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12

Intermolecular Forces: Liquids and Solids

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TYPES OF INTERMOLECULAR FORCES (NONCOVALENT INTERACTIONS)

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▶ Two of the many natural phenomena described in this chapter include the more ordered structure of the solid compared with the liquid state and the variation of density with the state of matter.

In this scene from Antarctica, water exists in all three states of matter—solid in the ice, liquid in the sea, and gas in the atmosphere. Solids, liquids, and gases were compared at the macroscopic and microscopic levels in Chapter 1 (Fig. 1-7).

When we make ice cubes by placing water in a tray in a freezer, energy is removed from the water molecules, which gradually slow down. Attractive (intermolecular) forces between the molecules take over, and the water solidifies into ice. When an ice cube melts, energy from the surroundings is absorbed by the water molecules, which overcome the intermolecular forces within the ice cube and enter the liquid state. In our study of gases, we intentionally sought conditions in which the intermolecular forces were negligible. This approach allowed us to describe gases with the ideal gas equation and to explain their behavior with the kinetic-molecular theory of gases. To describe the other states of matter—liquids and solids—we must first be able to identify the various intermolecular forces and then find situations in which the intermolecular forces are significant. We then consider some interesting properties of liquids and solids related to the strengths of these forces.

12-1 Intermolecular Forces

In our study of gases, we noted that at high pressures and low temperatures intermolecular forces cause gas behavior to depart from ideality. When these forces are sufficiently strong, a gas condenses to a liquid. That is, the intermolecular forces keep the molecules in such close proximity that they are confined to a definite volume, as expected for the liquid state.

Intermolecular forces are important in establishing the form and behavior of matter. The origin of intermolecular forces, those interactions between molecules, arises from the permanent and momentary unequal distribution of electron density within molecules.

Van der Waals Forces

(generally refer to all intermolecular forces between electrically neutral molecules)

Because helium forms no stable chemical bonds, we might expect it to remain a gas right down to 0 K. Although helium remains gaseous to very low temperatures, it does condense to a liquid at 4 K and freeze to a solid (at 25 atm pressure) at 1 K. These data suggest that intermolecular forces, even though very weak, must exist among He atoms. If the temperature is sufficiently low, these forces overcome thermal agitation and cause helium to condense. In this section, we will examine the types of intermolecular forces known collectively as **van der Waals forces**. The intermolecular forces contributing to the term $a(n/V)^2$ in the van der Waals equation for nonideal gases (equation 6.26) are of this type.

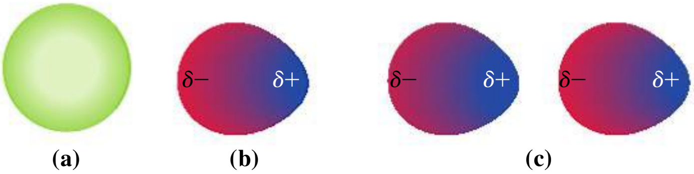
Instantaneous and Induced Dipoles

In describing electronic structures, we speak of electron charge density, or the probability that an electron is in a certain region at a given time. One probability is that at some particular instant—purely by chance—electrons are concentrated in one region of an atom or a molecule. This displacement of electrons causes a normally nonpolar species to become momentarily polar. An *instantaneous dipole* is formed. That is, the molecule has an instantaneous dipole moment. After this, electrons in a neighboring atom or molecule may be displaced to also produce a dipole. This is a process of induction (Fig. 12-1), and the newly formed dipole is called an *induced dipole.*

▲ FIGURE 12-1
The phenomenon of induction
The attraction of a balloon to a surface is a commonplace example of induction. The balloon is charged by rubbing, and the charged balloon induces an opposite charge on the surface. (See also Appendix B.)

Taken together, these two events lead to an intermolecular force of attraction (Fig. 12-2). We can call this an instantaneous dipole–induced dipole attraction, but the names more commonly used are **dispersion force** and **London force**. (In 1928, Fritz London offered a theoretical explanation of these forces.)

Polarizability is the term used to describe the relative tendency for a charge distribution to distort from its normal shape in an atom or a molecule. The greater this tendency, the more polarizable an atom or a molecule is said to be. Polarizability increases with atomic or molecular size (see the table on the next page), which is defined by the volume of the electron cloud around a substance. Also, in large molecules, some electrons, being farther from atomic nuclei, are less firmly held. These electrons are more easily displaced, and the polarizability



▲ FIGURE 12-2
Instantaneous and induced dipoles
(a) In the *normal condition*, a nonpolar molecule has a symmetrical charge distribution. **(b)** In the *instantaneous condition*, a displacement of the electronic charge produces an instantaneous dipole with a charge separation represented as $\delta+$ and $\delta-$. **(c)** In an *induced dipole*, the instantaneous dipole on the left induces a charge separation in the molecule on the right. The result is an instantaneous dipole–induced dipole attraction.

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that a bond dipole results from the separation of centers of positive and negative charge in a covalent bond, that a resultant dipole moment, μ, is a summation of bond dipoles taking into account their magnitudes and directions, and that a *polar* molecule (Section 10-7) is one that has a permanent resultant dipole moment.

Compound	Polarizability,* 10^{-25} cm^3	Molar Mass, amu	Boiling Point, K
H_2	7.90	2.0158	20.35
O_2	16.0	31.9988	90.19
N_2	17.6	28.0134	77.35
CH_4	26.0	16.04	109.15
C_2H_6	44.7	30.07	184.55
Cl_2	46.1	70.906	238.25
C_3H_8	62.9	44.11	231.05
CCl_4	105	153.81	349.95

*Sometimes polarizability is referred to as *polarizability volume.* Note that the units of polarizability given above have the units of volume. That provides a measure of the atomic or molecular volume.

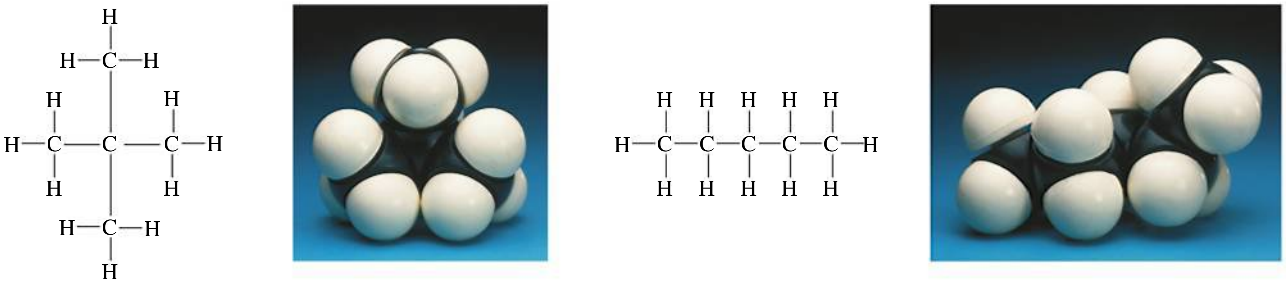
of the molecule increases. Because dispersion forces become stronger (more attractive) as polarizability increases, and because polarizability generally increases with molecular mass, the melting points and boiling points of molecular substances generally increase with increasing molecular mass. For instance, helium (atomic mass, 4 u) has a boiling point of 4 K, whereas radon (atomic mass, 222 u) has a boiling point of 211 K. The melting points and boiling points of the halogens increase in a similar way in the series F_2, Cl_2, Br_2, I_2 (recall Table 9.5).

▶ Recall from Chapter 3, a molecular substance is made up of molecules. The molecules interact with each other through relatively weak intermolecular forces. The atoms of a given molecule are held together by relatively strong covalent bonds.

The strength of dispersion forces also depends on *molecular shape.* Electrons in elongated molecules are more easily displaced than are those in small, compact, symmetrical molecules; the elongated molecules are more polarizable. Two substances with identical numbers and kinds of atoms but different molecular shapes (*isomers*) may have different properties. This idea is illustrated in Figure 12-3.

Dipole–Dipole Interactions

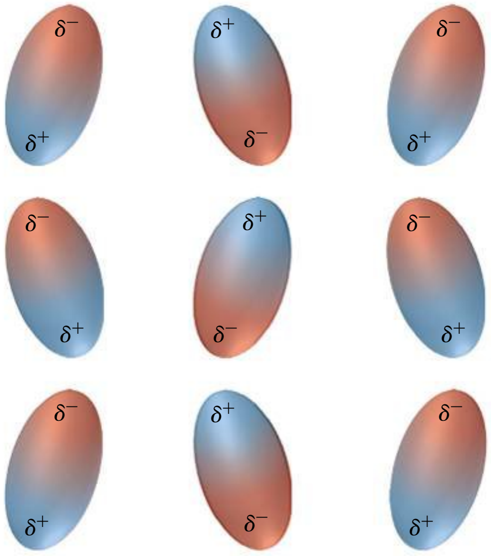
In a *polar* substance, the molecules have permanent dipole moments, so the molecules tend to line up with the positive end of one dipole directed toward the negative ends of neighboring dipoles (Fig. 12-4). This additional partial ordering of molecules can cause a substance to persist as a solid or liquid at temperatures higher than otherwise expected. Consider N_2, O_2, and NO. There are no electronegativity differences in N_2 and O_2, and both substances are nonpolar. In NO, conversely, there is an electronegativity difference, and the molecule has a slight dipole moment. Considering only dispersion forces, we would expect the boiling point of NO(l) to be intermediate to those of N_2(l) and O_2(l), but in the comparison on the next page, we see that it is not. NO(l) has the highest boiling point of the three because of its additional permanent dipole.



(a) Neopentane
bp = 9.5 °C

(b) Pentane
bp = 36.1 °C

▲ FIGURE 12-3
Molecular shapes and polarizability
The elongated pentane molecule is more polarized than is the compact neopentane molecule. Intermolecular forces are stronger in pentane than they are in neopentane. As a result, pentane boils at a higher temperature than neopentane.



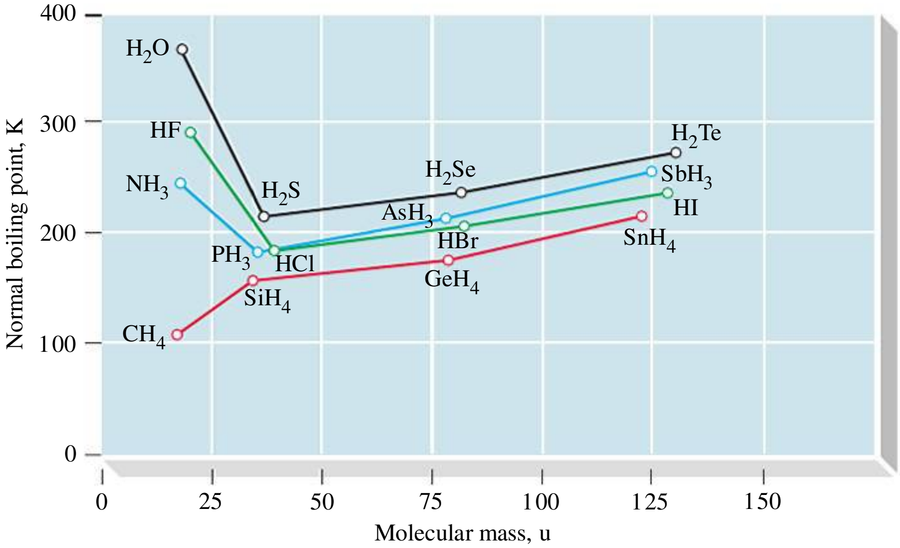
◀ FIGURE 12-4
Dipole–dipole interactions
Dipoles tend to arrange themselves with the positive end of one dipole pointed toward the negative end of a neighboring dipole. Ordinarily, thermal motion upsets this orderly array. Nevertheless, this tendency for dipoles to align themselves can affect physical properties, such as the melting points of solids and the boiling points of liquids.

N_2	NO	O_2
$\mu = 0$ (nonpolar) mol. mass = 28 u bp = 77.34 K	$\mu = 0.153$ D (polar) mol. mass = 30 u bp = 121.39 K	$\mu = 0$ (nonpolar) mol. mass = 32 u bp = 90.19 K

◀ The SI unit for dipole moment, C m, is inconvenient for expressing molecular dipole moments. The non-SI unit, debye (D), is often used. One debye is approximately 3.34×10^{-30} C m.

