SECTION 14.1

Intermolecular Forces and Phase Changes

Key Terms

- Intermolecular forces
- Intramolecular forces
- Dipole–dipole attraction
- Hydrogen bonding
- London dispersion forces
- Normal boiling point
- Heating/cooling curve
- Normal freezing point
- Molar heat of fusion
- Molar heat of vaporization

Objectives

- *To learn about dipole–dipole, hydrogen bonding, and London dispersion forces*
- *To understand the effect of intermolecular forces on the properties of liquids*
- *To learn some of the important features of water*
- *To learn about interactions among water molecules*
- *To understand and use heat of fusion and heat of vaporization*

In Chapter 13 we saw that the particles of a gas are far apart, are in rapid random motion, and have little effect on each other. Solids are obviously very different from gases.

Gases	**Solids**
• Low density	• High density
• Highly compressible	• Slightly compressible
• Fill container	• Rigid (keeps its shape)

These properties indicate that the components of a solid are close together and exert large attractive forces on each other.

The properties of liquids lie somewhere between those of solids and of gases—but not midway between, as can be seen from some of the properties of the three states of water. For example, it takes about seven times more energy to change liquid water to steam (a gas) at 100 °C than to melt ice to form liquid water at 0 °C.

$$H_2O(s) \rightarrow H_2O(l) \qquad \text{energy required} \approx 6 \text{ kJ/mol}$$

$$H_2O(l) \rightarrow H_2O(g) \qquad \text{energy required} \approx 41 \text{ kJ/mol}$$

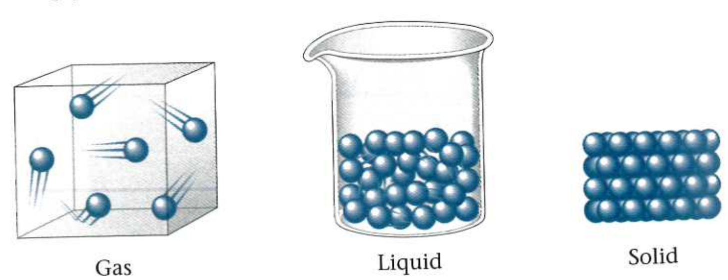
These values indicate that going from the liquid to the gaseous state involves a much greater change than going from the solid to the liquid. Therefore, we can conclude that the solid and liquid states are more similar than the liquid and gaseous states. This is also demonstrated by the densities of the three states of water (see **Table 14.1**). Note that water in its gaseous state is about 2000 times less dense than in the solid and liquid states and that the latter two states have very similar densities.

We find in general that the liquid and solid states show many similarities and are strikingly different from the gaseous state.

Table 14.1

Densities of the Three States of Water

State	Density (g/cm³)
solid (0 °C, 1 atm)	0.9168
liquid (25 °C, 1 atm)	0.9971
gas (100 °C, 1 atm)	5.88×10^{-4}



The best way to picture the solid state is in terms of closely packed, highly ordered particles in contrast to the widely spaced, randomly arranged particles of a gas. The liquid state lies in between, but its properties indicate that it much more closely resembles the solid than the gaseous state. It is useful to picture a liquid in terms of particles that are generally quite close together,

but with a more disordered arrangement than in the solid state and with some empty spaces. For most substances, the solid state has a higher density than the liquid. However, water is an exception to this rule. Ice has an unusual amount of empty space and so is less dense than liquid water, as indicated in Table 14.1.

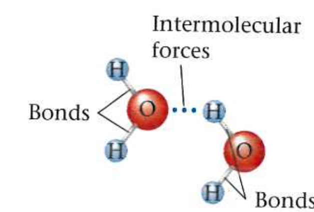
In this chapter we will explore the important properties of liquids and solids. We will illustrate many of these properties by considering one of the earth's most important substances: water.

Nitrogen, which forms a liquid at 77 K, is being poured causing moisture in the air to freeze to produce a fog.

