneously.



Λ Figure 8.7

As two water molecules come together to form a hydrogen bond, attractive electric forces cause them to accelerate toward each other. This results in an increase in their kinetic energies (the energy of motion), which is perceived on the macroscopic scale as heat energy.



Λ Figure 8.8

Heat energy must be added in order to separate two water molecules held together by a hydrogen bond. This heat energy causes the molecules to vibrate so rapidly that the hydrogen bond breaks.

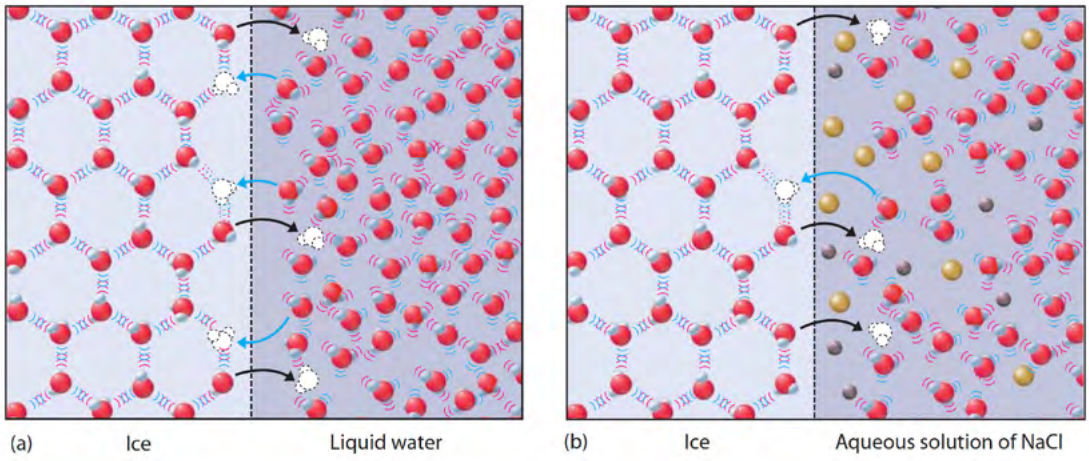
counterbalance each other. This means that if a mixture of ice and liquid water is maintained at exactly 0°C, the two phases are able to coexist indefinitely.

Anytime we want a mixture of ice and liquid water at 0°C to freeze solid, we need to favor the rate of ice formation. This is accomplished by removing heat (cooling it down), a process that facilitates the formation of hydrogen bonds. As shown in **Figure 8.7**, when water molecules come together to form a hydrogen bond, heat energy is released. In order for the molecules to remain hydrogen-bonded, this heat energy must be removed—otherwise, it can be reabsorbed by the molecules, causing them to separate. The removal of heat energy therefore allows hydrogen bonds to remain intact after they have formed. As a result, there is the tendency for the ice crystals to grow.

Conversely, we can get a mixture of ice and liquid water at 0°C to melt completely by adding heat. This heat energy goes into breaking apart the hydrogen bonds that hold the water molecules together in the form of ice, as shown in **Figure 8.8**. Because more hydrogen bonds between water molecules are breaking, the ice crystals tend to melt.

Solutes tend to inhibit crystal formation. Anytime a solute, such as table salt or sugar, is added to water, the solute molecules take up space, as you learned in Section 7.2. When a solute is added to a mixture of ice and liquid water at 0°C, the solute molecules effectively decrease the number of liquid water molecules at the solid–liquid interface, as **Figure 8.9** illustrates. With fewer liquid water molecules available to join the ice crystals, the rate of ice formation decreases. Because ice is a relatively pure form of water, the number of molecules moving from the solid phase to the liquid phase is not affected by the presence of solute. The net result is that the rate at which water molecules leave the solid phase is greater than the rate at which they enter the solid phase. This imbalance can be compensated for by decreasing the temperature to below 0°C. At lower temperatures, water molecules in the liquid phase move more slowly and coalesce more easily. Thus, the rate of crystal formation is increased.

In general, adding anything to water lowers the freezing point. Antifreeze is a practical application of this process. The salting of icy roads is another.



Λ Figure 8.9

(a) In a mixture of ice and liquid water at 0°C, the number of molecules entering the solid phase is equal to the number of molecules entering the liquid phase. (b) Adding a solute, such as sodium chloride, decreases the number of molecules entering the solid phase, because now there are fewer liquid molecules at the interface.

