

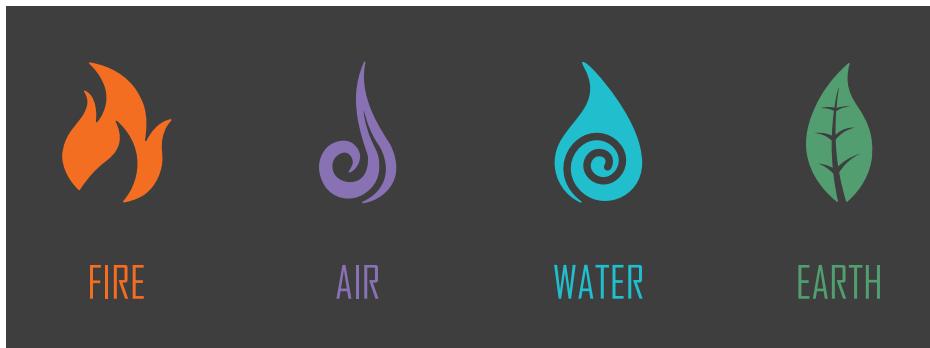
11

LIQUIDS AND INTERMOLECULAR FORCES

WHAT'S AHEAD

- 11.1 ► A Molecular Comparison of Gases, Liquids, and Solids
- 11.2 ► Intermolecular Forces
- 11.3 ► Select Properties of Liquids
- 11.4 ► Phase Changes
- 11.5 ► Vapor Pressure
- 11.6 ► Phase Diagrams
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11.1 | A Molecular Comparison of Gases, Liquids, and Solids



Empedocles lived around 2400 years ago, a citizen of the Greek city of Akragas, situated on what is now the island of Sicily. He was a philosopher and is best remembered for proposing four elements from which all matter was made: air, water, earth, and fire. We can understand his choice as it represents the three states of matter and energy, which is inseparable from all chemical reactions.

In this brief section, we remind ourselves of the differences between the states. At the end of this section, you should be able to

- Recognize the characteristic properties of the states

As we learned in Chapter 10, the molecules in a gas are widely separated and in a state of constant, chaotic motion. One of the key tenets of kinetic-molecular theory of gases is the assumption that we can neglect the interactions between molecules. The properties of liquids and solids are quite different from those of gases largely because the intermolecular forces in liquids and solids are much stronger. A comparison of the properties of gases, liquids, and solids is given in **Table 11.1**.

In liquids the intermolecular attractive forces are strong enough to hold particles close together. Thus, liquids are much denser and far less compressible than gases. Unlike gases, liquids have a definite volume, independent of the size and shape of their container. The attractive forces in liquids are not strong enough, however, to keep the particles from moving past one another. Thus, any liquid can be poured and assumes the shape of the container it occupies.

In solids the intermolecular attractive forces are strong enough to hold particles close together and to lock them virtually in place. Solids, like liquids, are not very compressible because the particles have little free space between them. Because the particles in a solid or liquid are fairly close together compared with those of a gas, we often refer to solids and liquids as *condensed phases*. We will study solids in Chapter 12. For now it is sufficient to know that the particles of a solid are not free to undergo long-range movement, which makes solids rigid.*

Figure 11.1 compares the three states of matter. *The state of a substance depends largely on the balance between the kinetic energies of the particles (atoms, molecules, or ions) and the interparticle energies of attraction.* The kinetic energies, which depend on temperature, tend to keep the particles apart and moving. The interparticle attractions tend to draw the particles together. Substances that are gases at room temperature have much weaker interparticle attractions than those that are liquids; substances that are liquids have weaker interparticle attractions than those that are solids. The different states of matter adopted by the halogens at room temperature—iodine is a solid, bromine is a liquid, and chlorine is a gas—are a direct consequence of a decrease in the strength of the intermolecular forces as we move from I_2 to Br_2 to Cl_2 .

We can change a substance from one state to another by heating or cooling, which changes the average kinetic energy of the particles. NaCl, for example, a solid at room temperature, melts at 1074 K and boils at 1686 K under a pressure of 101.3 kPa, and Cl_2 , a gas at room temperature, liquefies at 239 K and solidifies at 172 K under a pressure of 101.3 kPa. As the temperature of a gas decreases, the average kinetic energy of its particles decreases, allowing the attractions between the particles to draw the particles close together, forming a liquid, and then to virtually lock them in place, forming a solid. Increasing the pressure on a gas can also drive transformations from gas to liquid to solid because the increased pressure brings the molecules closer together, thus making intermolecular forces more effective. For example, propane (C_3H_8) is a gas at room temperature and 101.3 kPa, whereas liquefied propane (LP) is a liquid at room temperature because it is stored under much higher pressure.

TABLE 11.1 Characteristic Properties of the States of Matter

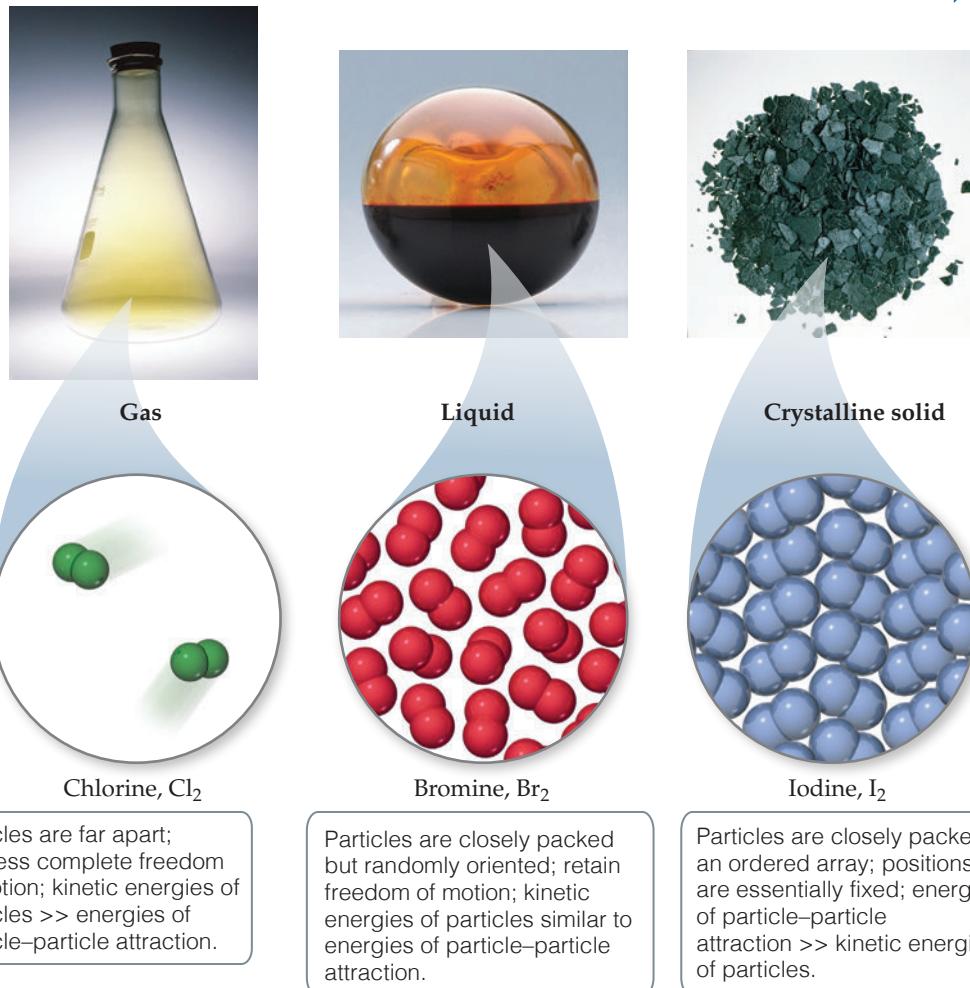
Gas	Liquid	Solid
Assumes both volume and shape of its container	Assumes shape of portion of container it occupies	Retains own shape and volume
Expands to fill its container	Does not expand to fill its container	Does not expand to fill its container
Is compressible	Is virtually incompressible	Is virtually incompressible
Flows readily	Flows readily	Does not flow
Diffusion within a gas occurs rapidly	Diffusion within a liquid occurs slowly	Diffusion within a solid occurs extremely slowly

*The atoms in a solid are able to vibrate in place. As the temperature of the solid increases, the vibrational motion increases.


Go Figure

For a given substance, do you expect the density of the substance in its liquid state to be closer to the density in the gaseous state or in the solid state?

Increasing intermolecular attractions



▲ **Figure 11.1 Gases, liquids, and solids.** Chlorine, bromine, and iodine are all diatomic molecules as a result of covalent bonding. However, due to differences in the strength of the intermolecular forces, they exist in three different states at room temperature and standard pressure: Cl₂ is a gas, Br₂ is a liquid, and I₂ is a solid.

Self-Assessment Exercise

- 11.1** A substance has a density of around 1 g/L. Is it likely to be a solid, liquid, or gas? Hint: think of the density of water for comparison.

- (a) Solid
- (b) Liquid
- (c) Gas

Exercises

- 11.2** (a) How does the average kinetic energy of molecules compare with the average energy of attraction between molecules in solids, liquids, and gases? (b) Why does increasing the temperature cause a solid substance to change in succession from a solid to a liquid to a gas? (c) What happens to a gas if you put it under extremely high pressure?
- 11.3** At room temperature, CO_2 is a gas, CCl_4 is a liquid, and C_{60} (fullerene) is a solid. List these substances in order of (a) increasing intermolecular energy of attraction and (b) increasing boiling point.
- 11.4** At standard temperature and pressure, the molar volumes of Cl_2 and NH_3 gases are 22.06 and 22.40 L, respectively.

(a) Given the different molecular weights, dipole moments, and molecular shapes, why are their molar volumes nearly the same? (b) On cooling to 160 K, both substances form crystalline solids. Do you expect the molar volumes to decrease or increase on cooling the gases to 160 K? (c) The densities of crystalline Cl_2 and NH_3 at 160 K are 2.02 and 0.84 g/cm³, respectively. Calculate their molar volumes. (d) Are the molar volumes in the solid state as similar as they are in the gaseous state? Explain. (e) Would you expect the molar volumes in the liquid state to be closer to those in the solid or gaseous state?

11.1 (c)

Answers to Self-Assessment Exercises



11.2 | Intermolecular Forces



The lotus plant grows in aquatic environments. To thrive in such an environment, the surface of a lotus leaf is highly water repellent. Scientists call surfaces with this property “superhydrophobic.” The superhydrophobic character of the lotus leaf not only allows it to float on water but also causes any water that falls on the leaf to bead up and roll off. The water drops collect dirt as they roll off, keeping the leaf clean, even in the muddy ponds and lakes where lotus plants tend to grow. Because of its self-cleaning properties, the lotus plant is considered a symbol of purity in many Eastern cultures.

By the end of this section, you should be able to

- Identify the intermolecular forces that exist within a substance.

What forces cause the lotus leaf to repel water so efficiently? Although this plant’s self-cleaning nature has been known for millennia, the effect was not fully understood until the 1970s, when scanning electron microscopy images revealed a rough leaf surface

(Figure 11.2). The rough surface helps minimize contact between water and leaf, and also minimizes contact between dirt and leaf so that the dirt does not stick.

The lotus effect has inspired scientists to design superhydrophobic surfaces for applications such as self-cleaning windows and water-repellent clothing. To understand the lotus effect and other phenomena involving liquids and solids, we must understand intermolecular forces, the forces that exist between molecules. Only by understanding the nature and strength of these forces can we understand how the composition and structure of a substance are related to its physical properties in the liquid or solid state.

The strengths of *intermolecular* forces, those forces acting between molecules, vary over a wide range but are generally much weaker than *intramolecular* forces—ionic, metallic, or covalent bonds (Figure 11.3). Less energy, therefore, is required to vaporize a liquid or melt a solid than to break covalent bonds. For example, only 16 kJ/mol is required to overcome the intermolecular attractions in liquid HCl to vaporize it. In contrast, the energy required to break the covalent bond in HCl is 431 kJ/mol. Thus, when a molecular substance such as HCl changes from solid to liquid to gas, the molecules remain intact.

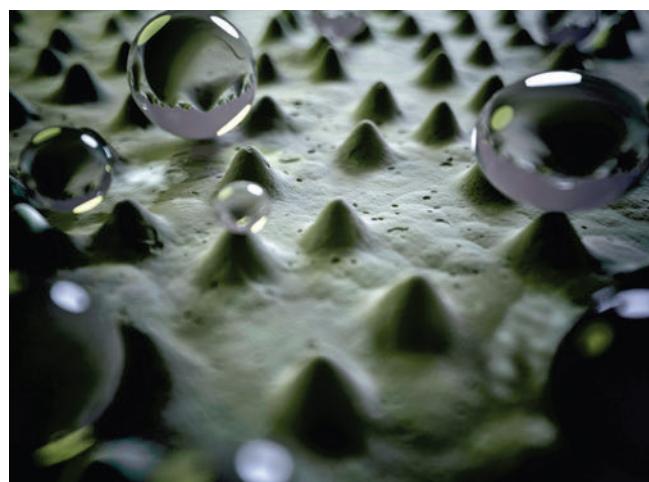
Many properties of liquids, including boiling points, reflect the strength of the intermolecular forces. A liquid boils when bubbles of its vapor form within the liquid. The molecules of the liquid must overcome their attractive forces to separate and form a vapor. The stronger the attractive forces, the higher the temperature at which the liquid boils. Similarly, the melting points of solids increase as the strengths of the intermolecular forces increase. As shown in Table 11.2, the melting and boiling points of substances in which the particles are held together by chemical bonds tend to be much higher than those of substances in which the particles are held together by intermolecular forces.

There are three types of intermolecular attractions that exist between electrically neutral molecules:

- dispersion forces
- dipole–dipole attractions
- hydrogen bonding.

The first two are collectively called *van der Waals forces* after Johannes van der Waals (1837–1923), who developed the equation for predicting the deviation of gases from ideal behavior. Another kind of attractive force, the ion-dipole force, is important in solutions.

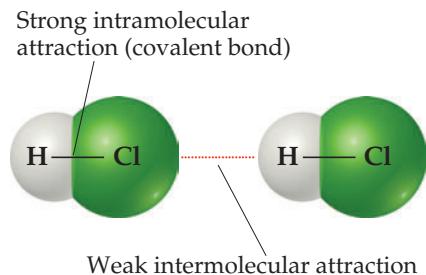
All intermolecular interactions are electrostatic, involving attractions between positive and negative species, much like ionic bonds. Why then are intermolecular forces so much weaker than ionic bonds? Recall from Equation 8.4 that electrostatic interactions



▲ Figure 11.2 A microscopic view of a water droplets on the surface of a lotus leaf.

Go Figure

How would you expect the H—Cl distance represented by the red dotted line to compare with the H—Cl distance within the HCl molecule?



▲ Figure 11.3 Intermolecular and intramolecular interactions.

TABLE 11.2 Melting and Boiling Points of Representative Substances

Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
<i>Chemical bonds</i>			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
<i>Intermolecular forces</i>			
Dispersion forces	Nitrogen (N ₂)	63	77
Dipole-dipole interactions	Hydrogen chloride (HCl)	158	188
Hydrogen bonding	Hydrogen fluoride (HF)	190	293

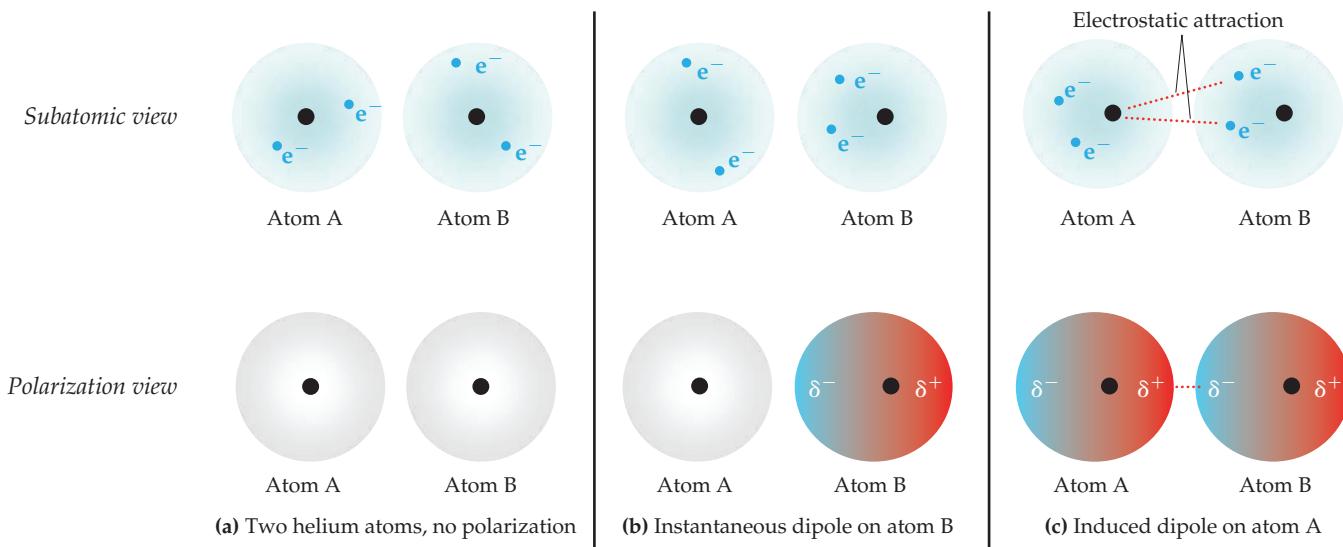
get stronger as the magnitude of the charges increases and weaker as the distance between charges increases. The charges responsible for intermolecular forces are generally much smaller than the charges in ionic compounds. For example, from its dipole moment it is possible to estimate charges of +0.178 and -0.178 for the hydrogen and chlorine ends of the HCl molecule, respectively (see Sample Exercise 8.5). Furthermore, the distances between molecules are often larger than the distances between atoms held together by chemical bonds.

Dispersion Forces

You might think there would be no electrostatic interactions between electrically neutral, nonpolar atoms and/or molecules. Yet some kind of attractive interactions must exist because nonpolar gases like helium, argon, and nitrogen can be liquefied. Fritz London, a German-American physicist, first proposed the origin of this attraction in 1930. London recognized that the motion of electrons in an atom or molecule can create an *instantaneous*, or momentary, dipole moment.

In a collection of helium atoms, for example, the *average* distribution of the electrons about each nucleus is spherically symmetrical, as shown in Figure 11.4(a). The atoms are nonpolar and so possess no permanent dipole moment. The *instantaneous* distribution of the electrons, however, can be different from the average distribution. If we could freeze the motion of the electrons at any given instant, both electrons could be on one side of the nucleus. At just that instant, the atom has an instantaneous dipole moment as shown in Figure 11.4(b). The motions of electrons in one atom influence the motions of electrons in its neighbors. The instantaneous dipole on one atom can induce an instantaneous dipole on an adjacent atom, causing the atoms to be attracted to each other as shown in Figure 11.4(c). This attractive interaction is called the **dispersion force** (also called *London dispersion forces* or *induced dipole–induced dipole interactions*). It is significant only when molecules are very close together.

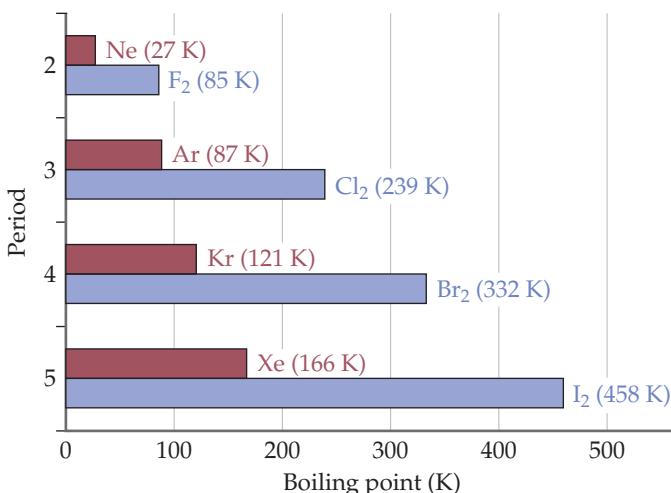
The strength of the dispersion force depends on the ease with which the charge distribution in a molecule can be distorted to induce an instantaneous dipole. The ease with which the charge distribution is distorted is called the molecule's **polarizability**. We can think of the polarizability of a molecule as a measure of the "squashiness" of its electron cloud: The greater the polarizability, the more easily the electron cloud can be distorted to give an instantaneous dipole. Therefore, more polarizable molecules have larger dispersion forces.



▲ **Figure 11.4** Dispersion forces. “Snapshots” of the charge distribution for a pair of helium atoms at three instants.

 Go Figure

Why is the boiling point of the halogen in each period greater than the noble gas?



▲ **Figure 11.5** Boiling points of the halogens and noble gases. This plot shows how the boiling points increase due to stronger dispersion forces as the atomic/molecular weight increases.

