

It's a wild dance floor
there at the molecular
level.

—ROALD HOFFMANN (1937—)

CHAPTER

12

Liquids, Solids, and Intermolecular Forces

Recall from Chapter 1 that matter exists primarily in three states (or phases): solid, liquid, and gas. In Chapter 6, we examined the gas state. In this chapter we turn to the solid and liquid states, known collectively as the *condensed states*. The solid and liquid states are more similar to each other than they are to the gas state. In the gas state, constituent particles—atoms or molecules—are separated by large distances and do not interact with each other very much. In the condensed states, constituent particles are close together and exert moderate to strong attractive forces on one another. Whether a substance is a solid, liquid, or gas at a given temperature depends on the structure of the particles that compose the substance. Remember the theme we have emphasized since Chapter 1 of this book: the properties of matter are determined by the properties of molecules and atoms. In this chapter, we see how the structure of a particular atom or molecule determines the state in which it will exist at a given temperature.



In the absence of gravity (such as in a space station), a sample of spilled water forms a perfect sphere. This behavior is a direct result of intermolecular forces—attractive forces that exist among the particles that compose matter.

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12.1 Water, No Gravity

In the space station there are no spills. When an astronaut squeezes a full water bottle, the water squirts out like it does on Earth, but instead of falling to the floor and forming a puddle, the water molecules stick together to form a floating, oscillating blob. Over time, the blob stops oscillating and forms a nearly perfect sphere. Why?

The reason is the main topic of this chapter: *intermolecular forces*, the attractive forces that exist among the particles that compose matter. The molecules that compose water are attracted to one another, much like a collection of small magnets are attracted to each other. These attractions hold the water together as a liquid (instead of a gas) at

room temperature. These forces also cause samples of water to clump together into a blob, which is clearly seen in the absence of gravity. Over time, irregularities in the shape of the blob smooth out, and the blob becomes a sphere. The sphere is the geometrical shape with the lowest surface area to volume ratio. By forming a sphere, the water molecules maximize their interaction with one another because the sphere results in the minimum number of molecules being at the surface of the liquid, where fewer interactions occur (compared to the interior of the liquid).



Intermolecular forces exist, not only among water molecules, but among all particles that compose matter. You can see the effect of these attractive forces in the image to the left, which shows an astronaut touching a floating blob of water in the absence of gravity. Notice how the water sticks to the astronaut's finger. The water molecules experience an attractive force to the molecules that compose skin. This attractive force deforms the entire blob of water. *Intermolecular forces exist among all the particles that compose matter.*

The state of a sample of matter—solid, liquid, or gas—depends on the magnitude of intermolecular forces among the constituent particles relative to the amount of thermal energy in the sample. Recall from Chapter 7 that the molecules and atoms composing matter are in constant random motion that increases with increasing temperature. The energy associated with this motion is *thermal energy*. When thermal energy is high relative to intermolecular forces, matter tends to be gaseous. When thermal energy is low relative to intermolecular forces, matter tends to be in a condensed state (liquid or solid). Intermolecular forces are therefore responsible for the very existence of condensed states.

12.2

Solids, Liquids, and Gases: A Molecular Comparison

We are all familiar with solids and liquids. Water, gasoline, rubbing alcohol, and nail polish remover are common liquids. Ice, dry ice, and diamond are familiar solids. What makes these states so different?

Differences between States of Matter

To illustrate the differences between the three common states of matter, Table 12.1 lists the density and molar volume of water in its three different states, along with molecular representations of each state. Notice that the densities of the solid and liquid states are

TABLE 12.1 ■ The Three States of Water

Phase	Temperature (°C)	Density (g/cm ³ , at 1 atm)	Molar Volume	Molecular View
Gas (steam)	100	5.90×10^{-4}	30.6 L	
Liquid (water)	20	0.998	18.0 mL	
Solid (ice)	0	0.917	19.6 mL	

much greater than the density of the gas state. Notice also that the solid and liquid states are more similar in density and molar volume to one another than they are to the gas state. The molecular representations show the reason for these differences. The molecules in liquid water and ice are in close contact with one another—essentially touching—whereas those in gaseous water are separated by large distances. The molecular representation of gaseous water in Table 12.1 is actually out of proportion—the water molecules in the figure should be much farther apart for their size. (Only a fraction of a molecule could be included in the figure if it were drawn to scale.) From the molar volumes, we know that 18.0 mL of liquid water (slightly more than a tablespoon) occupies 30.6 L when converted to gas at 100 °C (at atmospheric pressure). The low density of gaseous water is a direct result of this large separation between molecules.

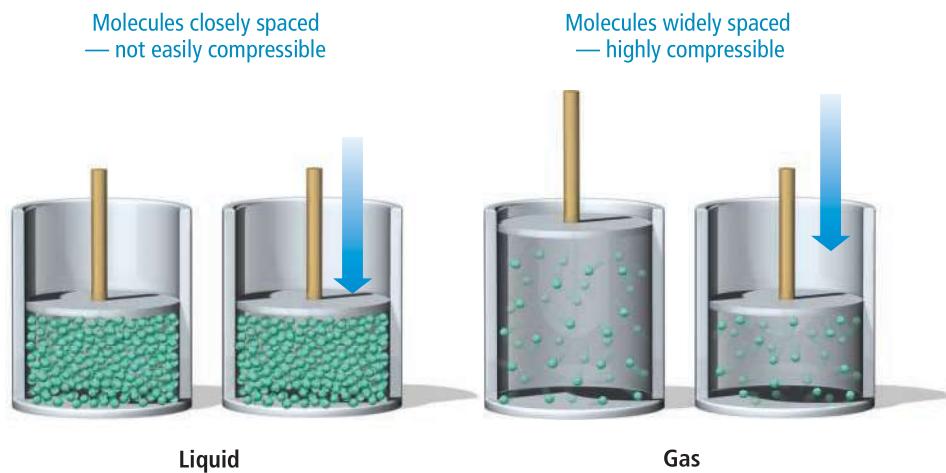
Notice also that, for water, the solid is slightly less dense than the liquid. This is *atypical* behavior. Most solids are slightly denser than their corresponding liquids because the molecules move closer together upon freezing. As we will discuss in Section 12.9, ice is less dense than liquid water because the unique crystal structure of ice results in water molecules moving slightly farther apart upon freezing.

A major difference between liquids and solids is the freedom of movement of the constituent molecules or atoms. Even though the atoms or molecules in a liquid are in close contact, thermal energy partially overcomes the attractions between them, allowing them to move around one another. This is not the case in solids; the atoms or molecules in a solid are virtually locked in their positions, only vibrating back and forth about a fixed point. Table 12.2 summarizes the properties of liquids and solids, as well as the properties of gases for comparison.

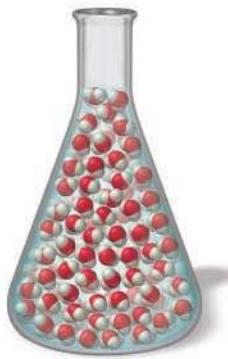
TABLE 12.2 ■ Properties of the States of Matter

State	Density	Shape	Volume	Strength of Intermolecular Forces (Relative to Thermal Energy)
Gas	Low	Indefinite	Indefinite	Weak
Liquid	High	Indefinite	Definite	Moderate
Solid	High	Definite	Definite	Strong

Liquids assume the shape of their containers (to the extent that they fill them) because the atoms or molecules that compose liquids are free to flow (or move around one another). When we pour water into a flask, the water flows and assumes the shape of the flask (Figure 12.1►). Liquids are not easily compressed because the molecules or atoms that compose them are already in close contact—they cannot be pushed much closer together. The molecules in a gas, by contrast, have a great deal of space between them and are easily forced into a smaller volume by an increase in external pressure (Figure 12.2▼).



▲ FIGURE 12.2 Gases Are Compressible Molecules in a liquid are closely spaced and are not easily compressed. Molecules in a gas have a great deal of space between them, making gases compressible.

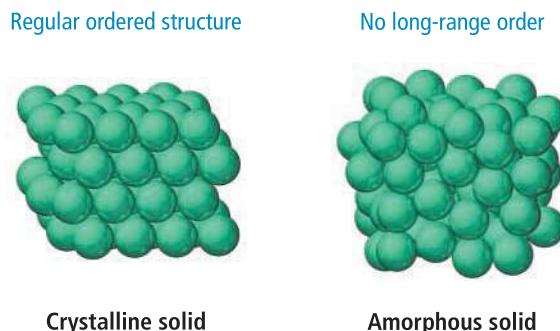


▲ FIGURE 12.1 Liquids Assume the Shapes of Their Containers When we pour water into a flask, it assumes the shape of the flask because water molecules are free to flow.

According to some definitions, an amorphous solid is considered a unique state, different from the normal solid state because it lacks any long-range order.

Solids have a definite shape because, in contrast to liquids and gases, the molecules or atoms that compose solids are fixed in place—each molecule or atom in a solid merely vibrates about a fixed point. Like liquids, solids have a definite volume and generally cannot be compressed because the molecules or atoms composing them are already in close contact. Solids may be **crystalline**, in which case the atoms or molecules that compose them are arranged in a well-ordered three-dimensional array, or they may be **amorphous**, in which case the atoms or molecules that compose them have no long-range order (Figure 12.3▼).

► FIGURE 12.3 Crystalline and Amorphous Solids In a crystalline solid, the arrangement of the particles displays long-range order. In an amorphous solid, the arrangement of the particles has no long-range order.



ANSWER NOW!



12.1 Cc

Conceptual Connection

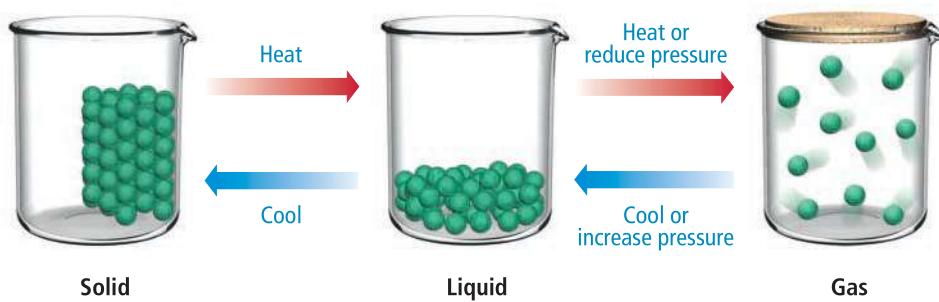
STATES OF MATTER

Which state of matter is compressible?

- (a) solid
- (b) liquid
- (c) gas

Changes between States

We can transform one state of matter to another by changing the temperature, pressure, or both. For example, we can convert solid ice to liquid water by heating, and liquid water to solid ice by cooling. The following diagram shows the three states of matter and the changes in conditions that commonly induce transitions between the states:



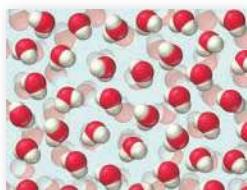
We can induce a transition between the liquid and gas state, not only by heating and cooling, but also by changing the pressure. In general, increases in pressure favor the denser state, so increasing the pressure of a gas sample results in a transition to the liquid state.

The most familiar example of this phenomenon occurs in the LP (liquefied petroleum) gas used as a fuel for outdoor grills and lanterns. LP gas is composed primarily of propane, a gas at room temperature and atmospheric pressure. However, it liquefies at pressures exceeding about 2.7 atm. The propane you buy in a tank is under pressure and therefore in the liquid form. When you open the tank, some of the propane escapes as a gas, lowering the pressure in the tank for a brief moment. Immediately, however, some of the liquid propane evaporates, replacing the gas that escaped. Storing gases like propane as liquids is efficient because, in their liquid form, they occupy much less space.

▲ The propane in an LP gas tank is in the liquid state. When you open the tank, some propane vaporizes and escapes as a gas.

STATE CHANGES

This molecular diagram shows a sample of liquid water:

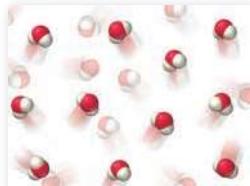


12.2
Cc
Conceptual Connection

ANSWER NOW!



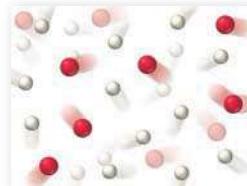
Which of the diagrams below best depicts the vapor emitted from a pot of boiling water?



(a)



(b)



(c)

12.3

Intermolecular Forces: The Forces That Hold Condensed States Together

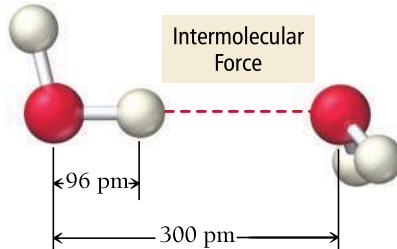
The structure of the particles that compose a substance determines the strength of the intermolecular forces that hold the substance together, which in turn determines whether the substance is a solid, liquid, or gas at a given temperature. At room temperature, moderate to strong intermolecular forces tend to result in liquids and solids (high melting and boiling points), and weak intermolecular forces tend to result in gases (low melting and boiling points).

Intermolecular forces originate from the interactions among charges, partial charges, and temporary charges on molecules (or atoms and ions), much as bonding forces originate from interactions among charged particles in atoms. Recall from Section 9.3 that according to Coulomb's law, the potential energy (E) of two oppositely charged particles (with charges q_1 and q_2) decreases (becomes more negative) with increasing magnitude of charge and with decreasing separation (r):

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \quad (\text{When } q_1 \text{ and } q_2 \text{ are opposite in sign, } E \text{ is negative.})$$

Therefore, as we have seen, protons and electrons are attracted to each other because their potential energy decreases as they get closer together. Similarly, molecules with partial or temporary charges are attracted to each other because *their* potential energy decreases as they get closer together. However, intermolecular forces, even the strongest ones, are generally *much weaker* than bonding forces.

The reason for the relative weakness of intermolecular forces compared to bonding forces is also related to Coulomb's law. Bonding forces are the result of large charges (the charges on protons and electrons) interacting at very close distances. Intermolecular forces are the result of smaller charges (as we shall see in the following discussion) interacting at greater distances. For example, consider the interaction between two water molecules in liquid water:



WATCH NOW!

KEY CONCEPT VIDEO 12.3
Intermolecular Forces

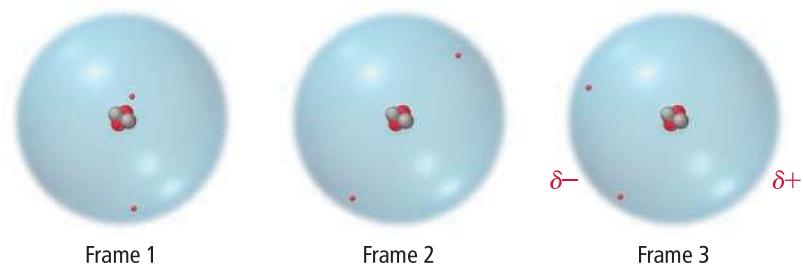
The length of an O—H bond in liquid water is 96 pm; however, the average distance between water molecules in liquid water is about 300 pm. The larger distances between molecules, as well as the smaller charges involved (the partial charges on the hydrogen and oxygen atoms), result in weaker forces. To break the O—H bonds in water, we have to heat the water to thousands of degrees Celsius. However, to completely overcome the intermolecular forces *between* water molecules, we have to heat water only to its boiling point, 100 °C (at sea level).

In this section, we examine several different types of intermolecular forces, including dispersion forces, dipole–dipole forces, hydrogen bonding, and ion-dipole forces. The first three of these can potentially occur in all substances; the last one occurs only in mixtures.

Dispersion Force

The nature of dispersion forces was first recognized by Fritz W. London (1900–1954), a German American physicist.

The one intermolecular force present between all molecules and atoms is the **dispersion force** (also called the London force). Dispersion forces are the result of fluctuations in the electron distribution within molecules or atoms. Since all atoms and molecules have electrons, they all exhibit dispersion forces. The electrons in an atom or molecule may, *at any one instant*, be unevenly distributed. Imagine a frame-by-frame movie of a helium atom in which each “frame” captures the position of the helium atom’s two electrons:



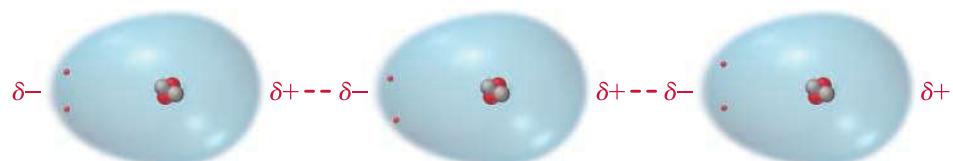
In any one frame, the electrons may not be symmetrically arranged around the nucleus. In frame 3, for example, helium’s two electrons are on the left side of the helium atom. At that instant, the left side has a slightly negative charge ($\delta-$). The right side of the atom, which temporarily has no electrons, has a slightly positive charge ($\delta+$) because of the charge of the nucleus. This fleeting charge separation is called an *instantaneous dipole* or a *temporary dipole*. As shown in Figure 12.4▼, an instantaneous dipole on one helium atom induces an instantaneous dipole on its neighboring atoms because the positive end of the instantaneous dipole attracts electrons in the neighboring atoms. The neighboring atoms then attract one another—the positive end of one instantaneous dipole attracting the negative end of another. This attraction is the dispersion force.

► FIGURE 12.4 Dispersion Interactions

Interactions The temporary dipole in one helium atom induces a temporary dipole in its neighbor. The resulting attraction between the positive and negative charges creates the dispersion force.

Dispersion Force

An instantaneous dipole on any one helium atom induces instantaneous dipoles on neighboring atoms, which then attract one another.



To polarize means to form a dipole moment (see Section 10.6).

The *magnitude* of the dispersion force depends on how easily the electrons in the atom or molecule can move or *polarize* in response to an instantaneous dipole, which in

turn depends on the size (or volume) of the electron cloud. A larger electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and therefore polarize more easily. If all other variables are constant, the dispersion force increases with increasing molar mass because molecules or atoms of higher molar mass generally have more electrons dispersed over a greater volume. For example, consider the boiling points of the noble gases displayed in Table 12.3. As the molar masses and electron cloud volumes of the noble gases increase, the greater dispersion forces result in increasing boiling points (because the atoms are more strongly attracted to one another).

Molar mass alone, however, does not always exactly correlate with the magnitude of the dispersion force. Compare the molar masses and boiling points of *n*-pentane and neopentane:



***n*-Pentane**
molar mass = 72.15 g/mol
boiling point = 36.1 °C

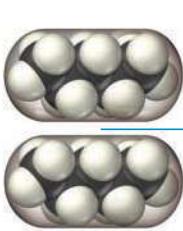


Neopentane
molar mass = 72.15 g/mol
boiling point = 9.5 °C

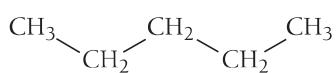
TABLE 12.3 ■ Boiling Points of the Noble Gases

Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165

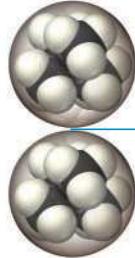
These molecules have identical molar masses, but *n*-pentane has a higher boiling point than neopentane. Why? Because the two molecules have different shapes. The *n*-pentane molecules are long and can interact with one another along their entire length, as shown in Figure 12.5(a)▼. In contrast, the bulky, round shape of neopentane molecules results in a smaller area of interaction between neighboring molecules, as shown in Figure 12.5(b)▼. The result is a lower boiling point for neopentane.



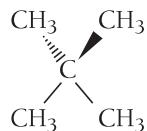
Large area for interaction



(a) *n*-Pentane



Small area for interaction



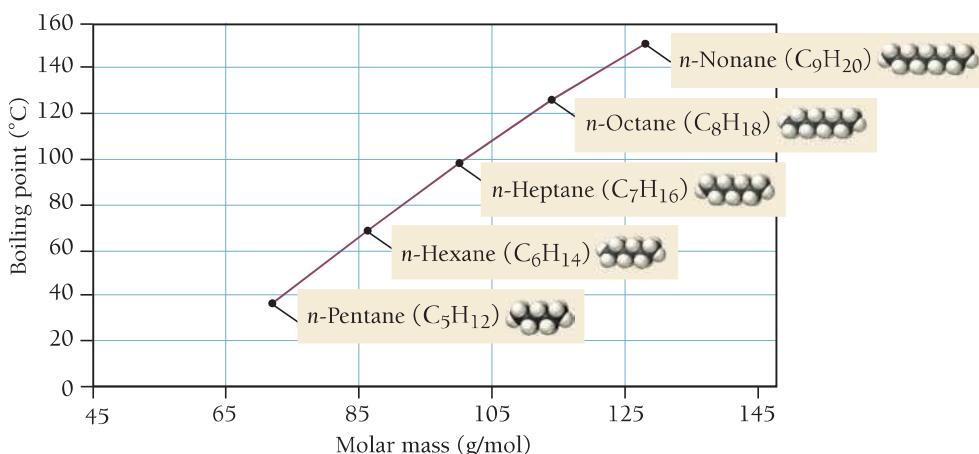
(b) Neopentane

▲ FIGURE 12.5 Dispersion Force and Molecular Shape (a) The straight shape of *n*-pentane molecules allows them to interact with one another along the entire length of the molecules. (b) The nearly spherical shape of neopentane molecules allows for only a small area of interaction. Thus, dispersion forces are weaker in neopentane than in *n*-pentane, resulting in a lower boiling point.

Although we must always consider molecular shape and other factors in predicting the magnitude of dispersion forces, molar mass can act as a guide when comparing dispersion forces within a family of similar elements or compounds as illustrated in Figure 12.6►.