A. Intermolecular Forces

Most substances consisting of small molecules are gases at normal temperatures and pressures. Examples are oxygen gas (contains O_2), nitrogen gas (contains N_2), methane gas (contains CH_4), and carbon dioxide gas (contains CO_2). A notable exception to this rule is water. Given the small size of its molecules we might expect water to be a gas at normal temperatures and pressures. Think about how different the world would be if water were a gas at 25 °C and 1 atm pressure. The oceans would be empty chasms, the Mississippi River would be a wide, dry ditch, and it would never rain! Life on earth as we know it would be impossible if water were a gas under normal conditions.

So why is water a liquid rather than a gas at normal temperatures and pressures? The answer has to do with something called **intermolecular forces**—forces that occur between the molecules.



Notice that molecules are held together by bonds, sometimes called **intramolecular forces**, that occur inside the molecules. Intermolecular forces exist *between* molecules. We have seen that covalent bonding forces within molecules arise from the sharing of electrons, but how do intermolecular forces arise? Actually several types of intermolecular forces exist. To illustrate one type, we will consider the forces that exist among water molecules.

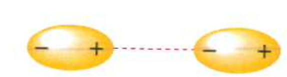
Intermolecular forces Attractive forces that occur between molecules

Intramolecular forces Attractive forces that occur between atoms in a molecule; chemical bonds

Active Reading Question

What type of force is represented by the lines in a Lewis structure? What type of force is responsible for holding molecules together in a solid or a liquid?

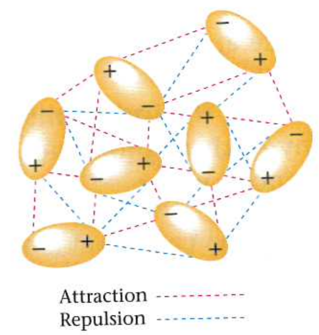
As we saw in Chapter 12, water is a polar molecule—it has a dipole moment. When molecules with dipole moments are put together, they orient themselves to take advantage of their charge distributions. Molecules with dipole moments can attract each other by lining up so that the positive and negative ends are close to each other, as shown here.



Dipole–dipole attraction
The attractive force between the positively charged end of one polar molecule with the negatively charged end of another polar molecule

Hydrogen bonding
Special name for unusually strong dipole–dipole attractions that occur among molecules in which hydrogen is bonded to a highly electronegative atom (such as nitrogen, oxygen, or fluorine)

This is called a **dipole–dipole attraction**. In the liquid, the dipoles find the best compromise between attraction and repulsion, as shown here.



Dipole–dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they become weaker as the distance between the dipoles increases. In the gas phase, where the molecules are usually very far apart, these forces are relatively unimportant.

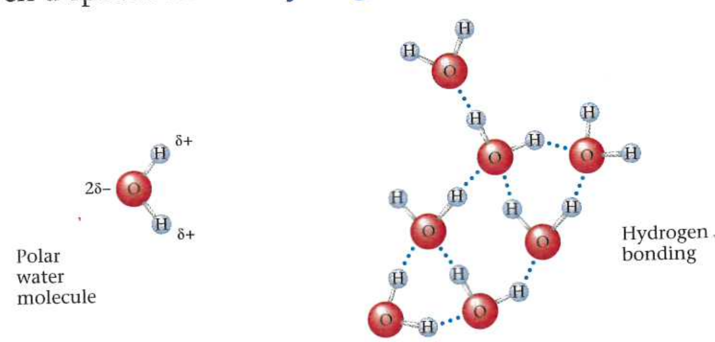
Hydrogen Bonding

Particularly strong dipole–dipole forces occur between molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine. Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, which is made possible by the very small size of the hydrogen atom. Because dipole–dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding**.

CRITICAL THINKING

You have learned the difference between intermolecular forces and intramolecular forces.

What if intermolecular forces were stronger than intramolecular forces? What differences could you observe in the world?



