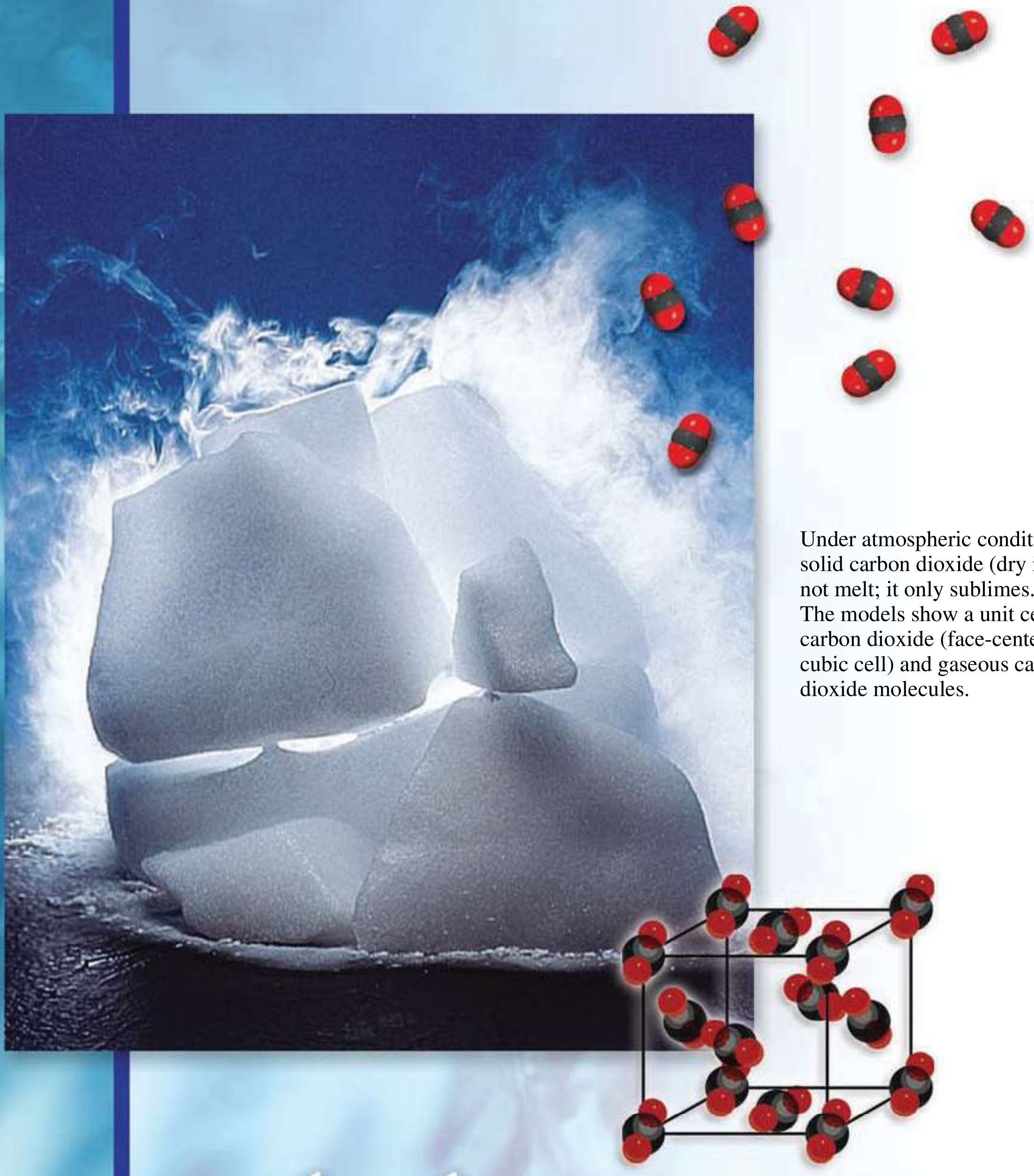
Intermolecular Forces and Liquids and Solids



Under atmospheric conditions, solid carbon dioxide (dry ice) does not melt; it only sublimes. The models show a unit cell of carbon dioxide (face-centered cubic cell) and gaseous carbon dioxide molecules.