In general, polarizability increases as the number of electrons in an atom or molecule increases. The strength of dispersion forces therefore tends to increase with increasing atomic or molecular size. Because molecular size and mass generally parallel each other, *dispersion forces tend to increase in strength with increasing molecular weight*. We can see this in the boiling points of the halogens and noble gases (Figure 11.5), where dispersion forces are the only intermolecular forces at work. In both families the atomic/molecular weight increases on moving down the periodic table. The higher atomic/molecular weights translate into stronger dispersion forces, which in turn lead to higher boiling points.

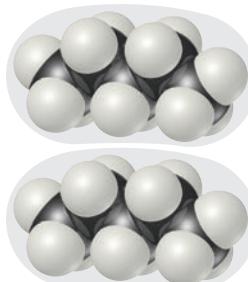
Molecular shape also influences the magnitude of dispersion forces. For example, pentane and dimethylpropane (Figure 11.6) have the same molecular formula (C_5H_{12}), yet the boiling point of pentane is about 27 K higher than that of dimethylpropane. The difference can be traced to the different shapes of the two molecules. Intermolecular attraction is greater for pentane because the molecules can come in contact over the entire length of the long, somewhat cylindrical molecules. Less contact is possible between the more compact and nearly spherical dimethylpropane molecules.

Dipole–Dipole Interactions

The presence of a permanent dipole moment in polar molecules gives rise to **dipole–dipole interactions**. These interactions originate from electrostatic attractions between the partially positive end of one molecule and the partially negative end of a neighboring molecule. Repulsions can also occur when the positive (or negative) ends of two molecules are in close proximity. Dipole–dipole interactions are effective only when molecules are very close together.

To see the effect of dipole–dipole interactions, we compare the boiling points of two compounds of similar molecular weight: acetonitrile (CH_3CN , MW 41 u, bp 355 K) and propane ($CH_3CH_2CH_3$, MW 44 u, bp 231 K). Acetonitrile is a polar molecule, with a dipole moment of 3.9 D, so dipole–dipole interactions are present. However, propane is essentially nonpolar, which means that dipole–dipole interactions are absent. Because acetonitrile and propane have similar molecular weights, dispersion forces are similar for these two molecules. Therefore, the higher boiling point of acetonitrile can be attributed to dipole–dipole interactions.

Linear molecule—larger surface area enhances intermolecular contact and increases dispersion force.



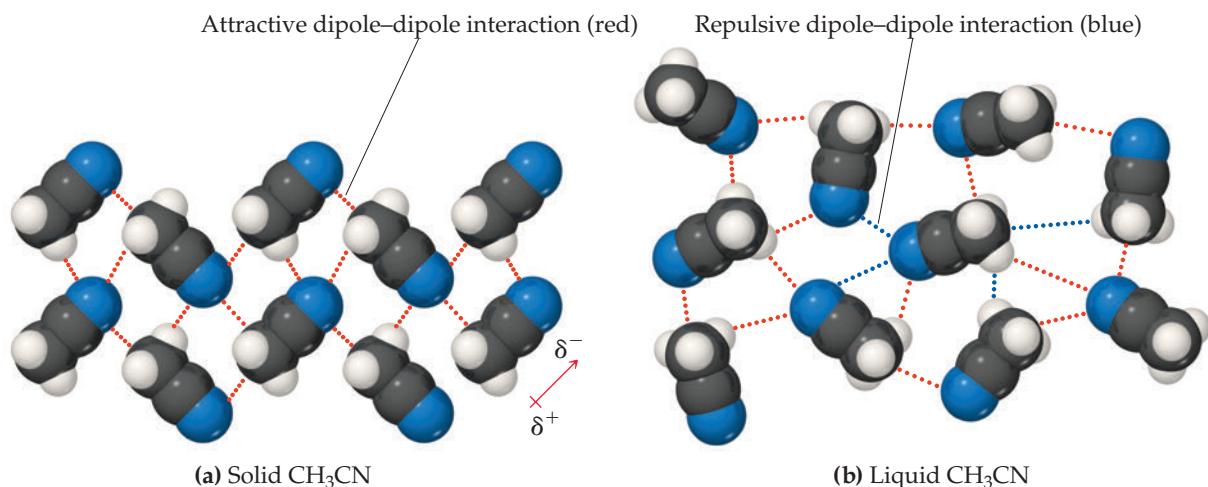
Pentane (C_5H_{12})
bp = 309.4 K

Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force.



Dimethylpropane (C_5H_{12})
bp = 282.7 K

▲ **Figure 11.6** Molecular shape affects intermolecular attraction. Molecules of *n*-pentane make more contact with each other than do neopentane molecules. Thus, *n*-pentane has stronger intermolecular attractive forces and therefore a higher boiling point.



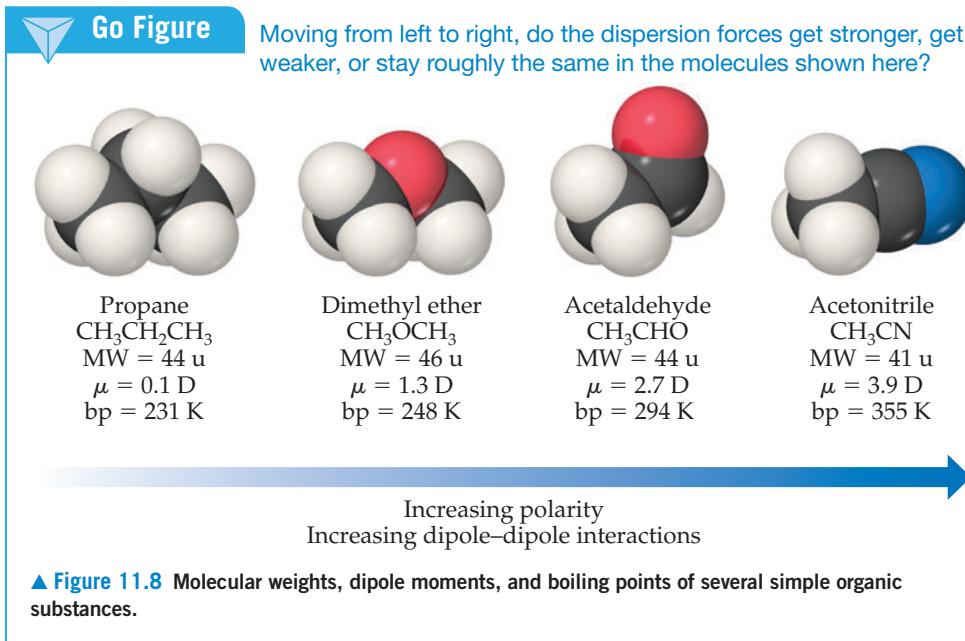
▲ **Figure 11.7** Dipole–dipole interactions. The dipole–dipole interactions in (a) crystalline CH_3CN and (b) liquid CH_3CN .

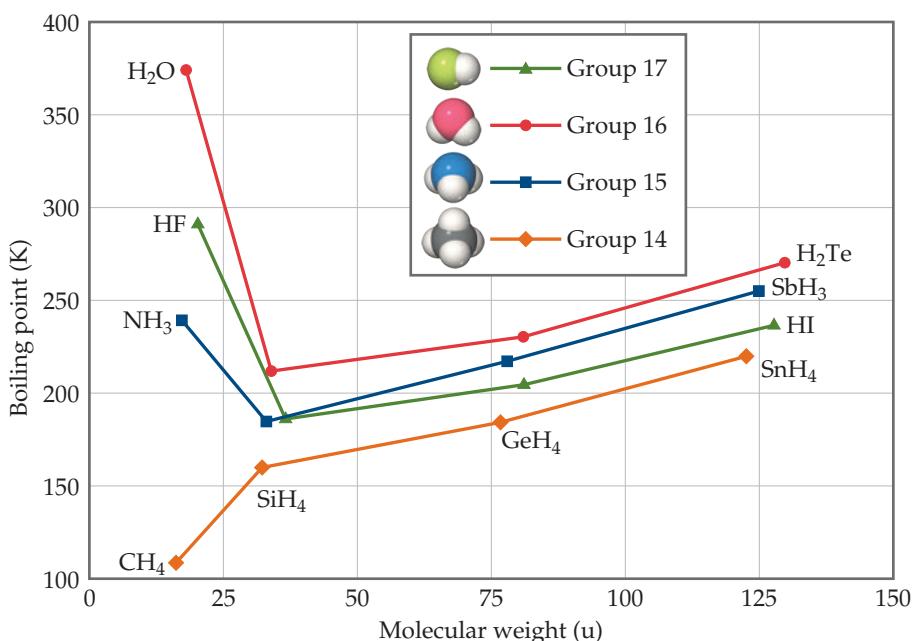
To better understand these forces, consider how CH_3CN molecules pack together in the solid and liquid states. In the solid [Figure 11.7(a)], the molecules are arranged with the negatively charged nitrogen end of each molecule close to the positively charged $-\text{CH}_3$ ends of its neighbors. In the liquid [Figure 11.7(b)], the molecules are free to move with respect to one another, and their arrangement becomes more disordered. This means that, at any given instant, both attractive and repulsive dipole–dipole interactions are present. However, not only are there more attractive interactions than repulsive ones, but also molecules that are attracting each other spend more time near each other than do molecules that are repelling each other. The overall effect is a net attraction strong enough to keep the molecules in liquid CH_3CN from moving apart to form a gas.

For molecules of approximately equal mass and size, the strength of intermolecular attractions increases with increasing polarity, a trend we see in Figure 11.8. Notice how the boiling point increases as the dipole moment increases.

Hydrogen Bonding

Figure 11.9 shows the boiling points of the binary compounds that form between hydrogen and the elements in Groups 14 through 17. The boiling points of the compounds containing



Go FigureExplain the difference in boiling points between PH_3 and AsH_3 .

▲ Figure 11.9 Boiling points of the covalent hydrides of the elements in Groups 14–17 as a function of molecular weight.

Group 14 elements (CH_4 through SnH_4 , all nonpolar) increase systematically moving down the group. This is the expected trend because polarizability and, hence, dispersion forces generally increase as molecular weight increases. The heavier members of Groups 15, 16, and 17 follow the same trend, but NH_3 , H_2O , and HF have boiling points that are much higher than expected. In fact, these three compounds also have many other characteristics that distinguish them from other substances of similar molecular weight and polarity. For example, water has a high melting point, a high specific heat, and a high heat of vaporization. Each of these properties indicates that the intermolecular forces are abnormally strong.

The strong intermolecular attractions in HF , H_2O , and NH_3 result from *hydrogen bonding*. A **hydrogen bond** is an attraction between a hydrogen atom attached to a highly electronegative atom (usually F, O, or N) and a nearby small electronegative atom in another molecule or chemical group. Thus, H—F, H—O, or H—N bonds in one molecule can form hydrogen bonds with an F, O, or N atom in another molecule. Several examples of hydrogen bonds are shown in Figure 11.10, including the hydrogen bond that exists between the H atom in an H_2O molecule and the O atom of an adjacent H_2O molecule. Notice in each case that the H atom in the hydrogen bond interacts with a nonbonding electron pair.

Hydrogen bonds can be considered a special type of dipole-dipole attraction. Because N, O, and F are so electronegative, a bond between hydrogen and any of these elements is quite polar, with hydrogen at the positive end (remember the + on the right-hand side of the dipole symbol represents the positive end of the dipole):



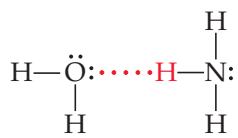
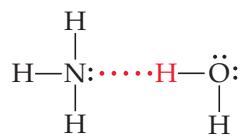
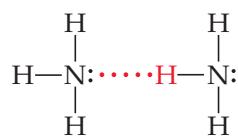
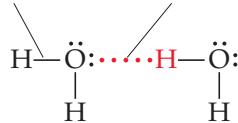
The hydrogen atom has no inner electrons. Thus, the positive side of the dipole has the concentrated charge of the nearly bare hydrogen nucleus. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the electron-poor hydrogen is so small, it can approach an electronegative atom very closely and, thus, interact strongly with it.

Hydrogen bonding plays important roles in many chemical systems, especially those of biological significance. For example, hydrogen bonding helps stabilize the three-dimensional structure of proteins, which is critical to their function. Hydrogen bonding is also responsible for the double-helical structure of DNA, which is key to its genetic function.

Go Figure

To form a hydrogen bond, what must the nonhydrogen atom (N, O, or F) involved in the bond possess?

Covalent bond, *intramolecular* Hydrogen bond, *intermolecular*



▲ Figure 11.10 Hydrogen bonding.

Hydrogen bonding occurs between an H atom that is bonded to N, O, or F in one molecule and an N, O, or F atom in another molecule.



Sample Exercise 11.1

Identifying Substances That Can Form Hydrogen Bonds

In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), fluoromethane (CH_3F), hydrogen sulfide (H_2S)?

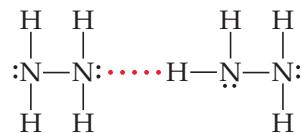
SOLUTION

Analyze We are given the chemical formulas of four compounds and asked to predict whether they can participate in hydrogen bonding. All the compounds contain H, but hydrogen bonding usually occurs only when the hydrogen is covalently bonded to N, O, or F.

Plan We analyze each formula to see if it contains N, O, or F directly bonded to H. There also needs to be a nonbonding pair of electrons on an electronegative atom (usually N, O, or F) in a nearby molecule, which can be revealed by drawing the Lewis structure for the molecule.

Solve The foregoing criteria eliminate CH_4 and H_2S , which do not contain H bonded to N, O, or F. They also eliminate CH_3F , whose Lewis structure shows a central C atom surrounded by three H atoms and an F atom. (Carbon always forms four bonds, whereas hydrogen and fluorine form one each.) Because the molecule contains a C—F bond and not an H—F bond, it does not form hydrogen bonds. In H_2NNH_2 , however, we find N—H bonds, and the Lewis structure shows a nonbonding pair of electrons on

each N atom, telling us hydrogen bonds can exist between the molecules:



Check Although we can generally identify substances that participate in hydrogen bonding based on their containing N, O, or F covalently bonded to H, drawing the Lewis structure for the interaction provides a way to check the prediction.

► Practice Exercise

Which of the following substances is most likely to be a liquid at room temperature?

- (a) formaldehyde, H_2CO
- (b) fluoromethane, CH_3F
- (c) hydrogen cyanide, HCN
- (d) hydrogen peroxide, H_2O_2
- (e) hydrogen sulfide, H_2S

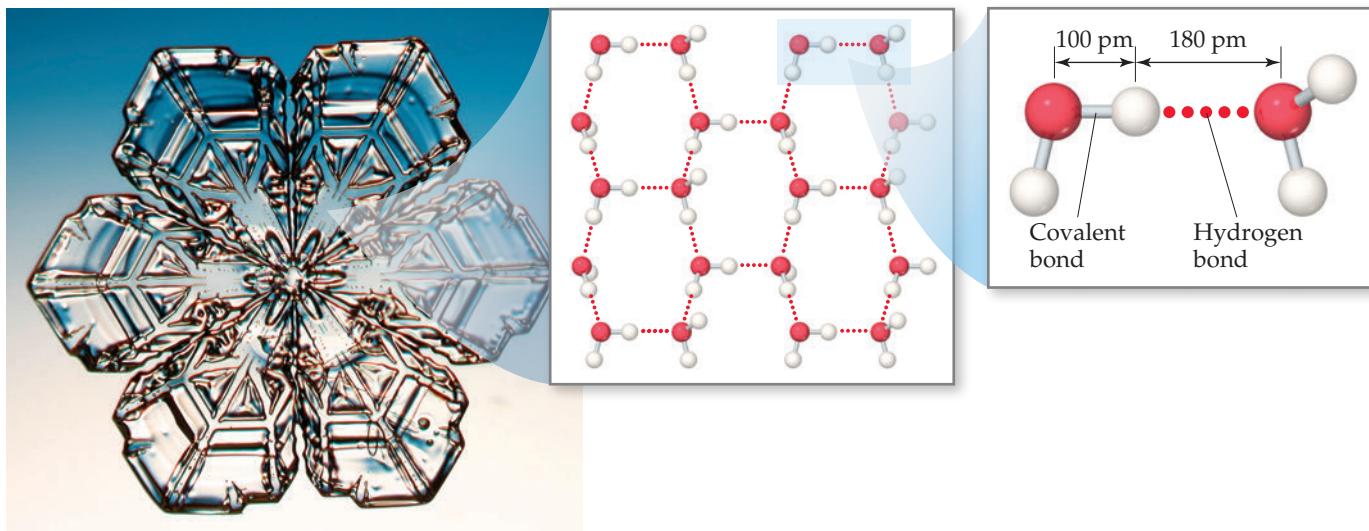
One remarkable consequence of hydrogen bonding is seen in the densities of ice and liquid water. In most substances the molecules in the solid are more densely packed than those in the liquid, making the solid phase denser than the liquid phase. By contrast, the density of ice at 0°C (0.917 g/mL) is less than that of liquid water at 0°C (1.00 g/mL), so ice floats on liquid water.

The lower density of ice can be understood in terms of hydrogen bonding. In ice, the H_2O molecules assume the ordered, open arrangement shown in **Figure 11.11**. This



Go Figure

What is the approximate $\text{H}-\text{O}\cdots\text{H}$ bond angle in ice, where $\text{H}-\text{O}$ is the covalent bond and $\text{O}\cdots\text{H}$ is the hydrogen bond?



▲ **Figure 11.11** Hydrogen bonding in ice. The empty channels in the structure of ice make water less dense as a solid than as a liquid.

arrangement optimizes hydrogen bonding between molecules, with each H₂O molecule forming hydrogen bonds to four neighboring H₂O molecules. These hydrogen bonds, however, create the cavities seen in the middle image of Figure 11.11. When ice melts, the motions of the molecules cause the structure to collapse. The hydrogen bonding in the liquid is more random than that in the solid but is strong enough to hold the molecules close together. Consequently, liquid water has a denser structure than ice, meaning that a given mass of water occupies a smaller volume than the same mass of ice.

The expansion of water upon freezing (**Figure 11.12**) is responsible for many phenomena we take for granted. It causes icebergs to float and water pipes to burst in cold weather. The lower density of ice compared to liquid water also profoundly affects life on Earth. Because ice floats, it covers the top of the water when a lake freezes, thereby insulating the water. If ice were denser than water, ice forming at the top of a lake would sink to the bottom, and the lake could freeze solid. Most aquatic life could not survive under these conditions.

Ion-Dipole Forces

An **ion-dipole force** exists between an ion and a polar molecule (**Figure 11.13**). Cations are attracted to the negative end of a dipole, and anions are attracted to the positive end. The magnitude of the attraction increases as either the ionic charge or the magnitude of the dipole moment increases. Ion-dipole forces are especially important for solutions of ionic substances in polar liquids, such as a solution of NaCl in water.

Comparing Intermolecular Forces

We can identify the intermolecular forces operative in a substance by considering its composition and structure. *Dispersion forces are found in all substances.* The strength of these attractive forces increases with increasing molecular weight and depends on molecular shapes. With polar molecules dipole-dipole interactions are also operative, but these interactions often make a smaller contribution to the total intermolecular attraction than do dispersion forces. For example, in liquid HCl, dispersion forces are estimated to account for more than 80% of the total attraction between molecules, while dipole-dipole attractions account for the rest. Hydrogen bonds, when present, make an important contribution to the total intermolecular interaction.

In general, the energies associated with dispersion forces are 0.1–30 kJ/mol. The wide range reflects the wide range in polarizabilities of molecules. By comparison, the energies associated with dipole-dipole interactions and hydrogen bonds are approximately 2–15 kJ/mol and 10–40 kJ/mol, respectively. Ion-dipole forces tend to be stronger than the aforementioned intermolecular forces, with energies typically exceeding 50 kJ/mol. All these interactions are considerably weaker than covalent and ionic bonds, which have energies that are hundreds of kilojoules per mole.

Figure 11.14 presents a systematic way of identifying the intermolecular forces in a particular system.

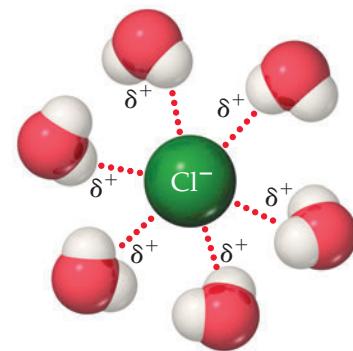
It is important to realize that the effects of all these attractions are additive. For example, acetic acid, CH₃COOH, and 1-propanol, CH₃CH₂CH₂OH, have the same molecular weight, 60 u, and both are capable of forming hydrogen bonds. However, a pair of acetic acid molecules can form two hydrogen bonds, whereas a pair of 1-propanol molecules can form only one (**Figure 11.15**). Hence, the boiling point of acetic acid is higher. These effects can be important, especially for very large polar molecules such as proteins, which have multiple dipoles and hydrogen-bonding groups over their surfaces. These molecules can be held together in solution to a surprisingly high degree due to the presence of multiple attractive interactions.



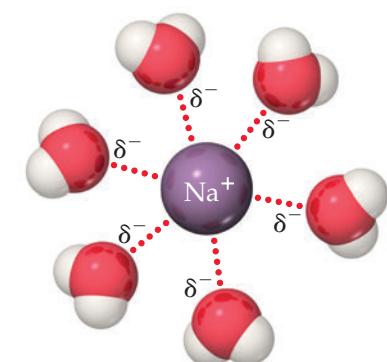
▲ **Figure 11.12** Expansion of water upon freezing.