Hydrogen Bonding

Figure 12-5, in which the boiling points of a series of similar compounds are plotted as a function of molecular mass, demonstrates some features that we cannot explain by the types of intermolecular forces considered to this point. The hydrogen compounds (hydrides) of the group 14 elements display normal behavior; that is, the boiling points increase regularly as the molecular mass increases. But there are three striking exceptions in groups 15, 16, and 17. The boiling points of NH_3, H_2O, and HF are as high or higher than those of any other hydride in their group—not lowest, as we might expect. A special type of intermolecular force



▲ FIGURE 12-5
Comparison of boiling points of some hydrides of the elements of groups 14,15,16, and 17
The values for NH_3, H_2O, and HF are unusually high compared with those of other members of their groups.

EXAMPLE 12-1 Comparing Physical Properties of Polar and Nonpolar Substances

Which would you expect to have the higher boiling point, the hydrocarbon fuel butane, C_4H_{10}, or the organic solvent acetone, $(CH_3)_2CO$?

Analyze

Ordinarily, the first clue comes in a comparison of molecular masses. However, because the two substances have the same molecular mass (58 u), we have to look elsewhere for a factor on which to base our prediction.

The next consideration is the polarity of the molecules. The electronegativity difference between C and H is so small that we generally expect hydrocarbons, such as butane, to be nonpolar. However, we notice that one of the molecules contains a carbon-oxygen bond, and thus, a strong carbon-to-oxygen dipole. At times, it is helpful to sketch the structure of a molecule to see whether symmetrical features cause bond dipoles to cancel. It is not necessary to sketch the structure of the acetone molecule to deduce that it is a polar molecule. The $C{=}O$ bond dipole in acetone cannot be offset by other bond dipoles. Thus, acetone is polar.

Solve

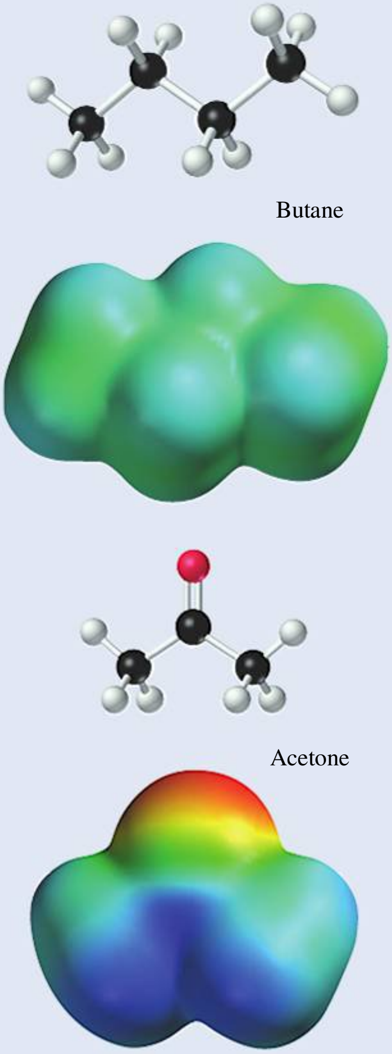
Given two substances with the same molecular mass, one polar and one nonpolar, we expect the polar substance—acetone—to have the higher boiling point. (The measured boiling points are butane, $-0.5\ ^\circ C$; acetone, $56.2\ ^\circ C$.)

Assess

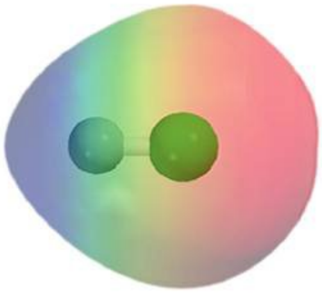
In general, when comparing the properties of different substances, we must consider the various types of intermolecular forces and the factors that affect the strength of each type of force. Although it wasn't important here, the three-dimensional shape of a molecule is usually a very important consideration and it is usually necessary to sketch the molecular structure to see how molecular shape plays a role.

PRACTICE EXAMPLE A: Which of the following substances would you expect to have the highest boiling point: C_3H_8, CO_2, CH_3CN? Explain.

PRACTICE EXAMPLE B: Arrange the following in the expected order of increasing boiling point: C_8H_{18}, $CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$, C_6H_5CHO (octane, butane, isobutane, and benzaldehyde respectively).



▲ **Butane and acetone**
The lower diagrams are electrostatic potential diagrams for butane and acetone. The red color indicates regions of high negative electrostatic potential.



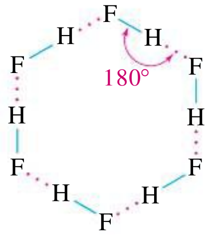
▲ **Electrostatic potential map of HF**

causes this exceptional behavior, as we see for hydrogen fluoride in Figure 12-6. The main points established in the figure are outlined below.

- The alignment of HF dipoles places an H atom between two F atoms. Because of the very small size of the H atom, the dipoles come close together and produce strong *dipole–dipole* attractions.
- Although an H atom is covalently bonded to one F atom, it is also weakly bonded to the F atom of a nearby HF molecule. This occurs through a lone pair of electrons on the F atom. Each H atom acts as a bridge between two F atoms.
- The bond angle between two F atoms bridged by an H atom (that is, the angle $F{-}HF\cdots F$) is about 180°.

The type of intermolecular force just described is called a hydrogen bond, although it is simply an electrostatic attraction and not an actual chemical bond like a covalent bond. In a **hydrogen bond** an H atom is covalently bonded to a highly electronegative atom, which attracts electron density away from the H nucleus. This in turn allows the H nucleus, a proton, to be simultaneously attracted to a lone pair of electrons on a highly electronegative atom in a neighboring molecule.

Hydrogen bonds are possible only with certain hydrogen-containing compounds because all atoms other than H have inner-shell electrons to shield their nuclei from attraction by lone-pair electrons of nearby atoms. Only F, O, and N easily meet the requirements for hydrogen-bond formation. Weak hydrogen bonding is occasionally encountered between an H atom of one molecule and a Cl or S atom in a neighboring molecule. Compared with other intermolecular forces, hydrogen bonds are relatively strong, having energies of the order of 15 to 40 $\mathrm{kJ\,mol^{-1}}$. By contrast, single covalent bonds (also known as intramolecular bonds) are much stronger still—greater than 150 $\mathrm{kJ\,mol^{-1}}$. (See Table 10.3 for further comparisons.)



▲ FIGURE 12-6

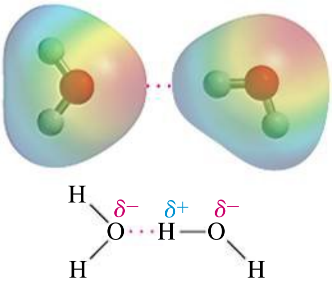
Hydrogen bonding in gaseous hydrogen fluoride

In gaseous hydrogen fluoride, many of the HF molecules are associated into cyclic $(HF)_6$ structures of the type pictured here. Each H atom is bonded to one F atom by a single covalent bond (—) and to another F atom through a hydrogen bond (···).

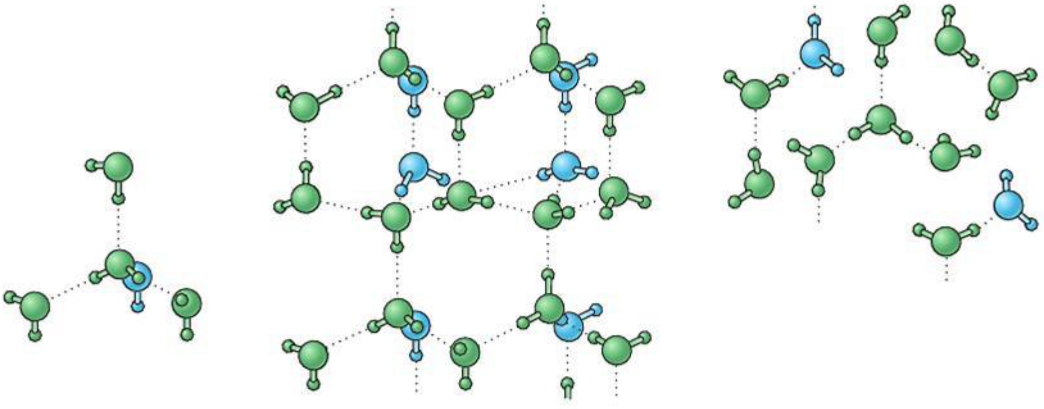
Hydrogen Bonding in Water

Ordinary water is certainly the most common substance in which hydrogen bonding occurs. Figure 12-7 shows how one water molecule is held to four neighbors in a tetrahedral arrangement by hydrogen bonds. In ice, hydrogen bonds hold the water molecules in a rigid but rather open structure. As ice melts, only a fraction of the hydrogen bonds are broken. One indication of this is the relatively low heat of fusion of ice (6.01 $\mathrm{kJ\,mol^{-1}}$). It is much less than we would expect if all the hydrogen bonds were to break during melting.

The open structure of ice shown in Figure 12-7(b) gives ice a low density. When ice melts, some of the hydrogen bonds are broken. This allows the water



▲ **Hydrogen bonding between H_2O molecules**



▲ FIGURE 12-7

Hydrogen bonding in water

(a) Each water molecule is linked to four others through hydrogen bonds. The arrangement is tetrahedral. Each H atom is situated along a line joining two O atoms, but closer to one O atom (100 pm) than to the other (180 pm). **(b)** For the crystal structure of ice, H atoms lie between pairs of O atoms, again closer to one O atom than to the other. (Molecules behind the plane of the page are light blue.) O atoms are arranged in bent hexagonal rings arranged in layers. This characteristic pattern is similar to the hexagonal shapes of snowflakes. **(c)** In the liquid, water molecules have hydrogen bonds to only some of their neighbours. This allows the water molecules to pack more densely in the liquid than in the solid.

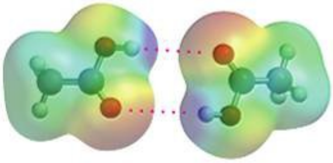
molecules to be more compactly arranged, accounting for the increase in density when ice melts. That is, the number of H_2O molecules per unit volume is greater in the liquid than in the solid.

As liquid water is heated above the melting point, hydrogen bonds continue to break. The molecules become even more closely packed, and the density of the liquid water continues to increase. Liquid water attains its maximum density at 3.98 °C. Above this temperature, the water behaves in a “normal” fashion: Its density decreases as temperature increases. The unusual freezing-point behavior of water explains why a freshwater lake freezes from the top down. When the water temperature falls below 4 °C, the denser water sinks to the bottom of the lake and the colder surface water freezes. The ice over the top of the lake then tends to insulate the water below from further heat loss. This allows fish to survive the winter in a lake that has been frozen over. Without hydrogen bonding, all lakes would freeze from the bottom up; and fish, small bottom-feeding animals, and aquatic plants would not survive the winter. The density relationship between liquid water and ice is compared in Figure 12-8 with the more common liquid–solid density relationship.

▲ FIGURE 12-8
Solid and liquid densities compared
The sight of ice cubes floating on liquid water (left) is a familiar one; ice is less dense than liquid water. The more common situation, however, is that of paraffin wax (right). Solid paraffin is denser than the liquid and sinks to the bottom of the beaker.

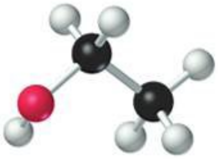
Other Properties Affected by Hydrogen Bonding

Water is one example of a substance whose properties are affected by hydrogen bonding. There are numerous others. In acetic acid, CH_3COOH, pairs of molecules tend to join together into *dimers* (double molecules), both in the liquid and in the vapor states (Fig. 12-9). Not all the hydrogen bonds are disrupted when liquid acetic acid vaporizes, and, as a result, the heat of vaporization is abnormally low.

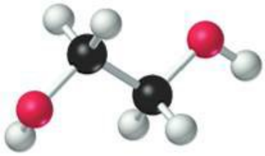


▲ FIGURE 12-9
An acetic acid dimer
Electrostatic potential maps showing hydrogen bonding.