11

Chapter Outline

A Look Ahead

- We begin by applying the kinetic molecular theory to liquids and solids and compare their properties with those of gases. (11.1)
- Next, we examine the different types of intermolecular forces between molecules and between ions and molecules. We also study a special type of intermolecular interaction called hydrogen bonding that involves hydrogen and electronegative elements nitrogen, oxygen, and fluorine. (11.2)
- We see that two important properties of liquids—surface tension and viscosity—can be understood in terms of intermolecular forces. (11.3)
- The major types of crystals are ionic, covalent, molecular, and metallic. Intermolecular forces help us understand their structure and physical properties such as density, melting point, and electrical conductivity. (11.6)
- We learn that solids can also exist in the amorphous form, which lacks orderly three-dimensional arrangement. A well-known example of an amorphous solid is glass. (11.7)
- We next study phase changes, or transitions among gas, liquids, and solids. We see that the dynamic equilibrium between liquid and vapor gives rise to equilibrium vapor pressure. The energy required for vaporization depends on the strength of intermolecular forces.
- The various types of phase transitions are summarized in a phase diagram, which helps us understand conditions under which a phase is stable and changes in pressure and/or temperature needed to bring about a phase transition. (11.9)

Although we live immersed in a mixture of gases that make up Earth's atmosphere, we are more familiar with the behavior of liquids and solids because they are more visible. Every day we use water and other liquids for drinking, bathing, cleaning, and cooking, and we handle, sit upon, and wear solids.

Molecular motion is more restricted in liquids than in gases; and in solids the atoms and molecules are packed even more tightly together. In fact, in a solid they are held in well-defined positions and are capable of little free motion relative to one another. In this chapter we will examine the structure of liquids and solids and discuss some of the fundamental properties of these two states of matter. We will also study the nature of transitions among gases, liquids, and solids.

11.1 The Kinetic Molecular Theory of Liquids and Solids

In Chapter 5 we used the kinetic molecular theory to explain the behavior of gases in terms of the constant, random motion of gas molecules. In gases, the distances between molecules are so great (compared with their diameters) that at ordinary temperatures and pressures (say, 25°C and 1 atm), there is no appreciable interaction between the molecules. Because there is a great deal of empty space in a gas—that is, space that is not occupied by molecules—gases can be readily compressed. The lack of strong forces between molecules also allows a gas to expand to fill the volume of its container. Furthermore, the large amount of empty space explains why gases have very low densities under normal conditions.

Liquids and solids are quite a different story. The principal difference between the condensed states (liquids and solids) and the gaseous state is the distance between molecules. In a liquid, the molecules are so close together that there is very little empty space. Thus, liquids are much more difficult to compress than gases, and they are also much denser under normal conditions. Molecules in a liquid are held together by one or more types of attractive forces, which will be discussed in Section 11.2. A liquid also has a definite volume, because molecules in a liquid do not break away from the attractive forces. The molecules can, however, move past one another freely, and so a liquid can flow, can be poured, and assumes the shape of its container.

In a solid, molecules are held rigidly in position with virtually no freedom of motion. Many solids are characterized by long-range order; that is, the molecules are arranged in regular configurations in three dimensions. There is even less empty space in a solid than in a liquid. Thus, solids are almost incompressible and possess definite shape and volume. With very few exceptions (water being the most important), the density of the solid form is higher than that of the liquid form for a given substance. It is not uncommon for two states of a substance to coexist. An ice cube (solid) floating in a glass of water (liquid) is a familiar example. Chemists refer to the different states of a substance that are present in a system as phases. A ***phase*** is *a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.* Thus, our glass of ice water contains both the solid phase and the liquid phase of water. In this chapter we will use the term "phase" when talking about changes of state involving one substance, as well as systems containing more than one phase of a substance. Table 11.1 summarizes some of the characteristic properties of the three phases of matter.

TABLE 11.1 Characteristic Properties of Gases, Liquids, and Solids

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

11.2 Intermolecular Forces

Intermolecular forces are *attractive forces between molecules.* Intermolecular forces are responsible for the nonideal behavior of gases described in Chapter 5. They exert even more influence in the condensed phases of matter—liquids and solids. As the temperature of a gas drops, the average kinetic energy of its molecules decreases. Eventually, at a sufficiently low temperature, the molecules no longer have enough energy to break away from the attraction of neighboring molecules. At this point, the molecules aggregate to form small drops of liquid. This transition from the gaseous to the liquid phase is known as *condensation.*

In contrast to intermolecular forces, ***intramolecular forces*** *hold atoms together in a molecule.* (Chemical bonding, discussed in Chapters 9 and 10, involves intramolecular forces.) Intramolecular forces stabilize individual molecules, whereas intermolecular forces are primarily responsible for the bulk properties of matter (for example, melting point and boiling point).