Go Figure

Why does the O side of H₂O point toward the Na⁺ ion?



Positive ends of polar molecules are oriented toward negatively charged anion.



Negative ends of polar molecules are oriented toward positively charged cation.

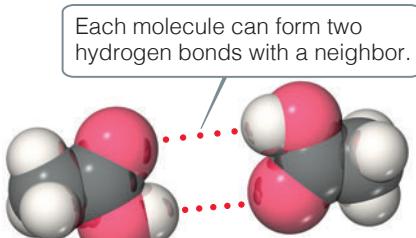
▲ **Figure 11.13** Ion-dipole forces.

**Go Figure**

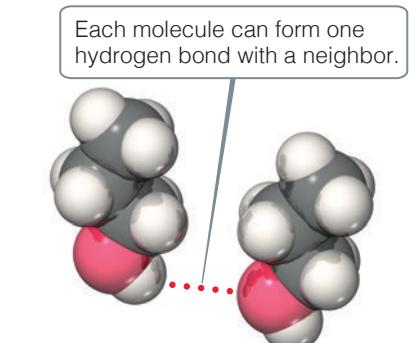
Can the energies of multiple dispersion forces between two molecules be larger than the energy of hydrogen bonding between the two molecules?

Type of intermolecular interaction	Atoms Examples: Ne, Ar	Nonpolar molecules Examples: BF ₃ , CH ₄	Polar molecules without OH, NH, or HF groups Examples: HCl, CH ₃ CN	Polar molecules containing OH, NH, or HF groups Examples: H ₂ O, NH ₃	Ionic solids dissolved in polar liquids Examples: NaCl in H ₂ O
Dispersion forces (0.1–30 kJ/mol)	✓	✓	✓	✓	✓
Dipole–dipole interactions (2–15 kJ/mol)			✓	✓	
Hydrogen bonding (10–40 kJ/mol)				✓	
Ion–dipole interactions (>50 kJ/mol)					✓

▲ **Figure 11.14** Checklist for determining intermolecular forces. Multiple types of intermolecular forces can be operating in a given substance or mixture. Note that dispersion forces occur in all substances.



Acetic acid, CH₃COOH
MW = 60 u
bp = 391 K



1-Propanol, CH₃CH₂CH₂OH
MW = 60 u
bp = 370 K

When comparing the relative strengths of intermolecular attractions, consider these generalizations:

- 1. When the molecules of two substances have comparable molecular weights and shapes, dispersion forces are approximately equal in the two substances.** Differences in the magnitudes of the intermolecular forces are due to differences in the strengths of dipole–dipole attractions. The intermolecular forces get stronger as molecule polarity increases, with those molecules capable of hydrogen bonding having the strongest interactions.
- 2. When the molecules of two substances differ widely in molecular weights, and there is no hydrogen bonding, dispersion forces tend to determine which substance has the stronger intermolecular attractions.** Intermolecular attractive forces are generally higher in the substance with higher molecular weight.

Self-Assessment Exercise

- 11.5** Rank the following molecules from lowest to highest boiling point: CH₃CH₂CH₂OH, CH₃CH₂CH₂CH₃, CH₃CH₂OCH₃
- (a) CH₃CH₂CH₂OH < CH₃CH₂CH₂CH₃ < CH₃CH₂OCH₃
 - (b) CH₃CH₂CH₂CH₃ < CH₃CH₂OCH₃ < CH₃CH₂CH₂OH
 - (c) CH₃CH₂OCH₃ < CH₃CH₂CH₂CH₃ < CH₃CH₂CH₂OH

▲ **Figure 11.15** Hydrogen bonding in acetic acid and 1-propanol. The greater the number of hydrogen bonds possible, the more tightly the molecules are held together and, therefore, the higher the boiling point.

Exercises

- 11.6** (a) Which is generally stronger, intermolecular interactions or intramolecular interactions? (b) Which of these kinds of interactions are broken when a liquid is converted to a gas?
- 11.7** Which type of intermolecular force accounts for each of these differences? (a) Acetone, $(\text{CH}_3)_2\text{CO}$, boils at 56°C ; dimethyl sulfoxide or DMSO, $(\text{CH}_3)_2\text{SO}$, boils at 189°C . (b) CCl_4 is a liquid at atmospheric pressure and room temperature, whereas CH_4 is a gas under the same conditions. (c) H_2O boils at 100°C but H_2S boils at -60°C . (d) 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) boils at 97°C , whereas 2-propanol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$) boils at 82.6°C .
- Acetone**
- DMSO**
- 11.8** True or false: (a) Molecules containing polar bonds must be polar molecules and have dipole-dipole forces. (b) For the halogen gases, the dispersion forces decrease while the boiling points increase as you go down the column in the periodic table. (c) In terms of the total attractive forces for a given substance, the more polar bonds there are in a molecule, the stronger the dipole-dipole interaction. (d) All other factors being the same, total attractive forces between linear molecules are greater than those between molecules whose shapes are nearly spherical. (e) The more electronegative the atom, the more polarizable it is.
- 11.9** Which member in each pair has the stronger intermolecular dispersion forces? (a) H_2O or CH_3OH , (b) CBr_3CBr_3 or CCl_3CCl_3 , (c) $\text{C}(\text{CH}_3)_4$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.
- 11.10** (a) What atoms must a molecule contain to participate in hydrogen bonding with other molecules of the same kind? (b) Which of the following molecules can form hydrogen bonds with other molecules of the same kind: CH_3F , CH_3NH_2 , CH_3OH , CH_3Br ?
- 11.11** Based on the type or types of intermolecular forces, predict the substance in each pair that has the higher boiling point: (a) propane (C_3H_8) or *n*-butane (C_4H_{10}), (b) diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) or 1-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), (c) sulfur dioxide (SO_2) or sulfur trioxide (SO_3), (d) phosphene (Cl_2CO) or formaldehyde (H_2CO).
- 11.12** Freon, CCl_2F_2 , and dichloromethane, CH_2Cl_2 , are common organic substances. Freon is a gas with a normal boiling point of -29.8°C ; dichloromethane's normal boiling point is 39.6°C . Which statement is the best explanation of these data? (a) Dichloromethane can form hydrogen bonds, but freon cannot. (b) Dichloromethane has a larger dipole moment than freon. (c) Freon is more polarizable than dichloromethane.

11.5 (b)

Answers to Self-Assessment Exercises



11.3 | Select Properties of Liquids



Honey is an example of a non-Newtonian fluid; that is, one in which viscosity changes with the applied stress. Another that you may be familiar with is a suspension of corn starch in water. In the case of honey, its viscosity increases as a sheer force is applied. Dip a spoon into a honey jar and try and stir it rapidly and you find the honey acts as a very viscous material. Remove the spoon and the honey flows smoothly off the spoon.

The intermolecular attractions we have just discussed can help us understand many familiar properties of liquids. In this section, we examine three: viscosity, surface tension, and capillary action.

By the end of this section, you should be able to

- Explain the concepts of viscosity, surface tension, and capillary action.



Sample Exercise 11.2

Predicting Types and Relative Strengths of Intermolecular Attractions

List the substances BaCl_2 , H_2 , CO , HF , and Ne in order of increasing boiling point.

SOLUTION

Analyze We need to assess the intermolecular forces in these substances and use that information to determine the relative boiling points.

Plan The boiling point depends in part on the attractive forces in each substance. We need to order these substances according to the relative strengths of the different kinds of intermolecular attractions.

Solve The attractive forces are stronger for ionic substances than for molecular ones, so BaCl_2 should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2 , 2 u; CO , 28 u; HF , 20 u; and Ne , 20 u. The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO , HF , and Ne are similar. Because HF can hydrogen-bond, it should have the highest boiling point of the three. Next is CO , which is slightly polar and has the highest

molecular weight. Finally, Ne , which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is, therefore,



Check The boiling points reported in the literature are H_2 , 20 K; Ne , 27 K; CO , 83 K; HF , 293 K; and BaCl_2 , 1813 K—in agreement with our predictions.

► Practice Exercise

List the substances Ar , Cl_2 , CH_4 , and CH_3COOH in order of increasing strength of intermolecular attractions.

- $\text{CH}_4 < \text{Ar} < \text{CH}_3\text{COOH} < \text{Cl}_2$
- $\text{Cl}_2 < \text{CH}_3\text{COOH} < \text{Ar} < \text{CH}_4$
- $\text{CH}_4 < \text{Ar} < \text{Cl}_2 < \text{CH}_3\text{COOH}$
- $\text{CH}_3\text{COOH} < \text{Cl}_2 < \text{Ar} < \text{CH}_4$
- $\text{Ar} < \text{Cl}_2 < \text{CH}_4 < \text{CH}_3\text{COOH}$



SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

▲ Figure 11.16 Comparing viscosities. The Society of Automotive Engineers (SAE) has established a numeric scale to indicate motor-oil viscosity.

Viscosity

Some liquids, such as molasses and motor oil, flow very slowly; others, such as water and gasoline, flow easily. The resistance of a liquid to flow is called **viscosity**. The greater a liquid's viscosity, the more slowly it flows. Viscosity can be measured by timing how long it takes a certain amount of the liquid to flow through a thin vertical tube (Figure 11.16). Viscosity can also be determined by measuring the rate at which steel balls fall through the liquid. The balls fall more slowly as the viscosity increases. The SI unit for viscosity is kg/m s .

The viscosity of a liquid is related to how easily its molecules flow past one another. It depends on the attractive forces between molecules and on whether the shapes and flexibility of the molecules are such that they tend to become entangled (for example, long molecules can become tangled like spaghetti). For a series of related compounds, viscosity increases with molecular weight, as illustrated in Table 11.3.

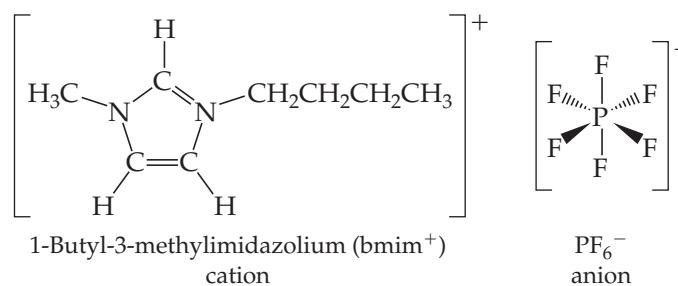
TABLE 11.3 Viscosities of a Series of Hydrocarbons at 20 °C

Substance	Formula	Viscosity (kg/m s)
Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	3.26×10^{-4}
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	4.09×10^{-4}
Octane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	5.42×10^{-4}
Nonane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	7.11×10^{-4}
Decane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.42×10^{-3}

CHEMISTRY PUT TO WORK Ionic Liquids

The strong electrostatic attractions between cations and anions explain why most ionic compounds are solids at room temperature, with high melting and boiling points. However, the melting point of an ionic compound can be low if the ionic charges are not too high and the cation-anion distance is sufficiently large. For example, the melting point of NH_4NO_3 , where both cation and anion are larger polyatomic ions, is 170°C . If the ammonium cation is replaced by the even larger ethylammonium cation, $\text{CH}_3\text{CH}_2\text{NH}_3^+$, the melting point drops to 12°C , making ethylammonium nitrate a liquid at room temperature. Ethylammonium nitrate is an example of an *ionic liquid*: a salt that is a liquid at room temperature.

Not only is $\text{CH}_3\text{CH}_2\text{NH}_3^+$ larger than NH_4^+ but also it is less symmetric. In general, the larger and more irregularly shaped the ions in an ionic substance, the better the chances of forming an ionic liquid. Among the cations that form ionic liquids, one of the most widely used is the 1-butyl-3-methylimidazolium cation (abbreviated bmim^+ , Figure 11.17 and Table 11.4), which has two arms of different lengths coming off a five-atom central ring. This feature gives bmim^+ an irregular shape, which makes it difficult for the molecules to pack together in a solid.



▲ Figure 11.17 Representative ions found in ionic liquids.

TABLE 11.4 Melting Point and Decomposition Temperature of Four 1-Butyl-3-Methylimidazolium (bmim^+) Salts

Cation	Anion	Melting Point (°C)	Decomposition Temperature (°C)
bmim ⁺	Cl ⁻	41	254
bmim ⁺	I ⁻	-72	265
bmim ⁺	PF ₆ ⁻	10	349
bmim ⁺	BF ₄ ⁻	-81	403

Common anions found in ionic liquids include the PF_6^- , BF_4^- , and halide ions.

Ionic liquids have many useful properties. Unlike most molecular liquids, they are nonvolatile (that is, they don't evaporate readily) and nonflammable. They tend to remain in the liquid state at temperatures up to about 400 °C. Most molecular substances are liquids only at much lower temperatures, 100 °C or less in most cases. Because ionic liquids are good solvents for a wide range of substances, ionic liquids can be used for a variety of reactions and separations. These properties make them attractive replacements for volatile organic solvents in many industrial processes. Relative to traditional organic solvents, ionic liquids offer the promise of reduced volumes, safer handling, and easier reuse, thereby reducing the environmental impact of industrial chemical processes.

Related Exercises: 11.59, 11.17, 11.89

The viscosity of a substance decreases with increasing temperature. This can be seen in the viscosity of octane:

$$7.06 \times 10^{-4} \text{ kg/m s at } 0^\circ\text{C}$$

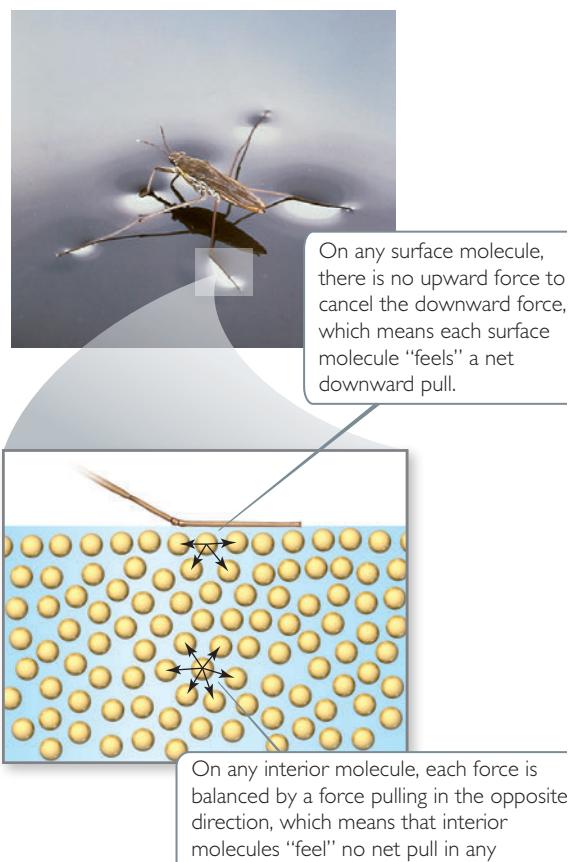
At higher temperatures, the greater average kinetic energy of the molecules overcomes the attractive forces between molecules.

Surface Tension

The surface of water behaves almost as if it had an elastic skin, as evidenced by the ability of certain insects to “walk” on water. This behavior is due to an imbalance of intermolecular forces at the surface of the liquid. As shown in [Figure 11.18](#), molecules in the interior are attracted equally in all directions, but those at the surface experience a net inward force. This net force tends to pull surface molecules toward the interior, thereby reducing the surface area and making the molecules at the surface pack closely together.

Because spheres have the smallest surface area for their volume, water droplets assume an almost spherical shape. This explains the tendency of water to “bead up” when it contacts a surface made of nonpolar molecules, like a lotus leaf or a newly waxed car.

A measure of the net inward force that must be overcome to expand the surface area of a liquid is given by its surface tension. **Surface tension** is the energy required to increase the surface area of a liquid by a unit amount. For example, the surface tension of water at 20°C is 7.29×10^{-2} J/m², which means that an energy of 7.29×10^{-2} J must be supplied to increase the surface area of a given amount of water by 1 m². Water has a



▲ **Figure 11.18** Molecular-level view of surface tension. The high surface tension of water keeps the water strider from sinking.

high surface tension because of its strong hydrogen bonds. The surface tension of mercury is even higher ($4.6 \times 10^{-1} \text{ J/m}^2$) because of even stronger metallic bonds between the atoms of mercury.

Capillary Action

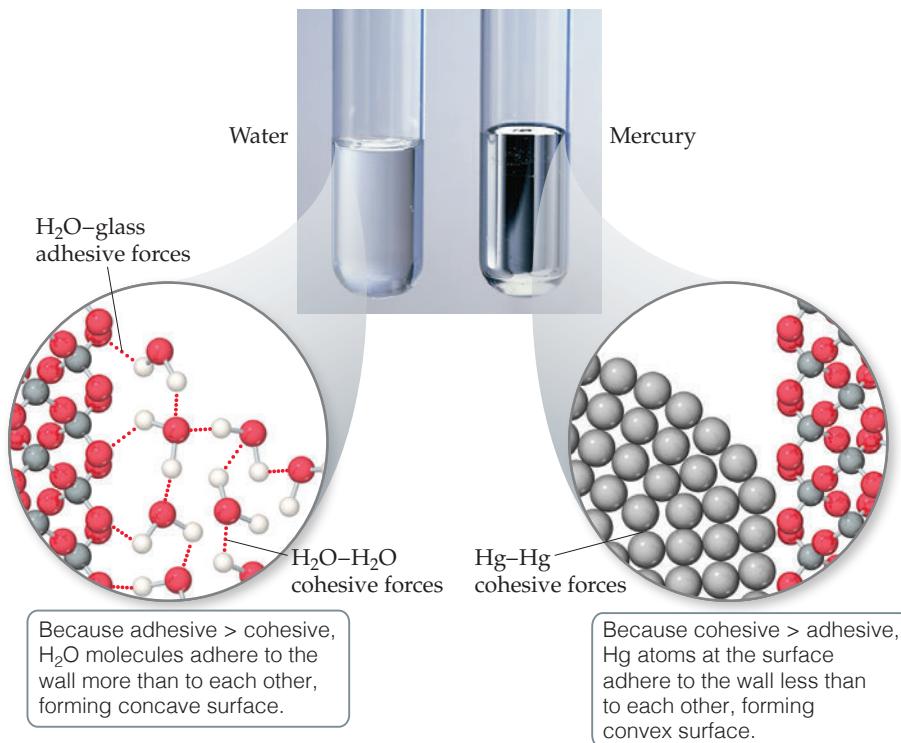
Intermolecular forces that bind similar molecules to one another, such as the hydrogen bonding in water, are called *cohesive forces*. Intermolecular forces that bind a substance to a surface are called *adhesive forces*. Water placed in a glass tube adheres to the glass because the adhesive forces between the water and the glass are greater than the cohesive forces between water molecules; glass is principally SiO_2 , which has a very polar surface. The curved surface, or *meniscus*, of the water is therefore U-shaped (Figure 11.19). For mercury, however, the situation is different. Mercury atoms can form bonds with one another but not with the glass. As a result, the cohesive forces are much greater than the adhesive forces and the meniscus is shaped like an inverted U.

When a small-diameter glass tube, or capillary, is placed in water, water rises in the tube. The rise of liquids up very narrow tubes is called **capillary action**. The adhesive forces between the liquid and the walls of the tube tend to increase the surface area of the liquid. The surface tension of the liquid tends to reduce the area, thereby pulling the liquid up the tube. The liquid climbs until the force of gravity on the liquid balances the adhesive and cohesive forces.

Capillary action is widespread. For example, towels absorb liquid, and "stay-dry" synthetic fabrics move sweat away from the skin by capillary action. Capillary action also plays a role in moving water and dissolved nutrients upward through plants.

Go Figure

If the inside surface of each tube were coated with wax, would the general shape of the water meniscus change? Would the general shape of the mercury meniscus change?



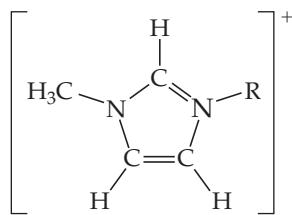
▲ **Figure 11.19** Meniscus shapes for water and mercury in glass tubes.

Self-Assessment Exercise

- 11.13** As the temperature increases, how do you expect the surface tension of a liquid to change?
- It would increase
 - It would decrease
 - It would stay the same

Exercises

- 11.14** Based on their composition and structure, list CH_3COOH , $\text{CH}_3\text{COOCH}_3$, and $\text{CH}_3\text{CH}_2\text{OH}$ in order of (a) increasing intermolecular forces, (b) increasing viscosity, (c) increasing surface tension.
- 11.15** Hydrazine (H_2NNH_2), hydrogen peroxide (HOOH), and water (H_2O) all have exceptionally high surface tensions compared with other substances of comparable molecular weights. (a) Draw the Lewis structures for these three compounds. (b) What structural property do these substances have in common, and how might that account for the high surface tensions?
- 11.16** (a) Would you expect the viscosity of 2-propanol, $(\text{CH}_3)_2\text{CHOH}$, to be larger or smaller than the viscosity of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$? (b) Would you expect the viscosity of 2-propanol to be smaller or larger than the viscosity of 1-propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$?
- 11.17** The generic structural formula for a 1-alkyl-3-methylimidazolium cation is



where R is a $-\text{CH}_2(\text{CH}_2)_n\text{CH}_3$ alkyl group. The melting points of the salts that form between the 1-alkyl-3-methylimidazolium cation and the PF_6^- anion are as follows: R = CH_2CH_3 (m.p. = 60°C), R = $\text{CH}_2\text{CH}_2\text{CH}_3$ (m.p. = 40°C), R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (m.p. = 10°C), and R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (m.p. = -61°C). Why does the melting point decrease as the length of alkyl group increases?