CONCEPT **CHECK**
How does a solute decrease the rate of freezing?

CHECK YOUR ANSWER
When a solute is present, there are fewer water molecules in contact with the surface of any ice crystal. This makes it more difficult for the ice crystal to grow.

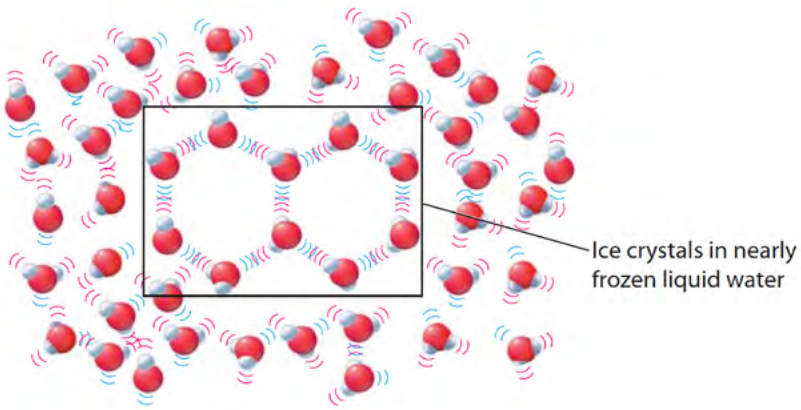
Water Is Densest at 4°C

When the temperature of a substance is increased, its molecules vibrate faster and move farther apart on average. The result is that the substance expands. With few exceptions, all phases of matter—solids, liquids, and gases—expand when heated and contract when cooled. In many cases, these changes in volume are not very noticeable, but with careful observation, you can usually detect them. Telephone wires, for instance, are longer and sag more on a hot summer day than on a cold winter day. Metal lids on glass jars can often be loosened by heating them under hot water. If one part of a piece of glass is heated or cooled more rapidly than adjacent parts, the resulting expansion or contraction may break the glass.

Within any given phase, water also expands with increasing temperature and contracts with decreasing temperature. This is true of all three phases—ice, liquid water, and water vapor. Liquid water at near-freezing temperatures, however, is an exception.

Liquid water at 0°C can flow just like any other liquid, but at 0°C, the temperature is cold enough that nanoscopic crystals of ice are able to form. These crystals slightly "bloat" the liquid water's volume, as shown in **Figure 8.10.** As the temperature is increased to above 0°C, more and more of these crystals collapse, and as a result, the volume of the liquid water *decreases*.

Figure 8.11 shows that between 0°C and 4°C, liquid water *contracts* as its temperature is raised. This contraction, however, continues only up to 4°C. As near-freezing liquid water is heated, there is a simultaneous tendency for the water to expand due to greater molecular motion. Between 0°C and 4°C, the decrease in volume caused by collapsing ice crystals is greater than the increase in volume caused by the faster-moving molecules. As a result, the water volume continues to decrease. At temperatures just above 4°C, expansion overrides contraction because most of the ice crystals have collapsed.