Generally, intermolecular forces are much weaker than intramolecular forces. It usually requires much less energy to evaporate a liquid than to break the bonds in the molecules of the liquid. For example, it takes about 41 kJ of energy to vaporize 1 mole of water at its boiling point; but about 930 kJ of energy are necessary to break the two O—H bonds in 1 mole of water molecules. The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapor phase. If it takes more energy to separate molecules of substance A than of substance B because A molecules are held together by stronger intermolecular forces, then the boiling point of A is higher than that of B. The same principle applies also to the melting points of the substances. In general, the melting points of substances increase with the strength of the intermolecular forces.

To discuss the properties of condensed matter, we must understand the different types of intermolecular forces. *Dipole-dipole, dipole-induced dipole,* and *dispersion forces* make up what chemists commonly refer to as ***van der Waals forces,*** after the Dutch physicist Johannes van der Waals (see Section 5.8). Ions and dipoles are attracted to one another by electrostatic forces called *ion-dipole forces,* which are *not* van der Waals forces. *Hydrogen bonding* is a particularly strong type of dipole-dipole interaction. Because only a few elements can participate in hydrogen bond formation, it is treated as a separate category. Depending on the phase of a substance, the nature of chemical bonds, and the types of elements present, more than one type of interaction may contribute to the total attraction between molecules, as we will see below.

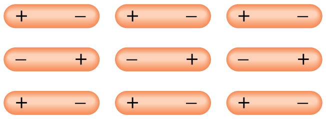


Figure 11.1 *Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.*

Dipole-Dipole Forces

Dipole-dipole forces are *attractive forces between polar molecules,* that is, between molecules that possess dipole moments (see Section 10.2). Their origin is electrostatic, and they can be understood in terms of Coulomb's law. The larger the dipole moment, the greater the force. Figure 11.1 shows the orientation of polar molecules in a solid. In liquids, polar molecules are not held as rigidly as in a solid, but they tend to align in a way that, on average, maximizes the attractive interaction.

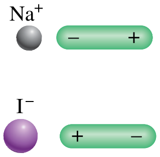


Figure 11.2 *Two types of ion-dipole interaction.*

Ion-Dipole Forces

Coulomb's law also explains ***ion-dipole forces,*** which *attract an ion (either a cation or an anion) and a polar molecule to each other* (Figure 11.2). The strength of this