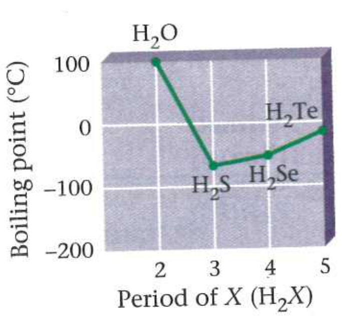


Figure 14.1
The boiling points of the covalent hydrides of elements in Group 6

Hydrogen bonding has a very important effect on various physical properties. For example, the boiling points for the covalent compounds of hydrogen with the elements in Group 6 are given in **Figure 14.1.** Note that the boiling point of water is much higher than would be expected from the trend shown by the other members of the series. Why? Because the especially large electronegativity value of the oxygen atom compared with that of other group members causes the O—H bonds to be much more polar than the S—H, Se—H, or Te—H bonds. This leads to very strong hydrogen-bonding forces among the water molecules. An unusually large quantity of energy is required to overcome these interactions and separate the molecules to produce the gaseous state. That is, water molecules tend to remain together in the liquid state even at relatively high temperatures, hence the very high boiling point of water.

Active Reading Question

What observation shows us that hydrogen bonding is quite strong?

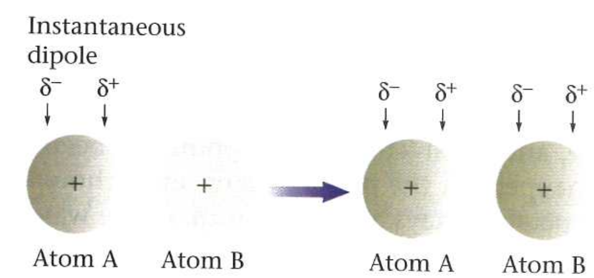
London Dispersion Forces

Even molecules without dipole moments must exert forces on each other. We know this because all substances—even the noble gases—exist in the liquid and solid states at very low temperatures. There must be forces to hold the atoms or molecules as close together as they are in these condensed states. The forces that exist among noble gas atoms and nonpolar molecules are called **London dispersion forces**. To understand the origin of these forces, consider a pair of noble gas atoms. Although we usually assume that the electrons of an atom are uniformly distributed about the nucleus,

London dispersion forces
Relatively weak intermolecular forces resulting from a temporarily uneven distribution of electrons that induces a dipole in a neighbor

No polarity

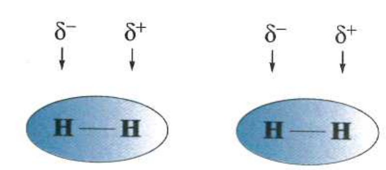
this is apparently not true at every instant. Atoms can develop a temporary dipolar arrangement of charge as the electrons move around the nucleus. This *instantaneous dipole* can then *induce* a similar dipole in a neighboring atom.



The interatomic attraction thus formed is both weak and short-lived, but it can be very significant for large atoms and large molecules, as we will see.

The motions of the atoms must be greatly slowed down before the weak London dispersion forces can lock the atoms into place to produce a solid. This explains, for instance, why the noble gas elements have such low freezing points (see **Table 14.2**).

Nonpolar molecules such as H_2, N_2, and I_2, none of which has a permanent dipole moment, also attract each other by London dispersion forces.



Molecule A Molecule B
Instantaneous dipole on A induces a dipole on B.

London forces become more significant as the sizes of atoms or molecules increase. Larger size means there are more electrons available to form the dipoles.

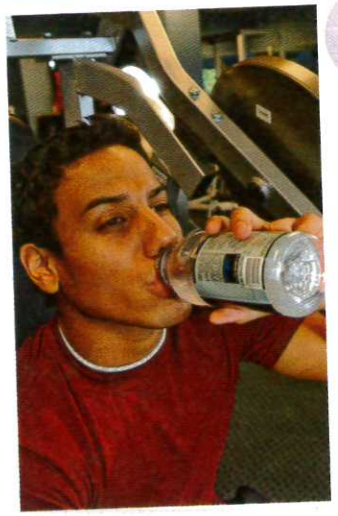
Table 14.2
The Freezing Points of the Group 8 Elements

Element	Freezing Point (°C)
helium*	–272.0 (25 atm)
neon	–248.6
argon	–189.4
krypton	–157.3
xenon	–111.9

*Helium will not freeze unless the pressure is increased above 1 atm.