► FIGURE 12.6 Boiling Points of the *n*-Alkanes

The boiling points of the *n*-alkanes rise with increasing molar mass and the consequent stronger dispersion forces.



ANSWER NOW!

**12.3**

Conceptual Connection

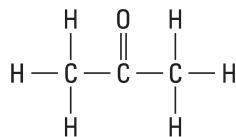
See Sections 10.6 and 11.5 to review how to determine if a molecule is polar.

DISPERSION FORCES Which halogen has the highest boiling point?

- (a) Cl_2 (b) Br_2 (c) I_2

Dipole–Dipole Force

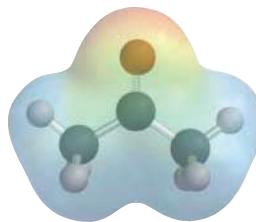
The **dipole–dipole force** exists between all molecules that are polar. Polar molecules have electron-rich regions (which have a partial negative charge) and electron-deficient regions (which have a partial positive charge). For example, consider acetone:



Structural formula



Space-filling model



Electrostatic potential map

The image on the right is an electrostatic potential map of acetone; we first saw these kinds of maps in Sections 10.6 and 11.5. Recall that the red areas indicate electron-rich regions in the molecule and that the blue areas indicate electron-poor regions.

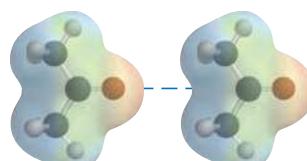
Notice that acetone has an electron-rich region surrounding the oxygen atom (because oxygen is more electronegative than the rest of the molecule) and electron-poorer regions surrounding the carbon and hydrogen atoms. The result is that acetone has a **permanent dipole** that can interact with other acetone molecules as shown in Figure 12.7▼.

Dipole–Dipole Interaction

The positive end of a polar molecule is attracted to the negative end of its neighbor.



Space-filling model



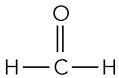
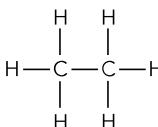
Electrostatic potential map

► FIGURE 12.7 Dipole–Dipole

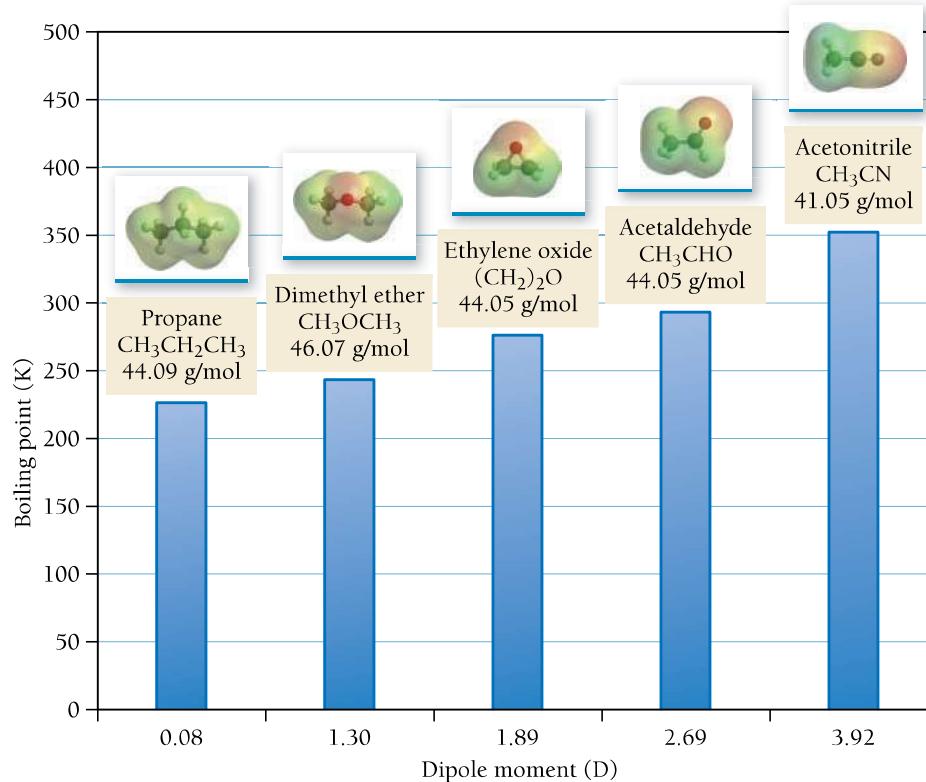
Interaction Molecules with permanent dipoles, such as acetone, are attracted to one another via dipole–dipole interactions.

The positive end of one permanent dipole attracts the negative end of another; this attraction is the dipole–dipole force. Polar molecules, therefore, have higher melting and boiling points than nonpolar molecules of similar molar mass.

Remember that all molecules (including polar ones) have dispersion forces. Polar molecules have, *in addition*, dipole–dipole forces. This additional attractive force raises their melting and boiling points relative to nonpolar molecules of similar molar mass. For example, consider formaldehyde and ethane:

Name	Formula	Molar Mass (g/mol)	Structure	bp (°C)	mp (°C)
Formaldehyde	CH ₂ O	30.03		-19.5	-92
Ethane	C ₂ H ₆	30.07		-88	-183

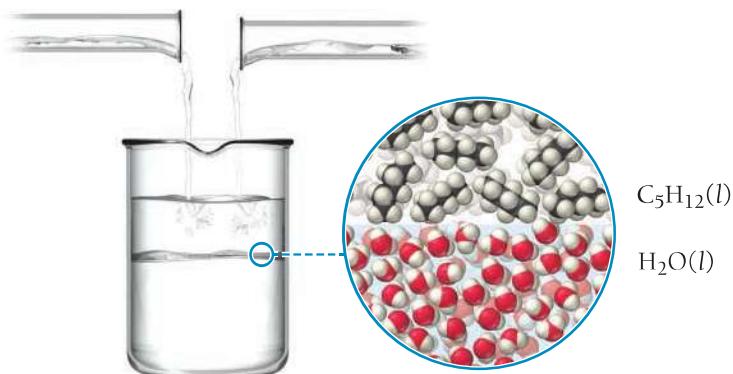
Formaldehyde is polar and has a higher melting point and boiling point than nonpolar ethane, even though the two compounds have the same molar mass. Figure 12.8▼ shows the boiling points of a series of molecules with similar molar mass but progressively greater dipole moments. Notice that the boiling points increase with increasing dipole moment.



◀ FIGURE 12.8 Dipole Moment and Boiling Point The molecules shown here all have similar molar masses but different dipole moments. The boiling points increase with increasing dipole moment.

The polarity of molecules is also important in determining the **miscibility**—the ability to mix without separating into two states—of liquids. This is especially true for water, which is highly polar. In general, polar liquids tend to be miscible with water, while nonpolar liquids are not. For example, pentane (C_5H_{12}) is nonpolar and does not mix with water (Figure 12.9►). Similarly, water and oil (nonpolar) do not mix. Consequently, oily hands or oily stains on clothes cannot be washed with plain water (see *Chemistry in Your Day: How Soap Works* in Section 11.5).

► FIGURE 12.9 Polar and Nonpolar Substances Water and pentane do not mix because water molecules are polar and pentane molecules are nonpolar.



WATCH NOW!

INTERACTIVE WORKED EXAMPLE 12.1

EXAMPLE 12.1 Dipole–Dipole Forces

Which molecules have dipole–dipole forces?

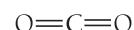
- (a) CO_2 (b) CH_2Cl_2 (c) CH_4

SOLUTION

A molecule has dipole–dipole forces if it is polar. To determine if a molecule is polar: (1) *determine if the molecule contains polar bonds* (Section 10.6); and (2) *determine if the polar bonds add together to form a net dipole moment* (Section 11.5).

- (a) CO_2

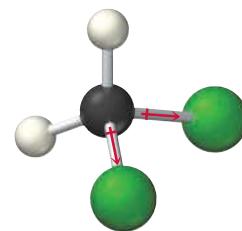
- (1) Since the electronegativity of carbon is 2.5 and that of oxygen is 3.5 (see Figure 10.8), CO_2 has polar bonds.
- (2) The geometry of CO_2 is linear. Consequently, the dipoles of the polar bonds cancel, so the molecule is *not polar* and does not have dipole–dipole forces.



No dipole forces present

- (b) CH_2Cl_2

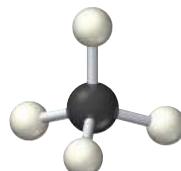
- (1) The electronegativity of C is 2.5, that of H is 2.1, and that of Cl is 3.0. Consequently, CH_2Cl_2 has two polar bonds ($\text{C}-\text{Cl}$) and two bonds that are nearly nonpolar ($\text{C}-\text{H}$).
- (2) The geometry of CH_2Cl_2 is tetrahedral. Because the $\text{C}-\text{Cl}$ bonds and the $\text{C}-\text{H}$ bonds are different, their dipoles do not cancel but sum to a net dipole moment. The molecule is polar and has dipole–dipole forces.



Dipole forces present

- (c) CH_4

- (1) The electronegativity of C is 2.5 and that of hydrogen is 2.1, so the $\text{C}-\text{H}$ bonds are nearly nonpolar.
- (2) In addition, since the geometry of the molecule is tetrahedral, any slight polarities that the bonds might have cancel. CH_4 is therefore nonpolar and does not have dipole–dipole forces.



No dipole forces present

FOR PRACTICE 12.1 Which molecules have dipole–dipole forces?

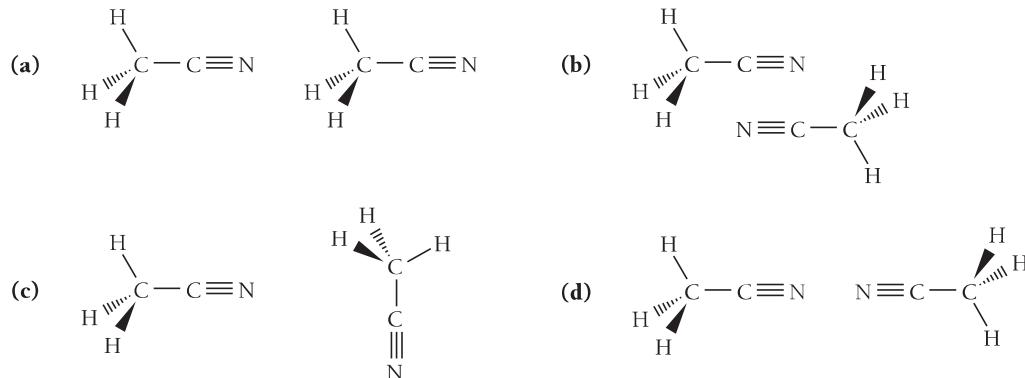
- (a) Cl_4 (b) CH_3Cl (c) HCl

DIPOLE-DIPOLE INTERACTION An electrostatic potential map for acetonitrile (CH_3CN), which is polar, is shown here: From this map, determine the geometry for how two acetonitrile molecules would interact with each other. Which of the orientations shown here is most likely?



12.4
Cc
Conceptual Connection

ANSWER NOW!



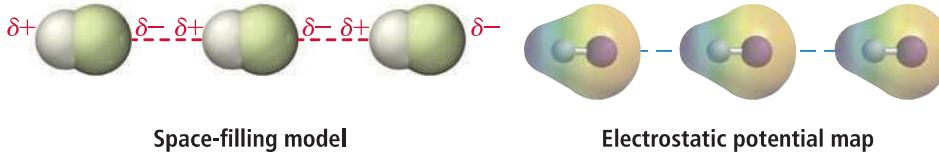
Hydrogen Bonding

Polar molecules containing hydrogen atoms bonded directly to small electronegative atoms—most importantly fluorine, oxygen, or nitrogen—exhibit an intermolecular force called **hydrogen bonding**. HF, NH_3 , and H_2O , for example, all exhibit hydrogen bonding. The hydrogen bond is a sort of *super* dipole–dipole force. The large electronegativity difference between hydrogen and any of these electronegative elements causes the hydrogen atom to have a fairly large partial positive charge ($\delta+$) within the bond, while the F, O, or N atom has a fairly large partial negative charge ($\delta-$). In addition, since these atoms are all quite small, the H atom on one molecule can approach the F, O, or N atom on an adjacent molecule very closely. The result is a strong attraction between the H atom on one molecule and the F, O, or N on its neighbor—an attraction called a **hydrogen bond**.

For example, in HF, the hydrogen atom in one molecule is strongly attracted to the fluorine atom on a neighboring molecule (Figure 12.10▼). The electrostatic potential maps in Figure 12.10 illustrate the large differences in electron density that result in unusually large partial charges.

Hydrogen Bonding

When H bonds directly to F, O, or N, the bonding atoms acquire relatively large partial charges, giving rise to strong dipole–dipole attractions between neighboring molecules.



◀ FIGURE 12.10 Hydrogen Bonding in HF

The hydrogen of one HF molecule, with its partial positive charge, is attracted to the fluorine of its neighbor, with its partial negative charge. This dipole–dipole interaction is an example of a hydrogen bond.

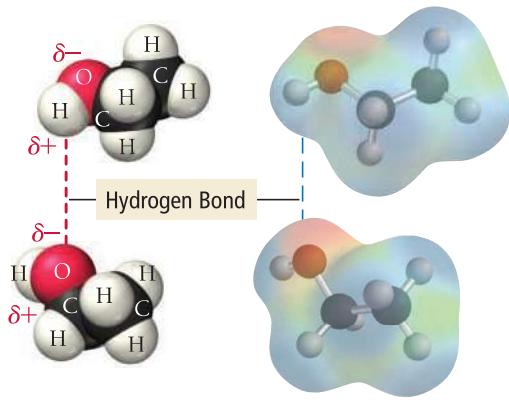
Hydrogen bonds should not be confused with chemical bonds. Chemical bonds occur between individual atoms within a molecule, whereas hydrogen bonds—like dispersion forces and dipole–dipole forces—are intermolecular forces that occur between molecules. A typical hydrogen bond is only 2–5% as strong as a typical covalent chemical bond. Hydrogen bonds are, however, the strongest of the three *intermolecular* forces we have discussed so far. Substances composed of molecules that form hydrogen bonds have higher melting and boiling points than comparable substances composed of molecules that do not form hydrogen bonds.

For example, consider ethanol and dimethyl ether:

Name	Formula	Molar Mass (g/mol)	Structure	bp (°C)	mp (°C)
Ethanol	C ₂ H ₆ O	46.07		CH ₃ CH ₂ OH	78.3 -114.1
Dimethyl ether	C ₂ H ₆ O	46.07		CH ₃ OCH ₃	-22.0 -138.5

Hydrogen Bonding in Ethanol

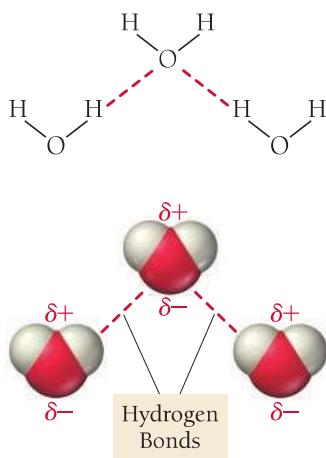
The partial positive charge on H is strongly attracted to the partial negative charge on O.



Space-filling model Electrostatic potential map

▲ **FIGURE 12.11** Hydrogen Bonding in Ethanol The left side shows the space-filling models, and the right side shows the electrostatic potential maps.

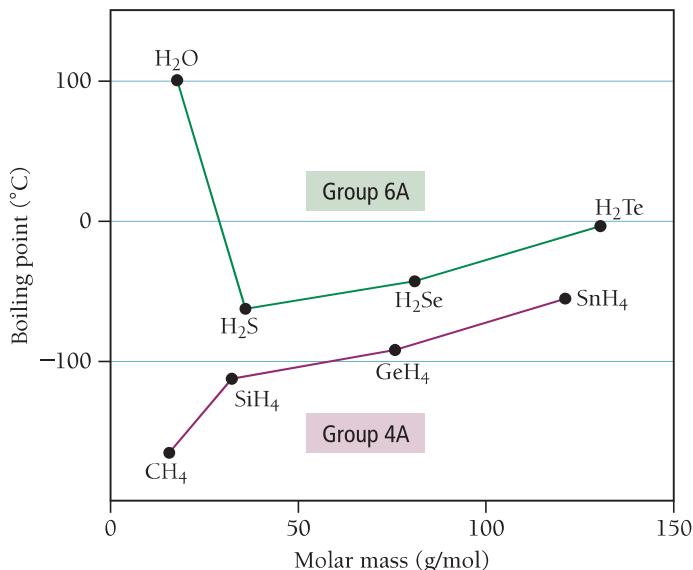
Hydrogen Bonding in Water



▲ **FIGURE 12.12** Hydrogen Bonding in Water

Since ethanol contains hydrogen bonded directly to oxygen, ethanol molecules form hydrogen bonds with each other, as shown in Figure 12.11◀. The hydrogen that is directly bonded to oxygen in an individual ethanol molecule is strongly attracted to the oxygen on neighboring molecules. This strong attraction (i.e., hydrogen bond) makes the boiling point of ethanol 78.3 °C. Consequently, ethanol is a liquid at room temperature. In contrast, dimethyl ether has an identical molar mass to ethanol but does not exhibit hydrogen bonding because in the dimethyl ether molecule, the oxygen atom is not bonded directly to hydrogen; this results in lower boiling and melting points, and dimethyl ether is a gas at room temperature.

Water is another good example of a molecule with hydrogen bonding (Figure 12.12▼). Figure 12.13▼ plots the boiling points of the simple hydrogen compounds of the group 4A and group 6A elements. In general, boiling points increase with increasing molar mass, as expected, based on increasing dispersion forces. However, because of hydrogen bonding, the boiling point of water (100 °C) is much higher than expected based on its molar mass (18.0 g/mol). Without hydrogen bonding, all the water on our planet would be gaseous.



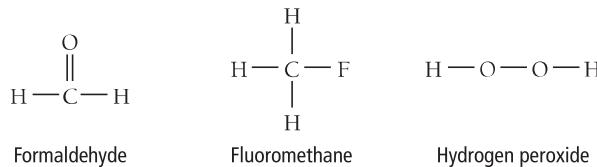
▲ **FIGURE 12.13** Boiling Points of Group 4A and 6A Compounds Because of hydrogen bonding, the boiling point of water is anomalous compared to the boiling points of other hydrogen-containing compounds.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 12.2

EXAMPLE 12.2 Hydrogen Bonding

One of these compounds is a liquid at room temperature. Which one and why?

**SOLUTION**

The three compounds have similar molar masses:

Formaldehyde	30.03 g/mol
Fluoromethane	34.03 g/mol
Hydrogen peroxide	34.02 g/mol

As a result, the strengths of their dispersion forces are similar. All three compounds are also polar, so they have dipole–dipole forces. Hydrogen peroxide, however, is the only one of these compounds that also contains H bonded directly to F, O, or N. Therefore, it also has hydrogen bonding and is likely to have the highest boiling point of the three. Since the example stated that only one of the compounds was a liquid, it is safe to assume that hydrogen peroxide is the liquid. Note that, although fluoromethane *contains* both H and F, H is not *directly bonded* to F, so fluoromethane does not have hydrogen bonding as an intermolecular force. Similarly, formaldehyde *contains* both H and O, but H is not *directly bonded* to O, so formaldehyde does not exhibit hydrogen bonding either.

FOR PRACTICE 12.2 Which has the higher boiling point, HF or HCl? Why?

Ion-Dipole Force

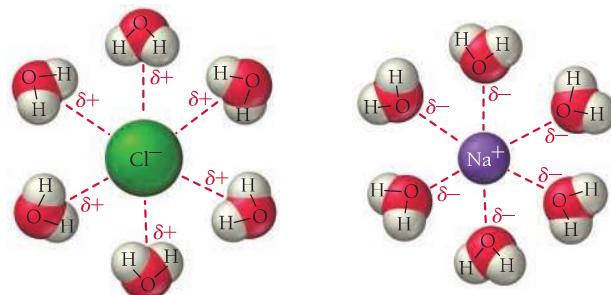
The **ion-dipole force** occurs when an ionic compound is mixed with a polar compound; it is especially important in aqueous solutions of ionic compounds. For example, when sodium chloride is mixed with water, the sodium and chloride ions interact with water molecules via ion-dipole forces, as shown in Figure 12.14▶. The positive sodium ions interact with the negative poles of water molecules, while the negative chloride ions interact with the positive poles. Ion-dipole forces are the strongest of the types of intermolecular forces discussed and are responsible for the ability of ionic substances to form solutions with water. We discuss aqueous solutions more thoroughly in Chapter 14.

Summarizing Intermolecular Forces (as shown in Table 12.4):

- Dispersion forces are present in all molecules and atoms and generally increase with increasing molar mass. These forces are always weak in small molecules but can be significant in molecules with high molar masses.
- Dipole–dipole forces are present in polar molecules.
- Hydrogen bonds, the strongest of the intermolecular forces that can occur in pure substances (second only to ion-dipole forces in general), are present in molecules containing hydrogen bonded directly to fluorine, oxygen, or nitrogen.
- Ion-dipole forces are present in mixtures of ionic compounds and polar compounds. These forces are very strong and are especially important in aqueous solutions of ionic compounds.

Ion-Dipole Forces

The positively charged end of a polar molecule such as H_2O is attracted to negative ions, and the negatively charged end of the molecule is attracted to positive ions.