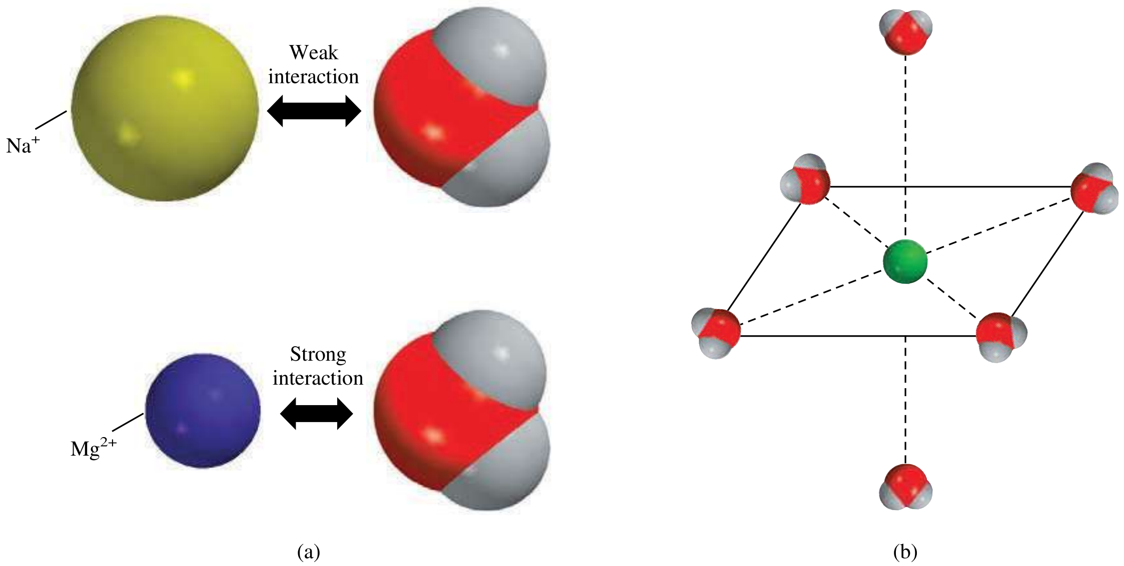


Figure 11.3 *(a) Interaction of a water molecule with a Na$^+$ ion and a Mg^{2+} ion. (b) In aqueous solutions, metal ions are usually surrounded by six water molecules in an octahedral arrangement.*

interaction depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the molecule. The charges on cations are generally more concentrated, because cations are usually smaller than anions. Therefore, a cation interacts more strongly with dipoles than does an anion having a charge of the same magnitude.

Hydration, discussed in Section 4.1, is one example of ion-dipole interaction. Heat of hydration (see p. 259) is the result of the favorable interaction between the cations and anions of an ionic compound with water. Figure 11.3 shows the ion-dipole interaction between the Na$^+$ and Mg^{2+} ions with a water molecule, which has a large dipole moment (1.87 D). Because the Mg^{2+} ion has a higher charge and a smaller ionic radius (78 pm) than that of the Na$^+$ ion (98 pm), it interacts more strongly with water molecules. (In reality, each ion is surrounded by a number of water molecules in solution.) Consequently, the heats of hydration for the Na$^+$ and Mg^{2+} ions are -405 kJ/mol and -1926 kJ/mol, respectively.[†] Similar differences exist for anions of different charges and sizes.

Dispersion Forces

What attractive interaction occurs in nonpolar substances? To learn the answer to this question, consider the arrangement shown in Figure 11.4. If we place an ion or a polar molecule near an atom (or a nonpolar molecule), the electron distribution of the atom (or molecule) is distorted by the force exerted by the ion or the polar molecule, resulting in a kind of dipole. The dipole in the atom (or nonpolar molecule) is said to be an ***induced dipole*** because *the separation of positive and negative charges in the atom (or nonpolar molecule) is due to the proximity of an ion or a polar molecule.* The attractive interaction between an ion and the induced dipole is called *ion-induced dipole interaction,* and the attractive interaction between a polar molecule and the induced dipole is called *dipole-induced dipole interaction.*

The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the *polarizability* of the atom or molecule—that is, the ease with which the electron distribution in the atom (or molecule) can be distorted. Generally, the larger the number of electrons and the more

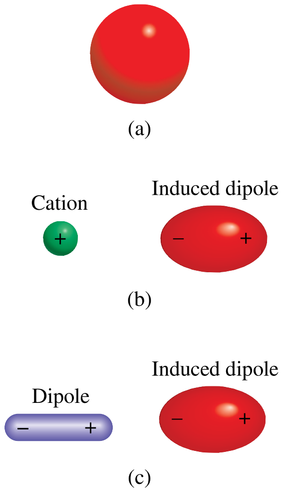


Figure 11.4 *(a) Spherical charge distribution in a helium atom. (b) Distortion caused by the approach of a cation. (c) Distortion caused by the approach of a dipole.*

[†] Heats of hydration of individual ions cannot be measured directly, but they can be reliably estimated.

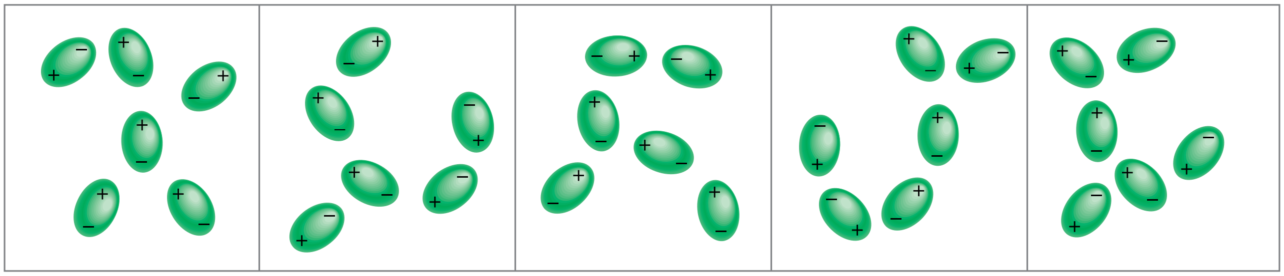


Figure 11.5 *Induced dipoles interacting with each other. Such patterns exist only momentarily; new arrangements are formed in the next instant. This type of interaction is responsible for the condensation of nonpolar gases.*

diffuse the electron cloud in the atom or molecule, the greater its polarizability. By *diffuse cloud* we mean an electron cloud that is spread over an appreciable volume, so that the electrons are not held tightly by the nucleus.