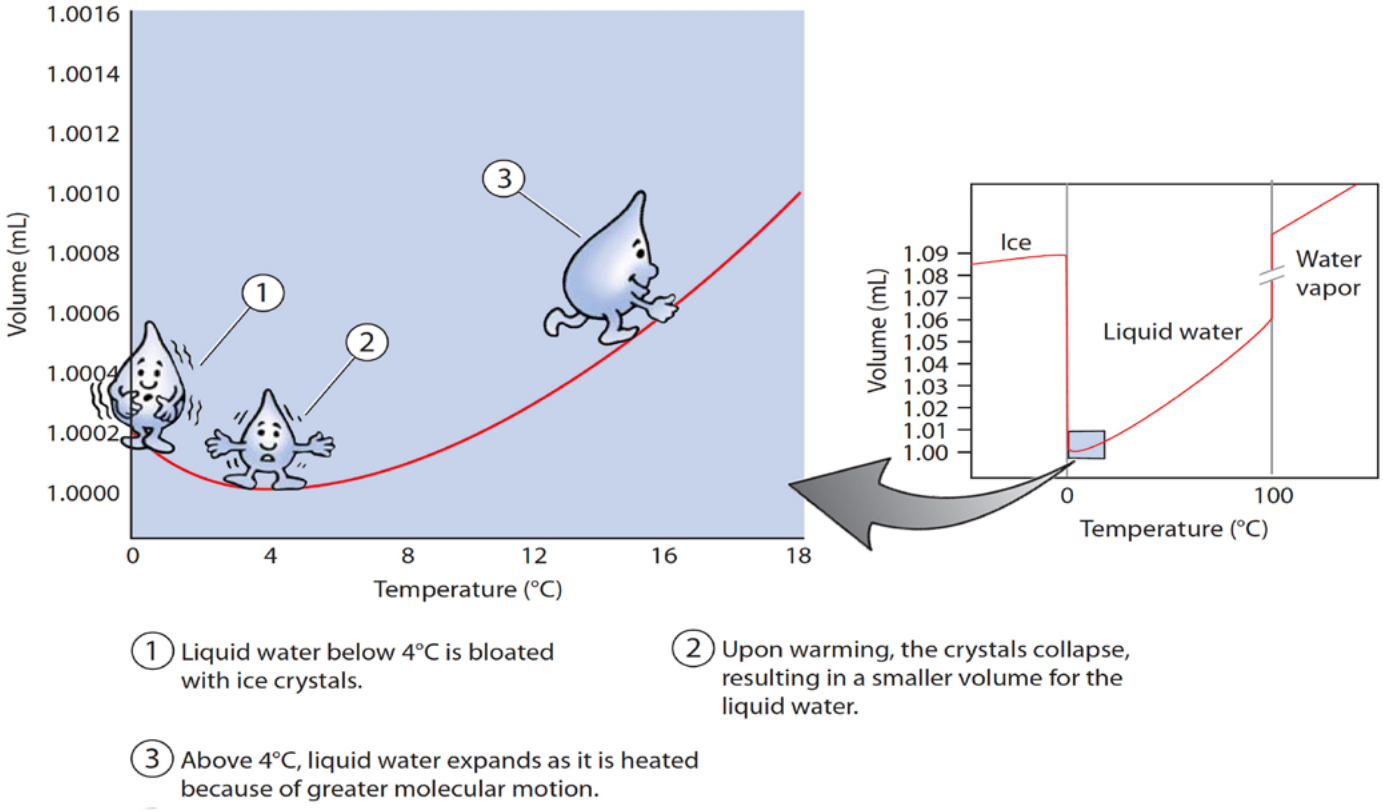
< Figure 8.10

Within a few degrees of 0°C, liquid water contains crystals of ice. The open structure of these crystals makes the volume of the water slightly greater than it would be without the crystals.

FOR YOUR INFORMATION

If left undisturbed, chilled purified bottled water can become "supercooled," which means it remains liquid at temperatures below 0°C. This happens because crystal formation usually requires a substrate, such as a microparticle, upon which to start growing. Upon opening, the bottle of supercooled water will rapidly turn into an icy slush. Similarly, during an ice storm, raindrops formed in warm upper layers of the atmosphere become supercooled as they pass through colder lower layers. Upon hitting the ground, tree branches, and power lines, the supercooled raindrops, known as freezing rain, quickly freeze. The results can be beautiful but also quite hazardous, especially for aircraft.

READING CHECK
What forms in 0°C liquid water?

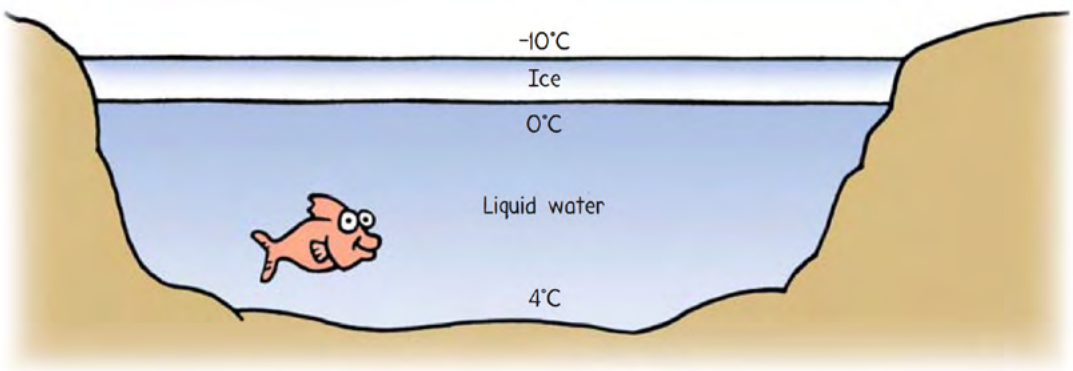


Λ Figure 8.11

Between 0°C and 4°C, the volume of liquid water decreases as the temperature increases. Above 4°C, water behaves the way all other substances do: its volume increases as its temperature increases. The volumes shown here are for a 1-gram sample.