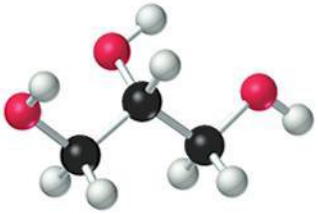
Certain trends in viscosity can also be explained by hydrogen bonding. In alcohols, the H atom in a —OH group in one molecule can form a hydrogen bond to the O atom in a neighboring alcohol molecule. An alcohol molecule with two —OH groups (a *diol*) has more possibilities for hydrogen-bond formation than a comparable alcohol with a single —OH group. Having stronger intermolecular forces, we expect the diol to flow more slowly, that is, to have a greater viscosity, than the simple alcohol. When still more —OH groups are present (*polyols*), we expect a further increase in viscosity. These comparisons are illustrated by the three common alcohols below. (The unit cP is a centipoise. The SI unit of viscosity is $1\ \text{N s m}^{-2} = 10\ \text{P}$. The Greek letter eta, η, is typically used as a symbol for viscosity.)



Ethyl alcohol
(ethanol)
at 20 °C: $\eta = 1.20$ cP



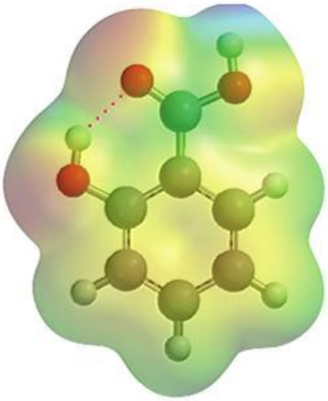
Ethylene glycol
(1,2-ethanediol)
at 20 °C: $\eta = 19.9$ cP



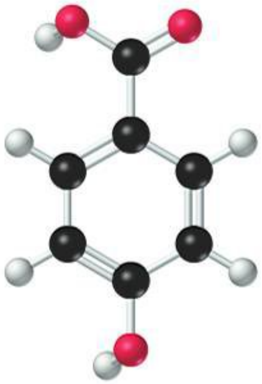
Glycerol
(1,2,3-propanetriol)
at 20 °C: $\eta = 1490$ cP

*Inter*molecular and *Intra*molecular Hydrogen Bonding

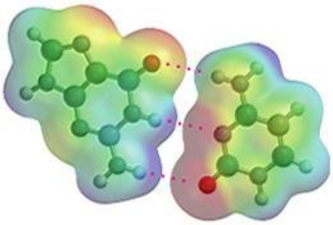
All the examples of hydrogen bonding presented to this point have involved an intermolecular force *between two molecules*, and this is called an *intermolecular hydrogen bond*. Another possibility occurs in molecules with an H atom covalently bonded to one highly electronegative atom (for example, O or N) and with another highly electronegative atom nearby in the same molecule. This type of hydrogen bonding *within a molecule* is called *intramolecular hydrogen bonding*. As shown in the molecular model of salicylic acid on the facing page, an intramolecular hydrogen bond (represented by a dotted line) joins the —OH group to the doubly bonded oxygen atom of the —COOH group on the same molecule. To underscore the importance of molecular geometry in establishing the conditions necessary for intramolecular hydrogen bonding, we need only turn to an isomer of salicylic acid called *para*-hydroxybenzoic acid. In this molecule, the H atom of the —COOH group is too close to the doubly bonded O atom of the same group to form a hydrogen bond, and the H atom of the —OH group on the opposite side of the molecule is too far away. Intramolecular hydrogen bonding does not occur in this situation.



▲ Electrostatic potential map of salicylic acid showing intramolecular hydrogen bonding. The double bond character of certain bonds are not shown in the ball-and-stick model.



▲ There is no intramolecular hydrogen bonding in *para*-hydroxybenzoic acid.



▲ **Hydrogen bonding between guanine (left) and cytosine(right)in DNA**

Hydrogen Bonding In Living Matter

Some chemical reactions in living matter involve complex structures, such as proteins and DNA, and in these reactions certain bonds must be easily broken and re-formed. Hydrogen bonding is the only type of bonding with energies of just the right magnitude to allow this, as we will discover in Chapter 27. We will also find that both intra- and intermolecular hydrogen bonding is involved in these complex structures.

Hydrogen bonding seems to provide an answer to the puzzle of how some trees are able to grow to great heights. In Chapter 6 (page 181), we learned that atmospheric pressure is capable of pushing a column of water to a maximum height of only about 10 m—other factors must be involved in transporting water to the tops of redwood trees up to 100 m tall. Hydrogen bonding seems to be a factor in transporting water in trees. Thin columns of water (in xylem, a plant tissue) extend from the roots to the leaves in the very tops of trees. In these columns, the water molecules are hydrogen-bonded to one another, with each water molecule acting like a link in a cohesive chain. When one water molecule evaporates from a leaf, another molecule in the chain moves to take its place and all the other molecules are pulled up the chain. Ultimately, a new water molecule joins the chain in the root system. In the next chapter, we will learn about another factor in transporting water in trees: osmotic pressure and its ability to force water through a membrane.

▲ **Sequoia trees**
The mystery of how these trees can bring water to leaves that are hundreds of feet up may be explained by hydrogen bonding.

12-1 CONCEPT ASSESSMENT

What are the types of intermolecular interactions in $CH_3CH_2NH_2(l)$, and which is the strongest?

TABLE 12.1 Intermolecular Forces and Properties of Selected Substances

	Molecular Mass, u	Dipole Moment, D	Van der Waals Forces		ΔH_{vap}, kJ mol^{-1}	Boiling Point, K
			% Dispersion	% Dipole		
F_2	38.00	0	100	0	6.86	85.01
HCl	36.46	1.08	81.4	18.6	16.15	188.11
HBr	80.92	0.82	94.5	5.5	17.61	206.43
HI	127.91	0.44	99.5	0.5	19.77	237.80

Summary of van der Waals Forces

When assessing the importance of van der Waals forces, consider the following statements.

- *Dispersion (London) forces exist between all molecules.* They involve displacements of all the electrons in molecules, and they increase in strength with increasing molecular mass. The forces also depend on molecular shapes.
- *Forces associated with permanent dipoles* involve displacements of electron pairs in bonds rather than in molecules as a whole. These forces are found only in substances with resultant dipole moments (polar molecules). Their existence *adds* to the effect of dispersion forces also present.
- *When comparing substances of roughly comparable molecular masses,* dipole forces can produce significant differences in properties such as melting point, boiling point, and enthalpy of vaporization.
- *When comparing substances of widely different molecular masses,* dispersion forces are usually more significant than dipole forces.

▶ In our discussion of London forces, we use molar mass only as a guide to the number of electrons present in a molecule; the forces holding a molecule in a liquid are not gravitational in nature.

Let's see how these statements relate to the data in Table 12.1, which includes a rough breakdown of van der Waals forces into dispersion forces and forces caused by dipoles. HCl and F_2 have comparable molecular masses, but because HCl is polar, it has a significantly larger ΔH_{vap} and a higher boiling point. Within the series HCl, HBr, and HI, molecular mass increases sharply and ΔH_{vap} and boiling points increase in the order HCl < HBr < HI. The more polar nature of HCl and HBr relative to HI is not sufficient to reverse the trends produced by the increasing molecular masses—dispersion forces are the predominant intermolecular forces.

KEEP IN MIND

that the term *intermolecular forces* is used to classify a specific set of noncovalent interactions.

12-1 ARE YOU WONDERING...

Are there other types of intermolecular forces?

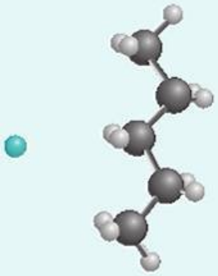
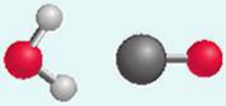
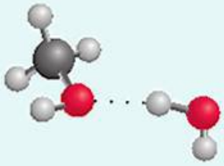
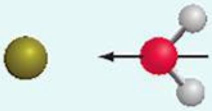
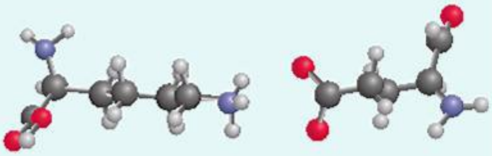
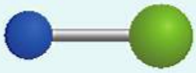
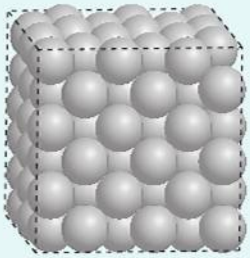
There are other types of intermolecular forces in addition to London dispersion, dipole–dipole, and hydrogen bonding. Table 12.2 summarizes some of the more commonly encountered intermolecular forces, along with their typical strengths.

In Table 12.2 one of the strongest forces between ions or molecules arises from the electrostatic attraction of opposite charge (ion–ion). This type of intermolecular force is what gives rise to the high melting points of ionic solids, along with their brittle nature. In such molecules as biomolecules, interactions between different charged groups, also known as salt bridges, increase their stability.

As we discovered in Chapter 11 molecules have dipole moments because of electronegativity differences between atoms. The dipole moment in a molecule will interact with a charged ion to form an ion–dipole interaction. Ion–dipole interactions are important in understanding the dissolution of salts.

In the absence of charges and dipole moments, other higher-order moments (e.g., quadrupole moments) become dominant. An example of quadrupole–quadrupole interactions would be between two CO_2 molecules.

TABLE 12.2 Summary of Noncovalent Interactions

Force	Energy,[a] kJ/mol	Example	Model
Intermolecular			
London dispersion	0.05–40	$CH_4 \cdots CH_4$	
Dipole–induced dipole	2–10	$CH_3(CO)CH_3 \ldots CH_5H_{12}$	
Ion–induced dipole	3–15	$Li^+ \ldots C_5H_{12}$	
Dipole–dipole	5–25	$H_2O \ldots CO$	
Hydrogen bond	10–40	$CH_3OH \ldots H_2O$	
Ion–dipole	40–600	$K^+ \ldots H_2O$	
Ion–ion	400–4000	$Lys^+ \ldots Glu^-$	
Interatomic			
London dispersion	0.05–40	$Ar \ldots Ar$	
Ion–ion	400–4000	$Na^+ \ldots Cl^-$	
Metallic	100–1000	$Ag \ldots Ag$	

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[a] These are gas phase values.

12-2 Some Properties of Liquids

Surface Tension

The observation of a needle floating on water, as pictured in Figure 12-10, is puzzling. Steel is much denser than water and should not float. Something must overcome the force of gravity on the needle, allowing it to remain suspended on the surface of the water. What is this special quality associated with the surface of liquid water?

▲ FIGURE 12-10
An effect of surface tension illustrated
Despite being denser than water, the needle is supported on the surface of the water. The property of surface tension accounts for this unexpected behaviour.

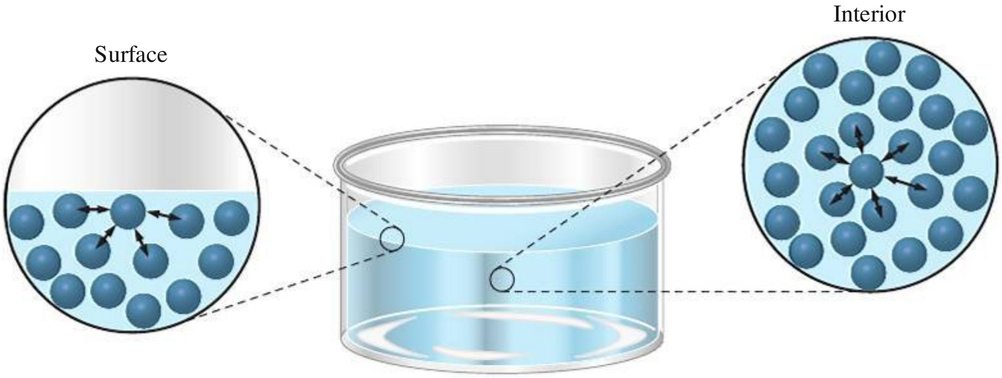
Figure 12-11 suggests an important difference in the forces experienced by molecules within the bulk of a liquid and by those at the surface. Interior molecules have more neighbors and experience more attractive intermolecular interactions than surface molecules. The increased number of attractions by neighboring molecules places an interior molecule in a more stable environment (lower energy state) than a surface molecule. Consequently, as many molecules as possible tend to enter the bulk of a liquid, while as few as possible remain at the surface. Thus, liquids tend to maintain a minimum surface area. To increase the surface area of a liquid requires that molecules be moved from the interior to the surface of a liquid, and this requires that work be done. The steel needle of Figure 12-10 remains suspended on the surface of the water because energy is required to spread the surface of the water over the top of the needle.