Active Reading Question

Rank intermolecular forces from weakest to strongest (given molecules of equal size).



Drinking water is important when exercising.

B. Water and Its Phase Changes

In the world around us we see many solids (soil, rocks, trees, concrete, and so on), and we are immersed in the gases of the atmosphere. But the liquid we most commonly see is water; it is virtually everywhere, covering about 70% of the earth's surface. Approximately 97% of the earth's water is found in the oceans, which are actually mixtures of water and huge quantities of dissolved salts.

Water is one of the most important substances on earth. It is crucial for sustaining the reactions within our bodies that keep us alive, but it also affects our lives in many indirect ways. The oceans help moderate the earth's temperature. Water cools automobile engines and nuclear power plants. Water provides a means of transportation on the earth's surface and acts as a medium for the growth of many of the creatures we use as food, and much more.

Pure water is a colorless, tasteless substance that at 1 atm pressure freezes to form a solid at 0 °C and vaporizes completely to form a gas at 100 °C. This means that (at 1 atm pressure) the liquid range of water occurs between the temperatures 0 °C and 100 °C.

DID YOU KNOW

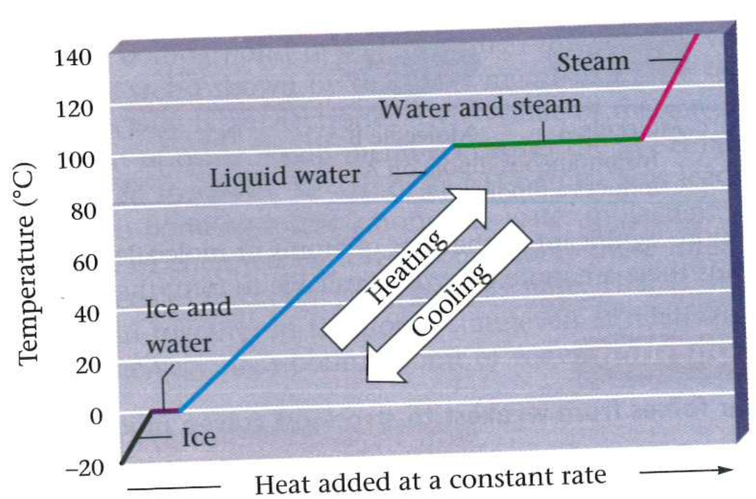
The water we drink often has a taste because of the substances dissolved in it.

Heating Water What happens when we heat liquid water? First the temperature of the water rises. Just as with gas molecules, the motions of the water molecules increase as it is heated. Eventually the temperature of the water reaches 100 °C; now bubbles develop in the interior of the liquid, float to the surface, and burst—the boiling point has been reached. An interesting thing happens at the boiling point: even though heating continues, the temperature stays at 100 °C until all the water has changed to vapor. Only when all of the water has changed to the gaseous state does the temperature begin to rise again. (We are now heating the vapor.) At 1 atm pressure, liquid water always changes to gaseous water at 100 °C, the **normal boiling point** for water.

Normal boiling point
The boiling temperature of a liquid under one atmosphere of pressure. The temperature at which the vapor pressure of a liquid is exactly one atmosphere.

The experiment just described is represented in **Figure 14.2**, which is called the **heating/cooling curve** for water. Going from left to right on this graph means energy is being added (heating). Going from right to left on the graph means that energy is being removed (cooling).

Figure 14.2
The heating/cooling curve for water heated or cooled at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point, because it takes almost seven times as much energy (and thus seven times the heating time) to vaporize liquid water as to melt ice.



Cooling Water When liquid water is cooled, the temperature decreases until it reaches 0 °C, where the liquid begins to freeze (see Figure 14.2). The temperature remains at 0 °C until all the liquid water has changed to ice and then begins to drop again as cooling continues. At 1 atm pressure, water freezes (or, in the opposite process, ice melts) at 0 °C. This is called the **normal freezing point** of water. Liquid and solid water can coexist indefinitely if the temperature is held at 0 °C. However, at temperatures below 0 °C liquid water freezes, while at temperatures above 0 °C ice melts.