11.13 (b)

Answers to Self-Assessment Exercises

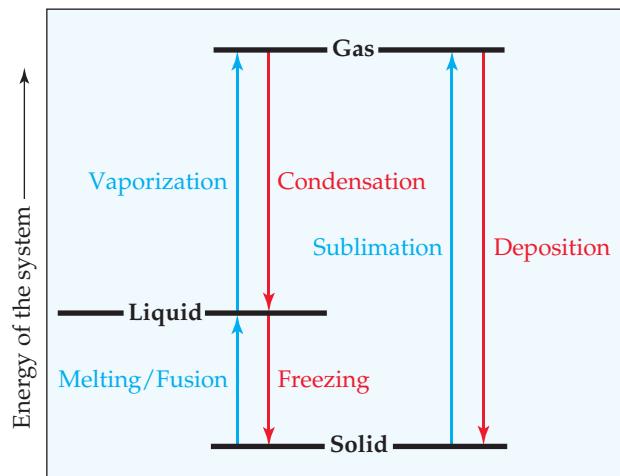
11.4 | Phase Changes





Go Figure

How is energy evolved in deposition related to those for condensation and freezing?



▲ **Figure 11.20** Phase changes and the names associated with them.

two states. **Figure 11.20** shows the names associated with these transformations, which are called either **phase changes** or *changes of state*.

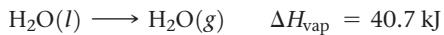
Energy Changes Accompany Phase Changes

Every phase change is accompanied by a change in the energy of the system. In a solid, for example, the particles (molecules, ions, or atoms) are in more or less fixed positions with respect to one another and closely arranged to minimize the energy of the system. As the temperature of the solid increases, the particles vibrate about their equilibrium positions with increasing energetic motion. When the solid melts, the particles begin moving freely relative to one another, which means their average kinetic energy increases.

Melting is called (somewhat confusingly) *fusion*. The increased freedom of motion of the particles requires energy, measured by the **heat of fusion** or *enthalpy of fusion*, ΔH_{fus} . The heat of fusion of ice, for example, is 6.01 kJ/mol:



As the temperature of the liquid increases, the particles move about more vigorously. The increased motion allows some particles to escape into the gas phase. As a result, the concentration of gas-phase particles above the liquid surface increases with temperature. These gas-phase particles exert a pressure called *vapor pressure*. We explore vapor pressure in Section 11.5. For now we just need to understand that vapor pressure increases with increasing temperature until it equals the external pressure above the liquid, typically atmospheric pressure. At this point the liquid boils—bubbles of the vapor form within the liquid. The energy required to cause the transition of a given quantity of the liquid to the vapor is called either the **heat of vaporization** or the *enthalpy of vaporization*, ΔH_{vap} . For water, the heat of vaporization is 40.7 kJ/mol.



Heat packs are often used for the on-site treatment of sports injuries. They consist of a flexible thick plastic bag divided into two compartments, one containing water and the other a salt. Breaking the seal between the compartments allows the salt to dissolve, and this is accompanied by a temperature change. Hot packs typically have magnesium sulfate or calcium chloride as the salt, which dissolves exothermically, while cold packs use ammonium nitrate or urea. These packs are for a single use. A variation is a reusable hot pack that contains a supercooled solution of sodium acetate and a small strip of metal. When the metal is bent, small changes on its surface initiate the crystallization of the sodium acetate from solution, releasing heat. The pack may be reused by heating it in boiling water to redissolve the sodium acetate, putting it aside and, without disturbing it, allowing it to cool to room temperature.

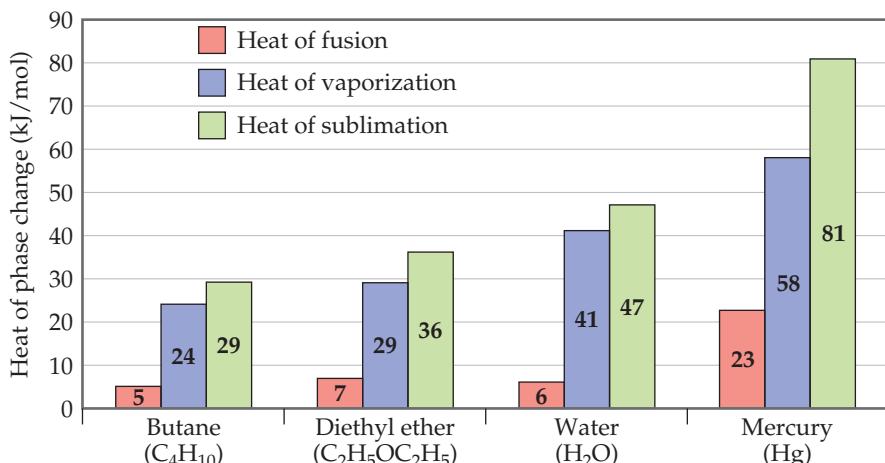
By the end of this section, you should be able to

- List the names of the various changes of state for a pure substance and indicate which are endothermic and which are exothermic.

Liquid water left uncovered in a glass eventually evaporates. An ice cube left in a warm room quickly melts. Solid CO₂ (sold as a product called dry ice) *sublimes* at room temperature; that is, it changes directly from solid to gas. In general, each state of matter—solid, liquid, gas—can transform into either of the other


Go Figure

Why does water have a higher heat of vaporization than diethyl ether?



▲ Figure 11.21 Heats of fusion, vaporization, and sublimation.

Figure 11.21 shows ΔH_{fus} and ΔH_{vap} values for four substances. The values of ΔH_{vap} tend to be larger than the values of ΔH_{fus} because in the transition from liquid to gas, particles must essentially sever all their interparticle attractions, whereas in the transition from solid to liquid, many of these attractive interactions remain operative.

The particles of a solid can move directly into the gaseous state. The enthalpy change required for this transition is called the **heat of sublimation**, denoted ΔH_{sub} . As illustrated in Figure 11.20, ΔH_{sub} is the sum of ΔH_{fus} and ΔH_{vap} . Thus, ΔH_{sub} for water is approximately 47 kJ/mol.

Phase changes show up in important ways in our everyday experiences. When we use ice cubes to cool a drink, for instance, the heat of fusion of the ice cools the liquid. We feel cool when we step out of a swimming pool or a warm shower because the liquid water's heat of vaporization is drawn from our bodies as the water evaporates from our skin. Our bodies use this mechanism to regulate body temperature, especially when we exercise vigorously in warm weather. A refrigerator also relies on the cooling effects of vaporization. Its mechanism contains an enclosed gas that can be liquefied under pressure. The liquid absorbs heat as it subsequently evaporates, thereby cooling the interior of the refrigerator.

What happens to the heat absorbed when the liquid refrigerant vaporizes? According to the first law of thermodynamics, this absorbed heat must be released when the gas condenses to liquid. As this phase change occurs, the heat released is dissipated through cooling coils in the back of the refrigerator. Just as for a given substance the heat of condensation is equal in magnitude to the heat of vaporization and has the opposite sign, so too the *heat of deposition* for a given substance is exothermic to the same degree that the heat of sublimation is endothermic; the *heat of freezing* is exothermic to the same degree that the heat of fusion is endothermic (see Figure 11.20).

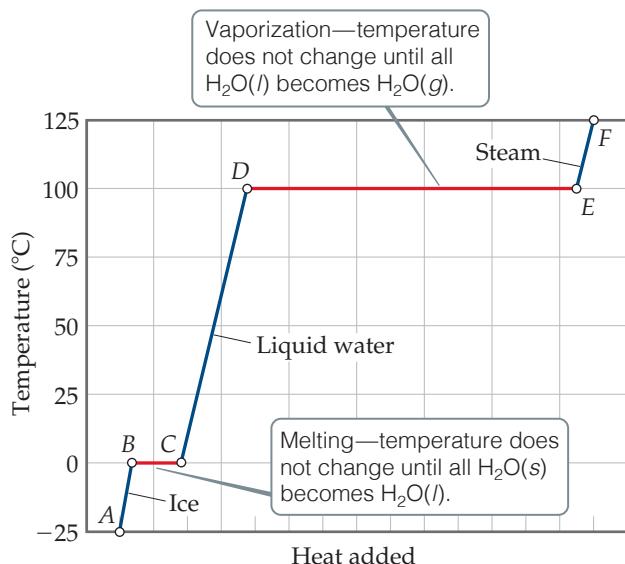
Heating Curves

When we heat an ice cube initially at -25°C and 101.3 kPa, the temperature of the ice increases. As long as the temperature is below 0°C , the ice cube remains in the solid state. When the temperature reaches 0°C , the ice begins to melt. Because melting is an endothermic process, the heat we add at 0°C is used to convert ice to liquid water, and *the temperature remains constant until all the ice has melted*. Once all the ice has melted, adding more heat causes the temperature of the liquid water to increase.



Go Figure

What process is occurring between points C and D?



▲ Figure 11.22 Heating curve for water. Changes that occur when 1.00 mol of H_2O is heated from $\text{H}_2\text{O}(s)$ at -25°C to $\text{H}_2\text{O}(g)$ at 125°C at a constant pressure of 101.3 kPa. Even though heat is being added continuously, the system temperature does not change during the two phase changes (red lines).

achieve a 1°C temperature change is greater than the amount we must add to achieve a 1°C temperature change in the same mass of ice.

Lines BC and DE show the conversion of one phase to another at a constant temperature. The temperature remains constant during these phase changes because the added energy is used to overcome the attractive forces between molecules rather than to increase their average kinetic energy. For line BC , the enthalpy change can be calculated by using ΔH_{fus} , and for line DE we can use ΔH_{vap} .

If we start with 1 mol of steam at 125°C and cool it, we move right to left across Figure 11.22. We first lower the temperature of the $\text{H}_2\text{O}(g)$ ($F \longrightarrow E$), then condense it ($E \longrightarrow D$) to $\text{H}_2\text{O}(l)$, and so forth.

Sometimes as we remove heat from a liquid, we can temporarily cool it below its freezing point without forming a solid. This phenomenon, called *supercooling*, occurs when the heat is removed so rapidly that the molecules have no time to assume the ordered structure of a solid. A supercooled liquid is unstable; particles of dust entering the solution or gentle stirring is often sufficient to cause the substance to solidify quickly.

Critical Temperature and Pressure

A gas normally liquefies at some point when pressure is applied. Suppose we have a cylinder fitted with a piston and the cylinder contains water vapor at 100°C . If we increase the pressure on the water vapor, liquid water will form when the pressure is 101.3 kPa. However, if the temperature is 110°C , the liquid phase does not form until the pressure is 143.3 kPa. At 374°C the liquid phase forms only at 22.06 MPa. Above this temperature, no amount of pressure causes a distinct liquid phase to form. Instead, as pressure increases, the gas becomes steadily more compressed. The highest temperature at which a distinct liquid phase can form is called the **critical temperature**. The **critical pressure** is the pressure required to bring about liquefaction at this critical temperature.

The critical temperature is the highest temperature at which a liquid can exist. Above the critical temperature, the kinetic energies of the molecules are greater than the attractive forces that lead to the liquid state regardless of how much the substance is

A graph of temperature versus amount of heat added is called a *heating curve*. Figure 11.22 shows the heating curve for transforming ice, $\text{H}_2\text{O}(s)$, initially at -25°C to steam, $\text{H}_2\text{O}(g)$, at 125°C . As heat is added at a constant rate, the heating curve forms distinct regions:

- Line AB : Heating increases the temperature of $\text{H}_2\text{O}(s)$ from -25 to 0°C .
- Line BC : Heating converts $\text{H}_2\text{O}(s)$ to $\text{H}_2\text{O}(l)$ as the ice melts at a constant temperature of 0°C .
- Line CD : Heating increases the temperature of the $\text{H}_2\text{O}(l)$ from 0°C to 100°C .
- Line DE : Heating converts $\text{H}_2\text{O}(l)$ to $\text{H}_2\text{O}(g)$ as the water boils at a constant temperature of 100°C .
- Line EF : Heating increases the temperature of the $\text{H}_2\text{O}(g)$ to 125°C .

We can calculate the enthalpy change of the system for each region of the heating curve. Lines AB , CD , and EF show the heating of a single phase from one temperature to another. As we saw in Section 5.5, the amount of heat needed to raise the temperature of a substance is given by the product of the specific heat, mass, and temperature change (Equation 5.21). The greater the specific heat of a substance, the more heat we must add to accomplish a certain temperature increase. Because the specific heat of water is greater than that of ice, the slope of line CD is less than that of line AB . This lesser slope means the amount of heat we must add to a given mass of liquid water to



Sample Exercise 11.3

Calculating ΔH for Temperature and Phase Changes

Calculate the enthalpy change upon converting 1.00 mol of ice at -25°C to steam at 125°C under a constant pressure of 1 atm. The specific heats of ice, liquid water, and steam are 2.03, 4.18, and 1.84 J/g K, respectively. For H_2O , $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$ and $\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$.

SOLUTION

Analyze Our goal is to calculate the total heat required to convert 1 mol of ice at -25°C to steam at 125°C .

Solve

For line *AB* in Figure 11.22, we are adding enough heat to ice to increase its temperature by 25°C . A temperature change of 25°C is the same as a temperature change of 25 K, so we can use the specific heat of ice to calculate the enthalpy change during this process:

For line *BC* in Figure 11.22, in which we convert ice to water at 0°C , we can use the molar enthalpy of fusion directly:

The enthalpy changes for lines *CD*, *DE*, and *EF* can be calculated in similar fashion:

Plan We can calculate the enthalpy change for each segment and then sum them to get the total enthalpy change (Hess's law, Section 5.6).

$$\begin{aligned} \text{AB: } \Delta H &= (1.00 \text{ mol})(18.0 \text{ g/mol})(2.03 \text{ J/g K})(25 \text{ K}) \\ &= 914 \text{ J} = 0.91 \text{ kJ} \end{aligned}$$

$$\text{BC: } \Delta H = (1.00 \text{ mol})(6.01 \text{ kJ/mol}) = 6.01 \text{ kJ}$$

$$\begin{aligned} \text{CD: } \Delta H &= (1.00 \text{ mol})(18.0 \text{ g/mol})(4.18 \text{ J/g K})(100 \text{ K}) \\ &= 7520 \text{ J} = 7.52 \text{ kJ} \end{aligned}$$

$$\text{DE: } \Delta H = (1.00 \text{ mol})(40.67 \text{ kJ/mol}) = 40.7 \text{ kJ}$$

$$\begin{aligned} \text{EF: } \Delta H &= (1.00 \text{ mol})(18.0 \text{ g/mol})(1.84 \text{ J/g K})(25 \text{ K}) \\ &= 830 \text{ J} = 0.83 \text{ kJ} \end{aligned}$$

The total enthalpy change is the sum of the changes of the individual steps:

$$\Delta H = 0.91 \text{ kJ} + 6.01 \text{ kJ} + 7.52 \text{ kJ} + 40.7 \text{ kJ} + 0.83 \text{ kJ} = 56.0 \text{ kJ}$$

Check The components of the total enthalpy change are reasonable relative to the horizontal lengths (heat added) of the lines in Figure 11.22. Notice that the largest component is the heat of vaporization.

► Practice Exercise

What information about water is needed to calculate the enthalpy change for converting 1 mol $\text{H}_2\text{O}(g)$ at 100°C to $\text{H}_2\text{O}(l)$ at 80°C ?

- (a) heat of fusion
- (b) heat of vaporization
- (c) heat of vaporization and specific heat of $\text{H}_2\text{O}(g)$
- (d) heat of vaporization and specific heat of $\text{H}_2\text{O}(l)$
- (e) heat of fusion and specific heat of $\text{H}_2\text{O}(l)$

compressed to bring the molecules closer together. *The greater the intermolecular forces, the higher the critical temperature of a substance.*

Several experimentally determined critical temperatures and pressures are listed in **Table 11.5**. Notice that nonpolar, low-molecular-weight substances, which have weak intermolecular attractions, have lower critical temperatures and pressures than substances that are polar or of higher molecular weight. Notice also that water and ammonia have exceptionally high critical temperatures and pressures as a consequence of strong intermolecular hydrogen-bonding forces.

Because they provide information about the conditions under which gases liquefy, critical temperatures and pressures are often of considerable importance to engineers and other people working with gases. Sometimes we want to liquefy a gas; other times we want to avoid liquefying it. It is useless to try to liquefy a gas by applying pressure if the gas is above its critical temperature. For example, O_2 has a critical temperature of 154.4 K. It must be cooled below this temperature before it can be liquefied by pressure. In contrast, ammonia has a critical temperature of 405.6 K. Thus, it can be liquefied at room temperature (approximately 295 K) by applying sufficient pressure.

When the temperature exceeds the critical temperature and the pressure exceeds the critical pressure, the liquid and gas phases are indistinguishable from each other, and

TABLE 11.5 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (MPa)
Nitrogen, N ₂	126.1	3.39
Argon, Ar	150.9	4.86
Oxygen, O ₂	154.4	5.04
Methane, CH ₄	190.0	4.60
Carbon dioxide, CO ₂	304.3	7.40
Phosphine, PH ₃	324.4	6.54
Propane, CH ₃ CH ₂ CH ₃	370.0	4.26
Hydrogen sulfide, H ₂ S	373.5	9.01
Ammonia, NH ₃	405.6	11.30
Water, H ₂ O	647.6	22.06

the substance is in a state called a **supercritical fluid**. A supercritical fluid expands to fill its container (like a gas), but the molecules are still quite closely spaced (like a liquid).

Like liquids, supercritical fluids can behave as solvents dissolving a wide range of substances. Using *supercritical fluid extraction*, the components of mixtures can be separated from one another. Supercritical fluid extraction has been successfully used to separate complex mixtures in the chemical, food, pharmaceutical, and energy industries. Supercritical CO₂ is a popular choice because it is relatively inexpensive and, if used in closed-loop systems, may be a way to reduce CO₂ emissions into the atmosphere.

Self-Assessment Exercise

- 11.18** What phases and enthalpy change are described by the term *deposition*?

- (a) Gas to liquid, exothermic change
 (b) Gas to solid, exothermic change

- (a) Gas to solid, endothermic change
 (b) Liquid to solid, exothermic change

Exercises

- 11.19** Name the phase transition in each of the following situations and indicate whether it is exothermic or endothermic: (a) Iodine solid turns to iodine gas when it is heated. (b) Snowflakes turn into water when they fall on an open palm. (c) Droplets of water appear on grass in a cold humid morning. (d) Dry ice gradually disappears when left at room temperature for some period of time.

- 11.20** Chloroethane (C₂H₅Cl) boils at 12 °C. When liquid C₂H₅Cl under pressure is sprayed on a room-temperature (25 °C) surface in air, the surface is cooled considerably. (a) What does this observation tell us about the specific heat of C₂H₅Cl(*g*) as compared with that of C₂H₅Cl(*l*)? (b) Assume that the heat lost by the surface is gained by chloroethane. What enthalpies must you consider if you were to calculate the final temperature of the surface?

- 11.21** CHClF₂ is a type of hydrochlorofluorocarbon (HCFC) that has a comparatively lower damaging effect on the ozone layer. It is used as a replacement for chlorofluorocarbons (CFCs). The heat of vaporization is 233.95 kJ/g. What mass of this substance must evaporate to freeze 15 g of water

initially at 15 °C? (The heat of fusion of water is 334 J/g; the specific heat of water is 4.18 J/g · K.)

- 11.22** Acetone, CH₃COCH₃, is a common organic solvent with relatively low melting point (178 K) and boiling point (329 K). The enthalpy of fusion of acetone is 5.72 kJ/mol, and its enthalpy of vaporization is 29.1 kJ/mol. The specific heats of solid and liquid acetone are 96 J/mol K and 125.5 J/mol K respectively. (a) How much heat is required to convert 23.0 g of acetone at 273 K to the vapor phase at 329 K? (b) How much heat is required to convert the same amount of acetone at 77 K to the vapor phase at 329 K?

- 11.23** Indicate whether each statement is true or false: (a) The critical pressure of a substance is the pressure at which it turns into a solid at room temperature. (b) The critical temperature of a substance is the highest temperature at which the liquid phase can form. (c) Generally speaking, the higher the critical temperature of a substance, the lower its critical pressure. (d) In general, the more intermolecular forces there are in a substance, the higher its critical temperature and pressure.