▲ FIGURE 12.14 Ion-Dipole Forces Ion-dipole forces exist between Na^+ and the negative ends of H_2O molecules and between Cl^- and the positive ends of H_2O molecules.

TABLE 12.4 ■ Types of Intermolecular Forces

Type	Present In	Molecular Perspective	Strength
Dispersion*	All molecules and atoms		0.05–20+ kJ/mol
Dipole–dipole	Polar molecules		3–20+ kJ/mol
Hydrogen bonding	Molecules containing H bonded to F, O, or N		10–40 kJ/mol
Ion–dipole	Mixtures of ionic compounds and polar compounds		30–100+ kJ/mol

*The dispersion force can become very strong (as strong and even stronger than the others) for molecules of high molar mass.

ANSWER NOW!

12.5
Cc
 Conceptual Connection
INTERMOLECULAR FORCES AND BOILING POINT

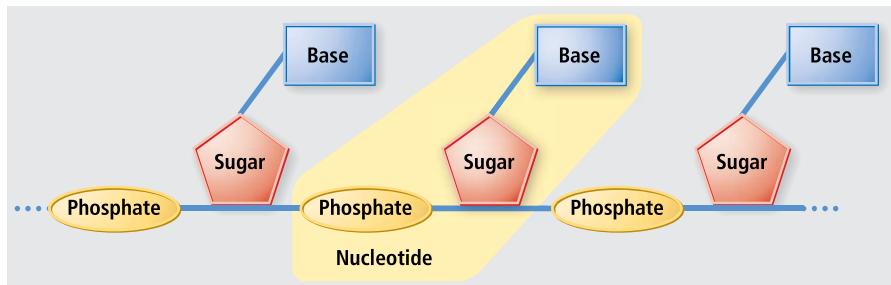
Which substance has the highest boiling point?

- (a) CH₃OH (b) CO (c) N₂

**CHEMISTRY AND MEDICINE****Hydrogen Bonding in DNA**

DNA is a long, chainlike molecule that acts as a blueprint for each living organism. Copies of DNA are passed from parent to offspring, which is how we inherit traits from our parents. A DNA molecule is composed of thousands of repeating units called *nucleotides* (Figure 12.15▼). Each nucleotide contains one of four different organic bases: adenine, thymine, cytosine, and

guanine (abbreviated A, T, C, and G). The sequence of these bases along DNA encodes the information that determines the nature of the proteins that are made in the body (proteins are the molecules that do most of the work in living organisms). Our proteins in turn determine many of our characteristics, including how we look, what diseases we are at risk of developing, and even our behavior.

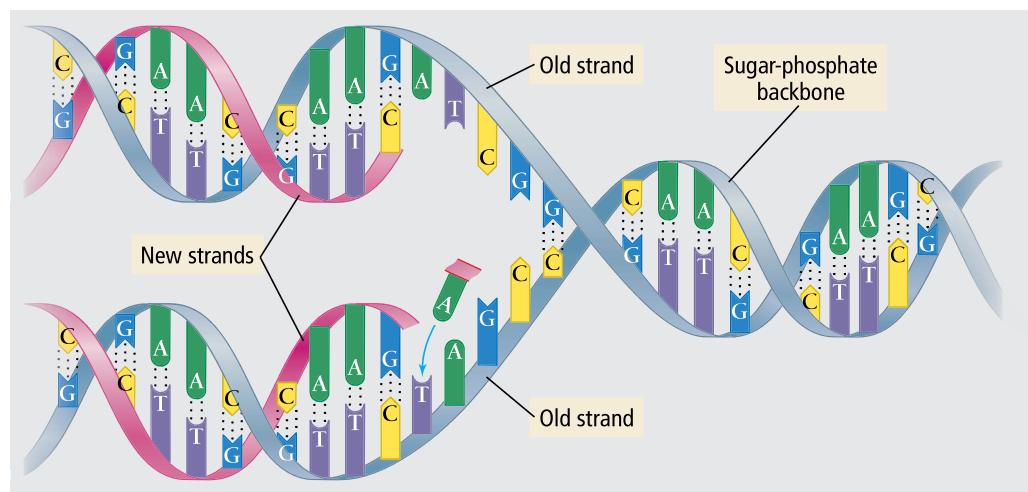
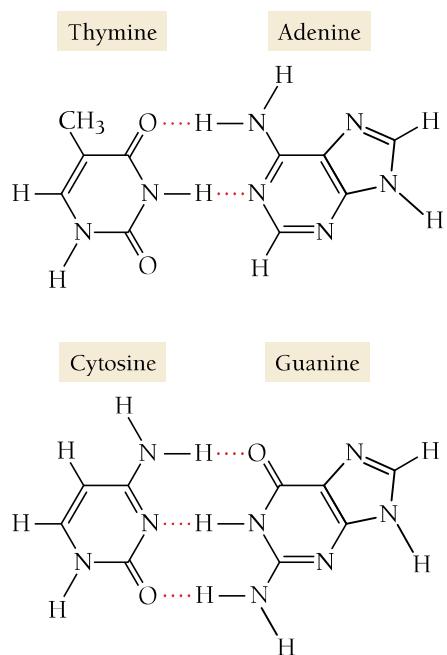
**◀ FIGURE 12.15** Nucleotides

The individual units in a DNA polymer are nucleotides. Each nucleotide contains one of four bases: adenine, thymine, cytosine, and guanine (abbreviated A, T, C, and G).

The replicating mechanism of DNA is related to its structure, which was discovered in 1953 by James Watson (1928–) and Francis Crick (1916–2004). DNA consists of two complementary strands wrapped around each other in the now famous double helix and linked by hydrogen bonds between the bases on each strand. Each base (A, T, C, and G) has a complementary partner with which it forms hydrogen bonds (Figure 12.16►); adenine (A) with thymine (T) and cytosine (C) with guanine (G). The hydrogen bonding is so specific that each base will pair only with its complementary partner. When a cell is going to divide, enzymes unzip the DNA molecule across the hydrogen bonds that join its two strands (Figure 12.17▼). Then new bases, complementary to the bases in each strand, are added along each of the original strands, forming hydrogen bonds with their complements. The result is two identical copies of the original DNA.

QUESTION Why would dispersion forces not work as a way to hold the two strands of DNA together? Why would covalent bonds not work?

► **FIGURE 12.16 Complementary Base Pairing via Hydrogen Bonds** The individual bases in DNA interact with one another via specific hydrogen bonds that form between A and T and between C and G.



◀ **FIGURE 12.17 Copying DNA** The two strands of the DNA molecule “unzip” by breaking the hydrogen bonds that join the base pairs. New bases complementary to the bases of each strand are assembled and joined together. The result is two molecules, each identical to the original one.

12.4

Intermolecular Forces in Action: Surface Tension, Viscosity, and Capillary Action

The most important manifestation of intermolecular forces is the very existence of liquids and solids. In liquids, we also observe several other manifestations of intermolecular forces, including surface tension, viscosity, and capillary action.

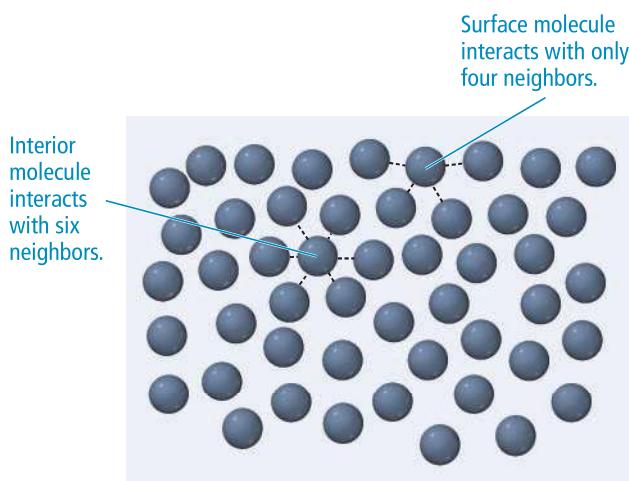
Surface Tension

A fly fisherman delicately casts a small fishing fly (a metal hook with a few feathers and strings attached to make it look like an insect) onto the surface of a moving stream. The fly floats on the surface of the water—even though the metal composing the hook is denser than water—and attracts trout. Why? The hook floats because of *surface tension*, the tendency of liquids to minimize their surface area.



▲ A trout fly can float on water because of surface tension.

Recall from Section 12.3 that the interactions between molecules lower their potential energy in much the same way that the interaction between protons and electrons lowers their potential energy, in accordance with Coulomb's law.



▲ FIGURE 12.18 The Origin of Surface Tension Molecules at the liquid surface have a higher potential energy than those in the interior. As a result, a liquid tends to minimize its surface area; its surface behaves like a "skin."



▲ FIGURE 12.19 Surface Tension in Action A paper clip floats on water because of surface tension.



▲ FIGURE 12.20 Spherical Water Droplets Tiny water droplets are not distorted much by gravity and form nearly perfect spheres held together by intermolecular forces between water molecules.

Figure 12.18▲ depicts the intermolecular forces experienced by a molecule at the surface of the liquid compared to those experienced by a molecule in the interior. Notice that a molecule at the surface has relatively fewer neighbors with which to interact, and it is therefore inherently less stable—it has higher potential energy—than those in the interior. (Remember that attractive interactions with other molecules lower potential energy.) In order to increase the surface area of the liquid, molecules from the interior have to be moved to the surface, and because molecules at the surface have a higher potential energy than those in the interior, this movement requires energy. Therefore, liquids tend to minimize their surface area. The **surface tension** of a liquid is the energy required to increase the surface area by a unit amount. For example, at room temperature, water has a surface tension of 72.8 mJ/m^2 ; it takes 72.8 mJ to increase the surface area of water by one square meter.

Why does surface tension allow the fly fisherman's hook to float on water? The tendency for liquids to minimize their surface area creates a kind of skin at the surface that resists penetration. For the fisherman's hook to sink into the water, the water's surface area must increase slightly—an increase that is resisted by the surface tension. We can observe surface tension by carefully placing a paper clip on the surface of water (Figure 12.19▲). The paper clip, even though it is denser than water, floats on the surface of the water. A slight tap on the clip provides the energy necessary to overcome the surface tension and causes the clip to sink.

Surface tension decreases as intermolecular forces decrease. You can't float a paper clip on benzene, for example, because the dispersion forces among the molecules composing benzene are significantly weaker than the hydrogen bonds among water molecules. The surface tension of benzene is only 28 mJ/m^2 , just 40% that of water.

Surface tension is also the reason for the behavior of water that we discussed in the chapter-opening section on water and gravity. You can see this behavior on Earth by looking at small water droplets (those not large enough to be distorted by gravity) on a leaf or a spider's web (Figure 12.20▲). Just as larger samples of water form spheres in the space station, so smaller samples form spheres on Earth. Why? In the same way that gravity pulls the matter of a planet or star inward to form a sphere, intermolecular forces among collections of water molecules pull the water into a sphere. As we discussed in Section 12.1, the sphere is the geometrical shape with the smallest ratio of surface area to volume; therefore, the formation of a sphere minimizes the number of molecules at the surface, minimizing the potential energy of the system.

Viscosity

Another manifestation of intermolecular forces is **viscosity**, the resistance of a liquid to flow. Motor oil, for example, is more viscous than gasoline, and maple syrup is more viscous than water. Viscosity is measured in a unit called the poise (P), defined as $1 \text{ g/cm} \cdot \text{s}$. The viscosity of water at room temperature is approximately one centipoise (cP). Viscosity is greater in substances with stronger intermolecular forces because if molecules are more strongly attracted to each other, they do not flow around each other as freely. Viscosity also depends on molecular shape, increasing in longer molecules that can interact over a greater area and possibly become entangled. Table 12.5 lists the viscosity of several hydrocarbons. Notice the increase in viscosity with increasing molar mass (and therefore increasing magnitude of dispersion forces) and with increasing length (and therefore increasing potential for molecular entanglement).

Viscosity also depends on temperature because thermal energy partially overcomes the intermolecular forces, allowing molecules to flow past each other more easily. Table 12.6 lists the viscosity of water as a function of temperature. Nearly all liquids become less viscous as temperature increases.

TABLE 12.5 ■ Viscosity of Several Hydrocarbons at 20 °C

Hydrocarbon	Molar Mass (g/mol)	Formula	Viscosity (cP)
n-Pentane	72.15	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.240
n-Hexane	86.17	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.326
n-Heptane	100.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.409
n-Octane	114.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.542
n-Nonane	128.3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.711

TABLE 12.6 ■ Viscosity of Liquid Water at Several Temperatures

Temperature (°C)	Viscosity (cP)
20	1.002
40	0.653
60	0.467
80	0.355
100	0.282



CHEMISTRY IN YOUR DAY

Viscosity and Motor Oil

Viscosity is an important property of the motor oil you put into your car. The oil must be thick enough to adequately coat engine surfaces to lubricate them, but also thin enough to be pumped easily into all the required engine compartments. Motor oil viscosity is usually reported on the SAE scale (named after the Society of Automotive Engineers). The higher the SAE rating, the more viscous the oil. The thinnest motor oils have SAE ratings of 5 or 10, whereas the thickest have SAE ratings of up to 50.

Before the 1950s, most automobile owners changed the oil in their engine to accommodate seasonal changes in weather—a higher SAE rating was required in the summer months and a lower rating in the winter. Today, the advent of multigrade oils allows car owners in many climates to keep the same oil all year long. Multigrade oils, such as the 10W-40 oil shown at right, contain polymers (long molecules made up of repeating structural units) that coil at low temperatures but unwind at high temperatures. At low temperatures, the coiled polymers—because of their compact shape—do not contribute very much to the oil's viscosity. As the temperature increases, however, the molecules unwind, and their long shape results in intermolecular forces and molecular entanglements that prevent the oil's viscosity from decreasing as

much as it would normally. The result is an oil whose viscosity is less temperature-dependent than it would be otherwise, allowing the same oil to be used over a wider range of temperatures. The 10W-40 designation indicates that the oil has an SAE rating of 10 at low temperatures and 40 at high temperatures.



Capillary Action

Medical technicians take advantage of **capillary action**—the ability of a liquid to flow against gravity up a narrow tube—when taking a blood sample. The technician pokes the patient's finger with a pin, squeezes some blood out of the puncture, and then collects



▲ Blood is drawn into a capillary tube by capillary action.



▲ **FIGURE 12.21 Capillary Action** The attraction of water molecules to the glass surface draws the liquid around the edge of the tube up the walls. The water in the rest of the column is pulled along by the attraction of water molecules to one another. As can be seen in this figure, the narrower the tube, the higher the liquid will rise.

WATCH NOW!

KEY CONCEPT VIDEO 12.5
Vaporization and Vapor Pressure

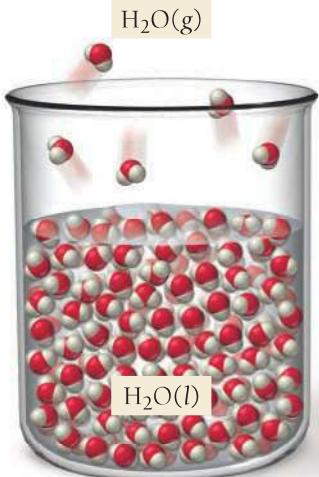
12.5 Vaporization and Vapor Pressure

We now turn our attention to *vaporization*, the process by which thermal energy can overcome intermolecular forces and produce a state change from liquid to gas.

We first discuss the process of vaporization itself, then the energetics of vaporization, and finally the concepts of *vapor pressure*, *dynamic equilibrium*, and *critical point*. Vaporization is a common occurrence that we experience every day and even depend on to maintain proper body temperature.

The Process of Vaporization

Imagine water molecules in a beaker at room temperature and open to the atmosphere (Figure 12.23). The molecules are in constant motion due to thermal energy. If we could actually see the molecules at the surface, we would witness what theoretical chemist Roald Hoffmann describes as a “wild dance floor” (see the chapter-opening quote) because of all the vibrating, jostling, and molecular movement. *The higher the temperature, the greater the average energy of the collection of molecules.* However, at any one time, some molecules have more thermal energy than the average and some have less.



◀ **FIGURE 12.23 Vaporization of Water** Some molecules in an open beaker have enough kinetic energy to vaporize from the surface of the liquid.

the blood with a thin tube. When the tube’s tip comes into contact with the blood, the blood is drawn into the tube by capillary action. The same force helps trees and plants draw water from the soil.

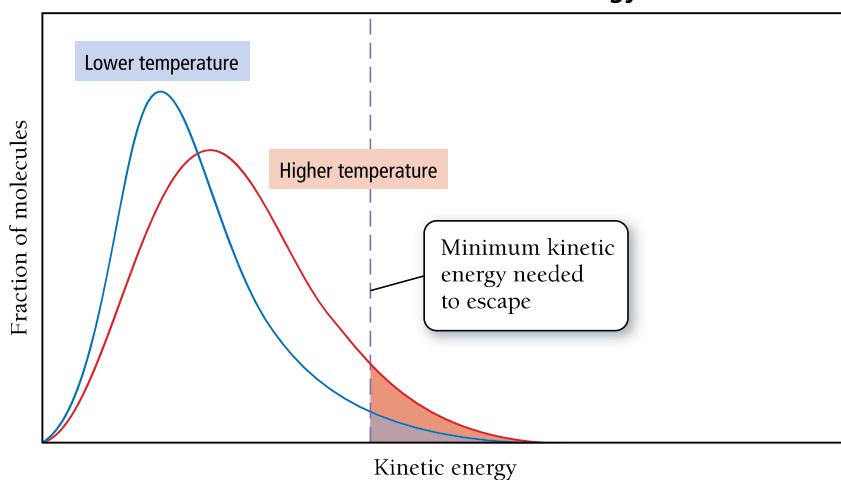
Capillary action results from a combination of two forces: the attraction between molecules in a liquid, called *cohesive forces*, and the attraction between these molecules and the surface of the tube, called *adhesive forces*. The adhesive forces cause the liquid to spread out over the surface of the tube, whereas the cohesive forces cause the liquid to stay together. If the adhesive forces are greater than the cohesive forces (as is the case for water in a glass tube), the attraction to the surface draws the liquid up the tube and the cohesive forces pull along those molecules not in direct contact with the tube walls (Figure 12.21◀). The water rises up the tube until the force of gravity balances the capillary action—the thinner the tube, the higher the rise. If the adhesive forces are less than the cohesive forces (as is the case for liquid mercury), the liquid does not rise up the tube at all (and in fact drops to a level below the level of the surrounding liquid).

We can see the result of the differences in the relative magnitudes of cohesive and adhesive forces by comparing the meniscus of water to the meniscus of mercury (Figure 12.22▶). (The meniscus is the curved shape of a liquid surface within a tube.) The meniscus of water is concave (rounded inward) because the *adhesive forces* are greater than the cohesive forces, causing the edges of the water to creep up the sides of the tube a bit, forming the familiar cupped shape. The meniscus of mercury is convex (rounded outward) because the *cohesive forces*—due to metallic bonding between the atoms—are greater than the adhesive forces. The mercury atoms crowd toward the interior of the liquid to maximize their interactions with each other, resulting in the upward bulge at the center of the surface.



▲ **FIGURE 12.22 Meniscuses of Water and Mercury** The meniscus of water is concave because water molecules are more strongly attracted to the glass wall than to one another. The meniscus of mercury is convex because mercury atoms are more strongly attracted to one another than to the glass walls.

Distribution of Thermal Energy



◀ FIGURE 12.24 Distribution of Thermal Energy The thermal energies of the molecules in a liquid are distributed over a range. The peak energy increases with increasing temperature.

The distributions of thermal energies for the molecules in a sample of water at two different temperatures are shown in Figure 12.24▲. The molecules at the high end of the distribution curve have enough energy to break free from the surface—where molecules are held less tightly than they are in the interior due to fewer neighbor–neighbor interactions—and into the gas state. This transition, from liquid to gas, is known as **vaporization**. Some of the water molecules in the gas state, at the low end of the energy distribution curve for the gaseous molecules, plunge back into the water and are captured by intermolecular forces. This transition, from gas to liquid, is the opposite of vaporization and is called **condensation**.

Although both vaporization and condensation occur in a beaker open to the atmosphere, under normal conditions (such as relatively dry air at room temperature) evaporation takes place at a greater rate because most of the newly evaporated molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the water level within an open beaker over time (usually several days).

What happens if we increase the temperature of the water within the beaker? Because of the shift in the energy distribution to higher energies (see Figure 12.24), more molecules now have enough energy to break free and evaporate, so vaporization occurs more quickly. What happens if we spill the water on the table or floor? The same amount of water is now spread over a wider area, resulting in more molecules at the surface of the liquid. Since molecules at the surface have the greatest tendency to evaporate—because they are held less tightly—vaporization also occurs more quickly in this case. You probably know from experience that water in a beaker or glass may take many days to evaporate completely, whereas the same amount of water spilled on a table or floor typically evaporates within a few hours (depending on the exact conditions).

What happens if the liquid in the beaker is not water, but some other substance with weaker intermolecular forces, such as acetone (the main component in nail polish remover)? The weaker intermolecular forces allow more molecules to evaporate at a given temperature, increasing the rate of vaporization. We call liquids that vaporize easily **volatile** and those that do not vaporize easily **nonvolatile**. Acetone is more volatile than water. Motor oil is virtually nonvolatile at room temperature.

Summarizing the Process of Vaporization:

- The rate of vaporization increases with increasing temperature.
- The rate of vaporization increases with increasing surface area.
- The rate of vaporization increases with decreasing strength of intermolecular forces.

VAPORIZATION

Which sample of water has the greatest rate of vaporization?