Normal freezing point
The freezing temperature of a liquid under one atmosphere of pressure

information

Remember that temperature is a measure of the random motions (average kinetic energy) of the particles in a substance.

Interestingly, water expands when it freezes. That is, one gram of ice at 0 °C has a greater volume than one gram of liquid water at 0 °C. This has very important practical implications. For instance, water in a confined space can break its container when it freezes and expands. This accounts for the bursting of water pipes and engine blocks that are left unprotected in freezing weather.

The expansion of water when it freezes also explains why ice cubes float. Recall that density is defined as mass/volume. When one gram of liquid water freezes, its volume becomes greater (it expands). Therefore, the *density* of one gram of ice is less than the density of one gram of water, because in the case of ice we divide by a slightly larger volume. For example, at 0 °C the density of liquid water is

$$\frac{1.00\text{ g}}{1.00\text{ mL}} = 1.00\text{ g/mL}$$

and the density of ice is

$$\frac{1.00\text{ g}}{1.09\text{ mL}} = 0.917\text{ g/mL}$$

The lower density of ice also means that ice floats on the surface of lakes as they freeze, providing a layer of insulation that helps prevent lakes and rivers from freezing solid in the winter. This means that aquatic life continues to have liquid water available through the winter.

C. Energy Requirements for the Changes of State

It is important to recognize that changes of state from solid to liquid and from liquid to gas are *physical* changes. No *chemical* bonds are broken in these processes. Ice, water, and steam all contain H_2O molecules. When water is boiled to form steam, water molecules are separated from each other (see **Figure 14.3**) but the individual molecules remain intact.

It takes energy to melt ice and to vaporize water, because intermolecular forces between water molecules must be overcome. In ice the molecules are virtually locked in place, although they can vibrate about their positions. When energy is added, the vibrational motions increase, and the molecules eventually achieve the greater movement and disorder characteristic of liquid water. The ice has melted. As still more energy is added, the gaseous state is eventually reached, in which the individual molecules are far apart

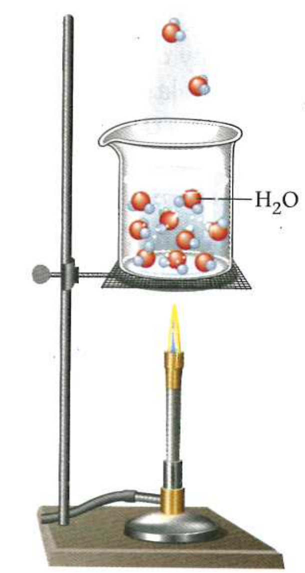


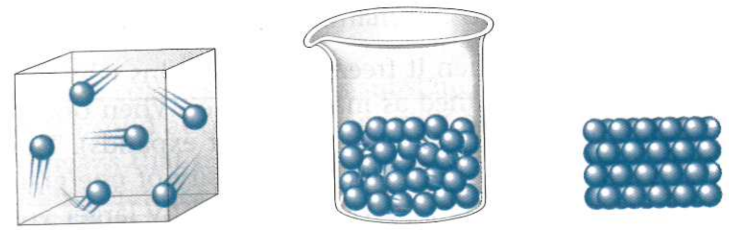
Figure 14.3
Both liquid water and gaseous water contain H_2O molecules. In liquid water the H_2O molecules are close together, whereas in the gaseous state the molecules are widely separated. The bubbles contain gaseous water.

Molar heat of fusion The energy required to melt one mole of a solid

Molar heat of vaporization The energy required to vaporize one mole of a liquid

and interact relatively little. However, the gas still consists of water molecules. It would take *much* more energy to overcome the covalent bonds and decompose the water molecules into their component atoms.