11.18 (b)



11.5 | Vapor Pressure

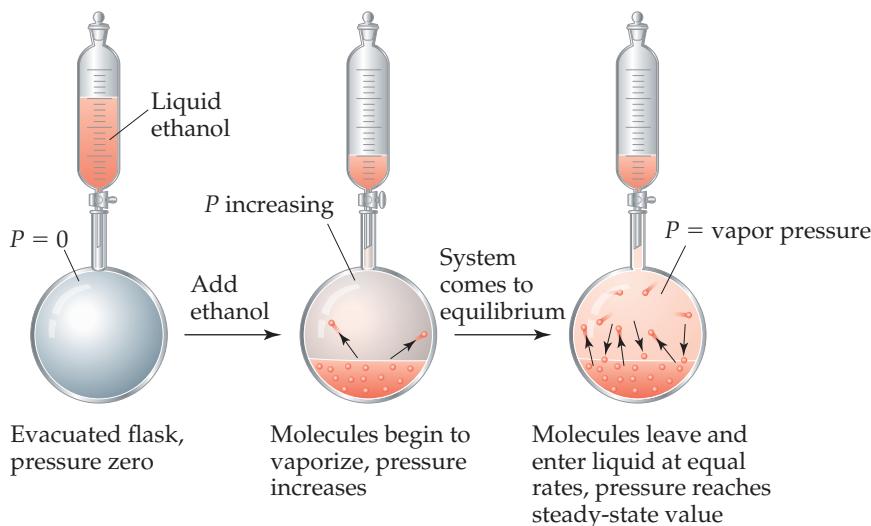


Smelling salts have a long history—there is mention of them in the writings of Pliny as well as Chaucer. Traditionally, they were used to revive someone that had fainted, but, in modern times, have been used to ‘freshen up’ athletes before a sporting fixture and to revive athletes on the field that have suffered an injury. This is no longer a recommended treatment as it may mask, or delay, the diagnosis of more serious neurological damage caused by concussion. The active component is ammonium carbonate, but this is often dissolved in a water-alcohol solution and accompanied by perfumes or pleasantly smelling compounds such as eucalyptus oil. The ammonium carbonate forms ammonia, which stimulates the respiratory system. It can also burn the tissue lining the nose and windpipe, so cautious use is required.

The volatility of a compound is the focus of this section, by the end of which you should be able to

- Understand what factors affect the volatility of a compound

Molecules can escape from the surface of a liquid into the gas phase by evaporation. Suppose we place a quantity of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) in an evacuated, closed container, as in **Figure 11.23**. The ethanol quickly begins to evaporate. As a result, the pressure



◀ **Figure 11.23** Vapor pressure over a liquid.

exerted by the vapor in the space above the liquid increases. After a short time, the pressure of the vapor attains a constant value, which we call the **vapor pressure**.

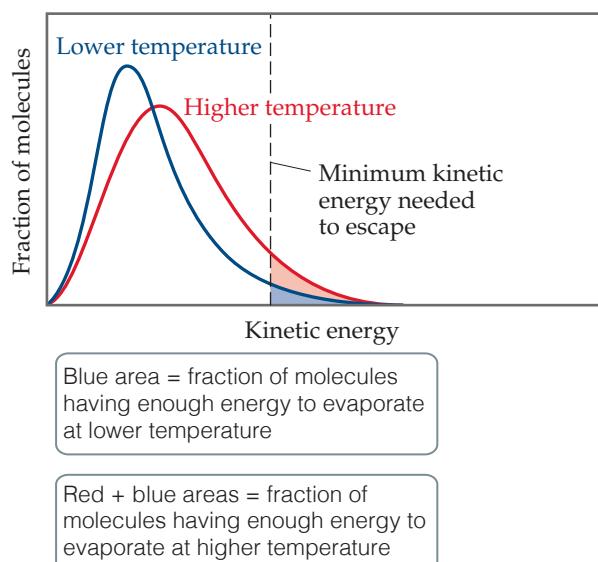
At any instant, some of the ethanol molecules at the liquid surface possess sufficient kinetic energy to overcome the attractive forces of their neighbors and, therefore, escape into the gas phase. As the number of gas-phase molecules increases, however, the probability increases that a molecule in the gas phase will strike the liquid surface and be recaptured by the liquid, as shown in the flask on the right in Figure 11.23. Eventually, the rate at which molecules return to the liquid equals the rate at which they escape. The number of molecules in the gas phase then reaches a steady value, and the pressure exerted by the vapor becomes constant.

The condition in which two opposing processes occur simultaneously at equal rates is called **dynamic equilibrium** (or simply *equilibrium*). Chemical equilibrium, which we encountered in Section 4.1, is a kind of dynamic equilibrium in which the opposing processes are chemical reactions.

A liquid and its vapor are in dynamic equilibrium when evaporation and condensation occur at equal rates. It may appear that nothing is occurring at equilibrium because there is no net change in the system. In fact, though, a great deal is happening as molecules continuously pass from liquid state to gas state and from gas state to liquid state. *The vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium.*

Go Figure

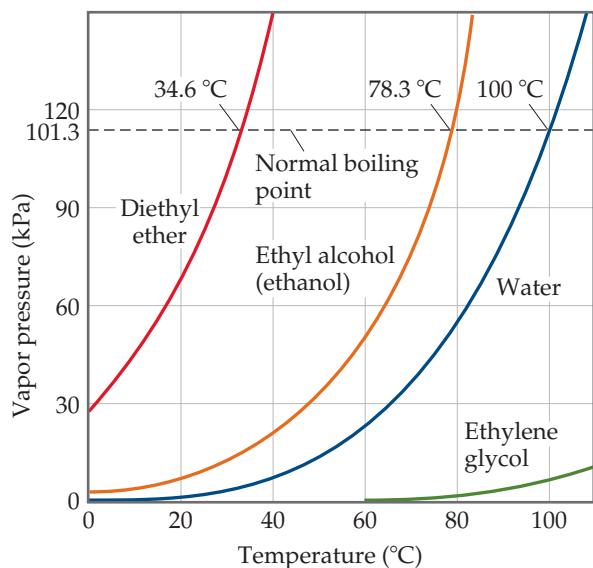
As the temperature increases, does the rate of molecules escaping into the gas phase increase or decrease?



▲ Figure 11.24 The effect of temperature on the distribution of kinetic energies in a liquid.

Go Figure

What is the vapor pressure of ethylene glycol at its normal boiling point?



▲ Figure 11.25 Vapor pressure for four liquids as a function of temperature.

Volatility, Vapor Pressure, and Temperature

When vaporization occurs in an open container, as when water evaporates from a bowl, the vapor moves away from the liquid. Little, if any, is recaptured at the surface of the liquid. Equilibrium never occurs, and the vapor continues to form until the liquid evaporates to dryness. Substances with high vapor pressure (such as gasoline) evaporate more quickly than substances with low vapor pressure (such as motor oil). Liquids that evaporate readily are said to be **volatile**.

Hot water evaporates more quickly than cold water because vapor pressure increases with increasing temperature. To see why this statement is true, we begin with the fact that the molecules of a liquid move at various speeds. Figure 11.24 shows the distribution of kinetic energies of the molecules at the surface of a liquid at two temperatures. (The curves are like those shown for gases in Section 10.6.) As the temperature is increased, the molecules move more energetically and more of them can break free from their neighbors and enter the gas phase, increasing the vapor pressure.

Figure 11.25 depicts the variation in vapor pressure with temperature for four common substances that differ greatly in volatility. Note that the vapor pressure in all cases increases nonlinearly with increasing temperature. The weaker the intermolecular forces in the liquid, the more easily molecules can escape and, therefore, the higher the vapor pressure at a given temperature.

Vapor Pressure and Boiling Point

The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external pressure, acting on the liquid surface. At this temperature, the thermal energy of the molecules is great enough for the molecules in the interior of the liquid to break free from their neighbors and enter the gas phase. As a result, bubbles of vapor form within the liquid. The boiling point increases as the external pressure increases. The boiling point of a liquid at 101.3 kPa pressure is called its **normal boiling point**. From Figure 11.25 we see that the normal boiling point of water is 100 °C.

The time required to cook food in boiling water depends on the water temperature. In an open container, that temperature is 100 °C, but it is possible to boil at higher temperatures. Pressure cookers work by allowing steam to escape only when it exceeds a predetermined pressure; the pressure above the water can therefore increase above atmospheric pressure. The higher pressure causes the water to boil at a higher temperature, thereby allowing the food to get hotter and to cook more rapidly.

The effect of pressure on boiling point also explains why it takes longer to cook food at high elevations than it does at sea level. The atmospheric pressure is lower at higher altitudes, so water boils at a temperature lower than 100 °C, and foods generally take longer to cook.

A CLOSER LOOK The Clausius–Clapeyron Equation

Notice that the plots in Figure 11.25 have a distinct shape: For each substance, the vapor-pressure curves sharply upward with increasing temperature. The relationship between vapor pressure and temperature is given by the *Clausius–Clapeyron equation*:

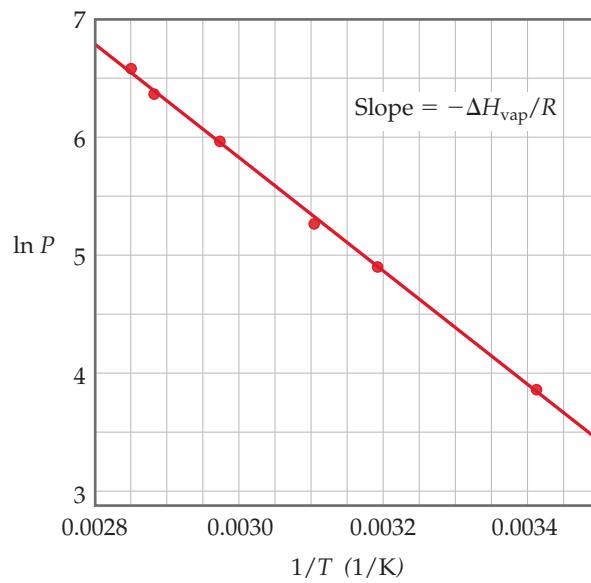
$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C \quad [11.1]$$

where P is the vapor pressure, T is the absolute temperature, R is the gas constant (8.314 J/mol K), ΔH_{vap} is the molar enthalpy of vaporization, and C is a constant. This equation predicts that a graph of $\ln P$ versus $1/T$ should give a straight line with a slope equal to $-\Delta H_{\text{vap}}/R$. Using this plot, we can determine the enthalpy of vaporization of a substance:

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

As an example of how we use the Clausius–Clapeyron equation, the vapor-pressure data for ethanol shown in Figure 11.25 are graphed as $\ln P$ versus $1/T$ in **Figure 11.26**. The data lie on a straight line with a negative slope. We can use the slope to determine ΔH_{vap} for ethanol, 38.56 kJ/mol. We can also extrapolate the line to obtain the vapor pressure of ethanol at temperatures above and below the temperature range for which we have data.

Related Exercises: 11.91–11.93



▲ **Figure 11.26** The natural logarithm of vapor pressure versus $1/T$ for ethanol.

Sample Exercise 11.4

Relating Boiling Point to Vapor Pressure

Use Figure 11.25 to estimate the boiling point of diethyl ether under an external pressure of 80 kPa atm.

SOLUTION

Analyze We are asked to read a graph of vapor pressure versus temperature to determine the boiling point of a substance at a particular pressure. The boiling point is the temperature at which the vapor pressure is equal to the external pressure.

Plan We estimate the location of that pressure on the graph, move horizontally to the vapor-pressure curve, and then drop vertically from the curve to estimate the temperature.

Solve The pressure equals 81 kPa. From Figure 11.25 we see that the boiling point at this pressure is about 27 °C, which is close to room temperature.

Comment We can make a flask of diethyl ether boil at room temperature by using a vacuum pump to lower the pressure above the liquid to about 81 kPa.

► Practice Exercise

Use Figure 11.25 to determine the external pressure if ethanol boils at 60 °C.

Self-Assessment Exercise

11.24 Which compound is more volatile at 25 °C: CCl₄ or CBr₄?

- (a) CCl₄
- (b) CBr₄

Exercises

11.25 Hydrogen peroxide, H₂O₂, has a normal boiling point of 150 °C. Based on the data given in Figure 11.25, would you expect hydrogen peroxide to have a higher or lower vapor pressure than water at 25 °C?

11.26 True or false: (a) CBr₄ is more volatile than CCl₄. (b) CBr₄ has a higher boiling point than CCl₄. (c) CBr₄ has weaker intermolecular forces than CCl₄. (d) CBr₄ has a higher vapor pressure at the same temperature than CCl₄.

11.27 You are high up in the mountains and boil water to make some tea. However, when you drink your tea, it is not as hot as it should be. You try again and again, but the water is just not hot enough to make a hot cup of tea. Which is the best explanation for this result? (a) High in the mountains, it is probably very dry, and so the water is rapidly evaporating from your cup and cooling it. (b) High in the mountains, it is probably very windy, and so the water is rapidly evaporating from your cup and cooling it. (c) High in the mountains,

the air pressure is significantly less than 101.3 kPa, so the boiling point of water is much lower than at sea level.

(d) High in the mountains, the air pressure is significantly less than 101.3 kPa, so the boiling point of water is much higher than at sea level.

11.28 Appendix B lists the vapor pressure of water at various external pressures. (a) Plot the data in Appendix B, vapor pressure versus temperature (°C). From your plot, estimate the vapor pressure of water at body temperature, 37 °C. (b) Explain the significance of the data point at 101.3 kPa, 100 °C. (c) A city at an altitude of 1525 m above sea level has a barometric pressure of 84.3 kPa. To what temperature would you have to heat water to boil it in this city? (d) A city at an altitude of 150 m below sea level would have a barometric pressure of 103.14 kPa. To what temperature would you have to heat water to boil it in this city?

11.24 (a)

Answers to Self-Assessment Exercises



11.6 | Phase Diagrams



Who would have thought that ice skating is all about the solid–liquid phase change in water! The weight of a person bearing on the thin blade of an ice skate generates a considerable pressure under the blade. Sufficient to temporarily melt the ice and drastically reduce the friction under the blade. The skater can glide fast and apparently effortlessly across the rink. As soon as the pressure on the water is released, it refreezes. By the end of this section, you should be able to

- Interpret the phase diagram of a substance

The equilibrium between a liquid and its vapor is not the only dynamic equilibrium that can exist between states of matter. Under appropriate conditions, a solid can be in equilibrium with its liquid or even with its vapor. The temperature at which solid and liquid phases coexist at equilibrium is the *melting point* of the solid or the *freezing point* of the liquid. Solids can also undergo evaporation and therefore possess a vapor pressure.

A **phase diagram** is a graphic way to summarize the conditions under which equilibria exist between the different states of matter. Such a diagram also allows us to predict which phase of a substance is present at any given temperature and pressure.

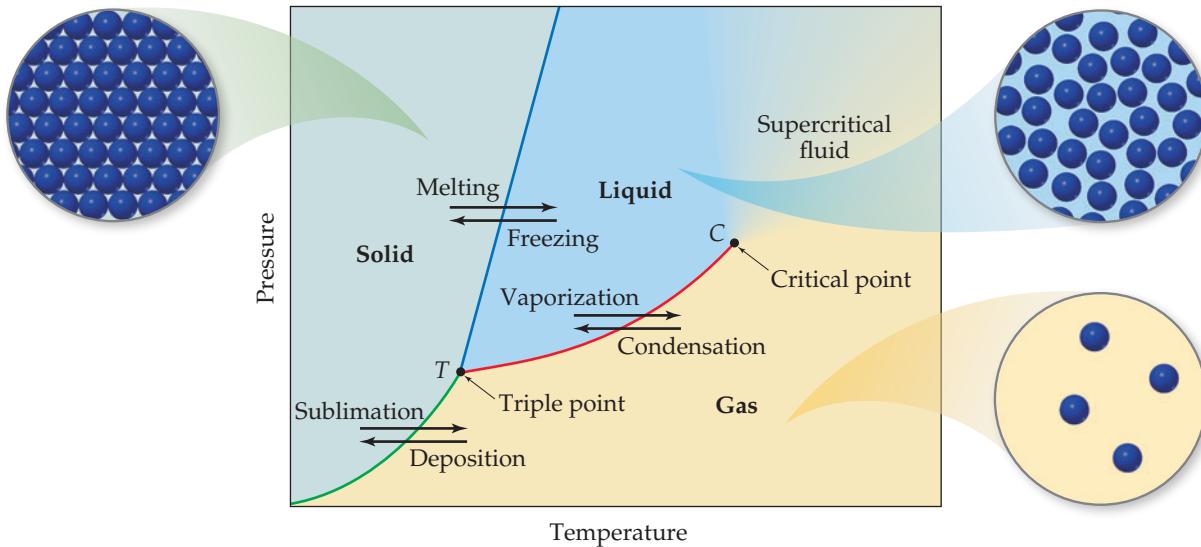
The phase diagram for any substance that can exist in all three phases of matter is shown in **Figure 11.27**. The diagram contains three important curves, each of which represents the temperature and pressure at which the various phases can coexist at equilibrium. The only substance present in the system is the one whose phase diagram is under consideration. The pressure shown in the diagram is either the pressure applied to the system or the pressure generated by the substance. The curves may be described as follows:

1. The red curve is the *vapor-pressure curve* of the liquid, representing equilibrium between the liquid and gas phases. The point on this curve where the vapor pressure is 101.3 kPa is the normal boiling point of the substance. The vapor-pressure curve ends at the **critical point** (C), which corresponds to the critical temperature and



Go Figure

Imagine that the pressure on the solid phase in the figure is decreased at constant temperature. If the solid eventually sublimes, what must be true about the temperature?



▲ Figure 11.27 Generic phase diagram for a pure substance. The green line is the sublimation curve, the blue line is the melting curve, and the red line is the vapor-pressure curve.

critical pressure of the substance. At temperatures and pressures beyond the critical point, the liquid and gas phases are indistinguishable from each other, and the substance is a *supercritical fluid*.

2. The green curve, the *sublimation curve*, separates the solid phase from the gas phase and represents the change in the vapor pressure of the solid as it sublimes at different temperatures. Each point on this curve represents a condition of equilibrium between the solid and the gas.
3. The blue curve, the *melting curve*, separates the solid phase from the liquid phase and represents the change in melting point of the solid with increasing pressure. Each point on this curve represents an equilibrium between the solid and the liquid. This curve usually slopes slightly to the right as pressure increases for most substances because the solid form is denser than the liquid form. An increase in pressure usually favors the more compact solid phase; thus, higher temperatures are required to melt the solid at higher pressures. The melting point at 101.3 kPa is the **normal melting point**.

Point *T*, where the three curves intersect, is the **triple point**, and here all three phases are in equilibrium. Any other point on any of the three curves represents equilibrium between two phases. Any point on the diagram that does not fall on one of the curves corresponds to conditions under which only one phase is present. The gas phase, for example, is stable at low pressures and high temperatures, whereas the solid phase is stable at low temperatures and high pressures. Liquids are stable in the region between the other two.

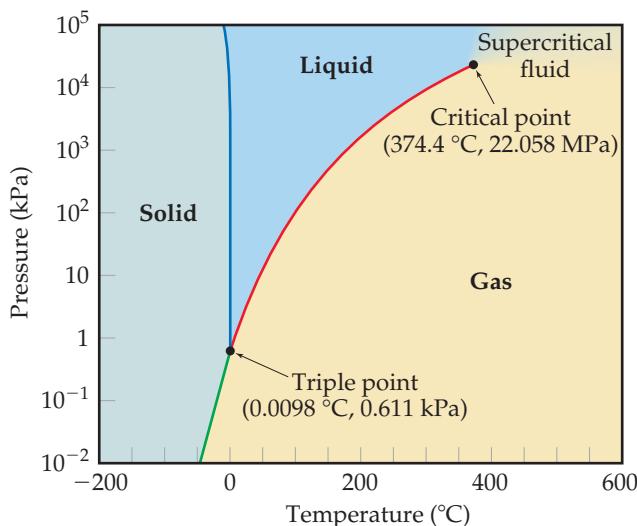
The Phase Diagrams of H₂O and CO₂

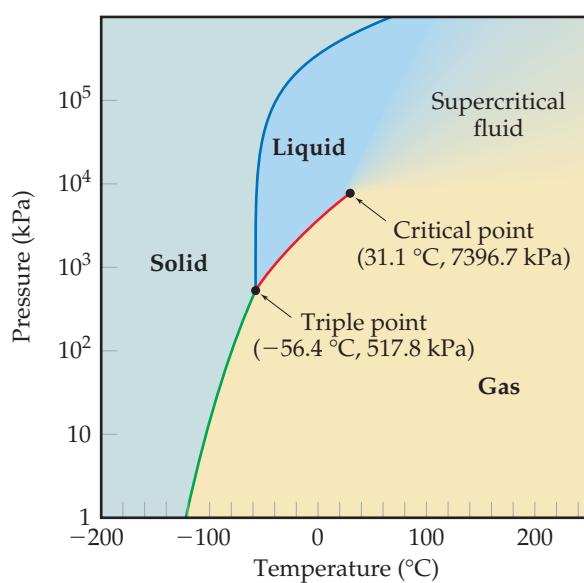
Figure 11.28 shows the phase diagram of H₂O. Because of the large range of pressures covered in the diagram, a logarithmic scale is used to represent pressure. The melting curve (blue line) of H₂O is atypical, slanting slightly to the left with increasing pressure, indicating that for water the melting point *decreases* with increasing pressure. This unusual behavior occurs because water is among the very few substances whose liquid form is more compact than its solid form, as we learned in Section 11.2.

If the pressure is held constant at 101.3 kPa, it is possible to move from the solid to liquid to gaseous regions of the phase diagram by changing the temperature, as we expect from our everyday encounters with water. The triple point of H₂O falls at a relatively low pressure, 0.611 kPa. Below this pressure, liquid water is not stable and ice sublimes to water vapor on heating. This property of water is used to “freeze-dry” foods and beverages. The food or beverage is frozen to a temperature below 0 °C. Next

► **Figure 11.28** Phase diagram of H₂O.

Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.





◀ **Figure 11.29** Phase diagram of CO_2 . Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.

it is placed in a low-pressure chamber (below 0.611 kPa) and then warmed so that the water sublimes, leaving behind dehydrated food or beverage.

The phase diagram for CO_2 is shown in **Figure 11.29**. The melting curve (blue line) behaves typically, slanting to the right with increasing pressure, telling us that the melting point of CO_2 increases with increasing pressure. Because the pressure at the triple point is relatively high, 517.8 kPa, CO_2 does not exist as a liquid at 101.3 kPa, which means that solid CO_2 does not melt when heated, but instead sublimes. Thus, CO_2 does not have a normal melting point; instead, it has a normal sublimation point, -78.5°C . Because CO_2 sublimes rather than melts as it absorbs energy at ordinary pressures, solid CO_2 (dry ice) is a convenient coolant.

Sample Exercise 11.5

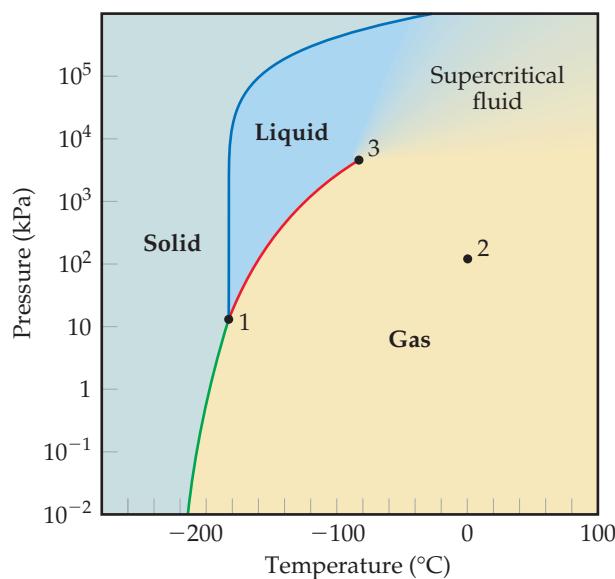
Interpreting a Phase Diagram

Use the phase diagram for methane, CH_4 , shown in **Figure 11.30** to answer the following questions. (a) What are the approximate temperature and pressure of the critical point? (b) What are the approximate temperature and pressure of the triple point? (c) Is methane a solid, liquid, or gas at 100 kPa and 0°C ? (d) If solid methane at 100 kPa is heated while the pressure is held constant, will it melt or sublime? (e) If methane at 100 kPa and 0°C is compressed until a phase change occurs, in which state is the methane when the compression is complete?

SOLUTION

Analyze We are asked to identify key features of the phase diagram and to use it to deduce what phase changes occur when specific pressure and temperature changes take place.

Plan We must identify the triple and critical points on the diagram and also identify which phase exists at specific temperatures and pressures.



▲ **Figure 11.30** Phase diagram of CH_4 . Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.

Continued

Solve

- (a) The critical point is the point where the liquid, gaseous, and supercritical fluid phases coexist. It is marked point 3 in the phase diagram and located at approximately -80°C and 5066 kPa.
- (b) The triple point is the point where the solid, liquid, and gaseous phases coexist. It is marked point 1 in the phase diagram and located at approximately -180°C and 10 kPa.
- (c) The intersection of 0°C and 1 atm is marked point 2 in the phase diagram. It is well within the gaseous region of the phase diagram.
- (d) If we start in the solid region at $P = 100$ kPa and move horizontally (this means we hold the pressure constant), we cross first into the liquid region, at $T \approx -180^\circ\text{C}$, and then into the gaseous region, at $T \approx -160^\circ\text{C}$. Therefore, solid methane melts when the pressure is 100 kPa. (For methane to sublime, the pressure must be below the triple point pressure.)

- (e) Moving vertically up from point 2, which is 100 kPa and 0°C , the first phase change we come to is from gas to supercritical fluid. This phase change happens when we exceed the critical pressure (~ 5066 kPa).

Check The pressure and temperature at the critical point are higher than those at the triple point, which is expected. Methane is the principal component of natural gas. So it seems reasonable that it exists as a gas at 1 atm and 0°C .

► Practice Exercise

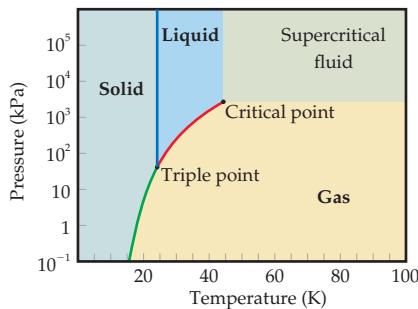
Use the phase diagram of methane to answer the following questions. (a) What is the normal boiling point of methane? (b) Over what pressure range does solid methane sublime? (c) Above what temperature does liquid methane not exist?

Self-Assessment Exercise

- 11.29** What phases are present at the triple point of a phase diagram?
- (a) solid and liquid
 - (b) solid and gas
 - (c) liquid and gas
 - (d) solid, liquid, and gas

Exercises

- 11.30** (a) What is the significance of the critical point in a phase diagram? (b) Why does the line that separates the gas and liquid phases end at the critical point?
- 11.31** Referring to Figure 11.29, describe the phase changes (and the temperatures at which they occur) when CO_2 is heated from -80 to -20°C at (a) a constant pressure of 300 kPa, (b) a constant pressure of 600 kPa.
- 11.32** The phase diagram for neon is



Use the phase diagram to answer the following questions.

(a) What is the approximate value of the normal melting point? (b) Over what pressure range will solid neon sublime? (c) At room temperature ($T = 25^\circ\text{C}$) can neon be liquefied by compressing it?

- 11.33** At 25°C gallium is a solid with a density of 5.91 g/cm^3 . Its melting point, 29.8°C , is low enough that you can melt it by holding it in your hand. The density of liquid gallium just above the melting point is 6.1 g/cm^3 . Based on this information, what unusual feature would you expect to find in the phase diagram of gallium?



11.29 (d)



11.7 | Liquid Crystals



Electronic paper (e-paper) is based on cholesteric liquid crystal technology. It is able to mimic the appearance of ordinary ink on paper and has numerous potential uses including thin displays on walls, electronic labels, and electronic book readers. It takes very little power to change the orientation of the liquid crystal molecules and, hence, affect the optical properties of the device.

By the end of this section, you should be able to

- Recognize the features of a molecule that make it a potential liquid crystal and the different liquid crystal phases that it may adopt.

In 1888, Friedrich Reinitzer, an Austrian botanist, discovered that the organic compound cholesteryl benzoate has an interesting and unusual property, shown in **Figure 11.31**. Solid cholesteryl benzoate melts at 145 °C, forming a viscous milky liquid; then at 179 °C the milky liquid becomes clear and remains that way at temperatures above 179 °C. When cooled, the clear liquid turns viscous and milky at 179 °C, and the milky liquid solidifies at 145 °C.

Reinitzer's work represents the first systematic report of what we call a **liquid crystal**, the term we use today for the viscous, milky state that some substances exhibit between the liquid and solid states.

This intermediate phase has some of the structure of solids and some of the freedom of motion of liquids. Because of the partial ordering, liquid crystals may be viscous and possess properties intermediate between those of solids and those of liquids. The region in which they exhibit these properties is marked by sharp transition temperatures, as in Reinitzer's sample. Just like solid, liquid, and gas phases, the liquid crystalline phase is represented by a distinct region on a phase diagram.

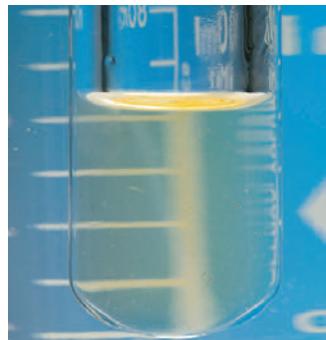
Today liquid crystals are used as pressure and temperature sensors and as liquid crystals displays (LCDs) in such devices as digital watches, televisions, and computers. They can be used for these applications because the weak intermolecular forces that hold the molecules together in the liquid crystalline phase are easily affected by changes in temperature, pressure, and electric fields.

Types of Liquid Crystals

Substances that form liquid crystals are often composed of rod-shaped molecules that are somewhat rigid. In the liquid phase, these molecules are oriented randomly. In the liquid crystalline phase, by contrast, the molecules are arranged in specific patterns as



$145\text{ }^{\circ}\text{C} < T < 179\text{ }^{\circ}\text{C}$
Liquid crystalline phase



$T > 179\text{ }^{\circ}\text{C}$
Liquid phase

▲ **Figure 11.31** Cholesteryl benzoate in its liquid and liquid crystalline states.

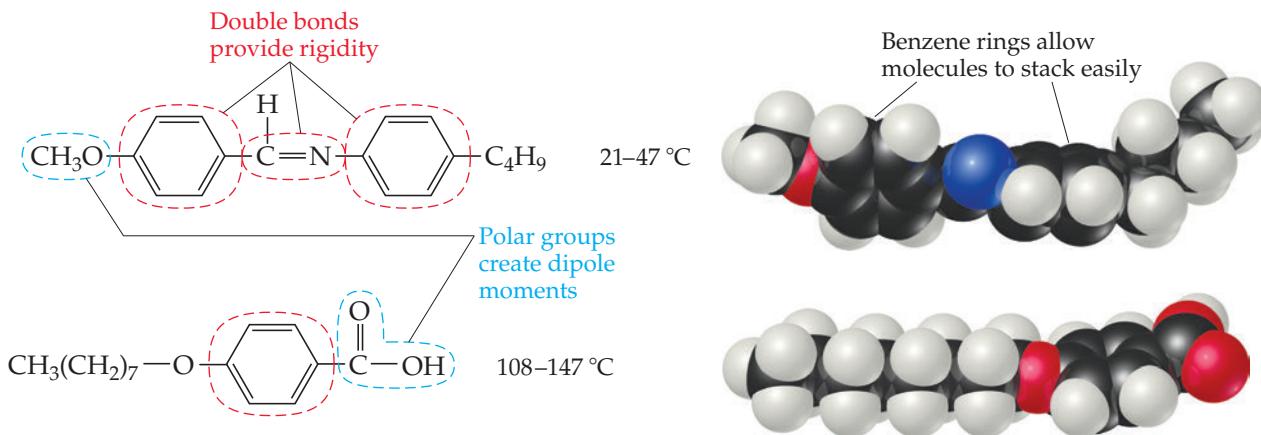
Liquid phase	Nematic liquid crystalline phase	Smectic A liquid crystalline phase	Smectic C liquid crystalline phase	Cholesteric liquid crystalline phase
Molecules arranged randomly	Long axes of molecules aligned, but ends are not aligned	Molecules aligned in layers, long axes of molecules perpendicular to layer planes	Molecules aligned in layers, long axes of molecules inclined with respect to layer planes	Molecules pack into layers, long axes of molecules in one layer rotated relative to the long axes in the layer above it

▲ **Figure 11.32 Molecular order in nematic, smectic, and cholesteric liquid crystals.** In the liquid phase of any substance, the molecules are arranged randomly, whereas in the liquid crystalline phases the molecules are arranged in a partially ordered way.

illustrated in **Figure 11.32**. Depending on the nature of the ordering, liquid crystals are classified as nematic, smectic A, smectic C, or cholesteric.

In a **nematic liquid crystal**, the molecules are aligned so that their long axes tend to point in the same direction but the ends are not aligned with one another. In **smectic A** and **smectic C liquid crystals**, the molecules maintain the long-axis alignment seen in nematic crystals, but in addition they pack into layers.

Two molecules that exhibit liquid crystalline phases are shown in **Figure 11.33**. The lengths of these molecules are much greater than their widths. The double bonds, including those in the benzene rings, add rigidity to the molecules, and the rings, because they are flat, help the molecules stack with one another. The polar $-\text{OCH}_3$ and $-\text{COOH}$ groups give rise to dipole-dipole interactions and promote alignment of the molecules. Thus, the molecules order themselves quite naturally along their long axes. They can, however, rotate around their axes and slide parallel to one another. In smectic liquid crystals, the intermolecular forces (dispersion



▲ **Figure 11.33 Molecular structure and liquid crystal temperature range for two typical liquid crystalline materials.**

forces, dipole-dipole attractions, and hydrogen bonding) limit the ability of the molecules to slide past one another.

In a **cholesteric liquid crystal**, the molecules are arranged in layers, with their long axes parallel to the other molecules within the same layer.* Upon moving from one layer to the next, the orientation of the molecules rotates by a fixed angle, resulting in a spiral pattern. These liquid crystals are so named because many derivatives of cholesterol adopt this structure.

CHEMISTRY AND LIFE Liquid Crystal Displays

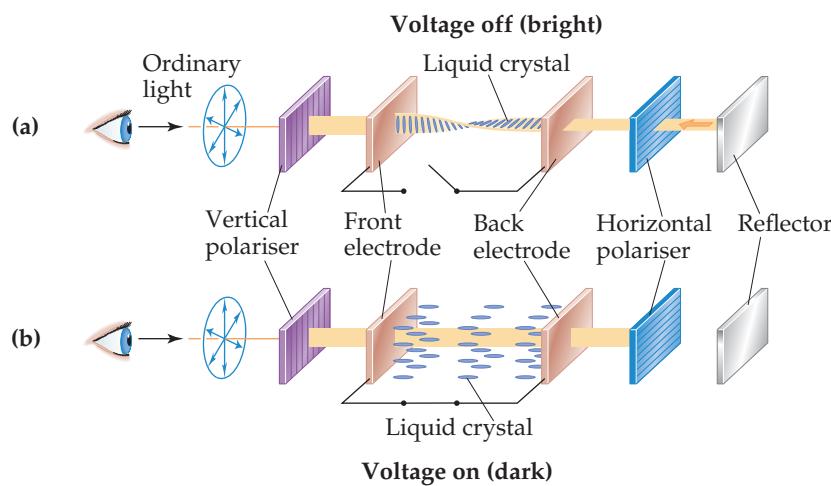
Liquid crystals displays (LCDs) are widely used in electronic devices such as watches, calculators and computer screens. These applications are possible because an applied electrical field changes the orientation of liquid crystal molecules and thus affects the optical properties of the device.

LCDs come in a variety of designs, but the structure illustrated in **Figure 11.34** is typical. A thin layer (5–20 µm) of liquid crystalline material is placed between electrically conducting, transparent glass electrodes. Ordinary light passes through a vertical polariser that permits light in only the vertical plane to pass. Using a special process during fabrication, the liquid crystal molecules are oriented so that the molecules at the front electrode are oriented vertically and those at the back electrode horizontally. The orientation of the molecules in between the two electrodes varies systematically from vertical to horizontal, as shown in Figure 11.34. The plane of polarisation of the light is turned by 90° as it passes through the liquid crystal layer and is thus in the correct orientation to pass through the horizontal polariser. In a watch display, a mirror reflects the light back, and the light

retraces its path, allowing the device to look bright. When a voltage is applied to the plates the liquid crystalline molecules align with the voltage, as shown in Figure 11.34. The light rays thus are not properly oriented to pass through the horizontal polariser, and the device appears dark. Displays of this kind are called ‘twisted nematic’. As the name implies, materials that order as nematic liquid crystals are used for this application.

Liquid crystal displays for computer and televisions employ a light source in place of the reflector, but the principle is the same. The screen is divided into a large number of tiny cells, with the voltages at points on the screen surface controlled by transistors made from thin films of amorphous silicon. Red-green-blue colour filters are employed to provide full colour. The entire display is refreshed at a frequency of about 60 Hz, so the display can change rapidly with respect to the response time of the human eye. Displays of this kind are remarkable technical achievements based on a combination of basic scientific discovery and creative engineering.

Related Exercises: 11.86, 11.87



◀ FIGURE 11.34 Schematic illustration of the operation of a twisted nematic liquid crystal display (LCD). (a) When the voltage is off, the molecules in the liquid crystal are aligned so that they rotate the polarisation of the light by 90°. This alignment allows light to pass through both the vertical and horizontal polarisers before being reflected and retracing its path to give a bright display. (b) When a voltage is applied to the electrodes the liquid crystal molecules align parallel to the light path. In this state the light retains the vertical polarisation and cannot pass through the horizontal polariser. The area covered by the front electrode therefore appears dark.

The molecular arrangement in cholesteric liquid crystals produces unusual coloring patterns with visible light. Changes in temperature and pressure change the order and, hence, the color. Cholesteric liquid crystals are used to monitor temperature changes in situations where conventional methods are not feasible. For example, they can detect hot spots in microelectronic circuits, which may signal the presence of flaws. They can also be fashioned into thermometers for measuring the skin temperature of infants. Because cholesteric liquid crystal displays can be built that draw very little power, they are also being investigated for use in electronic paper. Such applications are possible because an applied electrical field changes the orientation of liquid crystal molecules and thus affects the optical properties of the device.

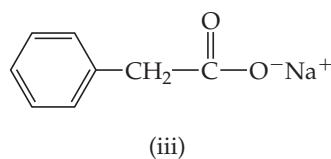
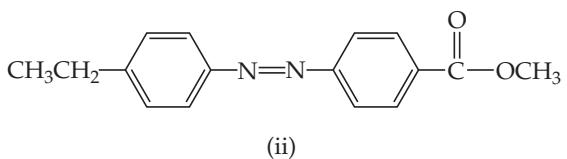
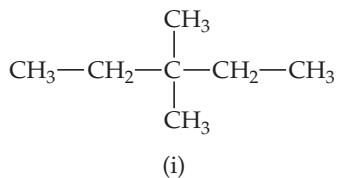
*Cholesteric liquid crystals are sometimes called chiral nematic phases because the molecules within each plane adopt an arrangement similar to a nematic liquid crystal.



Sample Exercise 11.6

Properties of Liquid Crystals

Which of these substances is most likely to exhibit liquid crystalline behavior?



SOLUTION

Analyze We have three molecules with different structures, and we are asked to determine which one is most likely to be a liquid crystalline substance.

Plan We need to identify all structural features that might induce liquid crystalline behavior.

Solve Molecule (i) is not likely to be liquid crystalline because the absence of double and/or triple bonds makes this molecule flexible rather than rigid. Molecule (iii) is ionic, and the generally high melting points of ionic materials make it unlikely that this substance is liquid crystalline. Molecule (ii) possesses the characteristic long axis and the kinds of structural features often seen in liquid crystals: The molecule has a rod-like shape, the double bonds and benzene rings provide rigidity, and the polar COOCH_3 group creates a dipole moment.

► Practice Exercise

Liquid crystalline phases are produced by which of the following?

- (a) short, flexible molecules
- (b) complete lack of order among molecules
- (c) three-dimensional order among molecules
- (d) highly branched molecules
- (e) rod-shaped molecules



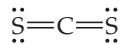
Sample Integrative Exercise

Putting Concepts Together

The substance CS_2 has a melting point of -110.8°C and a boiling point of 46.3°C . Its density at 20°C is 1.26 g/cm^3 . It is highly flammable. (a) What is the name of this compound? (b) List the intermolecular forces that CS_2 molecules exert on one another. (c) Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.) (d) The critical temperature and pressure for CS_2 are 552 K and 7903.3 kPa , respectively. Compare these values with those for CO_2 in Table 11.5 and discuss the possible origins of the differences.

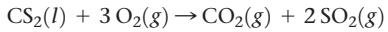
SOLUTION

- (a) The compound is named carbon disulfide, in analogy with the naming of other binary molecular compounds such as carbon dioxide.
- (b) Because there is no H atom, there can be no hydrogen bonding. If we draw the Lewis structure, we see that carbon forms double bonds with each sulfur:



Using the VSEPR model, we conclude that the molecule is linear and therefore has no dipole moment. Thus, there are no dipole-dipole forces. Only dispersion forces operate between the CS_2 molecules.

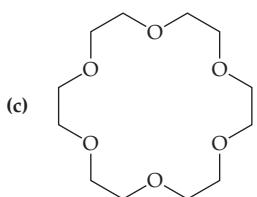
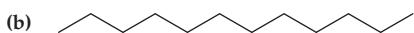
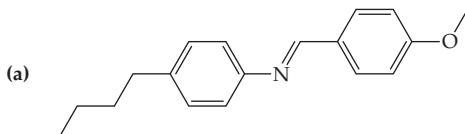
- (c) The most likely products of the combustion will be CO_2 and SO_2 . Under some conditions, SO_3 might be formed, but this would be the less likely outcome. Thus, we have the following equation for combustion:



- (d) The critical temperature and pressure of CS_2 (552 K and 7903.3 kPa , respectively) are both higher than those given for CO_2 in Table 11.5 (304 K and 7396.7 kPa , respectively). The difference in critical temperatures is especially notable. The higher values for CS_2 arise from the greater dispersion attractions between the CS_2 molecules compared with CO_2 . These greater attractions are due to the larger size of the sulfur compared to oxygen and, therefore, its greater polarizability.