Polarizability allows gases containing atoms or nonpolar molecules (for example, He and N_2) to condense. In a helium atom the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the specific positions of the electrons. This dipole moment is called an *instantaneous dipole* because it lasts for just a tiny fraction of a second. In the next instant the electrons are in different locations and the atom has a new instantaneous dipole, and so on. Averaged over time (that is, the time it takes to make a dipole moment measurement), however, the atom has no dipole moment because the instantaneous dipoles all cancel one another. In a collection of He atoms, an instantaneous dipole of one He atom can induce a dipole in each of its nearest neighbors (Figure 11.5). At the next moment, a different instantaneous dipole can create temporary dipoles in the surrounding He atoms. The important point is that this kind of interaction produces ***dispersion forces,*** *attractive forces that arise as a result of temporary dipoles induced in atoms or molecules.* At very low temperatures (and reduced atomic speeds), dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly.

A quantum mechanical interpretation of temporary dipoles was provided by Fritz London[†] in 1930. London showed that the magnitude of this attractive interaction is directly proportional to the polarizability of the atom or molecule. As we might expect, dispersion forces may be quite weak. This is certainly true for helium, which has a boiling point of only 4.2 K, or −269°C. (Note that helium has only two electrons, which are tightly held in the 1*s* orbital. Therefore, the helium atom has a low polarizability.)

For simplicity we use the term "intermolecular forces" for both atoms and molecules.

Dispersion forces, which are also called London forces, usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons. Furthermore, larger molar mass often means a bigger atom whose electron distribution is more easily disturbed because the outer electrons are less tightly held by the nuclei. Table 11.2 compares the melting points of similar substances that consist of nonpolar molecules. As expected, the melting point increases as the number of electrons in the molecule increases. Because these are all nonpolar molecules, the only attractive intermolecular forces present are the dispersion forces.

TABLE 11.2

Melting Points of Similar Nonpolar Compounds

Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

[†] Fritz London (1900–1954). German physicist. London was a theoretical physicist whose major work was on superconductivity in liquid helium.

In many cases, dispersion forces are comparable to or even greater than the dipole-dipole forces between polar molecules. For a dramatic illustration, let us compare the boiling points of CH_3F (−78.4°C) and CCl_4 (76.5°C). Although CH_3F has a dipole moment of 1.8 D, it boils at a much lower temperature than CCl_4, a nonpolar molecule. CCl_4 boils at a higher temperature simply because it contains more electrons. As a result, the dispersion forces between CCl_4 molecules are stronger than the dispersion forces plus the dipole-dipole forces between CH_3F molecules. (Keep in mind that dispersion forces exist among species of all types, whether they are neutral or bear a net charge and whether they are polar or nonpolar.)

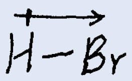
Example 11.1 shows that if we know the kind of species present, we can readily determine the types of intermolecular forces that exist between the species.

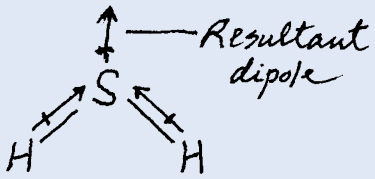
EXAMPLE 11.1

What type(s) of intermolecular forces exist between the following pairs: (a) HBr and H_2S, (b) Cl_2 and CBr_4, (c) I_2 and NO_3^-, (d) NH_3 and C_6H_6?

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

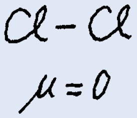
Solution (a) Both HBr and H_2S are polar molecules

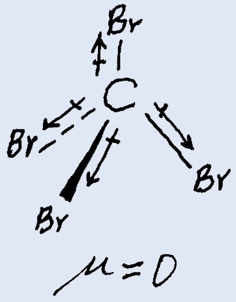




Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.