Surface tension is the energy, or work, required to increase the surface area of a liquid. Surface tension is often represented by the Greek letter gamma (γ) and has the units of energy per unit area, typically joules per square meter (J m^{-2}). As the temperature—and hence the intensity of molecular motion—increases, intermolecular forces become less effective. Less work is required to extend the surface of a liquid, meaning that surface tension *decreases* with *increased* temperature.

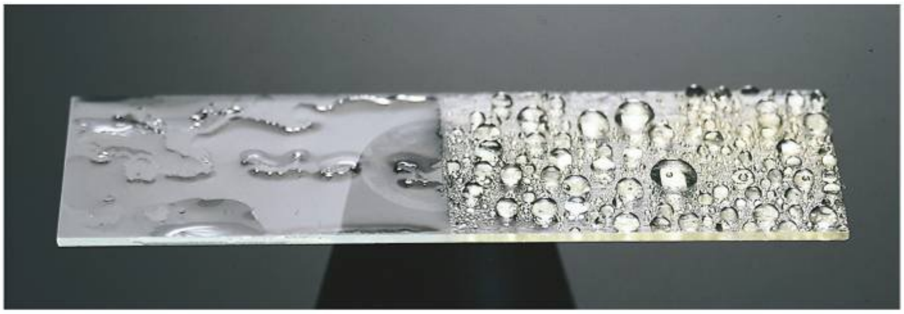
▶ The surface tension of water at 20 °C, for example, is $7.28 \times 10^{-2}\ \text{J m}^{-2}$, and that of mercury is more than six times as large, at $47.2 \times 10^{-2}\ \text{J m}^{-2}$.

When a drop of liquid spreads into a film across a surface, we say that the liquid *wets* the surface. Whether a drop of liquid wets a surface or retains its spherical shape and stands on the surface depends on the strengths of two types of intermolecular forces. The forces exerted between molecules holding them together in the drop are **cohesive forces**, and the forces between liquid molecules and the surface are **adhesive forces**. If cohesive forces are strong compared with adhesive forces, a drop maintains its shape. If adhesive forces are strong enough, the energy requirement for spreading the drop into a film is met through the work done by the collapsing drop.

Water wets many surfaces, such as glass and certain fabrics. This characteristic is essential to its use as a cleaning agent. If glass is coated with a film of oil



▲ FIGURE 12-11
Intermolecular forces in a liquid
Molecules at the surface are attracted only by other surface molecules and by molecules below the surface. Molecules in the interior experience forces from neighbouring molecules in all directions.



▲ FIGURE 12-12
Wetting of a surface
Water spreads into a thin film on a clean glass surface (left). If the glass is coated with oil or grease, the adhesive forces between the water and oil are not strong enough to spread the water, and droplets stand on the surface (right).

▲ FIGURE 12-13
Meniscus formation
Water wets glass (left). The meniscus is concave—the bottom of the meniscus is below the level of the water–glass contact line. Mercury does not wet glass. The meniscus is convex—the top of the meniscus is above the mercury–glass contact line.

or grease, water no longer wets the surface and water droplets stand on the glass, as shown in Figure 12-12. When we clean glassware in the laboratory, we have done a good job if water forms a uniform thin film on the glass. When we wax a car, we have done a good job if water uniformly beads up all along the surface.

Adding a detergent to water has two effects: The detergent solution dissolves grease to expose a clean surface, and the detergent lowers the surface tension of water. Lowering the surface tension means lowering the energy required to spread drops into a film. Substances that reduce the surface tension of water and allow it to spread more easily are known as *wetting agents*. They are used in applications ranging from dish washing to industrial processes.

Figure 12-13 illustrates another familiar observation. If the liquid in the glass tube is water, the water is drawn slightly up the walls of the tube by adhesive forces between water and glass. The interface between the water and the air above it, called a *meniscus*, is concave, or curved in. With liquid mercury, the meniscus is convex, or curved out. Cohesive forces in mercury, consisting of metallic bonds between Hg atoms, are strong; mercury does not wet glass. The effect of meniscus formation is greatly magnified in tubes of small diameter, called *capillary tubes*. In the *capillary action* shown in Figure 12-14, the water level inside the capillary tube is noticeably higher than outside. The soaking action of a sponge depends on the rise of water into capillaries of a fibrous material, such as cellulose. The penetration of water into soils also depends in part on capillary action. Conversely, mercury—with its strong cohesive forces and weaker adhesive forces—does not show a capillary rise. Rather, mercury in a glass capillary tube will have a lower level than the mercury outside the capillary.

▲ FIGURE 12-14
Capillary action
A thin film of water spreads up the inside walls of the capillary because of strong adhesive forces between water and glass (water wets glass). The pressure below the meniscus falls slightly. Atmospheric pressure then pushes a column of water up the tube to eliminate the pressure difference. The *smaller* the diameter of the capillary, the *higher* the liquid rises. Because its magnitude is also directly proportional to surface tension, capillary rise provides a simple experimental method of determining surface tension, described in Exercise 119.

Viscosity

Another property at least partly related to intermolecular forces is **viscosity**—a liquid's resistance to flow. The stronger the intermolecular forces of attraction, the greater the viscosity. When a liquid flows, one portion of the liquid moves with respect to neighboring portions. Cohesive forces within the liquid create an internal friction, which reduces the rate of flow. In liquids of low viscosity, such as ethyl alcohol and water, the effect is weak, and they flow easily. Liquids such as honey and heavy motor oil flow much more sluggishly. We say that they are *viscous*. One method of measuring viscosity is to time the fall of a steel ball through a certain depth of liquid (Fig. 12-15). The greater the viscosity of the liquid, the longer it takes for the ball to fall. Because intermolecular forces of attraction can be offset by higher molecular kinetic energies, viscosity generally *decreases* with *increased* temperature for liquids.

◀ For liquids, viscosity decreases with increasing temperature, but for gases, the viscosity increases with increasing temperature.

▲ FIGURE 12-15
Measuring Viscocity
By measuring the velocity of a ball dropping through a liquid, a measure of the liquid viscosity can be obtained.

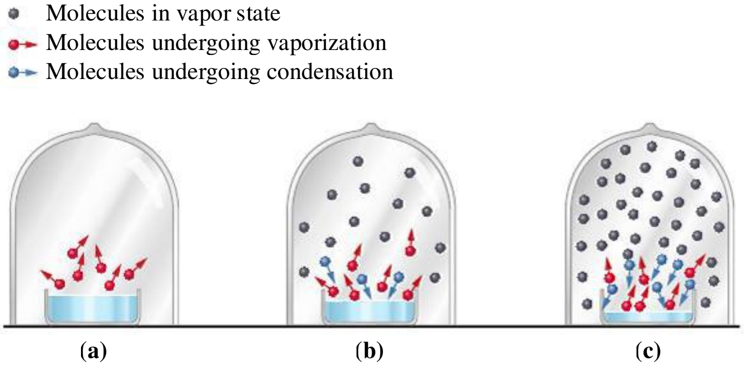
12-2 CONCEPT ASSESSMENT

The viscosity of automotive motor oil is designated by its SAE number, such as 40 W. When compared in a ball viscometer (Fig. 12-15), the ball drops much faster through 10 W oil than through 40 W oil. Which of these two oils provides better winter service in the Arctic region of Canada? Which is best suited for summer use in the American Southwest? Which oil has the stronger intermolecular forces of attraction?

Vapor Pressure

Water left in an open beaker evaporates completely. A different condition results if the beaker with the water is placed in a closed container. As shown in Figure 12-16, in a container with both liquid and vapor present, vaporization and condensation occur simultaneously. If sufficient liquid is present, eventually a condition is reached in which the amount of vapor remains constant. This condition is one of *dynamic equilibrium.* Dynamic equilibrium always implies that two opposing processes are occurring simultaneously and at equal rates.

▶ FIGURE 12-16
Establishing liquid–vapor equilibrium
(a) A liquid is allowed to evaporate into a closed container. Initially, only vaporization occurs. **(b)** Condensation begins. The rate at which molecules evaporate is greater than the rate at which they condense, and the number of molecules in the vapor state continues to increase. **(c)** The rate of condensation is equal to the rate of vaporization. The number of vapor molecules remains constant over time, as does the pressure exerted by this vapor.



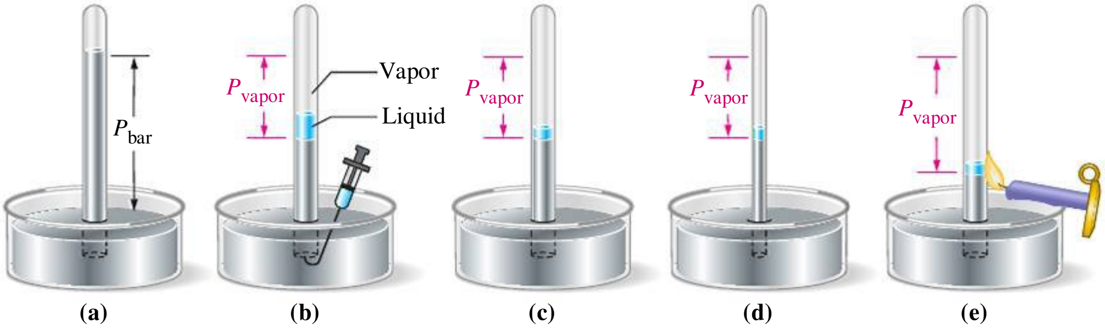
As a result, there is no net change with time once equilibrium has been established. A symbolic representation of the liquid–vapor equilibrium is shown below.

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

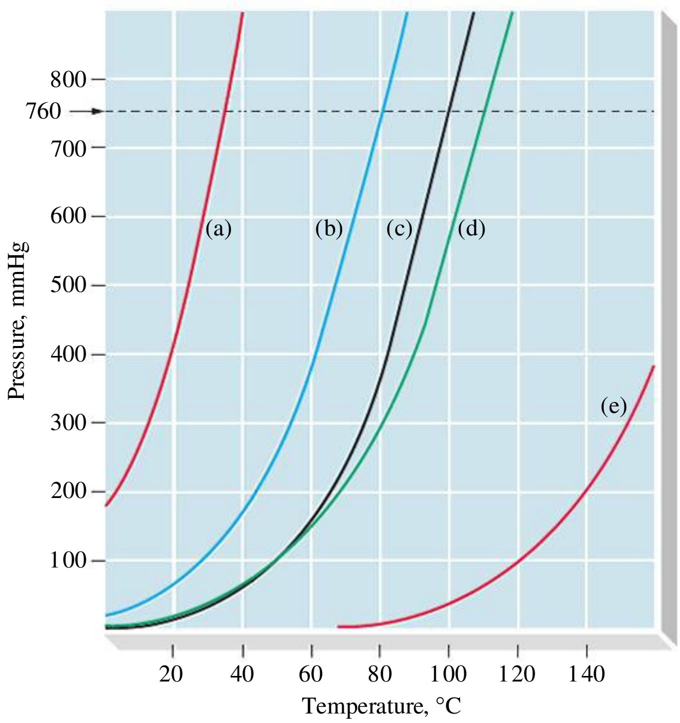
▶ Gasoline is a mixture of volatile hydrocarbons and is an important precursor of smog, whether it is vaporized from oil refineries, filling-station operations, automobile gas tanks, or power lawn mowers.

The pressure exerted by a vapor in dynamic equilibrium with its liquid is called the **vapor pressure**. Liquids with high vapor pressures at room temperature are said to be *volatile*, and those with very low vapor pressures are *nonvolatile*. Whether a liquid is volatile or not is determined primarily by the strengths of its intermolecular forces—the weaker these forces, the more volatile the liquid (the higher its vapor pressure). Diethyl ether and acetone are volatile liquids; at 25 °C their vapor pressures are 534 and 231 mmHg, respectively. Water at ordinary temperatures is a moderately volatile liquid; at 25 °C, its vapor pressure is 23.8 mmHg. Mercury is essentially a nonvolatile liquid; at 25 °C, its vapor pressure is 0.0018 mmHg.

As an excellent first approximation, the vapor pressure of a liquid depends only on the particular liquid and its temperature. Vapor pressure depends on neither the amount of liquid nor the amount of vapor, as long as some of each is present at equilibrium. These statements are illustrated in Figure 12-17. A graph of vapor pressure as a function of temperature is known as a **vapor pressure curve**. Vapor pressure curves always have the appearance of those in Figure 12-18: *Vapor pressure increases with temperature.* Vapor pressures of water at different temperatures are presented in Table 12.4.