- (a) A 100 mL sample of water at 25 °C in 100-mL beaker with a 5 cm diameter.
- (b) A 100 mL sample of water at 55 °C in 100-mL beaker with a 5 cm diameter.
- (c) A 100 mL sample of water at 25 °C in 250-mL beaker with a 7 cm diameter.
- (d) A 100 mL sample of water at 55 °C in 250-mL beaker with a 7 cm diameter.

12.6
Cc
Conceptual Connection

ANSWER NOW!



The Energetics of Vaporization

See Chapter 7 to review endothermic and exothermic processes.



▲ When we sweat, water evaporates from the skin. Since evaporation is endothermic, the result is a cooling effect.

The normal boiling point of a substance is its boiling point at a pressure of 1 atm, as discussed later in this section.

The sign conventions of ΔH were introduced in Chapter 7.

To understand the energetics of vaporization, consider again a beaker of water from the molecular point of view, except now imagine that the beaker is thermally insulated so that heat from the surroundings cannot enter the beaker. What happens to the temperature of the water left in the beaker as molecules evaporate? To answer this question, think about the energy distribution curve again (see Figure 12.24). The molecules that leave the beaker are the ones at the high end of the energy curve—the most energetic. If no additional heat enters the beaker, the average energy of the entire collection of molecules decreases—much as the class average on an exam goes down if you eliminate the highest-scoring students. So vaporization is an *endothermic* process; it takes energy to vaporize the molecules in a liquid. Another way to understand the endothermicity of vaporization is to remember that vaporization requires overcoming the intermolecular forces that hold liquids together. Since energy is needed to pull the molecules away from one another, the process is endothermic.

Our bodies use the endothermic nature of vaporization for cooling. When we overheat, we sweat and our skin is covered with liquid water. As this water evaporates, it absorbs heat from the body, cooling the skin. A fan makes us feel cooler because it blows newly vaporized water away from our skin, allowing more sweat to vaporize and causing even more cooling. High humidity, in contrast, slows down the net rate of evaporation, preventing cooling. When the air already contains large amounts of water vapor, the sweat evaporates more slowly, making the body's cooling system less efficient.

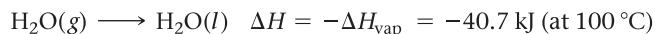
Condensation, the opposite of vaporization, is exothermic—heat is released when a gas condenses to a liquid. If you have ever accidentally put your hand above a steaming kettle or opened a bag of microwaved popcorn too soon, you may have experienced a *steam burn*. As the steam condenses to a liquid on your skin, it releases a lot of heat, causing the burn. The condensation of water vapor is also the reason that winter overnight temperatures in coastal regions, which tend to have water vapor in the air, do not get as low as in deserts, which tend to have dry air. As the air temperature in a coastal area drops, water condenses out of the air, releasing heat and preventing the temperature from dropping further. In deserts, the air contains almost no moisture to condense, so the temperature drop is more extreme.

The amount of heat required to vaporize one mole of a liquid to gas is its **heat (or enthalpy) of vaporization (ΔH_{vap})**. The heat of vaporization of water at its normal boiling point of 100 °C is +40.7 kJ/mol:



The heat of vaporization is always positive because the process is endothermic—energy must be absorbed to vaporize a substance. The heat of vaporization is somewhat temperature dependent. For example, at 25 °C the heat of vaporization of water is +44.0 kJ/mol, slightly more than it is at 100 °C because the water contains less thermal energy at 25 °C. Table 12.7 lists the heats of vaporization of several liquids at their boiling points and at 25 °C.

When a substance condenses from a gas to a liquid, the same amount of heat is involved, but the heat is emitted rather than absorbed:



When one mole of water condenses, it releases 40.7 kJ of heat. The sign of ΔH in this case is negative because the process is exothermic.

We can use the heat of vaporization of a liquid to calculate the amount of energy required to vaporize a given mass of the liquid (or the amount of heat given off by the condensation of a given mass of liquid), using concepts similar to those covered in

TABLE 12.7 ■ Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

Liquid	Chemical Formula	Normal Boiling Point (°C)	ΔH_{vap} (kJ/mol) at Boiling Point	ΔH_{vap} (kJ/mol) at 25 °C
Water	H ₂ O	100	40.7	44.0
Isopropyl alcohol	C ₃ H ₈ O	82.3	39.9	45.4
Acetone	C ₃ H ₆ O	56.1	29.1	31.0
Diethyl ether	C ₄ H ₁₀ O	34.6	26.5	27.1

Section 7.6 (stoichiometry of ΔH). The heat of vaporization is like a conversion factor between the number of moles of a liquid and the amount of heat required to vaporize it (or the amount of heat emitted when it condenses), as demonstrated in Example 12.3.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 12.3

EXAMPLE 12.3 Using the Heat of Vaporization in Calculations



Calculate the mass of water (in g) that can be vaporized at its boiling point with 155 kJ of heat.

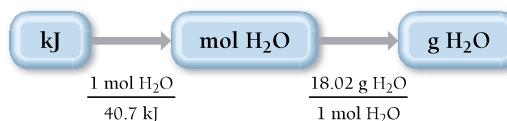
SORT You are given a certain amount of heat in kilojoules and asked to find the mass of water that can be vaporized.

GIVEN: 155 kJ

FIND: g H_2O

STRATEGIZE The heat of vaporization gives the relationship between heat absorbed and moles of water vaporized. Begin with the given amount of heat (in kJ) and convert to moles of water that can be vaporized. Then use the molar mass as a conversion factor to convert from moles of water to mass of water.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol (at } 100^\circ\text{C)}$$

$$18.02 \text{ g } H_2O = 1 \text{ mol } H_2O$$

SOLVE Follow the conceptual plan to solve the problem.

SOLUTION

$$155 \text{ kJ} \times \frac{1 \text{ mol } H_2O}{40.7 \text{ kJ}} \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 68.6 \text{ g } H_2O$$

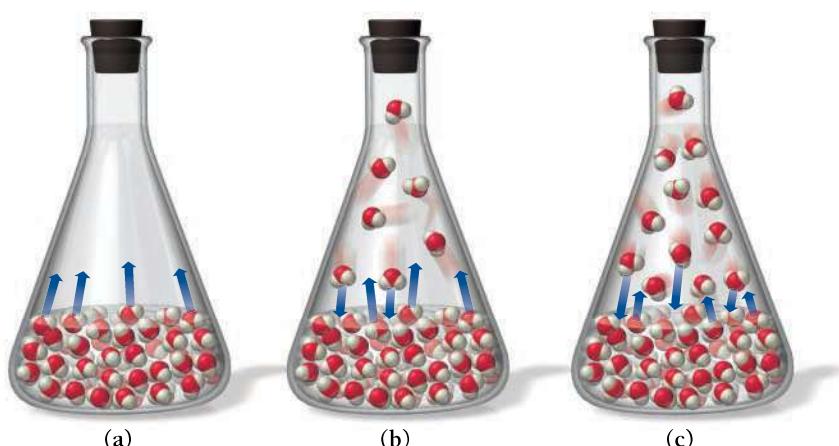
FOR PRACTICE 12.3 Calculate the amount of heat (in kJ) required to vaporize 2.58 kg of water at its boiling point.

FOR MORE PRACTICE 12.3 Suppose that 0.48 g of water at 25 °C condenses on the surface of a 55-g block of aluminum that is initially 25 °C. If the heat released during condensation goes only toward heating the metal, what is the final temperature (in °C) of the metal block? (The specific heat capacity of aluminum is 0.903 J/g °C.)

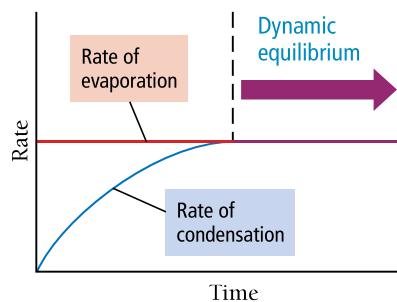
Vapor Pressure and Dynamic Equilibrium

We have already seen that if a container of water is left uncovered at room temperature, the water slowly evaporates away. What happens if the container is sealed? Imagine a sealed evacuated flask—one from which the air has been removed—containing liquid water, as shown in Figure 12.25▼. Initially, the water molecules evaporate, as they did in the open beaker. But because of the seal, the evaporated molecules cannot escape into the atmosphere. As water molecules enter the gas state, some start condensing

Dynamic equilibrium:
rate of evaporation = rate of condensation



◀ FIGURE 12.25 Vaporization in a Sealed Flask (a) When water is in a sealed container, water molecules begin to vaporize. (b) As water molecules build up in the gas state, they begin to recondense into the liquid. (c) When the rate of evaporation equals the rate of condensation, dynamic equilibrium is reached.



▲ FIGURE 12.26 Dynamic Equilibrium Dynamic equilibrium occurs when the rate of condensation is equal to the rate of evaporation.

Boyle's law is discussed in Section 6.3.

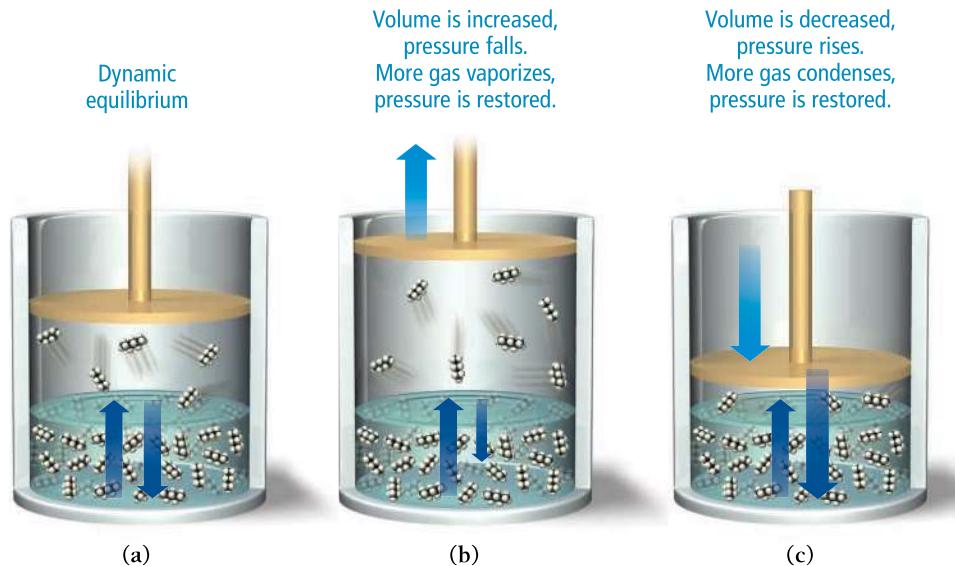
back into the liquid. As the concentration (or partial pressure) of gaseous water molecules increases, the rate of condensation also increases. However, as long as the water remains at a constant temperature, the rate of evaporation remains constant. Eventually, the rate of condensation and the rate of vaporization become equal—**dynamic equilibrium** has been reached (Figure 12.26). Condensation and vaporization continue at equal rates, and the concentration of water vapor above the liquid is constant.

The pressure of a gas in dynamic equilibrium with its liquid is its **vapor pressure**. The vapor pressure of a particular liquid depends on the intermolecular forces present in the liquid and the temperature. Weak intermolecular forces result in volatile (easily vaporizable) substances with high vapor pressures at a given temperature because the intermolecular forces are easily overcome by thermal energy. Strong intermolecular forces result in nonvolatile substances with low vapor pressures at a given temperature.

A liquid in dynamic equilibrium with its vapor is a balanced system that tends to return to equilibrium if disturbed. For example, consider a sample of *n*-pentane (a component of gasoline) at 25 °C in a cylinder equipped with a moveable piston (Figure 12.27(a)). The cylinder contains no other gases except *n*-pentane vapor in dynamic equilibrium with the liquid. Since the vapor pressure of *n*-pentane at 25 °C is 510 mmHg, the pressure in the cylinder is 510 mmHg.

Now, what happens when the piston is moved upward to expand the volume within the cylinder? Initially, the pressure in the cylinder drops below 510 mmHg, in accordance with Boyle's law. Then, however, more liquid vaporizes until equilibrium is reached once again (Figure 12.27(b)). If the volume of the cylinder is expanded again, the same thing happens—the pressure initially drops and more *n*-pentane vaporizes to bring the system back into equilibrium. Further expansion causes the same result *as long as some liquid n-pentane remains in the cylinder*.

Conversely, what happens if the piston is lowered, decreasing the volume in the cylinder? Initially, the pressure in the cylinder rises above 510 mmHg, but then some of the gas condenses into liquid until equilibrium is reached again (Figure 12.27(c)).



▲ FIGURE 12.27 Dynamic Equilibrium in *n*-Pentane (a) Liquid *n*-pentane is in dynamic equilibrium with its vapor. (b) When the volume is increased, the pressure drops and some liquid converts to gas to bring the pressure back up. (c) When the volume is decreased, the pressure increases and some gas converts to liquid to bring the pressure back down.

We describe the tendency of a system in dynamic equilibrium to return to equilibrium with the following general statement:

When a system in dynamic equilibrium is disturbed, the system responds so as to minimize the disturbance and return to a state of equilibrium.

If the pressure above a liquid-vapor system in equilibrium decreases, some of the liquid evaporates, restoring the equilibrium pressure. If the pressure increases, some of the vapor condenses, bringing the pressure back down to the equilibrium pressure. This basic principle—Le Châtelier’s principle—is applicable to any chemical system in equilibrium, as we shall see in Chapter 16.

VAPOR PRESSURE What happens to the vapor pressure of a substance when its surface area is increased at constant temperature?

- (a) The vapor pressure increases.
- (b) The vapor pressure remains the same.
- (c) The vapor pressure decreases.



Conceptual
Connection

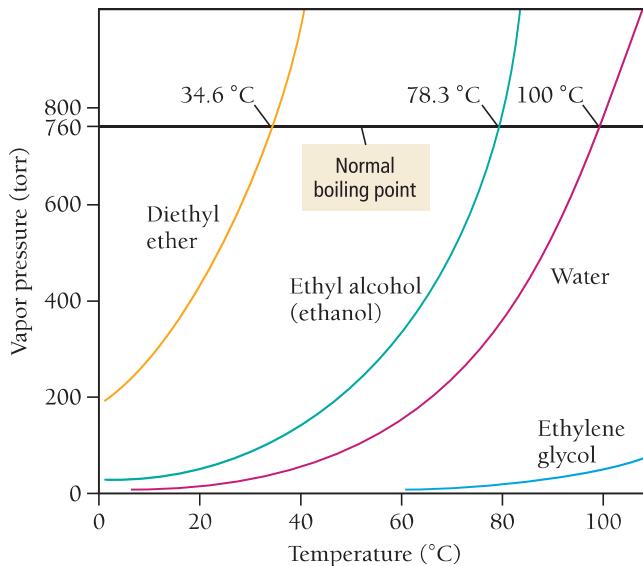
ANSWER NOW!



Temperature Dependence of Vapor Pressure and Boiling Point

When the temperature of a liquid increases, its vapor pressure rises because the higher thermal energy increases the number of molecules that have enough energy to vaporize (see Figure 12.24). Because of the shape of the thermal energy distribution curve, a small change in temperature makes a large difference in the number of molecules that have enough energy to vaporize, which results in a large increase in vapor pressure. For example, the vapor pressure of water at 25 °C is 23.3 torr, while at 60 °C the vapor pressure is 149.4 torr. Figure 12.28▼ plots the vapor pressure of water and several other liquids as a function of temperature.

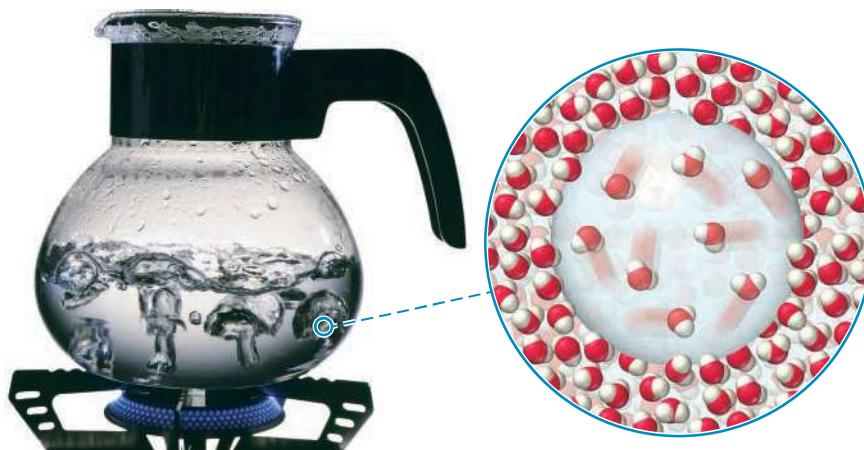
The **boiling point** of a liquid is *the temperature at which the liquid’s vapor pressure equals the external pressure*. When a liquid reaches its boiling point, the thermal energy is enough for molecules in the interior of the liquid (not just those at the surface) to break



▲ **FIGURE 12.28** Vapor Pressure of Several Liquids at Different Temperatures At higher temperatures, more molecules have enough thermal energy to escape into the gas state, so vapor pressure increases with increasing temperature.

► FIGURE 12.29 Boiling

A liquid boils when thermal energy is high enough to cause molecules in the interior of the liquid to become gaseous, forming bubbles that rise to the surface.



Sometimes you see bubbles begin to form in hot water below 100 °C. These bubbles are dissolved air—not gaseous water—leaving the liquid. Dissolved air comes out of water as you heat it because the solubility of a gas in a liquid decreases with increasing temperature (as we will see in Chapter 14).

free of their neighbors and enter the gas state (Figure 12.29▲). The bubbles in boiling water are pockets of gaseous water that form within the liquid water. The bubbles float to the surface and leave as gaseous water or steam.

The **normal boiling point** of a liquid is *the temperature at which its vapor pressure equals 1 atm*. The normal boiling point of pure water is 100 °C. However, at a lower pressure, water boils at a lower temperature. In Denver, Colorado, where the altitude is around 1600 meters (5200 feet) above sea level, for example, the average atmospheric pressure is about 83% of what it is at sea level, and water boils at approximately 94 °C. For this reason, it takes slightly longer to cook food in boiling water in Denver than in San Francisco (which is at sea level). Table 12.8 lists the boiling point of water at several locations of varied altitudes.

TABLE 12.8 ▀ Boiling Points of Water at Several Locations of Varied Altitudes

Location	Elevation (ft)	Approximate Pressure (atm)*	Approximate Boiling Point of Water (°C)
Mount Everest, Tibet (highest mountain peak on Earth)	29,029 ft.	0.32	78
Denali (formerly Mount McKinley), Alaska (highest mountain peak in North America)	20,310 ft.	0.46	83
Mount Whitney, California (highest mountain peak in 48 contiguous U.S. states)	14,505	0.60	87
Denver, Colorado (mile high city)	5,280	0.83	94
Boston, Massachusetts (sea level)	20	1.0	100

*The atmospheric pressure in each of these locations is subject to weather conditions and can vary significantly from these values.

Once the boiling point of a liquid is reached, additional heating only causes more rapid boiling; it does not raise the temperature of the liquid above its boiling point, as shown in the *heating curve* in Figure 12.30►. Therefore, at 1 atm, boiling water always has a temperature of 100 °C. *As long as liquid water is present, its temperature cannot rise above its boiling point.* After all the water has been converted to steam, the temperature of the steam can continue to rise beyond 100 °C.

ANSWER NOW!

12.8
Cc
Conceptual Connection



BOILING POINT Use Figure 12.28 to estimate the boiling point of water at an external pressure of 200 torr.