The energy required to melt 1 mol of a substance is called the **molar heat of fusion**. For ice, the molar heat of fusion is 6.02 kJ/mol. The energy required to change 1 mol of liquid to its vapor is called the **molar heat of vaporization**. For water, the molar heat of vaporization is 40.6 kJ/mol at 100 °C. Notice in Figure 14.2 that the plateau that corresponds to the vaporization of water is much longer than that for the melting of ice. This occurs because it takes much more energy (almost seven times as much) to vaporize a mole of water than to melt a mole of ice. This is consistent with our models of solids, liquids, and gases.



CHEMISTRY IN YOUR WORLD

Connection to Biology

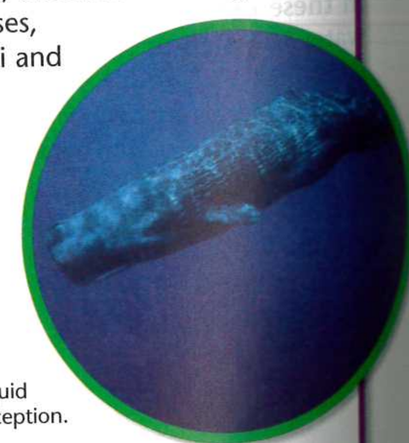
Whales Need Changes of State

Sperm whales are prodigious divers. They commonly dive a mile or more into the ocean, hovering at that depth in search of schools of squid or fish. To remain motionless at a given depth, the whale must have the same density as the surrounding water. Because the density of seawater increases with depth, the sperm whale has a system that automatically increases its density as it dives. This system involves the spermaceti organ found in the whale's head. Spermaceti is a waxy substance with the formula

$$CH_3-(CH_2)_{15}-O-\underset{\underset{\displaystyle O}{\|}}{C}-(CH_2)_{14}-CH_3$$

which is a liquid above 30 °C. At the ocean surface the spermaceti in the whale's head is a liquid, warmed by the flow of blood through the spermaceti organ. When the whale dives, this blood flow decreases and the colder water causes the spermaceti to begin freezing. Because solid spermaceti is more dense than the liquid state, the sperm whale's density increases as it dives, matching the increase in the water's density.* When the whale wants to resurface, blood flow through the spermaceti organ increases, remelting the spermaceti and making the whale more buoyant. So the sperm whale's sophisticated density-regulating mechanism is based on a simple change of state.

*For most substances, the solid state is more dense than the liquid state. Water is an important exception.



A sperm whale

In liquids, the particles (molecules) are relatively close together, so most of the intermolecular forces are still present. However, when the molecules go from the liquid to the gaseous state, they must be moved far apart. To separate the molecules enough to form a gas, virtually all of the intermolecular forces must be overcome, and this requires large quantities of energy.

Active Reading Question

Which is greater, the molar heat of fusion of water or the molar heat of vaporization of water? Why?

EXAMPLE 14.1

Calculating Energy Changes: Solid to Liquid

Calculate the energy required to melt 8.5 g of ice at 0 °C. The molar heat of fusion for ice is 6.02 kJ/mol.

Solution

Where do we want to go?

Energy to melt 8.5 g ice at 0 °C = ? kJ

What do we know?

- 8.5 g ice at 0 °C
- molar heat of fusion for ice = 6.02 kJ/mol
- molar mass H_2O = 18.02 g/mol

How do we get there?

- Convert the mass of water to moles since the heat of fusion for water is per mole of water.

$$8.5\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18\ \cancel{g\ H_2O}} = 0.47\ mol\ H_2O$$

- The molar heat of fusion represents the equivalence statement

6.02 kJ required for 1 mol H_2O

This leads to the conversion factor used below to calculate the energy required to melt 8.5 g ice:

$$0.47\ \cancel{mol\ H_2O} \times \frac{6.02\ kJ}{\cancel{mol\ H_2O}} = 2.8\ kJ$$

Does it make sense?

Since our sample is about $\frac{1}{2}$ mol the amount of energy should be about half the molar heat of fusion (6.02 kJ). Our answer is 2.8 kJ which is about half the molar heat of fusion.