▲ FIGURE 12-17
Vapour pressure illustrated
(a) A mercury barometer. **(b)** The pressure exerted by the vapor in equilibrium with a liquid injected to the top of the mercury column depresses the mercury level. **(c)** Compared with (b), the vapor pressure is independent of the volume of liquid injected. **(d)** Compared with (c), the vapor pressure is independent of the volume of vapor present. **(e)** Vapor pressure increases with an increase in temperature.



◀ FIGURE 12-18
Vapor pressure curves of several liquids
(a) Diethyl ether, $C_4H_{10}O$; **(b)** benzene, C_6H_6; **(c)** water, H_2O; **(d)** toluene, C_7H_8; **(e)** aniline, C_6H_7N. The normal boiling points are the temperatures at the intersection of the dashed line at $P = 760$ mmHg with the vapor pressure curves.

TABLE 12.4 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg
0.0	4.6	29.0	30.0	93.0	588.6
10.0	9.2	30.0	31.8	94.0	610.9
20.0	17.5	40.0	55.3	95.0	633.9
21.0	18.7	50.0	92.5	96.0	657.6
22.0	19.8	60.0	149.4	97.0	682.1
23.0	21.1	70.0	233.7	98.0	707.3
24.0	22.4	80.0	355.1	99.0	733.2
25.0	23.8	90.0	525.8	100.0	760.0
26.0	25.2	91.0	546.0	110.0	1074.6
27.0	26.7	92.0	567.1	120.0	1489.1
28.0	28.3				

Measuring Vapor Pressure

Figure 12-17 suggests one method of determining vapor pressure—inject a small sample of the target liquid at the top of a mercury barometer, and measure the depression of the mercury level. The method does not give very precise results, however, and it is not useful for measuring vapor pressures that are either very low or quite high. Better results are obtained with methods in which the pressure above a liquid is continuously varied and measured, and the liquid–vapor equilibrium temperature is recorded. In short, the boiling point of the liquid changes in accordance with the change in the pressure above the liquid, and the vapor pressure curve of the liquid can be traced. The pressure measurements are made with either a closed-end or open-end manometer (page 195). A method that is useful for determining very low vapor pressures is based on the rate of effusion of a gas through a tiny orifice. In this method, equations from the kinetic-molecular theory (Section 6-7) are applied. Example 12-3 illustrates a method (called the transpiration method) in which an inert gas is saturated with the vapor under study. Then the ideal gas equation is used to calculate the vapor pressure.

EXAMPLE 12-3 Using the Ideal Gas Equation to Calculate a Vapor Pressure

A sample of 113 L of helium gas at 1360 °C and prevailing barometric pressure is passed through molten silver at the same temperature. The gas becomes saturated with silver vapor, and the liquid silver loses 0.120 g in mass. What is the vapor pressure of liquid silver at 1360 °C?

Analyze

Let's assume that after the gas has become saturated with silver vapor, its volume remains at 113 L. This assumption will be valid if the vapor pressure of the silver is quite low compared with the barometric pressure. According to Dalton's law of partial pressures (page 213) we can deal with the silver vapor as if it were a single gas occupying a volume of 113 L.

Solve

The data required in the ideal gas equation are listed below.

$P = ?$

$V = 113\ \text{L}$

$R = 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$T = 1360 + 273.15 = 1633\ \text{K}$

$$n = 0.120\ \text{g Ag} \times \frac{1\ \text{mol Ag}}{107.9\ \text{g Ag}} = 0.00111\ \text{mol Ag}$$

$$P = \frac{nRT}{V}$$

$$P = \frac{0.00111\ \text{mol} \times 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 1633\ \text{K}}{113\ \text{L}}$$

$$= 1.32 \times 10^{-3}\ \text{atm}\ (1.00\ \text{Torr})$$

Assess

The assumption we made appears to be valid, because the experimental vapor pressure of liquid silver at 1360 °C is 1 mmHg or 1.32×10^{-2} atm.

PRACTICE EXAMPLE A: Equilibrium is established between liquid hexane, C_6H_{14}, and its vapor at 25.0 °C. A sample of the vapor is found to have a density of 0.701 g/L. Calculate the vapor pressure of hexane at 25.0 °C, expressed in Torr.

PRACTICE EXAMPLE B: With the help of Figure 12-18, estimate the density of the vapor in equilibrium with liquid diethyl ether at 20.0 °C.

Using Vapor Pressure Data

One use of vapor pressure data is in calculations dealing with the collection of gases over liquids, particularly water (Section 6-6). Another use, illustrated in Example 12-4, is in predicting whether a substance exists solely as a gas (vapor) or as a liquid and vapor in equilibrium.

EXAMPLE 12-4 Making Predictions with Vapor Pressure Data

As a result of a chemical reaction, 0.132 g H_2O is produced and maintained at a temperature of 50.0 °C in a closed flask of 525 mL volume. Will the water be present as liquid only, vapor only, or liquid and vapor in equilibrium (Fig. 12-19)?

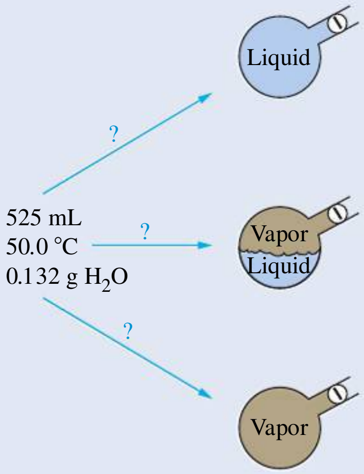
Analyze

Let's consider each of the three possibilities in the order that they are given.

Solve

LIQUID ONLY

With a density of about 1 g/mL, a 0.132 g sample of H_2O has a volume of only about 0.13 mL. There is no way that the sample could completely fill a 525 mL flask. The condition of liquid only is *impossible*.



◀ FIGURE 12-19
Predicting states of matter—Example 12.4 illustrated
For the conditions given on the left, which of the final conditions pictured on the right will result?

VAPOR ONLY

The portion of the flask that is not occupied by liquid water must be filled with something (it cannot remain a vacuum). That something is water vapor. The question is, will the sample vaporize completely, leaving no liquid? Let's use the ideal gas equation to calculate the pressure that would be exerted if the entire 0.132 g H_2O were present in the gaseous state.

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{0.132\ \text{g H}_2\text{O} \times \dfrac{1\ \text{mol H}_2\text{O}}{18.02\ \text{g H}_2\text{O}} \times 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 323.2\ \text{K}}{0.525\ \text{L}} \\ &= 0.370\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 281\ \text{mmHg} \end{aligned}$$

Now compare this calculated pressure with the vapor pressure of water at 50.0 °C (Table 12.4). The calculated pressure—281 mmHg—greatly exceeds the vapor pressure—92.5 mmHg. Water formed in the reaction as $H_2O(g)$ condenses to $H_2O(l)$ when the gas pressure reaches 92.5 mmHg, for this is the pressure at which the liquid and vapor are in equilibrium at 50.0 °C. The condition of vapor only is *impossible*.

LIQUID AND VAPOR

This is the only possibility for the final condition in the flask. Liquid water and water vapor coexist in equilibrium at 50.0 °C and 92.5 mmHg.

Assess

We found the solution to this problem through the application of the ideal gas equation and our understanding of vapor pressure. Note that in the first two steps, we considered the two extremes, with the first being just liquid water and the second all vapor.

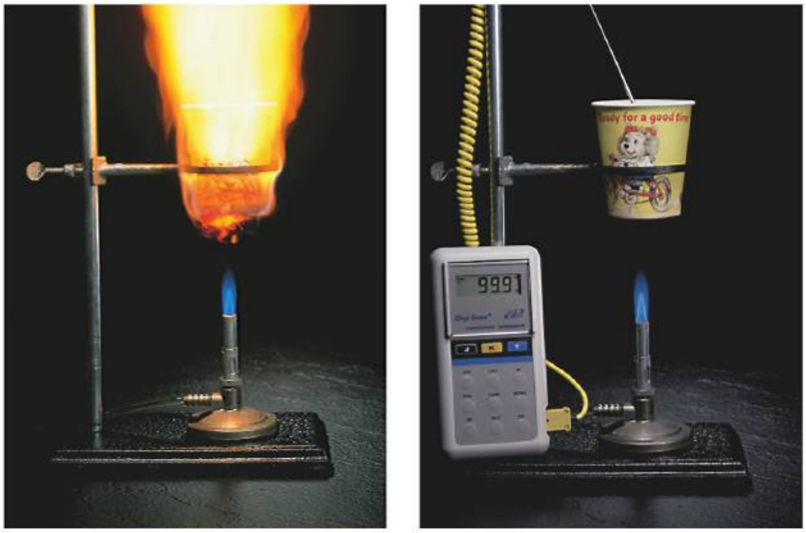
PRACTICE EXAMPLE A: If the reaction described in this example resulted in H_2O produced and maintained at 80.0 °C, would the water be present as vapor only or as liquid and vapor in equilibrium? Explain.

PRACTICE EXAMPLE B: For the situation described in Example 12.4, what mass of water is present as liquid and what mass as vapor?

Boiling and the Boiling Point

When a liquid is heated in a container *open to the atmosphere*, there is a particular temperature at which vaporization occurs throughout the liquid rather than simply at the surface. Vapor bubbles form within the bulk of the liquid, rise to the surface, and escape. The pressure exerted by escaping molecules equals that exerted by molecules of the atmosphere, and **boiling** is said to occur. During boiling, energy absorbed as heat is used only to convert molecules of liquid to vapor. The temperature remains constant until all the liquid has boiled away, as is dramatically illustrated in Figure 12-21. The temperature at which the vapor pressure of a liquid is equal to standard atmospheric pressure (1 atm = 760 mmHg) is the **normal boiling point**. In other words, the normal boiling point is the boiling point of a liquid at 1 atm pressure. The normal boiling points of several liquids can be determined from the intersection of the dashed line in Figure 12-18 with the vapor pressure curves for the liquids.

◀ When a pan of water is put on the stove to boil, small bubbles are usually observed as the water begins to warm. These are bubbles of dissolved air being expelled. Once the water boils, however, all the dissolved air is expelled and the bubbles consist only of water vapor.



◀ FIGURE 12-21
Bolling water in a paper cup
An empty paper cup heated over a Bunsen burner quickly bursts into flame. If a paper cup is filled with water, it can be heated for an extended time as the water boils. This is possible for three reasons: (1) Because of the high heat capacity of water, heat from the burner goes primarily into heating the water, not the cup. (2) As the water boils, large quantities of heat (ΔH_{vap}) are required to convert the liquid to its vapor. (3) The temperature of the cup does not rise above the boiling point of water as long as liquid water remains. The boiling point of 99.9 °C instead of 100.0 °C suggests that the prevailing barometric pressure was slightly below 1 atm.

Figure 12-18 also helps us see that the boiling point of a liquid varies significantly with barometric pressure. Shift the dashed line shown at $P = 760$ mmHg to higher or lower pressures, and the new points of intersection with the vapor pressure curves come at different temperatures. Barometric pressures below 1 atm are commonly encountered at high altitudes. At an altitude of 1609 m (that of Denver, Colorado), barometric pressure is about 630 mmHg. The boiling point of water at this pressure is 95 °C(203 °F). It takes longer to cook foods under conditions of lower boiling-point temperatures. A three–minute boiled egg takes longer than three minutes to cook. We can counteract the effect of high altitudes by using a pressure cooker. In a pressure cooker, the cooking water is maintained under higher-than-atmospheric pressure and its boiling temperature increases, for example, to about 120 °C at 2 atm pressure.

▶ A more extreme case is that on the summit of Mt. Everest, where a climber would barely be able to heat a cup of tea to 70 °C.

▲ **A liquid boils at low pressure**
Water boils when its vapor pressure equals the pressure on its surface. Bubbles form throughout the liquid.

12-3 CONCEPT ASSESSMENT

Why does a three-minute boiled egg take longer than three minutes to cook in Switzerland and not on Manhattan Island in New York City?