(a) 66 °C

(b) 84 °C

(c) 100 °C

(d) 0 °C

The Clausius–Clapeyron Equation

Now, let's return our attention to Figure 12.28. As we can see from the graph, the vapor pressure of a liquid increases with increasing temperature. However, *the relationship is not linear*. In other words, doubling the temperature results in more than doubling the vapor

pressure. The relationship between vapor pressure and temperature is exponential, and we can express it as follows:

$$P_{\text{vap}} = \beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \quad [12.1]$$

In this expression P_{vap} is the vapor pressure, β is a constant that depends on the gas, ΔH_{vap} is the heat of vaporization, R is the gas constant ($8.314 \text{ J/mol} \cdot \text{K}$), and T is the temperature in kelvins. We can rearrange Equation 12.1 by taking the natural logarithm of both sides:

$$\ln P_{\text{vap}} = \ln \left[\beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right] \quad [12.2]$$

Because $\ln AB = \ln A + \ln B$, we can rearrange the right side of Equation 12.2:

$$\ln P_{\text{vap}} = \ln \beta + \ln \left[\exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right] \quad [12.3]$$

Because $\ln e^x = x$ (see Appendix IB), we can simplify Equation 12.3:

$$\ln P_{\text{vap}} = \ln \beta + \frac{-\Delta H_{\text{vap}}}{RT} \quad [12.4]$$

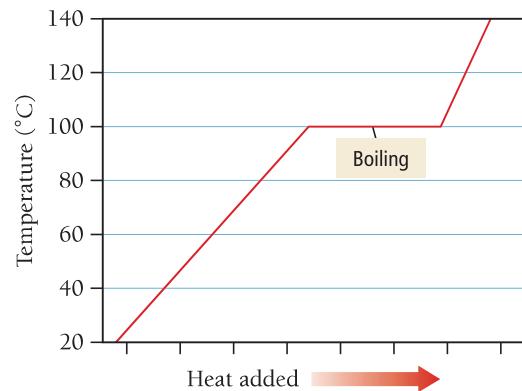
A slight additional rearrangement gives the following important result:

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + \ln \beta \quad \text{Clausius-Clapeyron equation}$$

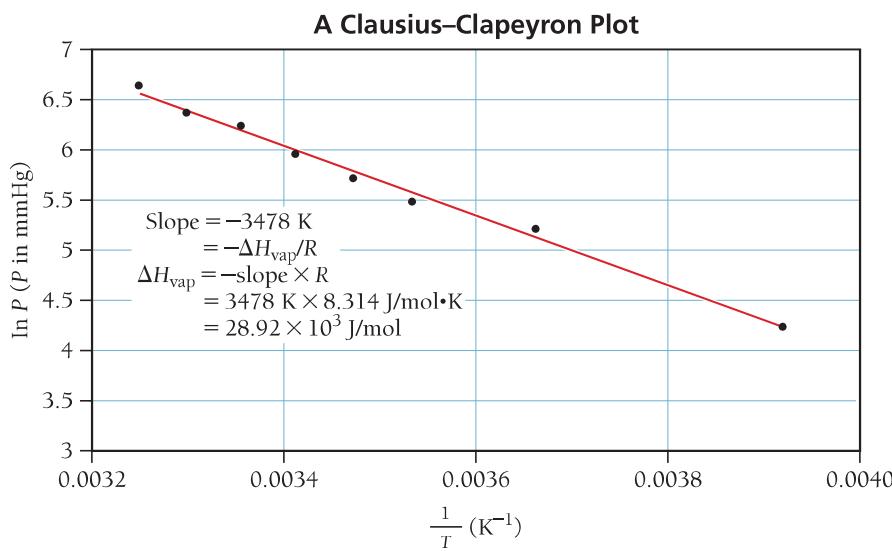
$$y = m(x) + b \quad (\text{equation for a line})$$

Notice the parallel relationship between the **Clausius-Clapeyron equation** and the equation for a straight line. Just as a plot of y versus x yields a straight line with slope m and intercept b , so a plot of $\ln P_{\text{vap}}$ (equivalent to y) versus $1/T$ (equivalent to x) gives a straight line with slope $-\Delta H_{\text{vap}}/R$ (equivalent to m) and y -intercept $\ln \beta$ (equivalent to b), as shown in Figure 12.31▼. The Clausius-Clapeyron equation gives a linear relationship—not between the vapor pressure and the temperature (which have an exponential relationship)—but between the *natural* logarithm of the vapor pressure and the *inverse* of temperature. This is a common technique in the analysis of chemical data. If two variables are not linearly related, it is often convenient to find ways to graph *functions of those variables* that are linearly related.

Using the Clausius-Clapeyron equation in this way ignores the relatively small temperature dependence of ΔH_{vap} .



▲ FIGURE 12.30 The Temperature during Boiling The temperature of water during boiling remains at 100°C .



◀ FIGURE 12.31 A Clausius-Clapeyron Plot for Diethyl Ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) A plot of the natural logarithm of the vapor pressure versus the inverse of the temperature in K yields a straight line with slope $-\Delta H_{\text{vap}}/R$.

The Clausius-Clapeyron equation leads to a convenient way to determine the heat of vaporization in the laboratory. We simply measure the vapor pressure of a liquid as a function of temperature and create a plot of the natural logarithm of the vapor pressure versus the inverse of the temperature. We then determine the slope of the line to find the heat of vaporization, as demonstrated in Example 12.4.

EXAMPLE 12.4 Using the Clausius–Clapeyron Equation to Determine Heat of Vaporization from Experimental Measurements of Vapor Pressure

The vapor pressure of dichloromethane is measured as a function of temperature, and the results are tabulated. From the results, determine the heat of vaporization of dichloromethane.

Temperature (K)	Vapor Pressure (torr)
200	0.8
220	4.5
240	21
260	71
280	197
300	391

SOLUTION

To find the heat of vaporization, use an Excel spreadsheet or a graphing calculator to plot the natural logarithm of vapor pressure ($\ln P$) as a function of the inverse of the temperature in kelvins ($1/T$). Then fit the points to a line and determine the slope of the line. The slope of the best-fitting line is -3773 K . Since the slope equals $-\Delta H_{\text{vap}}/R$, we find the heat of vaporization as follows:

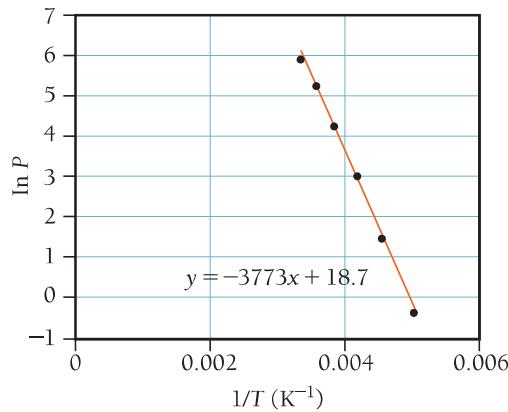
$$\text{slope} = -\Delta H_{\text{vap}}/R$$

$$\Delta H_{\text{vap}} = -\text{slope} \times R$$

$$= -(-3773 \text{ K})(8.314 \text{ J/mol} \cdot \text{K})$$

$$= 3.14 \times 10^4 \text{ J/mol}$$

$$= 31.4 \text{ kJ/mol}$$



FOR PRACTICE 12.4 The vapor pressure of carbon tetrachloride is measured as a function of the temperature, and the results are tabulated. Determine the heat of vaporization of carbon tetrachloride from the results.

Temperature (K)	Vapor Pressure (torr)
255	11.3
265	21.0
275	36.8
285	61.5
295	99.0
300	123.8

The Clausius–Clapeyron equation can also be expressed in a two-point form that we can use with just two measurements of vapor pressure and temperature to determine the heat of vaporization:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Clausius–Clapeyron equation (two-point form)}$$

The two-point method is generally inferior to plotting multiple points because fewer data points result in more chance for error.

We can use this form of the equation to predict the vapor pressure of a liquid at any temperature if we know the enthalpy of vaporization and the normal boiling point (or the vapor pressure at some other temperature), as demonstrated in Example 12.5.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 12.5

EXAMPLE 12.5

Using the Two-Point Form of the Clausius–Clapeyron Equation to Predict the Vapor Pressure at a Given Temperature



Methanol has a normal boiling point of 64.6 °C and a heat of vaporization (ΔH_{vap}) of 35.2 kJ/mol. What is the vapor pressure of methanol at 12.0 °C?

SORT You are given the normal boiling point of methanol (the temperature at which the vapor pressure is 760 mmHg) and the heat of vaporization. You are asked to find the vapor pressure at a specified temperature that is also given.

GIVEN: $T_1(\text{°C}) = 64.6 \text{ °C}$
 $P_1 = 760 \text{ torr}$
 $\Delta H_{\text{vap}} = 35.2 \text{ kJ/mol}$
 $T_2(\text{°C}) = 12.0 \text{ °C}$

FIND: P_2

STRATEGIZE The conceptual plan is essentially the Clausius–Clapeyron equation, which relates the given and find quantities.

CONCEPTUAL PLAN

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(Clausius–Clapeyron equation, two-point form)

SOLVE First, convert T_1 and T_2 from °C to K.

SOLUTION

$$\begin{aligned} T_1(\text{K}) &= T_1(\text{°C}) + 273.15 \\ &= 64.6 + 273.15 \\ &= 337.8 \text{ K} \\ T_2(\text{K}) &= T_2(\text{°C}) + 273.15 \\ &= 12.0 + 273.15 \\ &= 285.2 \text{ K} \end{aligned}$$

Then, substitute the required values into the Clausius–Clapeyron equation and solve for P_2 .

$$\begin{aligned} \ln \frac{P_2}{P_1} &= \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{P_2}{P_1} &= \frac{-35.2 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{285.2 \text{ K}} - \frac{1}{337.8 \text{ K}} \right) \\ &= -2.31 \end{aligned}$$

In order to isolate P_2 , you must take the inverse natural logarithm (or inv ln) of $\ln(P_2/P_1)$. Remember that $\text{inv ln}(\ln x) = x$.

$$\begin{aligned} \frac{P_2}{P_1} &= e^{-2.31} \\ P_2 &= P_1(e^{-2.31}) \\ &= 760 \text{ torr}(0.0993) \\ &= 75.4 \text{ torr} \end{aligned}$$

CHECK The units of the answer are correct. The magnitude of the answer makes sense because vapor pressure should be significantly lower at the lower temperature.

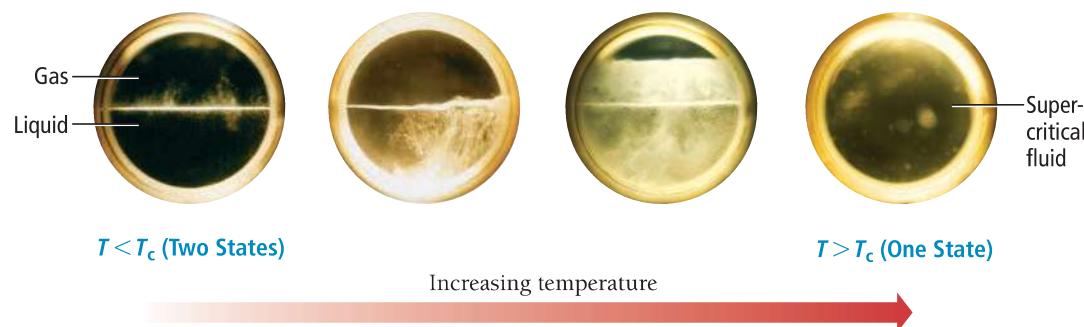
FOR PRACTICE 12.5 Propane has a normal boiling point of –42.0 °C and a heat of vaporization (ΔH_{vap}) of 19.04 kJ/mol. What is the vapor pressure of propane at 25.0 °C?

The Critical Point: The Transition to an Unusual State of Matter

We have considered the vaporization of a liquid in a container open to the atmosphere with and without heating, and the vaporization of a liquid in a *sealed* container without heating. We now examine the vaporization of a liquid in a *sealed* container *during heating*.

Consider liquid *n*-pentane in equilibrium with its vapor in a sealed container initially at 25 °C. At this temperature, the vapor pressure of *n*-pentane is 0.67 atm. What happens if we heat the liquid? As the temperature rises, more *n*-pentane vaporizes and the pressure within the container increases. At 100 °C, the pressure is 5.5 atm, and at

190 °C the pressure is 29 atm. As the temperature and pressure increase, more and more gaseous *n*-pentane is forced into the same amount of space, and the density of the *gas* gets higher and higher. At the same time, the increasing temperature causes the density of the *liquid* to become lower and lower. At 197 °C, the meniscus between the liquid and gaseous *n*-pentane disappears, and the gas and liquid states commingle to form a *supercritical fluid* (Figure 12.32▼). For any substance, the *temperature* at which this transition occurs is the **critical temperature (T_c)**. The liquid cannot exist (regardless of pressure) above this temperature. The *pressure* at which this transition occurs is the **critical pressure (P_c)**.



▲ FIGURE 12.32 Critical Point Transition As *n*-pentane is heated in a sealed container, it undergoes a transition to a supercritical fluid. At the critical point, the meniscus separating the liquid and gas disappears, and the fluid becomes supercritical—neither a liquid nor a gas.

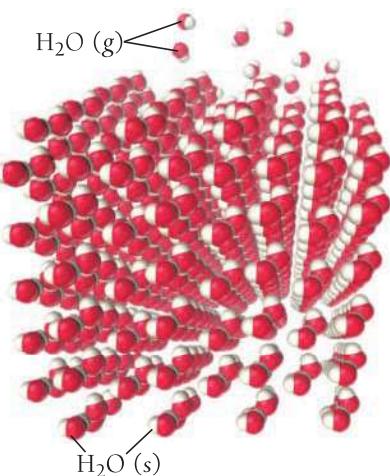
Researchers are interested in supercritical fluids because of their unique properties. A supercritical fluid has properties of both liquids and gases—it is in some sense intermediate between the two. Supercritical fluids can act as good solvents, selectively dissolving a number of compounds. For example, supercritical carbon dioxide is used as a solvent to extract caffeine from coffee beans. The caffeine dissolves in the supercritical carbon dioxide, but other substances—such as those responsible for the flavor of coffee—do not. Consequently, the caffeine is removed, and the flavor of the coffee is not substantially altered. The supercritical carbon dioxide is easily removed from the mixture by simply lowering the pressure below the critical pressure, at which point the carbon dioxide evaporates, leaving no residue.

12.6 Sublimation and Fusion

In Section 12.5, we examined a beaker of liquid water at room temperature from the molecular viewpoint. Now, let's examine a block of ice at –10 °C from the same molecular perspective, paying close attention to two common processes: sublimation and fusion.

Sublimation

Even though a block of ice is solid, the water molecules in the ice have thermal energy, which causes each one to vibrate about a fixed point. The motion is much less vigorous than that in a liquid, but it is significant nonetheless. As in liquids, at any instant some molecules in the block of ice have more thermal energy than the average and some have less. The molecules with high enough thermal energy can break free from the ice surface—where, as in liquids, molecules are held less tightly than in the interior due to fewer neighbor-neighbor interactions—and go directly into the gas state (Figure 12.33◀). This process is **sublimation**, the transition from solid to gas. Some of the water molecules in the gas state (those at the low end of the energy distribution curve for the gaseous molecules) collide with the surface of the ice and are captured by the intermolecular forces with other molecules. This process—the opposite of sublimation—is **deposition**, the transition from gas to solid. As is the case with liquids, the pressure of a gas in dynamic equilibrium with its solid is the vapor pressure of the solid.



▲ FIGURE 12.33 The Sublimation of Ice The water molecules at the surface of an ice cube can sublime directly into the gas state.

Although both sublimation and deposition occur on the surface of an ice block open to the atmosphere at $-10\text{ }^{\circ}\text{C}$, sublimation usually occurs at a greater rate than deposition because most of the newly sublimed molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the size of the ice block over time (even though the temperature is below the melting point).

If you live in a cold climate, you may have noticed the disappearance of ice and snow from the ground even though the temperature remains below $0\text{ }^{\circ}\text{C}$. Similarly, ice cubes left in the freezer for a long time slowly shrink, even though the freezer is always below $0\text{ }^{\circ}\text{C}$. In both cases, the ice is *subliming*, turning directly into water vapor. Ice also sublimes out of frozen foods. You may have noticed, for example, the gradual growth of ice crystals on the *inside* of airtight plastic food-storage bags in a freezer. The ice crystals are composed of water that has sublimed out of the food and redeposited on the surface of the bag or on the surface of the food. For this reason, food that remains frozen for too long becomes dried out. Such dehydration can be avoided to some degree by freezing foods to colder temperatures, a process called deep-freezing. The colder temperature lowers the vapor pressure of ice and preserves the food longer. Freezer burn on meats is another common manifestation of sublimation. When you improperly store meat (for example, in a container that is not airtight) sublimation continues unabated. The result is the dehydration of the surface of the meat, which becomes discolored and loses flavor and texture.

A substance commonly associated with sublimation is solid carbon dioxide or dry ice, which does not melt under atmospheric pressure no matter what the temperature is. However, at $-78\text{ }^{\circ}\text{C}$ the CO_2 molecules have enough energy to leave the surface of the dry ice and become gaseous through sublimation.

Fusion

Let's return to our ice block and examine what happens at the molecular level as we increase its temperature. The increasing thermal energy causes the water molecules to vibrate faster and faster. At the **melting point** ($0\text{ }^{\circ}\text{C}$ for water), the molecules have enough thermal energy to overcome the intermolecular forces that hold the molecules at their stationary points, and the solid turns into a liquid. This process is **melting** or **fusion**, the transition from solid to liquid. The opposite of melting is **freezing**, the transition from liquid to solid. Once the melting point of a solid is reached, additional heating only causes more rapid melting; it does not raise the temperature of the solid above its melting point (Figure 12.34►). Only after all of the ice has melted will additional heating raise the temperature of the liquid water past $0\text{ }^{\circ}\text{C}$. A mixture of water *and* ice always has a temperature of $0\text{ }^{\circ}\text{C}$ (at 1 atm pressure).

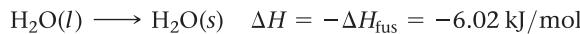
Energetics of Melting and Freezing

The most common way to cool a beverage quickly is to drop several ice cubes into it. As the ice melts, the drink cools because melting is endothermic—the melting ice absorbs heat from the liquid. The amount of heat required to melt 1 mol of a solid is the **heat of fusion** (ΔH_{fus}). The heat of fusion for water is 6.02 kJ/mol:

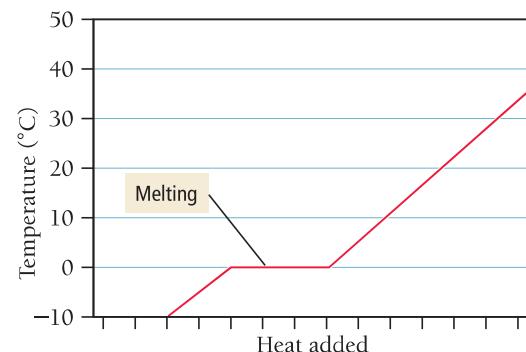


The heat of fusion is positive because melting is endothermic.

Freezing, the opposite of melting, is exothermic—heat is released when a liquid freezes into a solid. For example, as water in the freezer turns into ice, it releases heat, which must be removed by the refrigeration system of the freezer. If the refrigeration system did not remove the heat, the water would not completely freeze into ice. The heat released as the water began to freeze would warm the freezer, preventing further freezing. The change in enthalpy for freezing has the same magnitude as the heat of fusion but the opposite sign:



▲ Dry ice (solid CO_2) sublimes but does not melt at atmospheric pressure.



▲ FIGURE 12.34 Temperature during Melting

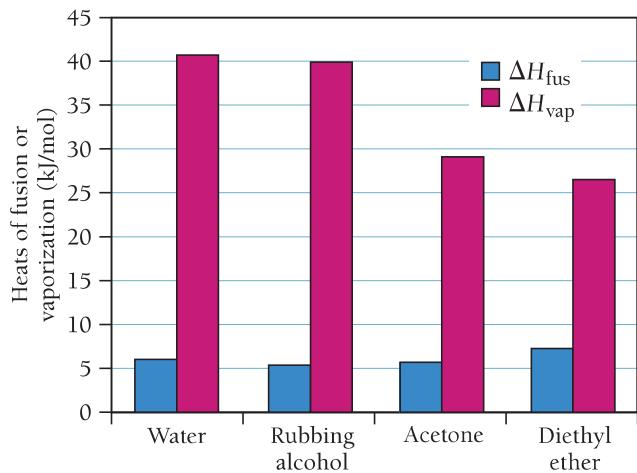
The temperature of water during melting remains at $0.0\text{ }^{\circ}\text{C}$ as long as both solid and liquid water remain.

The term *fusion* is used for melting because if we heat several crystals of a solid, they fuse into a continuous liquid upon melting.

Different substances have different heats of fusion as listed in Table 12.9.

TABLE 12.9 ■ Heats of Fusion of Several Substances

Liquid	Chemical Formula	Melting Point (°C)	ΔH_{fus} (kJ/mol)
Water	H ₂ O	0.00	6.02
Isopropyl alcohol	C ₃ H ₈ O	-89.5	5.37
Acetone	C ₃ H ₆ O	-94.8	5.69
Diethyl ether	C ₄ H ₁₀ O	-116.3	7.27



▲ FIGURE 12.35 Heat of Fusion and Heat of Vaporization Typical heats of fusion are significantly less than heats of vaporization.

In general, the heat of fusion for a substance is significantly less than its heat of vaporization (Figure 12.35). We have already seen that the solid and liquid states are closer to each other in many ways than they are to the gas state. It takes less energy to melt 1 mol of ice into liquid than it does to vaporize 1 mol of liquid water into gas because vaporization requires complete separation of molecules from one another, so the intermolecular forces must be completely overcome. Melting, in contrast, requires that intermolecular forces be only partially overcome, allowing molecules to move around one another while still remaining in contact.

The amount of heat required to sublime one mole of a solid to a gas is its **heat (or enthalpy) of sublimation (ΔH_{sub})**. Since enthalpy is a state function, the change in enthalpy of any two-step process is simply the sum of the changes in enthalpies of each step. Because the sublimation of a substance is equivalent to its fusion followed by its vaporization, the heat of sublimation is the sum of the heat of fusion and the heat of vaporization. For water, we calculate the heat of sublimation at 0 °C as follows:

$$\begin{aligned}\Delta H_{\text{sub}} &= \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \\ &= 6.01 \text{ kJ/mol} + 40.7 \text{ kJ/mol} \\ &= 46.7 \text{ kJ/mol}\end{aligned}$$

WATCH NOW!