Because of the effect of collapsing nanoscopic ice crystals, liquid water has its smallest volume and thus its greatest density at 4°C. (As discussed in Section 2.4, density is the amount of mass contained in a sample of anything divided by the volume of the sample.) By definition, 1 gram of pure water at this temperature has a volume of 1.0000 milliliter. As Figure 8.11 shows, 1 gram of liquid water at 0°C has an only slightly larger volume, 1.0002 milliliters. By comparison, 1 gram of ice at 0°C has a volume of 1.0870 milliliters. As can be seen in the small graph to the upper right in Figure 8.11, the volume of 1 gram of ice stays above 1.08 milliliters even below 0°C, meaning that even when ice is cooled to temperatures well below freezing, it is still less dense than liquid water.

Although liquid water at 4°C is only slightly denser than liquid water at 0°C, this small difference is of great importance in nature. Consider that if water were densest at its freezing point, as is true of most other liquids, the coldest water in a pond would settle to the bottom and the pond would freeze from the bottom up, destroying living organisms in winter months. Fortunately, this does not happen. As winter comes on and the temperature of the water drops, its density also drops. The entire volume of water in the pond does not cool all at once, however. Surface water cools first because it is in direct contact with the cold air. Being cooler than the underlying water, this surface water is denser and so sinks, with warmer water rising to replace it. That new batch of surface water then cools to the air temperature, gets denser as it does so, and sinks, only to be replaced by warmer water that cools. This process continues until the entire body of water has been cooled to 4°C. Then if the air temperature remains below 4°C, the surface water also cools to below 4°C. This surface water does not sink,



Λ Figure 8.12

As water cools to 4°C, it sinks. Then as water at the surface is cooled to below 4°C, it floats on top and can freeze. Only after surface ice forms can temperatures lower than 4°C extend down into the pond. This does not happen very readily, however, because surface ice insulates the liquid water from the cold air.

however, because at this colder temperature, it is now less dense than the water below it. Thus, cooler, less dense water stays on the surface, where it can cool further, eventually reach 0°C, and turn to ice. While this ice forms at the surface, the organisms that require a liquid environment are happily swimming below the ice in liquid water at a "warm" 4°C, as **Figure 8.12** illustrates.

An important effect of the vertical movement of water is the creation of vertical currents that, to the benefit of organisms living in the water, transport oxygen-rich surface water to the bottom and nutrient-rich bottom water to the surface. Marine biologists refer to this vertical cycling of water and nutrients as *upwelling*.

Very deep bodies of fresh water are not ice-covered even in the coldest of winters. This is because, as noted previously, all the water must be cooled to 4°C before the temperature of the surface water can drop below 4°C. For deep water, the winter is not long enough for this to occur.

If only some of the water in a pond is 4°C, this water lies on the bottom. Because of water's ability to resist changes in temperature (Section 8.5) and its poor ability to conduct heat, the bottom of deep bodies of water in cold regions is a constant 4°C year-round.

CHEMICAL CONNECTIONS

How is a raindrop connected to a campfire?

CONCEPT **CHECK**

What was the precise temperature at the bottom of Lake Michigan on New Year's Eve in 1901?

CHECK YOUR ANSWER

If a body of water has 4°C water, then the temperature at the bottom of that body of water is 4°C, for the same reason that rocks are at the bottom. Both 4°C water and rocks are denser than water at any other temperature. If the body of water is deep and in a region of short summers, as is the case for Lake Michigan, the water at the bottom is 4°C year-round.

FOR YOUR INFORMATION

In most cases, the thermal expansion of liquids is greater than the thermal expansion of solids. This is why you should never top off your car's gas tank on a warm summer day. Gasoline is cooled by its underground storage at the gas station. After you place it in your car's tank, it warms and begins to expand. If the tank and the gasoline expanded at the same rate, they would expand together and no overflow would occur. Similarly, if the expansion of the glass of a thermometer were as great as the expansion of the mercury, the mercury would not rise with increasing temperature. The reason the mercury in the thermometer rises with increasing temperature is that the expansion of the liquid mercury is greater than the expansion of the glass.