The Critical Point

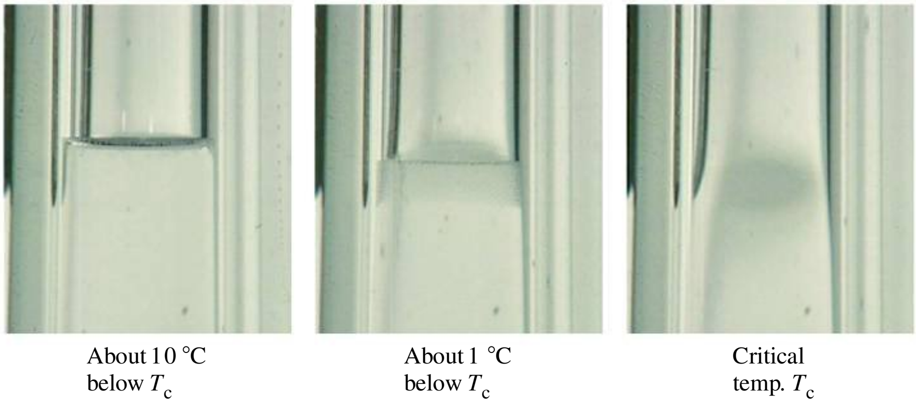
In describing boiling, we made an important qualification: Boiling occurs "in a container open to the atmosphere." If a liquid is heated in a *sealed* container, boiling does not occur. Instead, the temperature and vapor pressure rise continuously. Pressures many times atmospheric pressure may be attained. If just the right quantity of liquid is sealed in a glass tube and the tube is heated, as in Figure 12-22, the following phenomena can be observed:

- The density of the liquid decreases, that of the vapor increases, and eventually the two densities become equal.
- The surface tension of the liquid approaches zero. The interface between the liquid and vapor becomes less distinct and eventually disappears.

The **critical point** is the point at which these conditions are reached and the liquid and vapor become indistinguishable. The temperature at the critical point is the critical temperature, T_c, and the pressure is the critical pressure, P_c. The critical point is the highest point on a vapor pressure curve and represents the highest temperature at which the liquid can exist. Several critical temperatures and pressures are listed in Table 12.5.

A gas can be liquefied only at temperatures *below* its critical temperature, T_c. If room temperature is *below* T_c, this liquefaction can be accomplished just by applying sufficient pressure. If room temperature is *above* T_c, however, added pressure *and* a lowering of temperature to a value below T_c are required. We will comment further on the liquefaction of gases on page 523.

▶ Although the term *gas* can be used exclusively, sometimes the term *vapor* is used for the gaseous state at temperatures *below* T_c and gas at temperatures *above* T_c.



About 10 °C below T_c

About 1 °C below T_c

Critical temp. T_c

▶ FIGURE 12-22
Attainment of the critical point for benzene
In a sealed container, the meniscus separating a liquid from its vapor is just barely visible at the instant the critical point is reached. At the critical point—the liquid and vapor become indistinguishable.

TABLE 12.5 Some Critical Temperatures, T_c, and Critical Pressures, P_c

Substance	T_c, K	P_c, atm
"Permanent" gases[a]		
H_2	33.3	12.8
N_2	126.2	33.5
O_2	154.8	50.1
CH_4	191.1	45.8
"Nonpermanent" gases[b]		
CO_2	304.2	72.9
HCl	324.6	82.1
NH_3	405.7	112.5
SO_2	431.0	77.7
H_2O	647.3	218.3

[a] Permanent gases cannot be liquefied at 25 °C(298 K).

[b] Nonpermanent gases can be liquefied at 25 °C.

12-4 CONCEPT ASSESSMENT

Compare the critical temperatures of NH_3 and N_2 (Table 12.5). Which gas has the stronger intermolecular forces?

EXAMPLE 12-6 Relating Intermolecular Forces and Physical Properties

Arrange the following substances in the order in which you would expect their boiling points to increase: $CCl_4, Cl_2, ClNO, N_2$.

Analyze

Recall that boiling point trends are related to intermolecular forces. We should begin by identifying the types and strengths of intermolecular forces at work.

Solve

Three of the substances are nonpolar. For these, the strengths of dispersion forces, and hence the boiling points, should increase with increasing molecular mass, that is, $N_2 < Cl_2 < CCl_4$. ClNO has a molecular mass (65.5 u) comparable to that of Cl_2 (70.9 u), but the ClNO molecule is polar (bond angle $\approx 120°$). This suggests stronger intermolecular forces and a higher boiling point for ClNO than for Cl_2. We should not expect the boiling point of ClNO to be higher than that of CCl_4, however, because of the large difference in their molecular masses (65.5 u compared with 154 u). The expected order is $N_2 < Cl_2 < ClNO < CCl_4$. (The observed boiling points are 77.3, 239.1, 266.7, and 349.9 K, respectively.)

Assess

Even though one molecule (ClNO) is polar, it does not have the highest boiling point, indicating that dispersion forces can be stronger than dipole–dipole forces.

PRACTICE EXAMPLE A: Arrange the following in the expected order of increasing boiling point: Ne, He, $Cl_2, (CH_3)_2CO, O_2, O_3$.

PRACTICE EXAMPLE B: Following are some values of ΔH_{vap} for several liquids at their normal boiling points: H_2, 0.92 kJ mol^{-1}; CH_4, 8.16 kJ mol^{-1}; C_6H_6, 31.0 kJ mol^{-1}; CH_3NO_2, 34.0 kJ mol^{-1}. Explain the differences among these values.

12-5 CONCEPT ASSESSMENT

Explain why CCl_4 has a higher boiling point than CH_3Cl, despite the polarity of CH_3Cl.

12-3 Some Properties of Solids

We mentioned some properties of solids (for example, malleability, ductility) at the beginning of this text, and we will continue to consider additional properties. For now, we will comment on some properties that allow us to think of solids in relation to the other states of matter—liquids and gases.

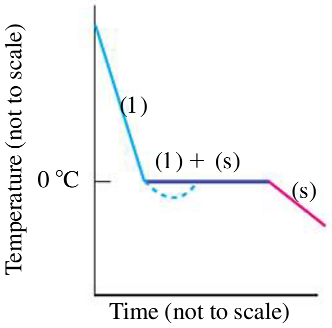
Melting and Melting Point

As a crystalline solid is heated, its atoms, ions, or molecules vibrate more vigorously. Eventually a temperature is reached at which these vibrations disrupt the ordered crystalline structure. The atoms, ions, or molecules can slip past one another, and the solid loses its definite shape and is converted to a liquid. This process is called **melting**, or fusion, and the temperature at which it occurs is the **melting point**. The reverse process, the conversion of a liquid to a solid, is called **freezing**, or solidification, and the temperature at which it occurs is the **freezing point**. The melting point of a solid and the freezing point of its liquid are identical. At this temperature, solid and liquid coexist in equilibrium.

If we add heat uniformly to a solid–liquid mixture at equilibrium, the temperature remains constant while the solid melts. Only when all the solid has melted does the temperature begin to rise. Conversely, if we remove heat uniformly from a solid–liquid mixture at equilibrium, the liquid freezes at a constant temperature. Perhaps the most familiar example of a melting (and freezing) point is that of water, 0 °C. This is the temperature at which liquid and solid water, in contact with air and under standard atmospheric pressure, are in equilibrium.

$$H_2O(s) \longrightarrow H_2O(l) \tag{12.3}$$

Here is an easy way to determine the freezing point of a liquid. Allow the liquid to cool, and measure the liquid temperature as it falls with time. When freezing begins, the temperature *remains constant* until all the liquid has frozen. Then the temperature is again free to fall as the solid cools. If we plot temperatures against time, we get a graph known as a *cooling curve*. Figure 12-23 is a



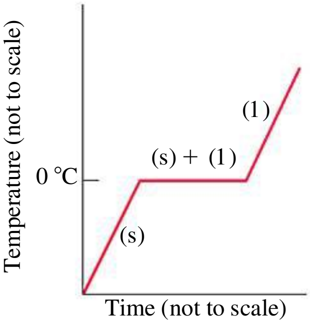
▲ FIGURE 12-23
Cooling curve for water
The broken-line portion represents the condition of supercooling that occasionally occurs.
(l) = liquid; (s) = solid.

TABLE 12.6 Some Melting Points

Substance	Melting Point, °C
Mercury, Hg	−38.9
Sodium, Na	97.8
Methyl alcohol, CH_3OH	−97.7
Ethyl alcohol, CH_3CH_3COOH	−114
Water, H_2O	0.0
Benzoic acid, C_6H_5COOH	122.4
Naphthalene, $C_{10}H_8$	80.2

cooling curve for water. We can also run this process backward, that is, by starting with the solid and adding heat. Now the temperature remains constant while melting occurs. This temperature–time plot is called a *heating curve.* Generally speaking, the appearance of the heating curve is that of a cooling curve that has been flipped from left to right. A heating curve for water is sketched in Figure 12-24.

Often, an experimentally determined cooling curve does not look quite like the solid-line plot in Figure 12-23. The temperature may drop below the freezing point without any solid appearing. This condition is known as *supercooling.* For a crystalline solid to start forming from a liquid at the freezing point, the liquid must contain some small particles (for example, suspended dust particles) on which crystals can form. If a liquid contains a very limited number of particles on which crystals can grow, it may supercool for a time before freezing. When a supercooled liquid does begin to freeze, however, the temperature rises back to the normal freezing point while freezing is completed. We can always recognize supercooling through a slight dip in a cooling curve just before the horizontal portion.



▲ FIGURE 12-24
Heating curve for water
This curve traces the changes that occur as ice is heated from below the melting point to produce liquid water somewhat above the melting point.

◀ Examples of supercooled substances are water droplets in the sky. They remain liquid at temperatures well below the freezing point. When they find a bit of dust on which they can nucleate, the droplets spontaneously turn to ice.

Sublimation

Like liquids, solids can also give off vapors, although because of the stronger intermolecular forces present, solids are generally not as volatile as liquids at a given temperature. The direct passage of molecules from the solid to the vapor state is called **sublimation**. The reverse process, the passage of molecules from the vapor to the solid state, is called **deposition**. When sublimation and deposition occur at equal rates, a dynamic equilibrium exists between a solid and its vapor. The vapor exerts a characteristic pressure called the *sublimation pressure.* A plot of sublimation pressure as a function of temperature is called a *sublimation curve.* At the sublimation point, sublimation (solid —> vapor) is equivalent to melting (solid —> liquid) followed by vaporization (liquid ⟶ vapor).

▲ FIGURE 12-25
Sublimation of iodine
Even at temperatures well below its melting point of 114 °C, solid iodine exhibits an appreciable sublimation pressure. Here, purple iodine vapor is produced at about 70 °C. Deposition of the vapor to solid iodine occurs on the colder walls of the flask.

Two familiar solids with significant sublimation pressures are ice and dry ice (solid carbon dioxide). If you live in a cold climate, you are aware that snow may disappear from the ground even though the temperature may fail to rise above 0 °C. Under these conditions, the snow does not melt; it sublimes. The sublimation pressure of ice at 0 °C is 4.58 mmHg. That is, the solid ice has a vapor pressure of 4.58 mmHg at 0 °C. If the air is not already saturated with water vapor, the ice will sublime. The sublimation and deposition of iodine are pictured in Figure 12-25.

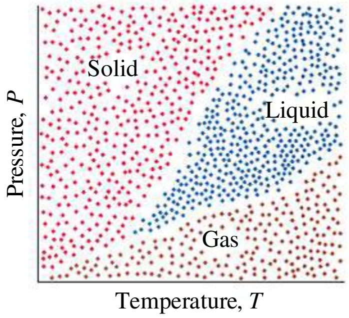
12-6 CONCEPT ASSESSMENT

Recall the discussion of dew and frost formation (see the Focus On feature for Chapter 6, *Earth's Atmosphere*, at www.masteringchemistry.com). Do the surroundings absorb or lose heat when water vapor condenses to dew or frost? Is the quantity of heat per gram of $H_2O(g)$ condensed the same whether the condensate is dew or frost? Explain.

12-4 Phase Diagrams

Imagine constructing a pressure–temperature graph in which each point on the graph represents a condition under which a substance might be found. At low temperatures and high pressures, such as the red points in Figure 12-26, we expect the atoms, ions, or molecules of a substance to be in a close orderly arrangement—a solid. At high temperatures and low pressures—the brown points in Figure 12-26—we expect the gaseous state; and at intermediate temperatures and pressures, we expect a liquid (blue points in Figure 12-26).

Figure 12-26 is a **phase diagram**, a graphical representation of the conditions of temperature and pressure at which solids, liquids, and gases (vapors) exist, either as single phases, or states, of matter or as two or more phases in equilibrium with one another. The different regions of the diagram correspond to single phases, or states, of matter. Straight or curved lines where single-phase regions adjoin represent two phases in equilibrium.