KEY CONCEPT VIDEO 12.7

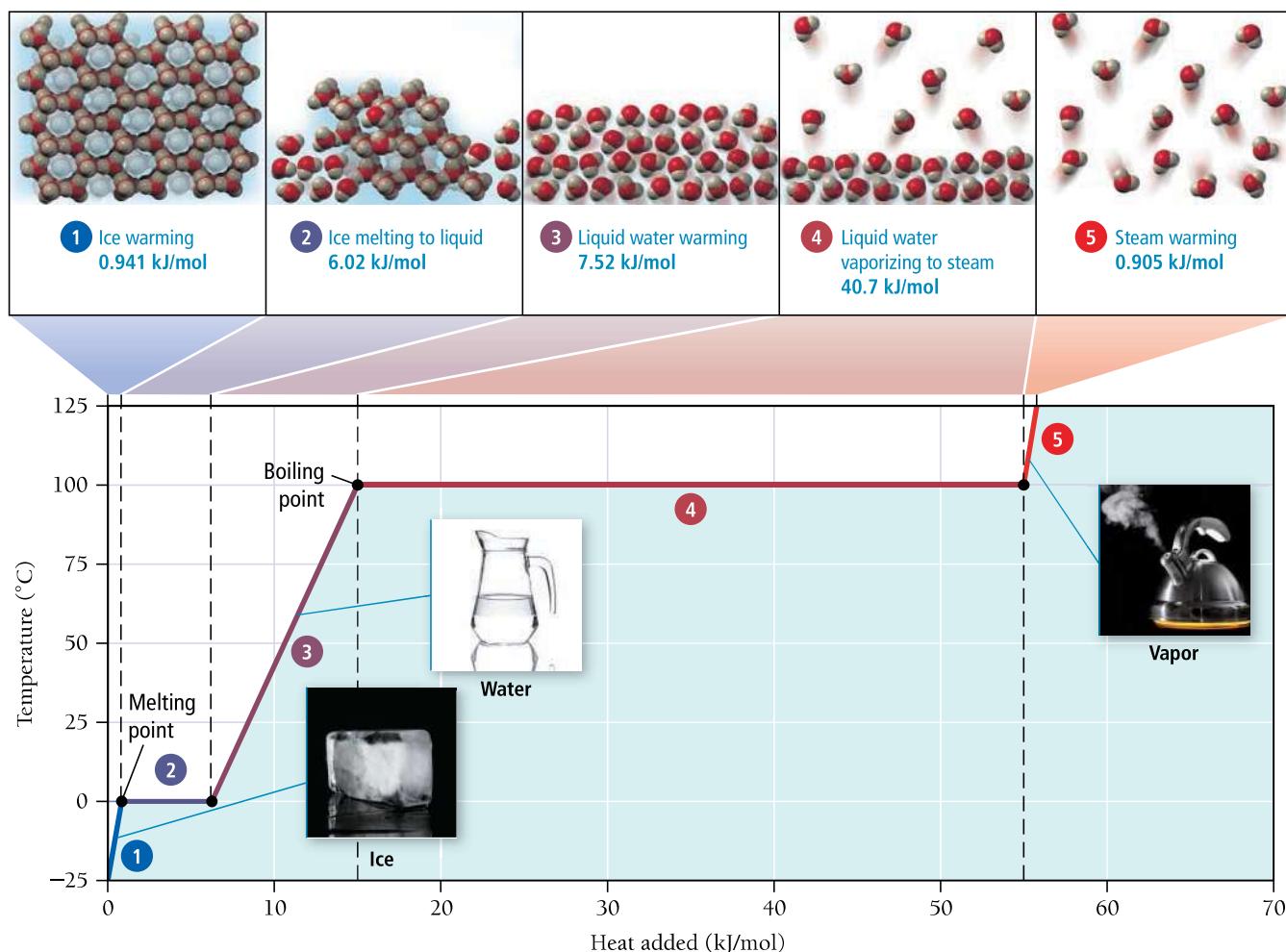
Heating Curve for Water

12.7

Heating Curve for Water

We can combine and build on the concepts from Sections 12.5 and 12.6 by examining the *heating curve* for 1.00 mol of water at 1.00 atm pressure shown in Figure 12.36. The *y*-axis of the heating curve represents the temperature of the water sample. The *x*-axis represents the amount of heat added (in kilojoules) during heating. In the diagram, we divide the process into five segments: (1) ice warming; (2) ice melting into liquid water; (3) liquid water warming; (4) liquid water vaporizing into steam; and (5) steam warming.

In two of these segments (2 and 4), the temperature is constant as heat is added because the added heat goes into producing the transition between states, not into increasing the temperature. The two states are in equilibrium during the transition, and the temperature remains constant. The amount of heat required to achieve the state change is given by $q = n\Delta H$.



▲ FIGURE 12.36 Heating Curve for Water

In the other three segments (1, 3, and 5), temperature increases linearly. These segments represent the heating of a single state in which the deposited heat raises the temperature in accordance with the substance's heat capacity ($q = mC_s \Delta T$). We examine each of these segments individually.

Segment 1

In segment 1, solid ice is warmed from -25°C to 0°C . Since no transition between states occurs here, the amount of heat required to heat the solid ice is given by $q = mC_s \Delta T$ (see Section 7.4), where C_s is the specific heat capacity of ice ($C_{s,\text{ice}} = 2.09\text{ J/g} \cdot ^{\circ}\text{C}$). For 1.00 mol of water (18.0 g), we calculate the amount of heat as follows:

$$\begin{aligned} q &= mC_{s,\text{ice}} \Delta T \\ &= 18.0\text{ g} \left(2.09 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \right) [0.0^{\circ}\text{C} - (-25.0^{\circ}\text{C})] \\ &= 941\text{ J} = 0.941\text{ kJ} \end{aligned}$$

So in segment 1, 0.941 kJ of heat is added to the ice, warming it from -25°C to 0°C .

Segment 2

In segment 2, the added heat does not change the temperature of the ice and water mixture because the heat is absorbed by the transition from solid to liquid. The amount of

heat required to convert the ice to liquid water is given by $q = n \Delta H_{\text{fus}}$, where n is the number of moles of water and ΔH_{fus} is the heat of fusion (see Section 12.6):

$$\begin{aligned} q &= n \Delta H_{\text{fus}} \\ &= 1.00 \text{ mol} \left(\frac{6.02 \text{ kJ}}{\text{mol}} \right) \\ &= 6.02 \text{ kJ} \end{aligned}$$

In segment 2, 6.02 kJ is added to the ice, melting it into liquid water. Notice that the temperature does not change during melting. The liquid and solid coexist at 0 °C as the melting occurs.

Segment 3

In segment 3, the liquid water warms from 0 °C to 100 °C. Since no transition between states occurs here, the amount of heat required to heat the liquid water is given by $q = mC_s \Delta T$, as in segment 1. However, now we must use the heat capacity of liquid water (not ice) for the calculation. For 1.00 mol of water (18.0 g), we calculate the amount of heat as follows:

$$\begin{aligned} q &= mC_{s, \text{liq}} \Delta T \\ &= 18.0 \text{ g} \left(4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (100.0^\circ\text{C} - 0.0^\circ\text{C}) \\ &= 7.52 \times 10^3 \text{ J} = 7.52 \text{ kJ} \end{aligned}$$

So in segment 3, 7.52 kJ of heat is added to the liquid water, warming it from 0 °C to 100 °C.

Segment 4

In segment 4, the water undergoes a second transition between states, this time from liquid to gas. The amount of heat required to convert the liquid to gas is given by $q = n \Delta H_{\text{vap}}$, where n is the number of moles and ΔH_{vap} is the heat of vaporization (see Section 12.5):

$$\begin{aligned} q &= n \Delta H_{\text{vap}} \\ &= 1.00 \text{ mol} \left(\frac{40.7 \text{ kJ}}{\text{mol}} \right) \\ &= 40.7 \text{ kJ} \end{aligned}$$

Thus, in segment 4, 40.7 kJ is added to the water, vaporizing it into steam. Notice that the temperature does not change during boiling. The liquid and gas coexist at 100 °C as the boiling occurs.

Segment 5

In segment 5, the steam warms from 100 °C to 125 °C. Since no transition between states occurs here, the amount of heat required to heat the steam is given by $q = mC_s \Delta T$ (as in segments 1 and 3) except that we must use the heat capacity of steam (2.01 J/g · °C):

$$\begin{aligned} q &= mC_{s, \text{steam}} \Delta T \\ &= 18.0 \text{ g} \left(2.01 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (125.0^\circ\text{C} - 100.0^\circ\text{C}) \\ &= 905 \text{ J} = 0.905 \text{ kJ} \end{aligned}$$

So in segment 5, 0.905 kJ of heat is added to the steam, warming it from 100 °C to 125 °C.

COOLING OF WATER WITH ICE You just saw that the heat capacity of ice is $C_{s,\text{ice}} = 2.09 \text{ J/g} \cdot ^\circ\text{C}$ and that the heat of fusion of ice is 6.02 kJ/mol. When a small ice cube at -10°C is put into a cup of water at room temperature, which of the following plays a greater role in cooling the liquid water: the warming of the ice from -10°C to 0°C , or the melting of the ice?

- (a) the warming of the ice from -10°C to 0°C
- (b) the melting of the ice



ANSWER NOW!



12.8

Phase Diagrams

Throughout most of this chapter, we have examined how the state of a substance changes in response to changes in temperature and pressure. We can combine both the temperature dependence and pressure dependence of the state of a particular substance in a graph called a *phase diagram*. A **phase diagram** is a map of the state or *phase* of a substance as a function of pressure (on the *y*-axis) and temperature (on the *x*-axis). In this section, we first examine the major features of a phase diagram, then turn to navigating within a phase diagram, and finally examine and compare the phase diagrams of selected substances.

WATCH NOW!

KEY CONCEPT VIDEO 12.8

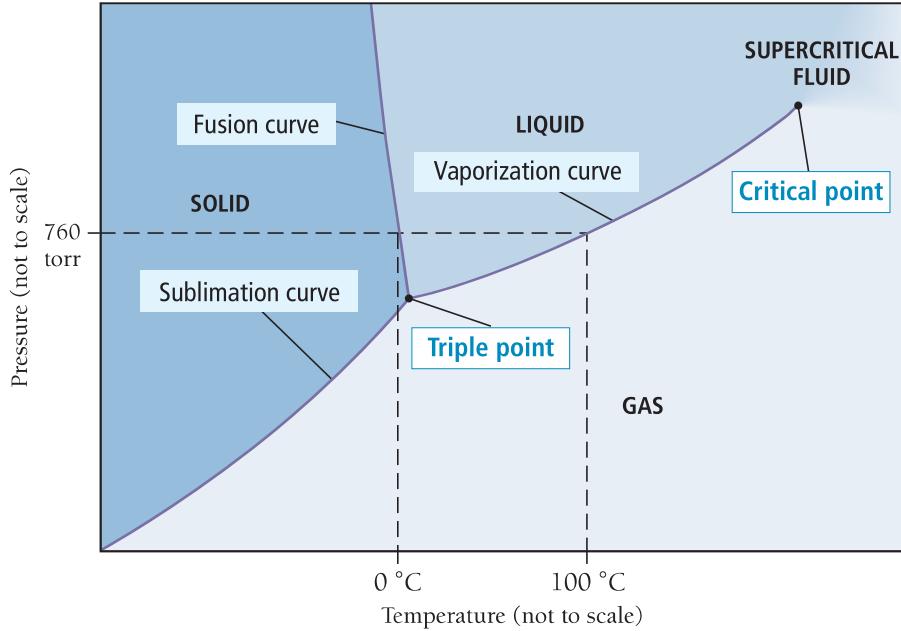
Phase Diagrams

The Major Features of a Phase Diagram

We can introduce the major features of a phase diagram by examining the phase diagram for water as an example (Figure 12.37▼). The *y*-axis displays the pressure in torr, and the *x*-axis displays the temperature in degrees Celsius. We categorize the main features of the phase diagram as regions, lines, and points.

Phase Diagram for Water

◀ FIGURE 12.37 Phase Diagram for Water



Regions

Each of the three main regions—solid, liquid, and gas—in the phase diagram represents conditions under which that particular state is stable. For example, under any of the temperatures and pressures within the liquid region in the phase diagram of water, the liquid is the stable state. Notice that the point 25°C and 760 torr falls within the liquid region, as we know

from everyday experience. In general, low temperature and high pressure favor the solid state, high temperature and low pressure favor the gas state, and intermediate conditions favor the liquid state. A sample of matter that is not in the state indicated by its phase diagram for a given set of conditions converts to that state when those conditions are imposed. For example, steam that is cooled to room temperature at 1 atm condenses to liquid.

Lines

Each of the lines (or curves) in the phase diagram represents a set of temperatures and pressures at which the substance is in equilibrium between the two states on either side of the line. In the phase diagram for water shown in Figure 12.37, consider the curved line beginning just beyond 0 °C separating the liquid from the gas. This line is the vaporization curve (also called the vapor pressure curve) for water that we examined in Section 12.5. At any of the temperatures and pressures that fall along this line, the liquid and gas states of water are equally stable and in equilibrium. For example, at 100 °C and 760 torr pressure, water and its vapor are in equilibrium—they are equally stable and coexist. The other two major lines in a phase diagram are the sublimation curve (separating the solid and the gas) and the fusion curve (separating the solid and the liquid).

The Triple Point

The triple point of a substance such as water can be reproduced anywhere to calibrate a thermometer or pressure gauge with a known temperature and pressure.

The triple point in a phase diagram represents the unique set of conditions at which the three states are equally stable and in equilibrium. In the phase diagram for water, the triple point occurs at 0.0098 °C and 4.58 torr. Under these unique conditions (and only under these conditions), the solid, liquid, and gas states of water are equally stable and coexist in equilibrium.

The Critical Point

As we discussed in Section 12.5, at the critical temperature and pressure, the liquid and gas states coalesce into a supercritical fluid. The **critical point** in a phase diagram represents the temperature and pressure above which a supercritical fluid exists.

Navigation within a Phase Diagram

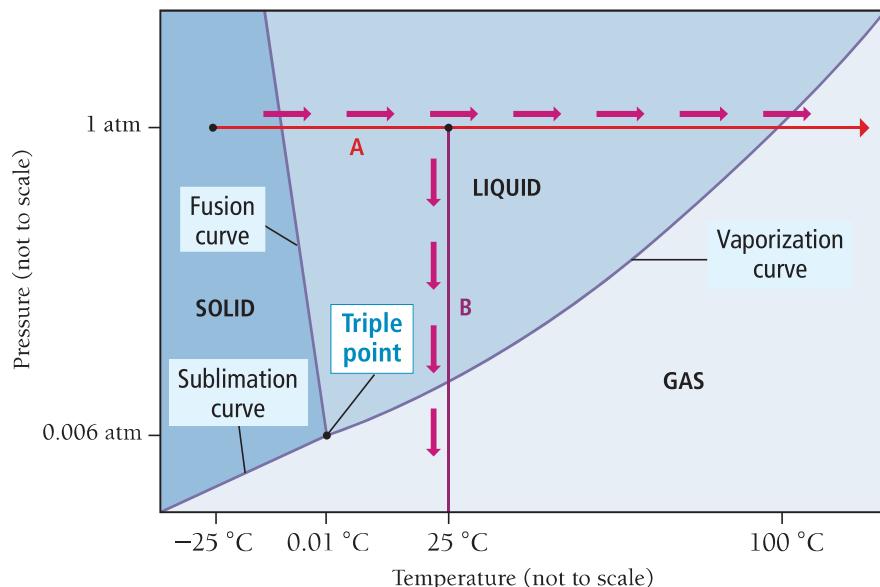
We can represent changes in the temperature or pressure of a sample of water as movement within the phase diagram. For example, suppose we heat a block of ice initially at 1.0 atm and –25 °C. We represent the change in temperature at constant pressure as movement along the line marked A in Figure 12.38▼. As the temperature rises, we move to the right along the line. At the fusion curve, the temperature stops rising,

and melting occurs until the solid ice is completely converted to liquid water. Crossing the fusion curve requires the complete transition from solid to liquid. Once the ice has completely melted, the temperature of the liquid water can begin to rise until the vaporization curve is reached. At this point, the temperature again stops rising and boiling occurs until all the liquid is converted to gas.

We represent a change in pressure with a vertical line on the phase diagram. For example, suppose we lower the pressure above a sample of water initially at 1.0 atm and 25 °C. We represent the change in pressure at constant temperature as movement along the line marked B in Figure 12.38. As the pressure drops, we move down the line and approach the vaporization curve. At the

▼ FIGURE 12.38 Navigation on the Phase Diagram for Water

Navigation within a Phase Diagram



vaporization curve, the pressure stops dropping and vaporization occurs until the liquid completely converts to vapor. Crossing the vaporization curve requires the complete transition from liquid to gas. Only after all the liquid has vaporized can the pressure continue to drop.

The Phase Diagrams of Other Substances

Next, let's examine the phase diagrams of iodine and carbon dioxide in Figure 12.39►. The phase diagrams are similar to the diagram of water in most of their general features, but some significant differences exist.

Note that the fusion curves for both carbon dioxide and iodine have a positive slope—as the temperature increases, the pressure also increases—in contrast to the fusion curve for water, which has a negative slope. The behavior of water is atypical. The fusion curve within the phase diagrams for most substances has a positive slope because increasing pressure favors the denser state, which for most substances is the solid state.

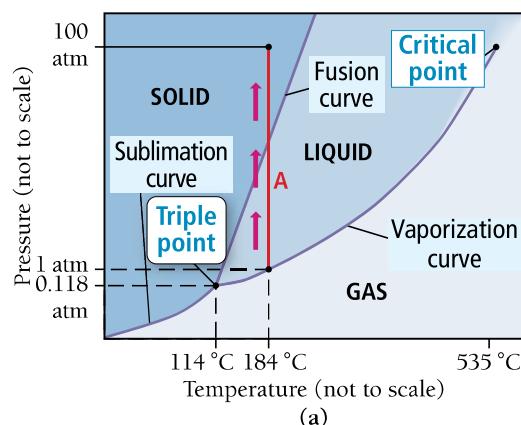
For example, suppose we increase the pressure on a sample of iodine from 1 atm to 100 atm at 184 °C, as shown by line A in Figure 12.39(a). Notice that this change crosses the fusion curve, converting the liquid into a solid. In contrast, a pressure increase from 1 atm to 100 atm at −0.1 °C in water causes a state transition from solid to liquid. Unlike most substances, the liquid state of water is actually denser than the solid state.

Both water and iodine have stable solid, liquid, and gaseous states at a pressure of 1 atm. However, notice that carbon dioxide has no stable liquid state at a pressure of 1 atm. If we increase the temperature of a block of solid carbon dioxide (dry ice) at 1 atm, as indicated by line B in Figure 12.39(b), we cross the sublimation curve at −78.5 °C. At this temperature, the solid sublimes to a gas, which is one reason that dry ice is useful (it does not melt into a liquid at atmospheric pressure). Carbon dioxide forms a liquid only above pressures of 5.1 atm.

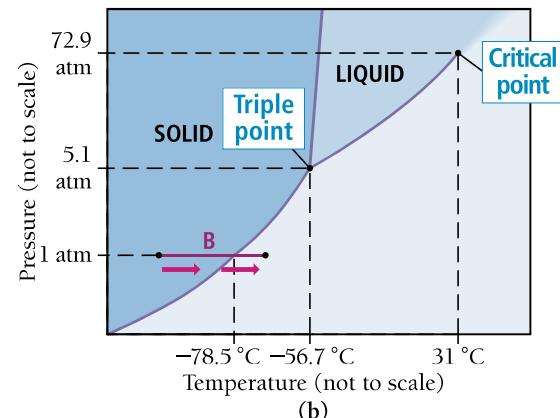
PHASE DIAGRAMS A substance has a triple point at −24.5 °C and 225 mmHg. What is most likely to happen to a solid sample of the substance as it is warmed from −35 °C to 0 °C at a pressure of 220 mmHg?

- (a) The solid melts into a liquid.
- (b) The solid sublimes into a gas.
- (c) Nothing (the solid remains solid).

Iodine



Carbon Dioxide



▲ FIGURE 12.39 Phase Diagrams for Other Substances (a) Iodine, (b) Carbon dioxide.

12.9

Water: An Extraordinary Substance

Water is the most common and important liquid on Earth. It fills our oceans, lakes, and streams. In its solid form, it caps our mountains, and in its gaseous form, it humidifies our air. We drink water, we sweat water, and we excrete bodily wastes dissolved in water. Indeed, the majority of our body mass *is* water. Life is impossible without water, and in most places on Earth where liquid water exists, life exists. Recent evidence for the existence of water on Mars has fueled hopes of finding life or evidence of past life there. And though it may not be obvious to us (because we take water for granted), this familiar substance has many remarkable properties.



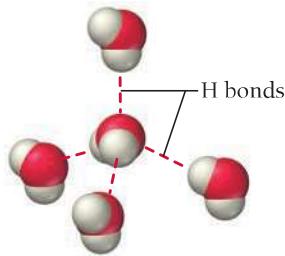
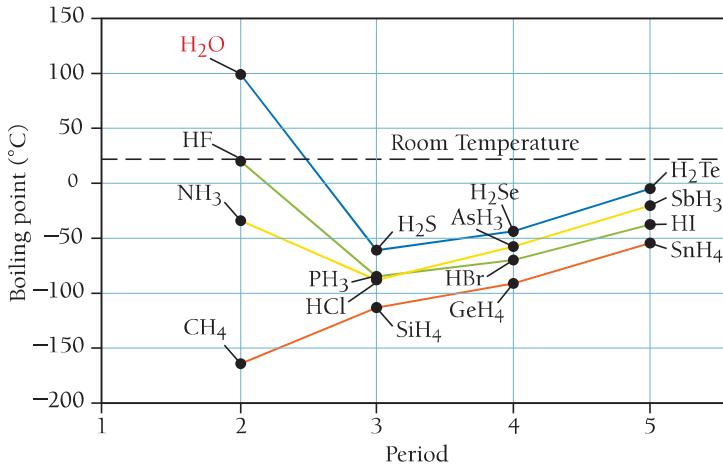
ANSWER NOW!