Self-Assessment Exercise

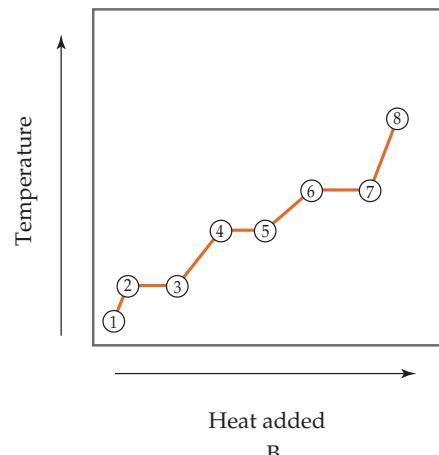
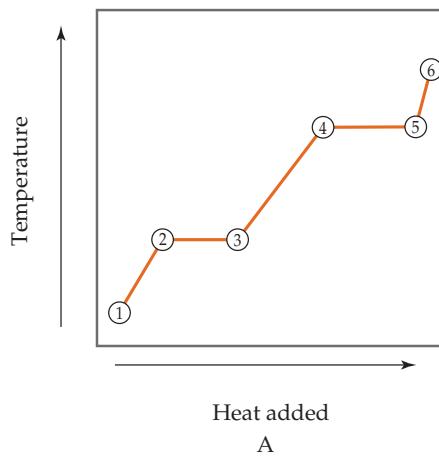
- 11.34** Which of the following substances is most likely to form a liquid crystal phase?



Exercises

- 11.35** In terms of the arrangement and freedom of motion of the molecules, how are the nematic liquid crystalline phase and an ordinary liquid phase similar? How are they different?

- 11.36** Two heating curves, A and B, are shown. In both cases, point 1 corresponds to the crystalline solid phase.



- (a) One of these graphs shows data for a liquid crystalline material. Which one? (b) In graph A, what process does the 2–3 line segment correspond to? (c) In graph B, what process does the 2–3 line segment correspond to? (d) In graph A, what process does the 3–4 line segment correspond to? (e) In graph B, what process does the 3–4 line segment correspond to?

- 11.37** Describe how a cholesteric liquid crystalline phase differs from a smectic A liquid crystalline phase.

- 11.38** The smectic liquid crystalline phase can be said to be more highly ordered than the nematic phase. In what sense is this true?

11.34 (a)



Chapter Summary and Key Terms

A MOLECULAR COMPARISON OF GASES, LIQUIDS, AND SOLIDS

(SECTION 11.1) Substances that are gases or liquids at room temperature are usually composed of molecules. In gases, the intermolecular attractive forces are negligible compared to the kinetic energies of the molecules; thus, the molecules are widely separated and undergo constant, chaotic motion. In liquids, the **intermolecular forces** are strong enough to keep the molecules in close proximity; nevertheless, the molecules are free to move with respect to one another. In solids, the intermolecular attractive forces are strong enough to restrain molecular motion and to force the particles to occupy specific locations in a three-dimensional arrangement.

INTERMOLECULAR FORCES (SECTION 11.2) Three types of intermolecular forces exist between neutral molecules: **dispersion forces**, **dipole-dipole interactions**, and **hydrogen bonding**. Dispersion forces operate between all molecules (and atoms, for atomic substances such as He, Ne, Ar, and so forth). As molecular weight increases, the **polarizability** of a molecule increases, which results in stronger dispersion forces. Molecular shape is also an important factor. Dipole-dipole forces increase in strength as the polarity of the molecule increases. Hydrogen bonding occurs in compounds containing O—H, N—H, and F—H bonds. Hydrogen bonds are generally stronger than dipole-dipole or dispersion forces. **Ion-dipole forces** are important in solutions in which ionic compounds are dissolved in polar solvents.

SELECT PROPERTIES OF LIQUIDS (SECTION 11.3) The stronger the intermolecular forces, the greater is the **viscosity**, or resistance to flow, of a liquid. **Surface tension** is a measure of the tendency of a liquid to maintain a minimum surface area. The surface tension of a liquid also increases as intermolecular forces increase in strength. The adhesion of a liquid to the walls of a narrow tube and the cohesion of the liquid account for **capillary action**.

PHASE CHANGES (SECTION 11.4) A substance may exist in more than one state of matter, or phase. **Phase changes** are transformations from one phase to another. Changes of a solid to liquid (melting), solid to gas (sublimation), and liquid to gas (vaporization) are all endothermic processes. Thus, the **heat of fusion** (melting), the **heat of sublimation**, and the **heat of vaporization** are all positive quantities. The reverse processes (freezing, deposition, and condensation) are exothermic.

A gas cannot be liquefied by application of pressure if the temperature is above its **critical temperature**. The pressure required to

liquefy a gas at its critical temperature is called the **critical pressure**. When the temperature exceeds the critical temperature and the pressure exceeds the critical pressure, the liquid and gas phases coalesce to form a **supercritical fluid**.

VAPOR PRESSURE (SECTION 11.5) The **vapor pressure** of a liquid is the partial pressure of the vapor when it is in **dynamic equilibrium** with the liquid. At equilibrium the rate of transfer of molecules from the liquid to the vapor equals the rate of transfer from the vapor to the liquid. The higher the vapor pressure of a liquid, the more readily it evaporates and the more **volatile** it is. Vapor pressure increases with temperature. Boiling occurs when the vapor pressure equals the external pressure. Thus, the **boiling point** of a liquid depends on pressure. The **normal boiling point** is the temperature at which the vapor pressure equals 101.3 kPa.

PHASE DIAGRAMS (SECTION 11.6) The equilibria between the solid, liquid, and gas phases of a substance as a function of temperature and pressure are displayed on a **phase diagram**. A line indicates equilibria between any two phases. The line through the melting point usually slopes slightly to the right as pressure increases, because the solid is usually more dense than the liquid. The melting point at 101.3 kPa is the **normal melting point**. The point on the diagram at which all three phases coexist in equilibrium is called the **triple point**. The **critical point** corresponds to the critical temperature and critical pressure. Beyond the critical point, the substance is a supercritical fluid.

LIQUID CRYSTALS (SECTION 11.7) A **liquid crystal** is a substance that exhibits one or more ordered phases at a temperature above the melting point of the solid. In a **nematic liquid crystal** the molecules are aligned along a common direction, but the ends of the molecules are not lined up. In a **smectic liquid crystal** the ends of the molecules are lined up so that the molecules form layers. In **smectic A liquid crystals** the long axes of the molecules line up perpendicular to the layers. In **smectic C liquid crystals** the long axes of molecules are inclined with respect to the layers. A **cholesteric liquid crystal** is composed of molecules that align parallel to each other within a layer, as they do in nematic liquid crystalline phases, but the direction along which the long axes of the molecules align rotates from one layer to the next to form a helical structure. Substances that form liquid crystals are generally composed of molecules with fairly rigid, elongated shapes, as well as polar groups to help align molecules through dipole-dipole interactions.

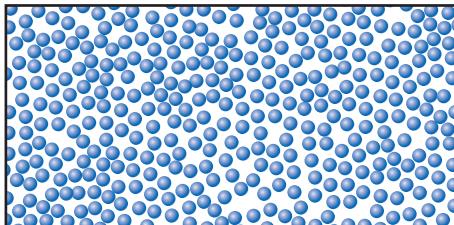
Learning Outcomes After studying this chapter, you should be able to:

- Identify the intermolecular attractive interactions (dispersion, dipole-dipole, hydrogen bonding, ion-dipole) that exist between molecules or ions based on their composition and molecular structure and compare the relative strengths of these intermolecular forces. (Section 11.2) *Related Exercises: 11.7, 11.10, 11.51, 11.56*
- Explain the concept of polarizability and how it relates to dispersion forces. (Section 11.2) *Related Exercises: 11.8, 11.9, 11.52, 11.53*
- Explain the concepts of viscosity, surface tension, and capillary action. (Section 11.3) *Related Exercises: 11.15, 11.61*
- List the names of the various changes of state for a pure substance and indicate which are endothermic and which are exothermic. (Section 11.4) *Related Exercises: 11.19, 11.75*
- Interpret heating curves and calculate the enthalpy changes related to temperature changes and phase changes. (Section 11.4) *Related Exercises: 11.22, 11.66*
- Define critical pressure, critical temperature, vapor pressure, normal boiling point, normal melting point, critical point, and triple point. (Sections 11.4, 11.5, and 11.6) *Related Exercises: 11.23, 11.26, 11.67, 11.69*
- Interpret and sketch phase diagrams. Explain how water's phase diagram differs from most other substances and why. (Section 11.6) *Related Exercises: 11.30, 11.31, 11.72, 11.73*
- Describe how the molecular arrangements characteristic of nematic, smectic, and cholesteric liquid crystals differ from ordinary liquids and from each other. Recognize the features of molecules that favor formation of liquid crystalline phases. (Section 11.7) *Related Exercises: 11.35, 11.78, 11.79*

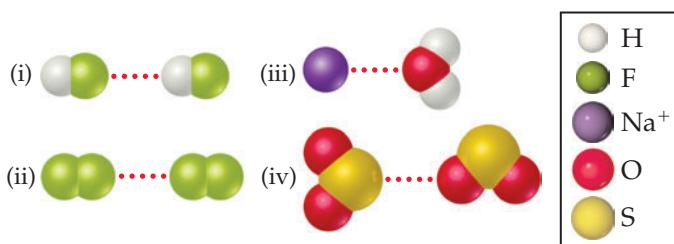
Exercises

Visualizing Concepts

- 11.39** (a) Does the diagram best describe a crystalline solid, a liquid, or a gas? (b) Explain. [Section 11.1]



- 11.40** (a) Which kind of intermolecular attractive force is shown in each case here?



- (b) Predict which of the four interactions is the weakest. [Section 11.2]

- 11.41** (a) Do you expect the viscosity of glycerol, $C_3H_5(OH)_3$, to be larger or smaller than that of 1-propanol, C_3H_7OH ? (b) Explain. [Section 11.3]

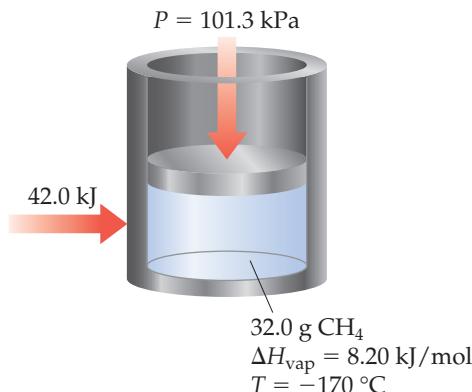


Glycerol

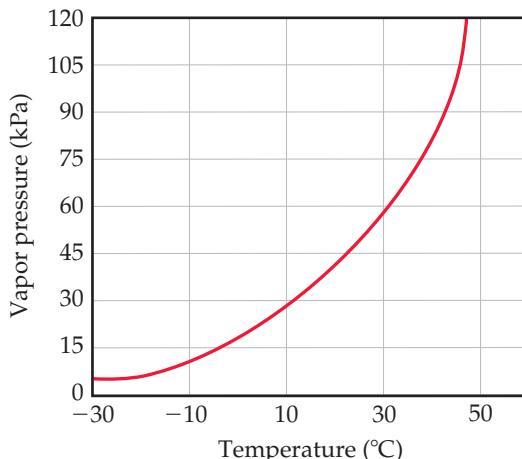


1-Propanol

- 11.42** If 42.0 kJ of heat is added to a 32.0 g sample of liquid methane under 101.3 kPa of pressure at a temperature of -170°C , what are the final state and temperature of the methane once the system equilibrates? Assume no heat is lost to the surroundings. The normal boiling point of methane is -161.5°C . The specific heats of liquid and gaseous methane are 3.48 and 2.22 J/g K, respectively. [Section 11.4]

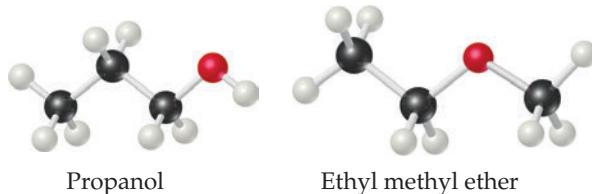


- 11.43** Using this graph of CS_2 data,



determine (a) the approximate vapor pressure of CS_2 at 30°C , (b) the temperature at which the vapor pressure equals 45 kPa, (c) the normal boiling point of CS_2 . [Section 11.5]

- 11.44** The molecules

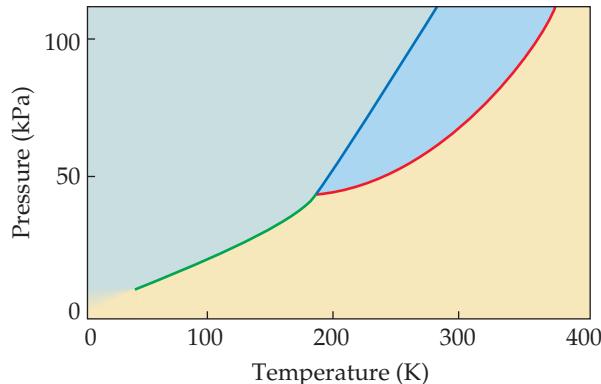


Propanol

Ethyl methyl ether

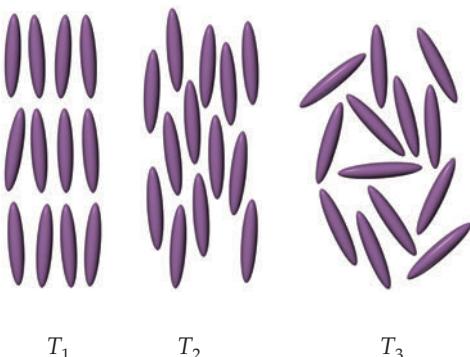
have the same molecular formula ($\text{C}_3\text{H}_8\text{O}$) but different chemical structures. (a) Which molecule(s), if any, can engage in hydrogen bonding? (b) Which molecule do you expect to have a larger dipole moment? (c) One of these molecules has a normal boiling point of 97.2°C , while the other one has a normal boiling point of 10.8°C . Assign each molecule to its normal boiling point. [Sections 11.2 and 11.5]

- 11.45** The phase diagram of a hypothetical substance is



- (a) Estimate the normal boiling point and freezing point of the substance. (b) What is the physical state of the substance under the following conditions? (i) $T = 150\text{ K}$, $P = 20\text{ kPa}$; (ii) $T = 100\text{ K}$, $P = 80\text{ kPa}$; (iii) $T = 300\text{ K}$, $P = 100\text{ kPa}$. (c) What is the triple point of the substance? [Section 11.6]

- 11.46** At three different temperatures, T_1 , T_2 , and T_3 , the molecules in a liquid crystal align in these ways:



(a) At which temperature or temperatures is the substance in a liquid crystalline state? At those temperatures, which type of liquid crystalline phase is depicted? (b) Which is the highest of these three temperatures? [Section 11.7]

Molecular Comparisons of Gases, Liquids, and Solids (Section 11.1)

- 11.47** List the three states of matter in order of (a) increasing molecular disorder and (b) increasing intermolecular attraction. (c) Which state of matter is most easily compressed?
- 11.48** As a metal such as lead melts, what happens to (a) the average kinetic energy of the atoms and (b) the average distance between the atoms?
- 11.49** Benzoic acid, C_6H_5COOH , melts at 122°C . The density in the liquid state at 130°C is 1.08 g/cm^3 . The density of solid benzoic acid at 15°C is 1.266 g/cm^3 . (a) In which of these two states is the average distance between molecules greater? (b) If you converted a cubic centimeter of liquid benzoic acid into a solid, would the solid take up more, or less, volume than the original cubic centimeter of liquid?

Intermolecular Forces (Section 11.2)

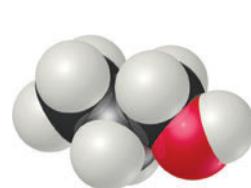
- 11.50** (a) Which type of intermolecular attractive force operates between all molecules? (b) Which type of intermolecular attractive force operates only between polar molecules? (c) Which type of intermolecular attractive force operates only between the hydrogen atom of a polar bond and a nearby small electronegative atom?
- 11.51** Describe the intermolecular forces that must be overcome to convert these substances from a liquid to a gas: (a) CF_4 , (b) NH_3 , (c) BCl_3 .
- 11.52** (a) List the following molecules in order of increasing polarizability: GeCl_4 , CH_4 , SiCl_4 , SiH_4 , and GeBr_4 . (b) Predict the order of boiling points of the substances in part (a).
- 11.53** Which member in each pair has the greater dispersion forces? (a) CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$, (b) NH_3 or $\text{N}(\text{CH}_3)_3$, (c) CH_2Cl_2 or CH_2Br_2 .
- 11.54** Butane and 2-methylpropane, whose space-filling models are shown here, are both nonpolar and have the same molecular formula, C_4H_{10} , yet butane has the higher boiling point (-0.5°C compared to -11.7°C). Explain.



Butane

2-Methylpropane

- 11.55** 1-Propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) and 2-propanol [$(\text{CH}_3)_2\text{CHOH}$], whose space-filling models are shown, have boiling points of 97.2 and 82.5°C , respectively. Explain why the boiling point of 1-propanol is higher, even though both have the molecular formula, $\text{C}_3\text{H}_8\text{O}$.



1-Propanol



2-Propanol

- 11.56** Rationalize the difference in boiling points in each pair: (a) $(\text{CH}_3)_2\text{O}$ (-23°C) and $\text{CH}_3\text{CH}_2\text{OH}$ (78°C), (b) CO_2 (-78.5°C) and CS_2 (46.2°C), (c) CH_3COCH_3 (50.5°C) and CH_3COOH (101°C).

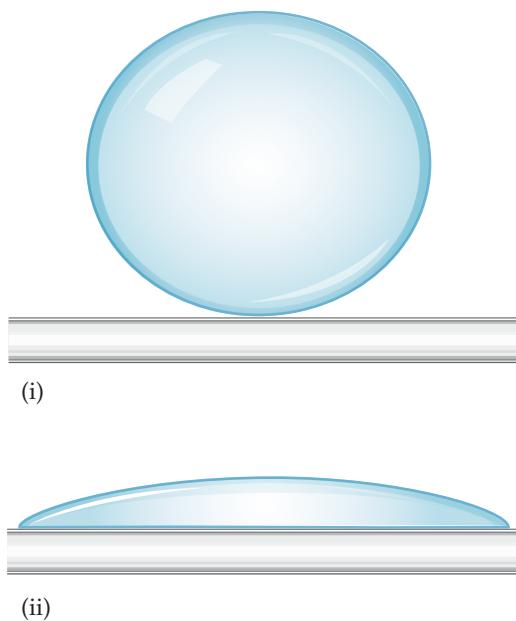
- 11.57** Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), the major substance in antifreeze, has a normal boiling point of 198°C . By comparison, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) boils at 78°C at atmospheric pressure. Ethylene glycol dimethyl ether ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$) has a normal boiling point of 83°C , and ethyl methyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_3$) has a normal boiling point of 11°C . (a) Explain why replacement of a hydrogen on the oxygen by a CH_3 group generally results in a lower boiling point. (b) What are the major factors responsible for the difference in boiling points of the two ethers?

- 11.58** Look up and compare the normal boiling points and normal melting points of H_2O and H_2S . Based on these physical properties, which substance has stronger intermolecular forces? What kinds of intermolecular forces exist for each molecule?

- 11.59** A number of salts containing the tetrahedral polyatomic anion, BF_4^- , are ionic liquids, whereas salts containing the somewhat larger tetrahedral ion SO_4^{2-} do not form ionic liquids. Explain this observation.

Select Properties of Liquids (Section 11.3)

- 11.60** (a) What is the relationship between surface tension and temperature? (b) What is the relationship between viscosity and temperature? (c) Why do substances with high surface tension also tend to have high viscosities?
- 11.61** Liquids can interact with flat surfaces just as they can with capillary tubes; the cohesive forces within the liquid can be stronger or weaker than the adhesive forces between liquid and surface:



- (a) In which of these diagrams, i or ii, do the adhesive forces between surface and liquid exceed the cohesive forces within the liquid? (b) Which of these diagrams, i or ii, represents what happens when water is on a nonpolar surface? (c) Which of these diagrams, i or ii, represents what happens when water is on a polar surface?

- 11.62** The boiling points, surface tensions, and viscosities of water and several alcohols are as shown in this table:

	Boiling Point (°C)	Surface Tension (J/m²)	Viscosity (kg/m s)
Water, H ₂ O	100	7.3×10^{-2}	0.9×10^{-3}
Ethanol, CH ₃ CH ₂ OH	78	2.3×10^{-2}	1.1×10^{-3}
1-Propanol, CH ₃ CH ₂ CH ₂ OH	97	2.4×10^{-2}	2.2×10^{-3}
1-Butanol, CH ₃ CH ₂ CH ₂ CH ₂ OH	117	2.6×10^{-2}	2.6×10^{-3}
Ethylene glycol, HOCH ₂ CH ₂ OH	197	4.8×10^{-2}	26×10^{-3}

- (a) From ethanol to 1-propanol to 1-butanol the boiling points, surface tensions, and viscosities all increase. What is the reason for this increase? (b) How do you explain the fact that 1-propanol and ethylene glycol have similar molecular weights (60 versus 62 u), yet the viscosity of ethylene glycol is more than 10 times larger than 1-propanol? (c) How do you explain the fact that water has the highest surface tension but the lowest viscosity?