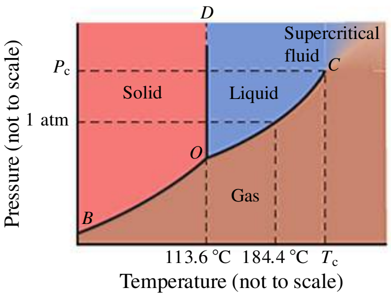
▲ FIGURE 12-26
Temperature, pressure, and states of matter
The outline of a phase diagram is suggested by the distribution of points. The red points identify the temperatures and pressures at which solid is the stable phase; the blue points identify the temperatures and pressures at which liquid is the stable phase; and the brown points represent the temperatures and pressures at which gas is the stable phase. (See also Figures 12-27 and 12-28.)

Iodine

One of the simplest phase diagrams is that of iodine shown in Figure 12-27. The curve OC is the vapor pressure curve of liquid iodine, and C is the critical point. OB is the sublimation curve of solid iodine. The nearly vertical line OD represents the effect of pressure on the melting point of iodine; it is called the *fusion curve.* The point O has a special significance. It defines the *unique* temperature and pressure at which the *three* states of matter, solid, liquid, and gas, coexist in equilibrium. It is called a **triple point**. For iodine, the triple point is at 113.6 °C and 91.6 mmHg. The normal melting point (113.6 °C) and the boiling point (184.4 °C) are the temperatures at which a line at $P = 1$ atm intersects the fusion and vapor pressure curves, respectively. Melting is essentially unaffected by pressure in the limited range from 91.6 mmHg to 1 atm, and the normal melting point and the triple point are at almost the same temperature.

The sublimation curve for iodine in Figure 12-27 appears to be a continuation of the vapor pressure curve, but if the data are plotted to scale, a discontinuity is seen at the triple point O. Moreover, this must *always* be the case. If these two curves were continuous, then the lines representing the variation of ln P with $1/T$ (Fig. 12-20) would have the same slope—but this is not possible. The value of ΔH_{vap} determines the slope of the vapor pressure line (recall equation 12.1), whereas ΔH_{sub} determines the slope of the sublimation line. However, these two enthalpy changes can never be the same, because $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}$.

The extreme range of temperatures and pressures required for the entire phase diagram precludes plotting it to scale. This is why the axes are labeled "not to scale."

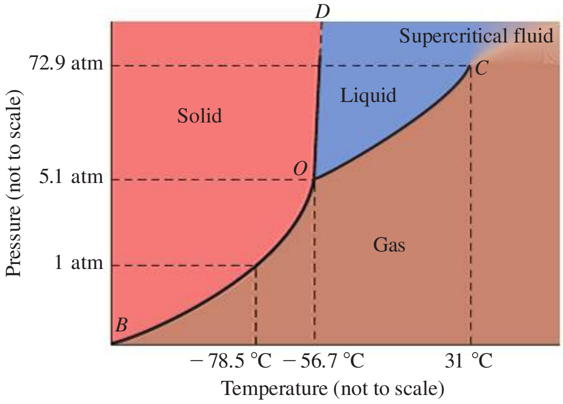


▲ FIGURE 12-27
Phase diagram for iodine
Note that the melting point and triple point temperatures for iodine are essentially the same. Generally, large pressure increases are required to produce even small changes in solid–liquid equilibrium temperatures. The pressure and temperature axes on a phase diagram are generally not drawn to scale so that the significant features of the diagram can be more readily emphasized.

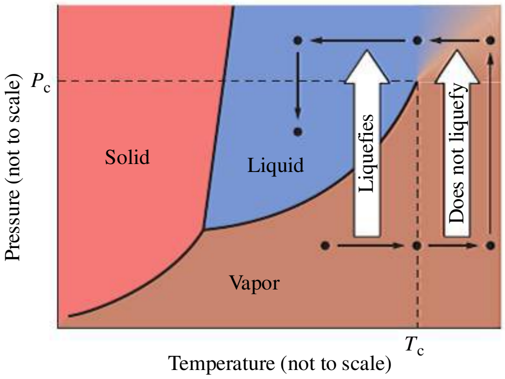
Carbon Dioxide

The case of carbon dioxide, shown in Figure 12-28, differs from that of iodine in one important respect—the pressure at the triple point O is greater than 1 atm. A line at $P = 1$ atm intersects the *sublimation curve,* not the vapor pressure curve. If solid CO_2 is heated in an open container, it sublimes away at a constant temperature of −78.5 °C. It *does not melt* at atmospheric pressure (and so is called "dry ice"). Because it maintains a low temperature and does not produce a liquid by melting, dry ice is widely used in freezing and preserving foods.

Liquid CO_2 can be obtained at pressures above 5.1 atm and it is most frequently encountered in CO_2 fire extinguishers. All three states of matter are involved in the action of these fire extinguishers. When the liquid CO_2 is released, most of it quickly vaporizes. The heat required for this vaporization is extracted from the remaining $CO_2(l)$, which has its temperature lowered to the point that it freezes and falls as a $CO_2(s)$ "snow." In turn, the $CO_2(s)$ quickly sublimes to $CO_2(g)$. All of this helps to quench a fire by displacing the air around the fire with a "blanket" of $CO_2(g)$ and by cooling the area somewhat.



▲ FIGURE 12-28
Phase diagram for carbon dioxide
Several aspects of this diagram are described in the text. An additional feature not shown here is the curvature of the fusion curve *OD* to the right at very high pressures, ultimately reaching temperatures above the critical temperature.



▲ FIGURE 12-29
Critical point and critical isotherm
Applying pressure to a gas at temperatures below the critical isotherm, T_c, causes a liquid to form with the appearance of a meniscus, a discontinuous phase change. Applying pressure above the critical isotherm simply increases the density of the supercritical fluid. In a path traced by the small arrows, gas changes to liquid without exhibiting a discontinuous phase transition.

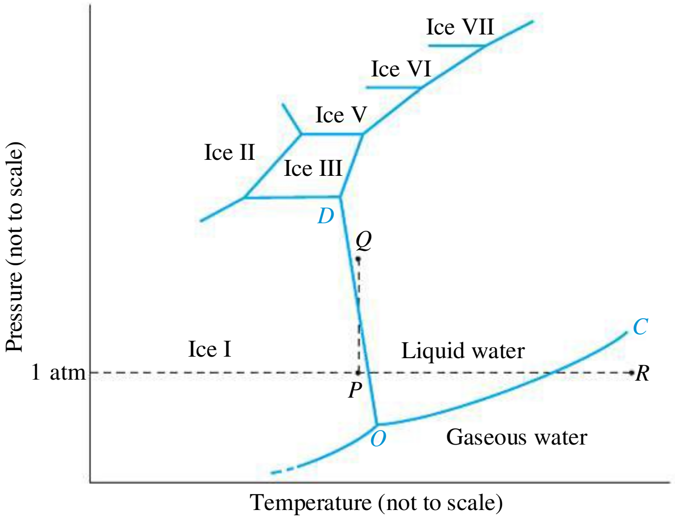
Supercritical Fluids

Because the liquid and gaseous states become identical and indistinguishable at the critical point, it is difficult to know what to call the state of matter at temperatures and pressures above the critical point. For example, this state of matter has the high density of a liquid and the low viscosity of a gas. The term that is now commonly used is *supercritical fluid* (SCF). Above the critical temperature, no amount of pressure can liquefy a supercritical fluid. Consider the generic phase diagram in Figure 12-29. The path of dots starting with a vapor below the critical isotherm takes us to a low-density gas above the isotherm. When the pressure is greatly increased, we produce a supercritical fluid of much greater density. If, while the pressure exceeds the critical pressure, P_c, the temperature is reduced below the critical temperature, we obtain a liquid. Even with further reduction of pressure, the sample remains in the liquid phase. In following the path described, we have gone from a gas to a liquid without observing a liquid–gas interface. The only way to observe the liquid–vapor interface is to cross the phase boundary below the critical temperature. Note that in the present case we could observe the liquid–vapor interface by lowering the pressure on the liquid to a point on the vapor pressure curve.

Although we do not ordinarily think of liquids or solids as being soluble in gases, *volatile* liquids and solids are. The mole fraction solubility is simply the ratio of the vapor pressure (or the sublimation pressure) to the total gas pressure. And liquids and solids become much more soluble in a gas that is above its critical pressure and temperature, mostly because the density of the SCF is high and approaches that of a liquid. Molecules in supercritical fluids, being in much closer proximity than in ordinary gases, can exert strong attractive forces on the molecules of a liquid or solid solute. SCFs display solvent properties similar to ordinary liquid solvents. To vary the pressure of an SCF means to vary its density and also its solvent properties. Thus, a given SCF, such as carbon dioxide, can be made to behave like many different solvents.

Until recently, the principal method of decaffeinating coffee was to extract the caffeine with a solvent, such as methylene chloride (CH_2Cl_2). This solvent is objectionable because it is hazardous in the workplace and difficult to completely remove from the coffee. Now, supercritical fluid CO_2 is used. In one process, green coffee beans are brought into contact with CO_2 at about 90 °C and 160 to 220 atm. The caffeine content of the coffee is reduced from its

▲ **Decaffeinated coffee**
"Naturally" decaffeinated coffee is made through a process that uses supercritical fluid CO_2 as a solvent to dissolve the caffeine in green coffee beans. Afterward, the beans are roasted and sold to consumers.



▶ FIGURE 12-30
Phase diagram for water
Point *O*, the triple point, is at 0.0098 °C and 4.58 mmHg. (The normal melting point is at exactly 0 °C and 760 mmHg.) The critical point, *C*, is at 374.1 °C and 218.2 atm. At point *D* the temperature is −22.0 °C and the pressure is 2045 atm. The negative slope of the fusion curve, *OD* (greatly exaggerated here), and the significance of the broken straight lines are discussed in the text.

normal 1% to 3% to about 0.02%. When the temperature and pressure of the CO_2 are reduced, the caffeine precipitates and the CO_2 is recycled.

Water

The phase diagram of water (Fig. 12-30) presents several new features. One is that the fusion curve *OD* has a *negative* slope; that is, it slopes toward the pressure axis. The melting point of ice *decreases* with an increase in pressure, and this is rather unusual behavior for a solid (bismuth and antimony also behave in this way). However, because large changes in pressure are required to produce even small decreases in the melting point, we do not commonly observe this melting behavior of ice. One example that has been given comes from ice-skating. Presumably, the pressure of the skate blades melts the ice, and the skater skims along on a thin lubricating film of liquid water. This explanation is unlikely, however, because the pressure of the blades doesn't produce a significant lowering of the melting point and certainly cannot explain the ability to skate on ice at temperatures much below the freezing point. (Recent experimental evidence suggests that molecules in a very thin surface layer on ice are mobile in the same way as in liquid water, and this mobility persists even at very low temperatures.)

▶ Since the L-S line in the phase diagram of water is negative, that means that ice floats. If ice did not float, then the polar seas would fill with ice that would never melt. Most solids are more dense than their liquid state. Water is, for us, a happy exception.

Another feature illustrated in the phase diagram of water is **polymorphism**, the existence of a solid substance in more than one form. Ordinary ice, called ice I, exists under ordinary pressures. The other forms exist only at high pressures. Polymorphism is more the rule than the exception among solids. Where it occurs, a phase diagram has triple points in addition to the usual solid-liquid-vapor triple point. For example at point *D* in Figure 12-30, ice I, ice III, and liquid H_2O are in equilibrium at −22.0 °C and 2045 atm. Note that the fusion curves for the forms of ice other than ice I have *positive* slopes. Thus, the triple point with ice VI, ice VII, and liquid water is at 81.6 °C and 21,700 atm.

▶ An increase in pressure to 125 atm lowers the freezing point of water by only about 1 °C.

Phases and Phase Transitions

What's the difference between a phase and a state of matter? These terms tend to be used synonymously, but there is a small distinction between them. As we have already noted, there are just *three* states of matter: solid, liquid, and gas. A *phase* is any sample of matter with definite composition and uniform properties that is distinguishable from other phases with which it is in contact. Thus, we can describe liquid water in equilibrium with its vapor as a two-phase mixture. The liquid is one phase and the gas, or vapor, is the other. In this case, the phases (liquid and gas) are the same as the states of matter present (liquid and gas).