▲ The European Space Agency (ESA) Mars Express Orbiter detected the presence of liquid water under the ice and dust on the planet's south pole.

Among liquids, water is unique. It has a low molar mass (18.02 g/mol), yet it is a liquid at room temperature. Other main-group hydrides have higher molar masses but lower boiling points, as shown in Figure 12.40▼. No other substance of similar molar mass (except HF) comes close to being a liquid at room temperature.

► **FIGURE 12.40 Boiling Points of Main-Group Hydrides** Water is the only common main-group hydride that is a liquid at room temperature.



▲ **FIGURE 12.41 Hydrogen Bonding in Water** A water molecule can form four strong hydrogen bonds with four other water molecules.



▲ When lettuce freezes, the water within its cells expands, rupturing them.

We can understand water's high boiling point (in spite of its low molar mass) by examining its molecular structure. The bent geometry of the water molecule and the highly polar nature of the O—H bonds result in a molecule with a significant dipole moment. Water's two O—H bonds (hydrogen directly bonded to oxygen) allow a water molecule to form strong hydrogen bonds with four other water molecules (Figure 12.41◀), resulting in a relatively high boiling point.

Water's high polarity allows it to dissolve many other polar and ionic compounds and even a number of nonpolar gases such as oxygen and carbon dioxide (by inducing a dipole moment in their molecules). Consequently, water is the main solvent within living organisms, transporting nutrients and other important compounds throughout the body. Water is the main solvent in our environment as well, allowing aquatic animals, for example, to survive by breathing dissolved oxygen and allowing aquatic plants to survive by using dissolved carbon dioxide for photosynthesis.

Recall from Section 7.4 that water has an exceptionally high specific heat capacity, which has a moderating effect on the climate of coastal cities. In some cities, such as San Francisco, for example, the daily fluctuation in temperature can be less than 10 °C. This same moderating effect occurs over the entire planet, two-thirds of which is covered by water. Without water, the daily temperature fluctuations on our planet might be more like those on Mars, where temperatures fluctuate 63 °C (113 °F) between midday and early morning. Imagine awakening to below-freezing temperatures, only to bake at summer desert temperatures in the afternoon! The presence of water on Earth and water's uniquely high specific heat capacity are largely responsible for our planet's much smaller daily fluctuations.

As we have discussed, the way water freezes is also unique. Unlike other substances, which contract upon freezing, water expands upon freezing. Consequently, ice is less dense than liquid water, which is why ice floats. This seemingly trivial property has significant consequences. The frozen layer of ice at the surface of a winter lake insulates the water in the lake from further freezing. If this ice layer sank, it would kill bottom-dwelling aquatic life and possibly allow the lake to freeze solid, eliminating virtually all life in the lake.

The expansion of water upon freezing, however, is one reason that most organisms do not survive freezing. When the water within a cell freezes, it expands and often ruptures the cell, just as water freezing within a pipe bursts the pipe. Many foods, especially those with high water content, do not survive freezing very well either. Have you ever tried, for example, to freeze your own vegetables? If you put lettuce or spinach in the freezer, it will be limp and damaged upon thawing. The frozen-food industry gets around this problem by *flash freezing* vegetables and other foods. In this process, foods are frozen nearly instantaneously, which prevents water molecules from settling into their preferred crystalline structure. Consequently, the water does not expand very much, and the food remains largely undamaged.



Water quality is critical to human health. Many human diseases—especially in developing nations—are caused by poor water quality. Several kinds of pollutants, including biological and chemical contaminants, can enter water supplies.



◀ Uncontaminated, sanitary water supplies are critical to human health.

Biological contaminants are microorganisms that cause diseases such as hepatitis, cholera, dysentery, and typhoid. They get into drinking water primarily when human or animal waste is dumped into bodies of water. Drinking water in developed nations is usually chemically treated to kill microorganisms. Water containing

biological contaminants poses an immediate danger to human health and should not be consumed. Boiling eliminates most biological contaminants from untreated water.

Chemical contaminants enter drinking water supplies as a result of industrial dumping, pesticide and fertilizer use, and household dumping. These contaminants include organic compounds, such as carbon tetrachloride and dioxin, and inorganic elements and compounds, such as mercury, lead, and nitrates. Because many chemical contaminants are neither volatile nor alive (like biological contaminants are), they are usually not eliminated through boiling.

The U.S. Environmental Protection Agency (EPA), under the Safe Drinking Water Act of 1974 and its amendments, sets standards that specify the maximum contamination level (MCL) of nearly 100 biological and chemical contaminants in water. Water providers that serve more than 25 people must periodically test the water they deliver to their consumers for these contaminants. If levels exceed the standards set by the EPA, the water provider must notify consumers and take appropriate measures to remove the contaminant from the water. According to the EPA, water from providers that serve more than 25 people should be safe to consume over a lifetime. If it is not safe to drink for a short period of time, providers must notify consumers.

QUESTION Why doesn't boiling eliminate nonvolatile contaminants such as lead?



QUIZ YOURSELF NOW!

Self-Assessment Quiz



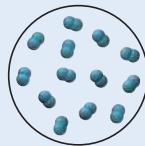
Q1. Which state of matter is compressible?

MISSED THIS? Read Section 12.2

- a) gas
- b) liquid
- c) solid
- d) none of the above

Q2. Liquid nitrogen boils at 77 K. The image shown below depicts a sample of liquid nitrogen.

MISSED THIS? Read Section 12.2



Which image best depicts the nitrogen after it has boiled?

- a)
- b)
- c)
- d)

Q3. Based on the expected intermolecular forces, which halogen has the highest boiling point?

MISSED THIS? Read Section 12.3; Watch KCV 12.3

- a) F₂
- b) Cl₂
- c) Br₂
- d) I₂

Q4. Which substance experiences dipole–dipole forces?

MISSED THIS? Read Section 12.3; Watch KCV 12.3, IWE 12.1

- a) CCl₄
- b) NF₃
- c) CS₂
- d) SO₃

Q5. One of these substances is a liquid at room temperature. Which one?

MISSED THIS? Read Section 12.3; Watch KCV 12.3, IWE 12.2

- a) CH₃OH
- b) CF₄
- c) SiH₄
- d) CO₂

Q6. Which property of a liquid increases with increasing temperature?

MISSED THIS? Read Sections 12.4, 12.5; Watch KCV 12.5

- a) surface tension
- b) viscosity
- c) vapor pressure
- d) none of the above

Q7. Determine the amount of heat (in kJ) required to vaporize 1.55 kg of water at its boiling point. For water, $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$ (at 100 °C).

MISSED THIS? Read Section 12.5; Watch KCV 12.5, IWE 12.3

- a) $3.50 \times 10^3 \text{ kJ}$
- b) $1.14 \times 10^6 \text{ kJ}$
- c) 2.11 kJ
- d) 686 kJ

—Continued on the next page

Continued—

- Q8.** The vapor pressure of a substance is measured over a range of temperatures. A plot of the natural log of the vapor pressure versus the inverse of the temperature (in kelvin) produces a straight line with a slope of -3.46×10^3 K. Find the enthalpy of vaporization of the substance.

MISSED THIS? Read Section 12.5

- 2.40×10^{-3} kJ/mol
- 28.8 kJ/mol
- 0.416 kJ/mol
- 3.22 kJ/mol

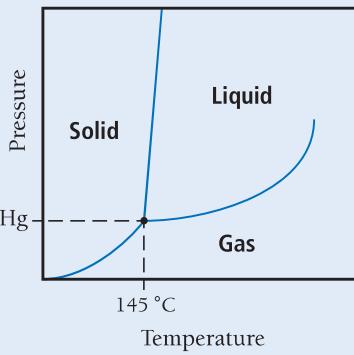
- Q9.** Acetic acid has a normal boiling point of 118 °C and a ΔH_{vap} of 23.4 kJ/mol. What is the vapor pressure (in mmHg) of acetic acid at 25 °C?

MISSED THIS? Read Section 12.5; Watch IWE 12.5

- 2.92×10^{-39} mmHg
- 7.16×10^3 mmHg
- 758 mmHg
- 80.6 mmHg

- Q10.** Consider the phase diagram shown here. A sample of the substance in the phase diagram is initially at 175 °C and 925 mmHg. What phase transition occurs when the pressure is decreased to 760 mmHg at constant temperature?

MISSED THIS? Read Section 12.8; Watch KCV 12.8



- solid to liquid
- liquid to gas
- solid to gas
- liquid to solid

Answers: 1. (a) 2. (d) 3. (d) 4. (b) 5. (a) 6. (c) 7. (a) 8. (b) 9. (d) 10. (b)

CHAPTER 12 IN REVIEW

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Section 12.8

phase diagram (527)
triple point (528)
critical point (528)

CONCEPTS

Solids, Liquids, and Intermolecular Forces (12.1, 12.2, 12.3)

- The forces that hold molecules or atoms together in a liquid or solid are intermolecular forces. The strength of the intermolecular forces in a substance determines its state.
- Dispersion forces are present in all elements and compounds; they arise from the fluctuations in electron distribution within atoms and molecules. These are the weakest intermolecular forces, but they are significant in molecules with high molar masses.
- Dipole-dipole forces, generally stronger than dispersion forces, are present in all polar molecules.
- Hydrogen bonding occurs in polar molecules that contain hydrogen atoms bonded directly to fluorine, oxygen, or nitrogen. These are among the strongest intermolecular forces.

- Ion-dipole forces occur when ionic compounds are mixed with polar compounds, and they are especially important in aqueous solutions.

Surface Tension, Viscosity, and Capillary Action (12.4)

- Surface tension results from the tendency of liquids to minimize their surface area in order to maximize the interactions between their constituent particles, thus lowering potential energy. Surface tension causes water droplets to form spheres and allows insects and paper clips to “float” on the surface of water.
- Viscosity is the resistance of a liquid to flow. Viscosity increases with increasing strength of intermolecular forces and decreases with increasing temperature.

- Capillary action is the ability of a liquid to flow against gravity up a narrow tube. It is the result of adhesive forces, the attraction between the molecules and the surface of the tube, and cohesive forces, the attraction between the molecules in the liquid.

Vaporization and Vapor Pressure (12.5, 12.7)

- Vaporization, the transition from liquid to gas, occurs when thermal energy overcomes the intermolecular forces present in a liquid. The opposite process is condensation. Vaporization is endothermic and condensation is exothermic.
- The rate of vaporization increases with increasing temperature, increasing surface area, and decreasing strength of intermolecular forces.
- The heat of vaporization (ΔH_{vap}) is the heat required to vaporize one mole of a liquid.
- In a sealed container, a liquid and its vapor come into dynamic equilibrium, at which point the rate of vaporization equals the rate of condensation. The pressure of a gas that is in dynamic equilibrium with its liquid is its vapor pressure.
- The vapor pressure of a substance increases with increasing temperature and with decreasing strength of its intermolecular forces.
- The boiling point of a liquid is the temperature at which its vapor pressure equals the external pressure.
- The Clausius–Clapeyron equation expresses the relationship between the vapor pressure of a substance and its temperature and can be used to calculate the heat of vaporization from experimental measurements.
- When a liquid is heated in a sealed container, it eventually forms a supercritical fluid, which has properties intermediate between a liquid and a gas. This occurs at critical temperature and critical pressure.

Fusion and Sublimation (12.6, 12.7)

- Sublimation is the transition from solid to gas. The opposite process is deposition.
- Fusion, or melting, is the transition from solid to liquid. The opposite process is freezing.
- The heat of fusion (ΔH_{fus}) is the amount of heat required to melt one mole of a solid. Fusion is endothermic.
- The heat of fusion is generally less than the heat of vaporization because intermolecular forces do not have to be completely overcome for melting to occur.

Phase Diagrams (12.8)

- A phase diagram is a map of the states of a substance as a function of its pressure (y-axis) and temperature (x-axis).
- The regions in a phase diagram represent conditions under which a single stable state (solid, liquid, gas) exists.
- The lines represent conditions under which two states are in equilibrium.
- The triple point represents the conditions under which all three states coexist.
- The critical point is the temperature and pressure above which a supercritical fluid exists.

The Uniqueness of Water (12.9)

- Water is a liquid at room temperature despite its low molar mass. Water forms strong hydrogen bonds, resulting in its high boiling point.
- The polarity of water enables it to dissolve many polar and ionic compounds and even nonpolar gases.
- Water expands upon freezing, so ice is less dense than liquid water. Water is critical both to the existence of life and to human health.

EQUATIONS AND RELATIONSHIPS

Clausius–Clapeyron Equation: Relationship between Vapor Pressure (P_{vap}), the Heat of Vaporization (ΔH_{vap}), and Temperature (T) (12.5)

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{RT} + \ln \beta \quad (\beta \text{ is a constant})$$

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

LEARNING OUTCOMES

Chapter Objectives	Assessment
Determine the intermolecular forces acting between molecules (12.2), (12.3)	Example 12.1 For Practice 12.1 Exercises 35–38
Predict physical properties based on intermolecular forces (12.4)	Example 12.2 For Practice 12.2 Exercises 39–52
Perform calculations using the heat of vaporization (12.5)	Example 12.3 For Practice 12.3 For More Practice 12.3 Exercises 53–60
Calculate the heat of vaporization and vapor pressure using the Clausius–Clapeyron equation (12.5)	Examples 12.4, 12.5 For Practice 12.4, 12.5 Exercises 61–66
Perform calculations using the heat of fusion (12.6)	Exercises 67–70
Calculate heats related to heating and cooling curves (12.7)	Exercises 71–72
Identify physical properties of a compound from its phase diagram (12.8)	Exercises 73–78
Describe the physical properties of water (12.9)	Exercises 79–82

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

1. Explain why water drops are spherical in the absence of gravity.
2. Why are intermolecular forces important?
3. What are the main properties of liquids (in contrast to gases and solids)?
4. What are the main properties of solids (in contrast to liquids and gases)?
5. What is the fundamental difference between an amorphous solid and a crystalline solid?
6. What factors cause transitions between the solid and liquid state? The liquid and gas state?
7. Describe the relationship between the state of a substance, its temperature, and the strength of its intermolecular forces.
8. From what kinds of interactions do intermolecular forces originate?
9. Why are intermolecular forces generally much weaker than bonding forces?
10. What is the dispersion force? What does the magnitude of the dispersion force depend on? How can you predict the magnitude of the dispersion force for closely related elements or compounds?
11. What is the dipole–dipole force? How can you predict the presence of dipole–dipole forces in a compound?
12. How is the polarity of a liquid generally related to its miscibility with water?
13. What is hydrogen bonding? How can you predict the presence of hydrogen bonding in a compound?
14. What is the ion–dipole force? Why is it important?
15. What is surface tension? How does surface tension result from intermolecular forces? How is it related to the strength of intermolecular forces?
16. What is viscosity? How does viscosity depend on intermolecular forces? What other factors affect viscosity?
17. What is capillary action? How does it depend on the relative strengths of adhesive and cohesive forces?
18. Explain what happens in the processes of vaporization and condensation. Why does the rate of vaporization increase with increasing temperature and surface area?
19. Why is vaporization endothermic? Why is condensation exothermic?
20. How is the volatility of a substance related to the intermolecular forces present within the substance?
21. What is the heat of vaporization for a liquid, and why is it useful?
22. Explain the process of dynamic equilibrium. How is dynamic equilibrium related to vapor pressure?
23. What happens to a system in dynamic equilibrium when it is disturbed in some way?
24. How is vapor pressure related to temperature? What happens to the vapor pressure of a substance when the temperature is increased? Decreased?
25. Define the terms *boiling point* and *normal boiling point*.
26. What is the Clausius–Clapeyron equation, and why is it important?
27. Explain what happens to a substance when it is heated in a closed container to its critical temperature.
28. What is sublimation? Give a common example of sublimation.
29. What is fusion? Is fusion exothermic or endothermic? Why?
30. What is the heat of fusion, and why is it important?
31. Examine the heating curve for water in Section 12.7 (Figure 12.36). Explain why the curve has two segments in which heat is added to the water but the temperature does not rise.
32. Examine the heating curve for water in Section 12.7 (Figure 12.36). Explain the significance of the slopes of each of the three rising segments. Why are the slopes different?
33. What is a phase diagram? Draw a generic phase diagram and label its important features. What is the significance of crossing a line in a phase diagram?
34. How do the properties of water differ from those of most other substances?

PROBLEMS BY TOPIC

Intermolecular Forces

35. Determine the kinds of intermolecular forces that are present in each element or compound.
MISSED THIS? Read Section 12.3; Watch KCV 12.3
a. N₂ b. NH₃ c. CO d. CCl₄
36. Determine the kinds of intermolecular forces that are present in each element or compound.
a. Kr b. NCl₃ c. SiH₄ d. HF
37. Determine the kinds of intermolecular forces that are present in each element or compound.
MISSED THIS? Read Section 12.3; Watch KCV 12.3
a. HCl b. H₂O c. Br₂ d. He
38. Determine the kinds of intermolecular forces that are present in each element or compound.
a. PH₃ b. HBr c. CH₃OH d. I₂

39. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
MISSED THIS? Read Section 12.3; Watch KCV 12.3, IWE 12.1, 12.2
a. CH₄ b. CH₃CH₃ c. CH₃CH₂Cl d. CH₃CH₂OH
40. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
a. H₂S b. H₂Se c. H₂O
41. In each pair of compounds, pick the one with the higher boiling point. Explain your reasoning.
MISSED THIS? Read Section 12.3; Watch KCV 12.3, IWE 12.2
a. CH₃OH or CH₃SH b. CH₃OCH₃ or CH₃CH₂OH
c. CH₄ or CH₃CH₃
42. In each pair of compounds, pick the one with the higher boiling point. Explain your reasoning.
a. NH₃ or CH₄ b. CS₂ or CO₂
c. CO₂ or NO₂

43. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain your reasoning.
MISSED THIS? Read Sections 12.3, 12.5; Watch KCV 12.3, 12.5
- Br_2 or I_2
 - H_2S or H_2O
 - NH_3 or PH_3

44. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain your reasoning.
- CH_4 or CH_3Cl
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or CH_3OH
 - CH_3OH or H_2CO

45. Determine whether each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved.
MISSED THIS? Read Section 12.3

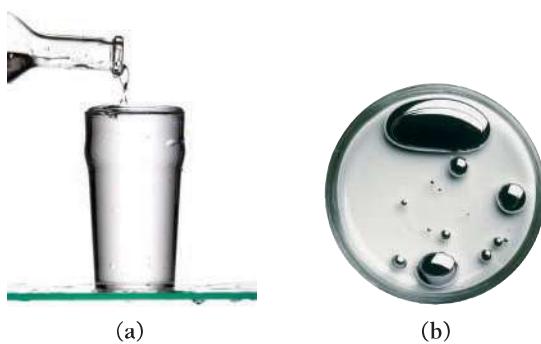
- CCl_4 and H_2O
- KCl and H_2O
- Br_2 and CCl_4
- $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O

46. Determine whether each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 - CBr_4 and H_2O
 - LiNO_3 and H_2O
 - CH_3OH and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

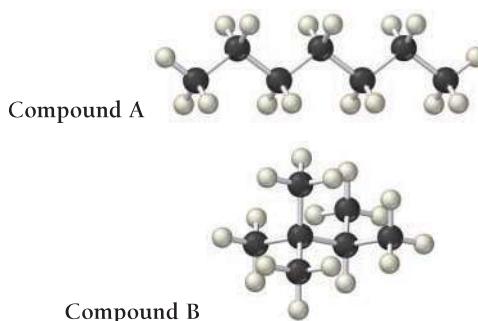
Surface Tension, Viscosity, and Capillary Action

47. Which compound would you expect to have greater surface tension: acetone [$(\text{CH}_3)_2\text{CO}$] or water (H_2O)? Explain.
MISSED THIS? Read Section 12.4

48. Water (a) “wets” some surfaces and beads up on others. Mercury (b), in contrast, beads up on almost all surfaces. Explain this difference.

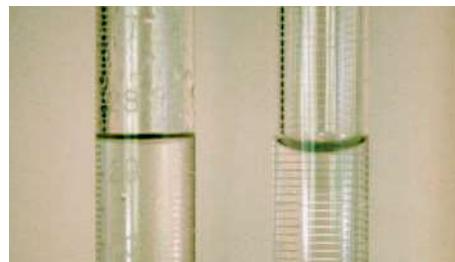


49. The structures of two isomers of heptane are shown. Which of these two compounds would you expect to have the greater viscosity? **MISSED THIS? Read Section 12.4**



50. Explain why the viscosity of multigrade motor oils is less temperature-dependent than that of single-grade motor oils.

51. Water in a glass tube that contains grease or oil residue displays a flat meniscus (left), whereas water in a clean glass tube displays a concave meniscus (right). Explain this observation.
MISSED THIS? Read Section 12.4



52. When a thin glass tube is put into water, the water rises 1.4 cm. When the same tube is put into hexane, the hexane rises only 0.4 cm. Explain.

Evaporation and Vapor Pressure

53. Which evaporates more quickly: 55 mL of water in a beaker with a diameter of 4.5 cm or 55 mL of water in a dish with a diameter of 12 cm? Is the vapor pressure of the water different in the two containers? Explain.

MISSED THIS? Read Section 12.5; Watch KCV 12.5

54. Which evaporates more quickly: 55 mL of water (H_2O) in a beaker or 55 mL of acetone [$(\text{CH}_3)_2\text{CO}$] in an identical beaker under identical conditions? Is the vapor pressure of the two substances different? Explain.

55. Spilling room-temperature water over your skin on a hot day cools you down. Spilling room-temperature vegetable oil over your skin on a hot day does not. Explain the difference.