Phase Changes (Section 11.4)

- 11.63** Name the phase transition in each of the following situations and indicate whether it is exothermic or endothermic: (a) Ice-cream melts at room temperature. (b) Potato slices become crisp when fried. (c) Droplets of water appear on the lid of a food container containing freshly baked bread. (d) You can see your own breath on a cold day.
- 11.64** (a) What phase change is represented by the “heat of vaporization” of a substance? (b) Is the process of vaporization

endothermic or exothermic? (c) If you compare a substance’s heat of vaporization to the amount of heat released during condensation, which one is generally larger (consider the numerical value only)?

- 11.65** For many years drinking water has been cooled in hot climates by evaporating it from the surfaces of canvas bags or porous clay pots. How many grams of water can be cooled from 35 to 20 °C by the evaporation of 60 g of water? (The heat of vaporization of water in this temperature range is 2.4 kJ/g. The specific heat of water is 4.18 J/g K.)
- 11.66** Due to the environmental concern of fluorocarbons as refrigerants, a refrigerant based on a mixture of hydrocarbons was used as a replacement. It is a patented blend of ethane, propane, butane, and isobutane. Isobutane has a normal boiling point of -12 °C. The molar specific heat of liquid phase and gas phase isobutane are 129.7 J/mol K and 95.2 J/mol K respectively. The heat of vaporization for this compound is 21.3 kJ/mol. Calculate the heat required to convert 25.0 g of isobutane from a liquid at -50 °C to a gas at 40 °C.

- 11.67** The critical temperatures and pressures of a series of halogenated methanes are as follows:

Compound	CCl ₃ F	CCl ₂ F ₂	CClF ₃	CF ₄
Critical temperature (K)	471	385	302	227
Critical pressure (MPa)	4.41	4.11	3.87	3.75

(a) List the intermolecular forces that occur for each compound. (b) Predict the order of increasing intermolecular attraction, from least to most, for this series of compounds. (c) Predict the critical temperature and pressure for CCl₄ based on the trends in this table. Look up the experimentally determined critical temperatures and pressures for CCl₄, using a source such as the *CRC Handbook of Chemistry and Physics*, and suggest a reason for any discrepancies.

Vapor Pressure (Section 11.5)

- 11.68** Which of the following affects the vapor pressure of a liquid? (a) Volume of the liquid, (b) surface area, (c) intermolecular attractive forces, (d) temperature, (e) density of the liquid.
- 11.69** (a) Place the following substances in order of increasing volatility: CH₄, CBr₄, CH₂Cl₂, CH₃Cl, CHBr₃, and CH₂Br₂. (b) How do the boiling points vary through this series? (c) Explain your answer to part (b) in terms of intermolecular forces.
- 11.70** (a) Two pans of water are on different burners of a stove. One pan of water is boiling vigorously, while the other is boiling gently. What can be said about the temperature of the water in the two pans? (b) A large container of water and a small one are at the same temperature. What can be said about the relative vapor pressures of the water in the two containers?
- 11.71** Using the vapor-pressure curves in Figure 11.25, (a) estimate the boiling point of diethyl ether at an external pressure of 133.7 kPa, (b) estimate the external pressure at which ethylene glycol will boil at 100 °C, (c) estimate the boiling point of ethanol at 26.7 kPa, (d) estimate the external pressure at which water will boil at 80 °C.

Phase Diagrams (Section 11.6)

- 11.72** (a) What is the significance of the triple point in a phase diagram? (b) Could you measure the triple point of water by measuring the temperature in a vessel in which water vapor, liquid water, and ice are in equilibrium under 101.3 kPa of air? Explain.
- 11.73** Referring to Figure 11.28, describe all the phase changes that would occur in each of the following cases: (a) Water vapor originally at 500 Pa and -0.5°C is slowly compressed at constant temperature until the final pressure is 2000 kPa. (b) Water originally at 100.0°C and 50 kPa is cooled at constant pressure until the temperature is -10°C .
- 11.74** Use the phase diagram of neon to answer the following questions. (a) What would you observe when the pressure of neon is reduced from 101.3 kPa to 0.1013 kPa at 20 K? (b) What can you say about the strength of the intermolecular forces in neon and krypton based on the critical points of Ne and Kr (see Table 11.5)?
- 11.75** The fact that water on Earth can readily be found in all three states (solid, liquid, and gas) is in part a consequence of the fact that the triple point of water ($T = 0.01^{\circ}\text{C}$, $P = 608 \text{ Pa}$) falls within a range of temperatures and pressures found on Earth. Saturn's largest moon Titan has a considerable amount of methane in its atmosphere. The conditions on the surface of Titan are estimated to be $P = 162 \text{ kPa}$ and $T = -178^{\circ}\text{C}$. As seen from the phase diagram of methane (Figure 11.30), these conditions are not far from the triple point of methane, raising the tantalizing possibility that

solid, liquid, and gaseous methane can be found on Titan.

- (a) In what state would you expect to find methane on the surface of Titan? (b) On moving upward through the atmosphere, the pressure will decrease. If we assume that the temperature does not change, what phase change would you expect to see as we move away from the surface?

Liquid Crystals (Section 11.7)

- 11.76** What observations made by Reinitzer on cholesterol benzoate suggested that this substance possesses a liquid crystalline phase?
- 11.77** Indicate whether each statement is true or false: (a) The liquid crystal state is another phase of matter, just like solid, liquid, and gas. (b) Liquid crystalline molecules are generally spherical in shape. (c) Molecules that exhibit a liquid crystalline phase do so at well-defined temperatures and pressures. (d) Molecules that exhibit a liquid crystalline phase show weaker-than-expected intermolecular forces. (e) Molecules containing only carbon and hydrogen are likely to form liquid crystalline phases. (f) Molecules can exhibit more than one liquid crystalline phase.
- 11.78** For a given substance, the liquid crystalline phase tends to be more viscous than the liquid phase. Why?
- 11.79** It often happens that a substance possessing a smectic liquid crystalline phase just above the melting point passes into a nematic liquid crystalline phase at a higher temperature. Account for this type of behavior.

Additional Exercises

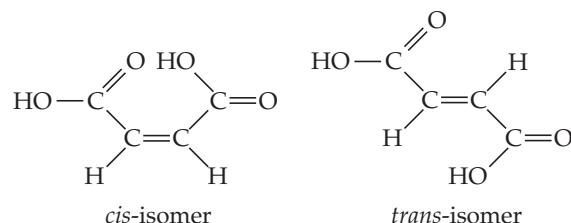
- 11.80** As the intermolecular attractive forces between molecules increase in magnitude, do you expect each of the following to increase or decrease in magnitude? (a) Vapor pressure, (b) heat of vaporization, (c) boiling point, (d) freezing point, (e) viscosity, (f) surface tension, (g) critical temperature.
- 11.81** This table lists the density of substance X at various temperatures and at 101.3 kPa. The normal melting point of substance X is 80 K.

Temperature (K)	Density (mol/L)
90	35.2
100	33.8
110	32.1
120	0.136
140	0.110
160	0.0893
180	0.0796

- (a) Over what temperature range is substance X a solid? (b) Over what temperature range is X a liquid? (c) Over what temperature range in the table is X a gas? (d) Estimate the normal boiling point of X. (e) Given that X is a nonpolar molecule, suggest the kind of intermolecular forces in X.
- 11.82** Suppose you have two colorless molecular liquids A and B whose boiling points are 78°C and 112°C respectively and both are at atmospheric pressure. Which of the following statements is correct? For each statement that is not correct, modify the statement so that it is correct. (a) Both A and B are liquids with identical vapor pressure at room temperature of 25°C . (b) Liquid A must consist of nonpolar molecules with lower molecular weight than B. (c) Both liquids A and B have higher total intermolecular forces than

water. (d) Liquid A is more volatile than liquid B because it has a lower boiling point. (e) At 112°C both liquids have a vapor pressure of 1 atm.

- 11.83** Two isomers of butenedioic acid with the planar structures are shown here:



- (a) Which of the two isomers will have the stronger intermolecular hydrogen bonding? (b) One isomer has a melting point of 135°C and the other 287°C . Which isomer has which melting point?

- 11.84** This table shows some physical properties of compounds containing O-H groups.

Liquid	Molecular Weight	Experimental Dipole Moment	Boiling Point
CH ₃ OH	32.04	1.7	64.7°C
CH ₃ CH ₂ CH ₂ OH	74.12	1.66	117.7°C
HOCH ₂ CH ₂ OH	62.07	1.5	197.3°C

Which of the following statements best explains these data? (a) The larger the dipole moment, the stronger the intermolecular forces, and therefore the boiling point is lowest for the molecule with the largest dipole moment. (b) The dis-

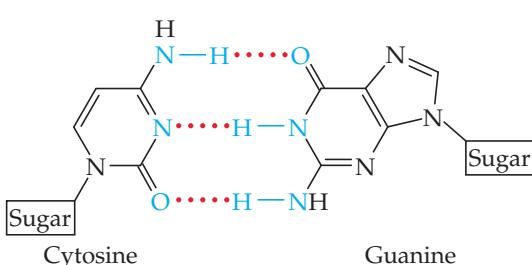
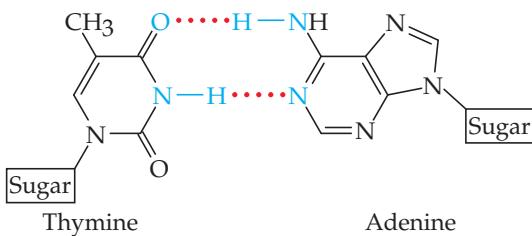
persion forces increase from CH_3OH $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{OH}$; since the boiling point also increases in this order, the dispersion forces must be the major contributing factor for the boiling point trend; (c) $\text{HOCH}_2\text{CH}_2\text{OH}$ has two groups capable of hydrogen bonding per molecule, whereas CH_3OH and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ have only one; therefore, $\text{HOCH}_2\text{CH}_2\text{OH}$ has the highest boiling point.

- 11.85** This table shows the normal boiling points of some compounds containing $\text{C}=\text{O}$ groups.

Compound	Structure	Normal Boiling Point (°C)
$\text{C}_2\text{H}_4\text{O}$ (ethanal)		20.2
CH_2O_2 (methanoic acid)		100.8
$\text{C}_2\text{H}_4\text{O}_2$ (ethanoic acid)		118.1
$\text{C}_3\text{H}_6\text{O}_2$ (methyl ethanoate)		56.9

(a) Which of these compounds exhibit dispersion interactions? (b) Which of these compounds exhibit dipole-dipole interactions? (c) Which of these compounds exhibit hydrogen bonding? (d) Why is the boiling point of ethanoic acid higher than that of methanoic acid? (e) Why is the boiling point of ethanal the lowest of all?

- 11.86** The DNA double helix (opening picture of section 9.2) at the atomic level looks like a twisted ladder, where the “rungs” of the ladder consist of molecules that are hydrogen-bonded together. Sugar and phosphate groups make up the sides of the ladder. Shown are the structures of the adenine-thymine (AT) “base pair” and the guanine-cytosine (GC) base pair:



You can see that AT base pairs are held together by two hydrogen bonds and the GC base pairs are held together by three hydrogen bonds. Which base pair is more stable to heating? Why?

- 11.87** Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) and pentane (C_5H_{12}) are both liquids at room temperature and room pressure, and have about the same molecular weight. (a) One of these liquids is much more viscous than the other. Which one do you predict is more viscous? (b) One of these liquids has a much lower normal boiling point (36.1°C) compared to the other one (198°C). Which liquid has the lower normal boiling point? (c) One of these liquids is the major component in antifreeze in automobile engines. Which liquid would you expect to be used as antifreeze? (d) One of these liquids is used as a “blowing agent” in the manufacture of polystyrene foam because it is so volatile. Which liquid would you expect to be used as a blowing agent?

- 11.88** Use the normal boiling points
 propane (C_3H_8) -42.1°C
 butane (C_4H_{10}) -0.5°C
 pentane (C_5H_{12}) 36.1°C
 hexane (C_6H_{14}) 68.7°C
 heptane (C_7H_{16}) 98.4°C
- to estimate the normal boiling point of octane (C_8H_{18}). Explain the trend in the boiling points.

- 11.89** One of the attractive features of ionic liquids is their low vapor pressure, which in turn tends to make them nonflammable. Why do you think ionic liquids have lower vapor pressures than most room-temperature molecular liquids?

- 11.90** (a) When you exercise vigorously, you sweat. How does this help your body cool? (b) A flask of water is connected to a vacuum pump. A few moments after the pump is turned on, the water begins to boil. After a few minutes, the water begins to freeze. Explain why these processes occur.

- 11.91** The following table gives the vapor pressure of tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) as a function of temperature:

Temperature (°C)	Vapor Pressure (Pa)
-50	99
-10	3630
0	6390
30	26,800
50	58,600

(a) By plotting these data in a suitable fashion, determine whether the Clausius-Clapeyron equation (Equation 11.1) is obeyed. If it is obeyed, use your plot to determine ΔH_{vap} for $\text{C}_4\text{H}_8\text{O}$. (b) Use these data to determine the boiling point of the compound.

- 11.92** Suppose the vapor pressure of a substance is measured at two different temperatures. (a) By using the Clausius-Clapeyron equation (Equation 11.1) derive the following relationship between the vapor pressures, P_1 and P_2 , and the absolute temperatures at which they were measured, T_1 and T_2 :

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

(b) Gasoline is a mixture of hydrocarbons, a component of which is octane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Octane has a vapor pressure of 1.86 kPa at 25°C and a vapor pressure of 19.3 kPa at 75°C . Use these data and the equation in part (a) to calculate the heat of vaporization of octane. (c) By using the equation in part (a) and the data given in part (b), calculate the normal boiling point of octane. Compare your answer to the one you obtained from Exercise 11.88. (d) Calculate the vapor pressure of octane at -30°C .

- 11.93** The following data present the temperatures at which certain vapor pressures are achieved for dichloromethane (CH_2Cl_2) and methyl iodide (CH_3I):

Vapor Pressure (kPa)	1.33	5.33	13.33	53.33
T for CH_2Cl_2 (°C)	-43.3	-22.3	-6.3	24.1
T for CH_3I (°C)	-45.8	-24.2	-7.0	25.3

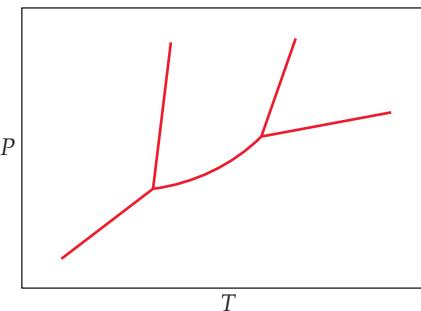
(a) Which of the two substances is expected to have the greater dipole–dipole forces? Which is expected to have the greater dispersion forces? Based on your answers, explain why it is difficult to predict which compound would be more volatile. (b) Which compound would you expect to have the higher boiling point? Check your answer in a reference book such as the *CRC Handbook of Chemistry and Physics*. (c) The order of volatility of these two substances changes as the temperature is increased. What quantity must be different for the two substances for this phenomenon to occur? (d) Substantiate your answer for part (c) by drawing an appropriate graph.

- 11.94** Solid CO_2 is called dry ice. It sublimes at an atmospheric pressure of -78.5 °C. The triple point of CO_2 is -56.6 °C

at 517.8 kPa. CO_2 becomes a supercritical fluid at 31 °C and 7.487 MPa. Using these data, construct a phase diagram for CO_2 , labeling all the regions of your diagram.

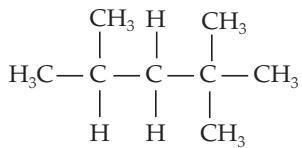
- 11.95** A watch with a liquid crystal display (LCD) does not function properly when it is exposed to low temperatures during a trip to Antarctica. Explain why the LCD might not function well at low temperature.

- 11.96** A particular liquid crystalline substance has the phase diagram shown in the figure. By analogy with the phase diagram for a nonliquid crystalline substance, identify the phase present in each area.



Integrative Exercises

- 11.97** In Table 11.3, we saw that the viscosity of a series of hydrocarbons increased with molecular weight, doubling from the six-carbon molecule to the ten-carbon molecule. (a) The eight-carbon hydrocarbon, octane, has an isomer, iso-octane. Would you predict that iso-octane would have a larger or smaller viscosity than octane? Why? (b) Predict the relative order of boiling points of the hydrocarbons in Table 11.4, from lowest to highest. (c) The surface tension of



2,2,4-Trimethylpentane or iso-octane

the hydrocarbon liquids in Table 11.4 does increase from hexane to decane, but only by a rather small amount (20% overall, compared to the doubling of viscosity). Which of these statements is the most likely explanation for this phenomenon? (i) The flexibility of the molecules has a much larger effect on viscosity than on surface tension. (ii) Viscosity only depends on molecular weight, but surface tension depends on molecular weight and on intermolecular forces. (iii) Larger molecules can make larger liquid droplets and therefore have lower surface tension. (d) Nonane has a viscosity of 7.11×10^{-4} kg/m s at 20 °C. *n*-octyl alcohol, $\text{CH}_3(\text{CH}_2)_7\text{OH}$, has almost the same molecular weight as nonane, but its viscosity is 1.01×10^{-2} kg/m s at 20 °C. Which of the following statements is the most likely explanation for this phenomenon? (i) The stronger the intermolecular forces in a liquid, the smaller its viscosity. (ii) The stronger the intermolecular forces in a liquid, the larger its viscosity.

- 11.98** Rubbing alcohol is the common name for 2-propanol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$). (a) Draw the three-dimensional structure of the 2-propanol molecule and predict the geometry around each carbon atom. (b) Is the 2-propanol mole-

cule polar or nonpolar? (c) What kinds of intermolecular attractive forces exist between the 2-propanol molecules? (d) The isomer 1-propanol has the same molecular weight as 2-propanol, yet 2-propanol boils at 82.6 °C and 1-propanol boils at 97.2 °C. Explain the difference.

- 11.99** The table shown here lists the molar heats of vaporization for several organic compounds. Use specific examples from this list to illustrate how the heat of vaporization varies with (a) molar mass, (b) molecular shape, (c) molecular polarity, (d) hydrogen-bonding interactions. Explain these comparisons in terms of the nature of the intermolecular forces at work. (You may find it helpful to draw out the structural formula for each compound.)

Compound	Heat of Vaporization (kJ/mol)
$\text{CH}_3\text{CH}_2\text{CH}_3$	19.0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	27.6
$\text{CH}_3\text{CHBrCH}_3$	31.8
CH_3COCH_3	32.0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	33.6
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	47.3

- 11.100** The vapor pressure of acetone (CH_3COCH_3) at 19 °C is 5.33 kPa. A 3.50-g sample of acetone is placed in a 2.00 L container at 22 °C. If the container is closed and the acetone is allowed to reach equilibrium with its vapor, how many grams of liquid acetone remain? (Assume that the vapor behaves like an ideal gas.)

- 11.101** Propane (C_3H_8) is pressurized into liquid and stored in cylinders to be used as a fuel. The normal boiling point of propane is listed as -42 °C. (a) When converting propane into liquid at room temperature of 25 °C, would you expect the pressure in the tank to be greater or less than atmospheric pressure? How does the pressure within the tank depend on how much liquid propane is in it? (b) Suppose the fuel tank leaks and a few liters of propane escape rapidly. What do you expect would happen to the temperature of the

remaining liquid propane in the tank? Explain. (c) How much heat must be added to vaporize 20 g of propane if its heat of vaporization is 18.8 kJ/mol? What volume does this amount of propane occupy at 100 kPa and 25 °C?

11.102 Using information in Appendices B and C, calculate the minimum grams of methane, CH_4 , that must be combusted to provide the energy necessary to convert 0.20 kg of ice at –10 °C to liquid water at 70 °C.

11.103 The vapor pressure of a volatile liquid can be determined by slowly bubbling a known volume of gas through it at a known temperature and pressure. In an experiment, 8.00 L of argon

gas is passed through 11.7872 g of liquid hexane C_6H_{14} at 30.0 °C. The mass of the remaining liquid after the experiment is 4.875 g. Assuming that the gas becomes saturated with hexane vapor and that the total gas volume and temperature remain constant, what is the vapor pressure of hexane?

11.104 The relative humidity of air is calculated by the ratio of the partial pressure of water in the air to the equilibrium vapor pressure of water at the same temperature times 100%. The average temperature and humidity of the Sahara are 40 °C and 25%, respectively. How many molecules of water are present in 1 m^3 of air in the Sahara?

Design an Experiment

Intermolecular forces are very important for predicting the physical properties of molecular substances. Sometimes, however, it is difficult to explain or predict trends in these properties because all the possible intermolecular forces can be operating at the same time, and there is a wide range of energies for these interactions. Consider ammonia, NH_3 . It is a gas at $P = 101.3 \text{ kPa}$, $T = 25^\circ\text{C}$. Ammonia can be liquefied at –33.5 °C ($P = 101.3 \text{ kPa}$). Methylamine, CH_3NH_2 , is a derivative of ammonia and is also a gas at

$P = 101.3 \text{ kPa}$, $T = 25^\circ\text{C}$. Methylamine can be liquefied at –6.4 °C ($P = 101.3 \text{ kPa}$).

Use these experimental data to determine which molecule has the stronger intermolecular attractive interactions, ammonia or methylamine; and suggest reasons for your conclusion. Based on your reasons, what other experiments could you do with these molecules, or related molecules, to test your hypothesis?