We can describe the equilibrium mixture at the triple point *D* in Figure 12-30 as a *three-phase* mixture, even though only *two* states of matter are present (solid and liquid). Two of the phases are in the solid state—the polymorphic forms ice I and ice III. For mixtures of two or more components, different phases may exist in the liquid state as well as in the solid state. For example, most mixtures of triethylamine, $N(CH_2CH_3)_3$, and water at 25 °C separate into two physically distinct liquid phases. One is a saturated solution of triethylamine in water and the other, a saturated solution of water in triethylamine. Because the pressure–temperature diagrams we have been describing can accommodate all the phases in a system, we call them *phase* diagrams. We call the crossing of a two-phase curve in a phase diagram a *phase transition*.

Listed below are six common names assigned to phase transitions.

melting $(s \longrightarrow l)$	freezing $(l \longrightarrow s)$
vaporization $(l \longrightarrow g)$	condensation $(g \longrightarrow l)$
sublimation $(s \longrightarrow g)$	deposition $(g \longrightarrow s)$

Following are two useful generalizations about the changes that occur when crossing a two-phase equilibrium curve in a phase diagram.

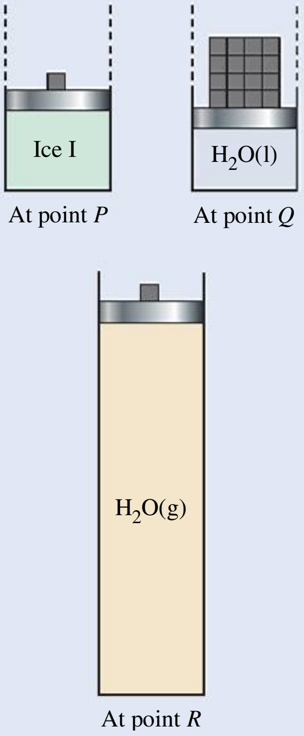
- From lower to higher temperatures along a *constant-pressure* line (an isobar), (Heat is absorbed.)
- From lower to higher pressures along a *constant-temperature* line (an isotherm), volume *decreases*. (The phase at the higher pressure has the higher density.)

The second generalization helps us to understand why a fusion curve usually has a positive slope. Typical behavior is for a solid to have a greater density than the corresponding liquid. Example 12-7 illustrates how we can use a phase diagram to describe the phase transitions that a substance can undergo.

◀ Because ice I is less dense than $H_2O(l)$, the fusion curve *OD* in Figure 12-30 has a negative slope.

EXAMPLE 12-7 Interpreting a Phase Diagram

A sample of ice is maintained at 1 atm and at a temperature represented by point *P* in Figure 12-30. Describe what happens when (a) the temperature is raised, at constant pressure, to point *R*, and (b) the pressure is raised, at constant temperature, to point *Q*. The sketches Figure 12-31 suggest the conditions at points *P*, *Q*, and *R*.



At point *P* At point *Q*

At point *R*

◀ FIGURE 12-31
Example 12-7 illustrated
A sample of pure water is confined in a cylinder by a freely moving piston surmounted by weights to establish the confining pressure. Sketched here are conditions at the points labeled *P*, *Q*, and *R* in Figure 12-30. The transition from point *P* to *Q* is accomplished by changing the pressure at constant temperature (isothermal). The transition from point *P* to *R* is accomplished by changing the temperature at constant pressure (isobaric).

Analyze

Recall that the lines separating the different phases represent coexistence lines. At these coexistence lines, the system is a mixture of both phases. On either side of those lines, the system is in that particular phase. Also recall that as the system moves from one phase to another at the coexistence lines, the temperature remains constant until all of one phase is converted to another.

Solve

(a) When the temperature reaches a point on the fusion curve *OD* (0 °C), ice begins to melt. The temperature remains constant as ice is converted to liquid. When melting is complete, the temperature

(continued)

again increases. No vapor appears in the cylinder until the temperature reaches 100 °C, at which point the vapor pressure is 1 atm. When all the liquid has vaporized, the temperature is again free to rise to a final value of *R*.

(b) Because solids are not very compressible, very little change occurs until the pressure reaches the point of intersection of the constant-temperature line *PQ* with the fusion curve *OD*. Here melting begins. A significant *decrease* in volume occurs (about 10%) as ice is converted to liquid water. After melting, additional pressure produces very little change because liquids are not very compressible.

Assess

Phase diagrams are very useful for understanding the conditions needed to observe the different phases of matter. We should now be able to use the phase diagram in Figure 12-30 to determine the pressure required to observe sublimation instead of melting.

PRACTICE EXAMPLE A: With as much detail as possible, describe the phase changes that would occur if a sample of water represented by point *R* in Figure 12-30 were brought first to point *P* and then to point *Q*.

PRACTICE EXAMPLE B: Draw a sketch showing the condition prevailing along the line *PR* when 1.00 mol of water has been brought to the point where exactly one-half of it has vaporized. Compare this to the condition at point *R* in Figure 12-31, assuming that this is also based on 1.00 mol of water. For example, is the volume of the system the same as that in Figure 12-31? If not, is it larger or smaller, and by how much? Assume that the temperature at point *R* is the same as the critical temperature of water and that water vapor behaves as an ideal gas.

12-7 CONCEPT ASSESSMENT

One method of restoring water-damaged books after a fire is extinguished in a library is by "freeze drying" them in evacuated chambers. Describe how this method might work.

Ionic Solids

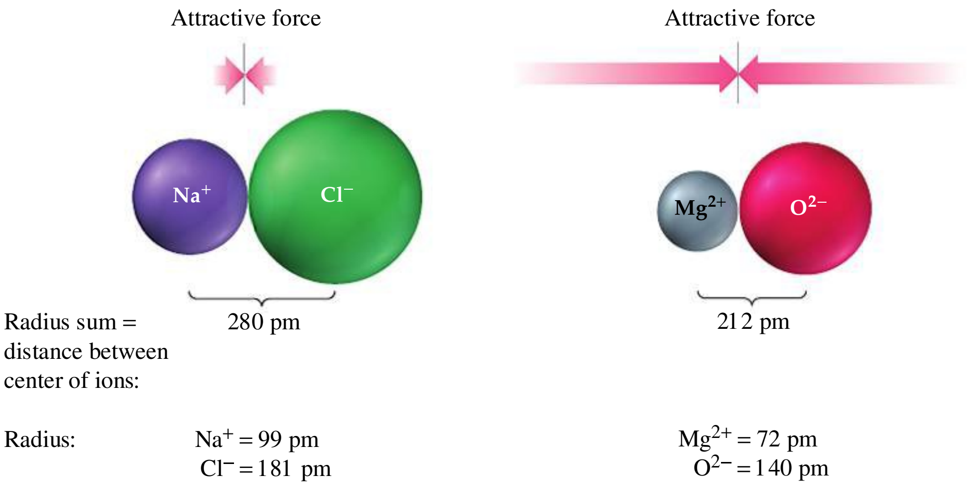
When predicting properties of an ionic solid, we often face this question: How difficult is it to break up an ionic crystal and separate its ions? This question is addressed by the *lattice energy* of a crystal. Let us define **lattice energy** as the energy given off when separated *gaseous* ions positive and negative come together to form *one mole* of a *solid* ionic compound. Lattice energies can be useful in making predictions about the melting points and water solubilities of ionic compounds.

The attractive force between a pair of oppositely charged ions increases with increased charge on the ions and with decreased ionic sizes.

This idea is based on Coulomb's law (Appendix B) and illustrated in Figure 12-36.

For most ionic compounds, lattice energies are great enough that ions do not readily detach themselves from the crystal and pass into the gaseous state. Ionic solids do not sublime at ordinary temperatures. We can melt ionic solids by supplying enough thermal energy to disrupt the crystalline lattice. In general, the higher the lattice energy of an ionic compound, the higher is its melting point.

The energy required to break up an ionic crystal when it dissolves results from the interaction of ions in the crystal with molecules of the solvent. The extent to which an ionic solid dissolves in a solvent, however, depends only in part on the lattice energy of the ionic solid. As a rough rule, though, the lower the lattice energy, the greater the quantity of an ionic solid that can be dissolved in a given quantity of solvent.



▲ FIGURE 12-36

Interionic forces of attraction

Because of the higher charges on the ions and the closer proximity of their centers, the interionic attractive force between Mg^{2+} and O^{2-} is about seven times as great as between Na^+ and Cl^-.

EXAMPLE 12-8 Predicting Physical Properties of Ionic Compounds

Which has the higher melting point, KI or CaO?

Analyze

Trends in melting points, just as we observed for boiling points, depend on intermolecular forces. For ionic compounds the melting points are dependent on the interionic forces, which are related to Coulomb's law.

Solve

Ca^{2+} and O^{2-} are more highly charged than K^+ and I^-. Also, Ca^{2+} is smaller than K^+, and O^{2-} is smaller than I^-. We would expect the interionic forces in crystalline CaO to be much larger than in KI. CaO should have the higher melting point. (The observed melting points are 677 °C for KI and 2590 °C for CaO.)

Assess

We see that two factors contribute to the interionic forces in this problem. The first is the charge and the second is the radius of each ion.

PRACTICE EXAMPLE A: Cite one ionic compound that you would expect to have a lower melting point than KI and one with a higher melting point than CaO.

PRACTICE EXAMPLE B: Which would you expect to have the greater solubility in water, NaI or $MgCl_2$? Explain.

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The acronym LCD, which stands for liquid crystal display, needs little introduction. Using the word liquid to describe crystals appears contradictory based upon the material in this chapter. For a discussion of the properties and uses of materials that we call liquid crystals, go to the Focus On feature for Chapter 12, Liquid Crystals, on the MasteringChemistry website.

Summary

12-1 Intermolecular Forces—The intermolecular forces that occur between molecules are collectively known as **van der Waals forces**. The most common intermolecular forces of attraction are those between instantaneous and induced dipoles (**dispersion forces**, or **London forces**). The magnitudes of dispersion forces depend on how easily electron displacements within molecules cause a temporary imbalance of electron charge distribution, that is, on the **polarizability** of the molecule. In polar substances, there are also dipole–dipole forces. Some hydrogen-containing substances exhibit significant intermolecular attractions called **hydrogen bonds,** in which H atoms bonded to highly electronegative atoms—N, O, or F—in a molecule are simultaneously attracted to other highly electronegative atoms in the same molecule or in different molecules. Hydrogen bonding has a profound effect on physical properties, such as boiling points (Fig. 12-5) and is a vital intermolecular force in living systems.

12-2 Some Properties of Liquids—**Surface tension**, the energy required to extend the surface of a liquid, and **viscosity,** a liquid's resistance to flow, are properties related to intermolecular forces. Familiar phenomena such as drop shape, meniscus formation, and capillary action depend on surface tension. Specifically, these phenomena are influenced by the balance between **cohesive forces**, intermolecular forces between molecules in a liquid, and **adhesive forces**, intermolecular forces between liquid molecules and a surface. **Vapor pressure,** the pressure exerted by a vapor in equilibrium with a liquid, is a measure of the volatility of a liquid and is related to the strength of intermolecular forces. The conversion of a liquid to a vapor is called **vaporization** or **evaporation**; the reverse process is called **condensation**. The dependence of vapor pressure on temperature is represented by a **vapor pressure curve** (Fig. 12-18). When the pressure exerted by the escaping molecules from the surface of the liquid equals the pressure exerted by the molecules in the atmosphere, **boiling** is said to occur. The **normal boiling point** is the temperature at which the vapor pressure of the liquid equals 1 atm. The **critical point** is the condition of temperature and pressure at which a liquid and its vapor become indistinguishable (Fig. 12-22).

12-3 Some Properties of Solids When crystalline solids are heated, a temperature is reached where the solid state is converted to a liquid and **melting** occurs. The temperature at which this occurs is the **melting point**. When liquids are cooled, the crystalline material will form during the process of **freezing**, and the temperature at which this occurs is the **freezing point**. Under certain conditions solids can directly convert into vapor by the process of **sublimation**. The reverse process is called **deposition**. Among the properties of a solid affected by intermolecular forces are its sublimation (vapor) pressure and its melting point.

12-4 Phase Diagrams—A **phase diagram** (Figs. 12-24 to 12-28) is a graphical plot of conditions under which solids, liquids, and gases (vapors) exist, as single phases or as two or more phases in equilibrium with one another. Significant points on a phase diagram are the **triple point** (where all three phases coexist), melting point, boiling point, and critical point, beyond which a supercritical fluid is possible. Some substances can exist in different forms in the solid state.