MISSED THIS? Read Section 12.5; Watch KCV 12.5

56. Why is the heat of vaporization of water greater at room temperature than it is at its boiling point?

57. The human body obtains 915 kJ of energy from a candy bar. If this energy were used to vaporize water at 100.0 °C, how much water (in liters) could be vaporized? (Assume the density of water is 1.00 g/mL.)

MISSED THIS? Read Section 12.5; Watch KCV 12.5, IWE 12.3

58. A 100.0-mL sample of water is heated to its boiling point. How much heat (in kJ) is required to vaporize it? (Assume a density of 1.00 g/mL.)

59. Suppose that 0.95 g of water condenses on a 75.0-g block of iron that is initially at 22 °C. If the heat released during condensation goes only to warming the iron block, what is the final temperature (in °C) of the iron block? (Assume a constant enthalpy of vaporization for water of 44.0 kJ/mol.)

MISSED THIS? Read Section 12.5; Watch KCV 12.5, IWE 12.3

60. Suppose that 1.15 g of rubbing alcohol ($\text{C}_3\text{H}_8\text{O}$) evaporates from a 65.0-g aluminum block. If the aluminum block is initially at 25 °C, what is the final temperature of the block after the evaporation of the alcohol? Assume that the heat required for the vaporization of the alcohol comes only from the aluminum block and that the alcohol vaporizes at 25 °C.

61. This table displays the vapor pressure of ammonia at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of ammonia.

MISSED THIS? Read Section 12.5

Temperature (K)	Pressure (torr)
200	65.3
210	134.3
220	255.7
230	456.0
235	597.0

62. This table displays the vapor pressure of nitrogen at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of nitrogen.

Temperature (K)	Pressure (torr)
65	130.5
70	289.5
75	570.8
80	1028
85	1718

63. Ethanol has a heat of vaporization of 38.56 kJ/mol and a normal boiling point of 78.4 °C. What is the vapor pressure of ethanol at 15 °C?

MISSED THIS? Read Section 12.5; Watch IWE 12.5

64. Benzene has a heat of vaporization of 30.72 kJ/mol and a normal boiling point of 80.1 °C. At what temperature does benzene boil when the external pressure is 445 torr?

65. Carbon disulfide has a vapor pressure of 363 torr at 25 °C and a normal boiling point of 46.3 °C. Find ΔH_{vap} for carbon disulfide.

MISSED THIS? Read Section 12.5; Watch IWE 12.5

66. Methylamine has a vapor pressure of 344 torr at -25 °C and a boiling point of -6.4 °C. Find ΔH_{vap} for methylamine.

Sublimation and Fusion

67. How much energy is released when 65.8 g of water freezes?

MISSED THIS? Read Section 12.6

68. Calculate the amount of heat required to completely sublime 50.0 g of solid dry ice (CO_2) at its sublimation temperature. The heat of sublimation for carbon dioxide is 32.3 kJ/mol.

69. An 8.5-g ice cube is placed into 255 g of water. Calculate the temperature change in the water upon the complete melting of the ice. Assume that all of the energy required to melt the ice comes from the water.

MISSED THIS? Read Section 12.6

70. How much ice (in grams) would have to melt to lower the temperature of 352 mL of water from 25 °C to 5 °C? (Assume the density of water is 1.0 g/mL.)

71. How much heat (in kJ) is required to warm 10.0 g of ice, initially at -10.0 °C, to steam at 110.0 °C? The heat capacity of ice is 2.09 J/g·°C, and that of steam is 2.01 J/g·°C.

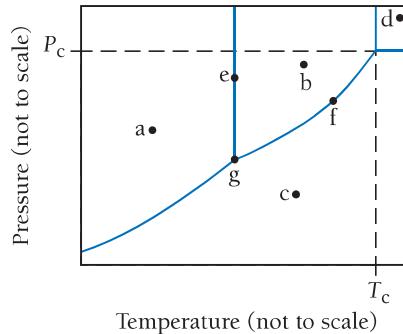
MISSED THIS? Read Section 12.7; Watch KCV 12.7

72. How much heat (in kJ) is evolved in converting 1.00 mol of steam at 145 °C to ice at -50 °C? The heat capacity of steam is 2.01 J/g·°C, and that of ice is 2.09 J/g·°C.

Phase Diagrams

73. Consider the phase diagram shown here. Identify the states present at points *a* through *g*.

MISSED THIS? Read Section 12.8; Watch KCV 12.8

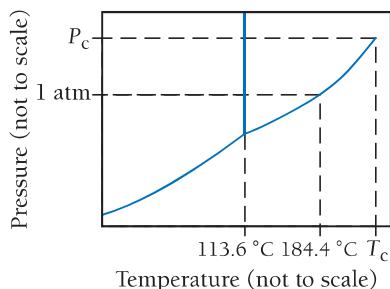


74. Consider the phase diagram for iodine shown here.

- What is the normal boiling point for iodine?
- What is the melting point for iodine at 1 atm?

- c. What state is present at room temperature and normal atmospheric pressure?

- d. What state is present at 186 °C and 1.0 atm?



75. Nitrogen has a normal boiling point of 77.3 K and a melting point (at 1 atm) of 63.1 K. Its critical temperature is 126.2 K, and its critical pressure is 2.55×10^4 torr. It has a triple point at 63.1 K and 94.0 torr. Sketch the phase diagram for nitrogen. Does nitrogen have a stable liquid state at 1 atm?

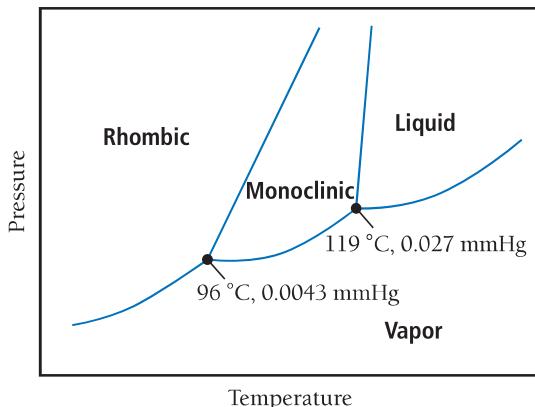
MISSED THIS? Read Section 12.8; Watch KCV 12.8

76. Argon has a normal boiling point of 87.2 K and a melting point (at 1 atm) of 84.1 K. Its critical temperature is 150.8 K, and its critical pressure is 48.3 atm. It has a triple point at 83.7 K and 0.68 atm. Sketch the phase diagram for argon. Which has the greater density, solid argon or liquid argon?

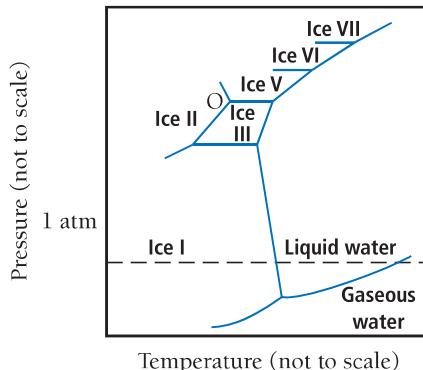
77. The phase diagram for sulfur is shown here. The rhombic and monoclinic states are two solid states with different structures.

MISSED THIS? Read Section 12.8; Watch KCV 12.8

- Below what pressure does solid sulfur sublime?
- Which of the two solid states of sulfur is more dense?



78. The high-pressure phase diagram of ice is shown here. Notice that, under high pressure, ice can exist in several different solid forms. What three forms of ice are present at the triple point marked O? How does the density of ice II compare to ice I (the familiar form of ice)? Would ice III sink or float in liquid water?



The Uniqueness of Water

79. Water has a high boiling point given its relatively low molar mass. Why?
MISSED THIS? Read Section 12.9

80. Water is a good solvent for many substances. What is the molecular basis for this property, and why is it significant?
81. Explain the role of water in moderating Earth's climate.
MISSED THIS? Read Section 12.9
82. How is the density of solid water compared to that of liquid water atypical among substances? Why is this significant?

CUMULATIVE PROBLEMS

83. Explain the observed trend in the melting points of the hydrogen halides.

HI	-50.8 °C
HBr	-88.5 °C
HCl	-114.8 °C
HF	-83.1 °C

84. Explain the observed trend in the boiling points of these compounds.

H ₂ Te	-2 °C
H ₂ Se	-41.5 °C
H ₂ S	-60.7 °C
H ₂ O	100 °C

85. The vapor pressure of water at 25 °C is 23.76 torr. If 1.25 g of water is enclosed in a 1.5-L container, will any liquid be present? If so, what mass of liquid?

86. The vapor pressure of CCl₃F at 300 K is 856 torr. If 11.5 g of CCl₃F is enclosed in a 1.0-L container, will any liquid be present? If so, what mass of liquid?

87. Examine the phase diagram for iodine shown in Figure 12.39(a). What state transitions occur as we uniformly increase the pressure on a gaseous sample of iodine from 0.01 atm at 185 °C to 100 atm at 185 °C? Make a graph, analogous to the heating curve for water shown in Figure 12.36. Plot pressure versus time during the pressure increase.

88. Carbon tetrachloride displays a triple point at 249.0 K and a melting point (at 1 atm) of 250.3 K. Which state of carbon tetrachloride is more dense, the solid or the liquid? Explain.

89. Four ice cubes at exactly 0 °C with a total mass of 53.5 g are combined with 115 g of water at 75 °C in an insulated container. If no heat is lost to the surroundings, what is the final temperature of the mixture?

90. A sample of steam with a mass of 0.552 g and at a temperature of 100 °C condenses into an insulated container holding 4.25 g of water at 5.0 °C. Assuming that no heat is lost to the surroundings, what is the final temperature of the mixture?

91. Draw a heating curve (such as the one in Figure 12.36) for 1 mole of methanol beginning at 170 K and ending at 350 K. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	176 K
Boiling point	338 K
ΔH_{fus}	2.2 kJ/mol
ΔH_{vap}	35.2 kJ/mol
C_s , solid	105 J/K
C_s , liquid	81.3 J/mol · K
C_s , gas	48 J/mol · K

92. Draw a heating curve (such as the one in Figure 12.36) for 1 mol of benzene beginning at 0 °C and ending at 100 °C. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	5.4 °C
Boiling point	80.1 °C
ΔH_{fus}	9.9 kJ/mol
ΔH_{vap}	30.7 kJ/mol
C_s , solid	118 J/mol · K
C_s , liquid	135 J/mol · K
C_s , gas	104 J/mol · K

93. Air conditioners not only cool air but dry it as well. A room in a home measures 6.0 m × 10.0 m × 2.2 m. If the outdoor temperature is 30 °C and the partial pressure of water in the air is 85% of the vapor pressure of water at this temperature, what mass of water must be removed from the air each time the volume of air in the room is cycled through the air conditioner? (Assume that all of the water must be removed from the air.) The vapor pressure for water at 30 °C is 31.8 torr.

94. A sealed flask contains 0.55 g of water at 28 °C. The vapor pressure of water at this temperature is 28.35 mmHg. What is the minimum volume of the flask in order that no liquid water be present in the flask?

95. Based on the phase diagram of CO₂ shown in Figure 12.39(b), describe the state changes that occur when the temperature of CO₂ is increased from 190 K to 350 K at a constant pressure of (a) 1 atm, (b) 5.1 atm, (c) 10 atm, and (d) 100 atm.

96. Consider a planet where the pressure of the atmosphere at sea level is 2500 mmHg. Does water behave in a way that can sustain life on the planet?

CHALLENGE PROBLEMS

97. Liquid nitrogen can be used as a cryogenic substance to obtain low temperatures. Under atmospheric pressure, liquid nitrogen boils at 77 K, allowing low temperatures to be reached. However, if the nitrogen is placed in a sealed, insulated container connected to a vacuum pump, even lower temperatures can be reached. Why? If the vacuum pump has sufficient capacity and is left on for an extended period of time, the liquid nitrogen will start to freeze. Explain.

98. Given that the heat of fusion of water is -6.02 kJ/mol, the heat capacity of H₂O(l) is 75.2 J/mol · K, and the heat capacity of H₂O(s) is 37.7 J/mol · K, calculate the heat of fusion of water at -10 °C.
99. The heat of combustion of CH₄ is 890.4 kJ/mol, and the heat capacity of H₂O is 75.2 J/mol · K. Find the volume of methane measured at 298 K and 1.00 atm required to convert 1.00 L of water at 298 K to water vapor at 373 K.

- 100.** Two liquids, A and B, have vapor pressures at a given temperature of 24 mmHg and 36 mmHg, respectively. We prepare solutions of A and B at a given temperature and measure the total pressures above the solutions. We obtain these data:

Solution	Amt A (mol)	Amt B (mol)	P (mmHg)
1	1	1	30
2	2	1	28
3	1	2	32
4	1	3	33

Predict the total pressure above a solution of 5 mol A and 1 mol B.

- 101.** Three 1.0-L flasks, maintained at 308 K, are connected to each other with stopcocks. Initially, the stopcocks are closed. One of the flasks contains 1.0 atm of N₂; the second, 2.0 g of H₂O; and the third, 0.50 g of ethanol, C₂H₆O. The vapor pressure of H₂O at 308 K is 42 mmHg, and that of ethanol is 102 mmHg. The stopcocks are then opened and the contents mix freely. What is the pressure?

- 102.** Butane (C₄H₁₀) has a heat of vaporization of 22.44 kJ/mol and a normal boiling point of -0.4°C . A 250-mL sealed flask contains 0.55 g of butane at -22°C . How much butane is present as a liquid? If the butane is warmed to 25°C , how much is present as a liquid?

CONCEPTUAL PROBLEMS

- 103.** The following image is an electrostatic potential map for ethylene oxide, (CH₂)₂O, a polar molecule. Use the electrostatic potential map to predict the geometry for how one ethylene oxide molecule interacts with another. Draw structural formulas, using the 3D bond notation introduced in Section 11.4, to show the geometry of the interaction.



- 104.** One prediction of global warming is the melting of global ice, which may result in coastal flooding. A criticism of this prediction is that the melting of icebergs does not increase ocean levels any more than the melting of ice in a glass of water increases the level of liquid in the glass. Is this a valid criticism? Does the melting of an ice cube in a cup of water raise the level of the liquid in the cup? Why or why not? In response to this criticism, scientists have asserted that they are not worried about melting icebergs, but rather the melting of ice sheets that sit on the continent of Antarctica. Would the melting of this ice increase ocean levels? Why or why not?

- 105.** The rate of vaporization depends on the surface area of the liquid. However, the vapor pressure of a liquid does not depend on the surface area. Explain.

- 106.** Substance A has a smaller heat of vaporization than substance B. Which of the two substances will undergo a larger change in vapor pressure for a given change in temperature?

- 107.** The density of a substance is greater in its solid state than in its liquid state. If the triple point in the phase diagram of the substance is below 1.0 atm, which will necessarily be at a lower temperature, the triple point or the normal melting point?

- 108.** A substance has a heat of vaporization of ΔH_{vap} and a heat of fusion of ΔH_{fus} . Express the heat of sublimation in terms of ΔH_{vap} and ΔH_{fus} .

- 109.** Examine the heating curve for water in Section 12.7 (Figure 12.36). If heat is added to the water at a constant rate, which of the three segments in which temperature is rising will have the least steep slope? Why?

- 110.** A root cellar is an underground chamber used to store fruits, vegetables, and even meats. In extreme cold, farmers put large vats of water into the root cellar to prevent the fruits and vegetables from freezing. Explain why this works.

- 111.** Suggest an explanation for the observation that the heat of fusion of a substance is always smaller than its heat of vaporization.

- 112.** Refer to Figure 12.36 to answer each question.

- A sample of steam begins on the line segment labeled 5 on the graph. Is heat absorbed or released in moving from the line segment labeled 5 to the line segment labeled 3? What is the sign of q for this change?
- In moving from left to right along the line segment labeled 2 on the graph, heat is absorbed, but the temperature remains constant. Where does the heat go?
- How would the graph change if it were for another substance (other than water)?

QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 113.** The boiling points of three compounds are tabulated here.

Molar Mass	Boiling Point
2-hexanone	100.16 128°C
heptane	100.20 98°C
1-hexanol	102.17 156°C

Answer the following questions without looking up the structures for these molecules: Which compound experiences hydrogen bonding? Which compound is polar but is unable to experience hydrogen bonding? Which is neither polar nor capable of hydrogen bonding? Explain your answers.

Active Classroom Learning

- 114.** The vapor pressure for pure water and pure acetone is measured as a function of temperature. In each case, a graph of the log of the vapor pressure versus $1/T$ is found to be a straight line. The slope of the line for water is -4895 K , and the slope of the line for acetone is -3765 K . Determine ΔH_{vap} for each substance. Account for the difference by discussing the molecular structure of the two molecules.

- 115.** Based on the heating curve for water, does it take more energy to melt a mole of water or to boil a mole of water? Does it take more energy to warm the solid, the liquid, or the gas by 10°C ? Explain your answers clearly.

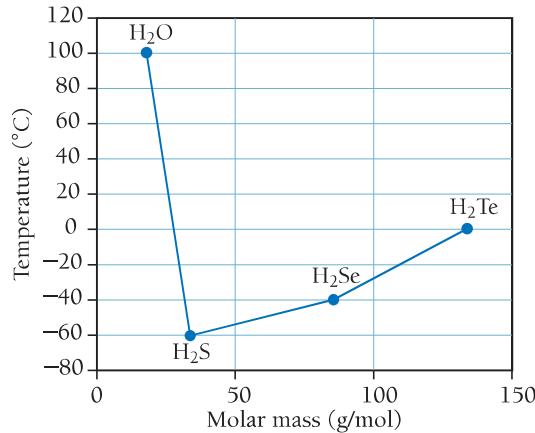
- 116.** Sketch the phase diagram for carbon dioxide. If you have carbon dioxide at 1.0 atm and 25°C , could you make it a liquid by cooling it down? How could you make it a liquid at 25°C ? If you increase the pressure of carbon dioxide that is at body temperature (37°C), will it ever liquefy?



DATA INTERPRETATION AND ANALYSIS

Intermolecular Forces of Group 6A Hydrides

117. We have seen that molar mass and molecular structure influence the boiling point of a substance. We can see these two factors at work in the boiling points of the group 6A hydrides shown in the following graph.



▲ Boiling Point versus Molar Mass of Group 6A Hydrides

In order to disentangle the effects of molar mass and molecular structure on the boiling point, consider the data in the following table.

Compound	Molar Mass (g/mol)	n-Boiling Point (°C)	Dipole Moment (D)	Polarizability (10^{-24} cm 3)
H ₂ O	18.01	100	1.85	1.45
H ₂ S	34.08	-60	1.10	3.81
H ₂ Se	80.98	-42.2	0.41	4.71
H ₂ Te	129.6	-2.2	0.22	5.01

Use the information in the graph and the table to answer the following questions.

- Does molar mass alone correlate with the trend in the boiling points for the group 6A hydrides?
- Which boiling points in the graph correlate with polarizability? What type of intermolecular force correlates with polarizability?
- Use the data in the table to explain the anomalously high boiling point of water.



ANSWERS TO CONCEPTUAL CONNECTIONS

States of Matter

- 12.1** (c) Gases are compressible because the atoms or molecules in a gas are separated by large distances. An increase in pressure forces the atoms or molecules closer together, reducing the gas's volume.

State Changes

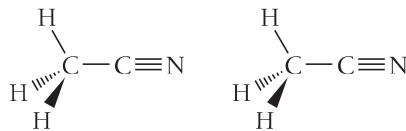
- 12.2** (a) When water boils, it simply changes state from liquid to gas. Water molecules do not decompose during boiling.

Dispersion Forces

- 12.3** (c) I₂ has the highest boiling point because it has the highest molar mass. Since the halogens are all similar in other ways, we expect I₂ to have the greatest dispersion forces and therefore the highest boiling point (and in fact it does).

Dipole–Dipole Interaction

- 12.4** (a)



Since acetonitrile is polar, the more negative end (in the electrostatic potential map) is attracted to the positive end (in the electrostatic potential map) of its neighbor.

Intermolecular Forces and Boiling Point

- 12.5** (a) CH₃OH. The compounds all have similar molar masses, so the dispersion forces are similar in all three. CO is polar, but because CH₃OH contains H directly bonded to O, it has hydrogen bonding, resulting in the highest boiling point.

Vaporization

- 12.6** (d) The rate of vaporization increases with increasing temperature and with increasing surface area. This sample has the combined highest temperature and highest surface. (The 250-mL beaker has a greater diameter than the 100-mL beaker, and therefore the water is spread out over a greater area.)

Vapor Pressure

- 12.7** (b) Although the *rate of vaporization* increases with increasing surface area, the *vapor pressure* of a liquid is independent of surface area. An increase in surface area increases both the rate of vaporization and the rate of condensation—the effects exactly cancel, and the vapor pressure does not change.

Boiling Point

- 12.8** (a) According to Figure 12.28, water has a vapor pressure of 200 torr at about 66 °C, so at an external pressure of 200 torr, water boils at 66 °C.

Cooling of Water with Ice

- 12.9** (b) The warming of the ice from -10 °C to 0 °C absorbs only 20.9 J/g of ice. The melting of the ice, however, absorbs about 334 J/g of ice. (You can obtain this value by dividing the heat of fusion of water by its molar mass.) Therefore, the melting of the ice produces a larger temperature decrease in the water than does the warming of the ice.

Phase Diagrams

- 12.10** (b) The solid will sublime into a gas. Since the pressure is below the triple point, the liquid state is not stable.