(b) Both Cl_2 and CBr_4 are nonpolar, so there are only dispersion forces between these molecules.





(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

Practice Exercise Name the type(s) of intermolecular forces that exists between molecules (or basic units) in each of the following species: (a) LiF, (b) CH_4, (c) SO_2.

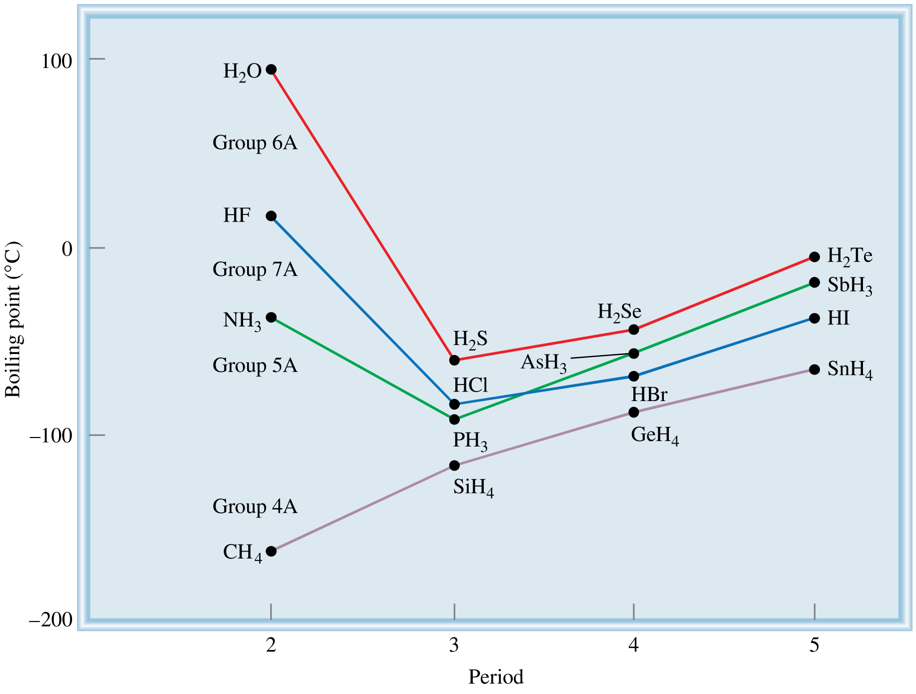
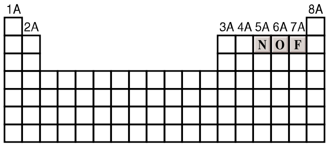


Figure 11.6 *Boiling points of the hydrogen compounds of Groups 4A, 5A, 6A, and 7A elements. Although normally we expect the boiling point to increase as we move down a group, we see that three compounds (NH_3, H_2O, and HF) behave differently. The anomaly can be explained in terms of intermolecular hydrogen bonding.*

The Hydrogen Bond

Normally, the boiling points of a series of similar compounds containing elements in the same periodic group increase with increasing molar mass. This increase in boiling point is due to the increase in dispersion forces for molecules with more electrons. Hydrogen compounds of Group 4A follow this trend, as Figure 11.6 shows. The lightest compound, CH_4, has the lowest boiling point, and the heaviest compound, SnH_4, has the highest boiling point. However, hydrogen compounds of the elements in Groups 5A, 6A, and 7A do not follow this trend. In each of these series, the lightest compound (NH_3, H_2O, and HF) has the highest boiling point, contrary to our expectations based on molar mass. This observation must mean that there are stronger intermolecular attractions in NH_3, H_2O, and HF, compared to other molecules in the same groups. In fact, this particularly strong type of intermolecular attraction is called the ***hydrogen bond,*** which is *a special type of dipole-dipole interaction between the hydrogen atom in a polar bond, such as N—H, O—H, or F—H, and an electronegative O, N, or F atom.* The interaction is written

$$\text{A—H} \cdots \text{B} \qquad \text{or} \qquad \text{A—H} \cdots \text{A}$$



The three most electronegative elements that take part in hydrogen bonding.

A and B represent O, N, or F; A—H is one molecule or part of a molecule and B is a part of another molecule; and the dotted line represents the hydrogen bond. The three atoms usually lie in a straight line, but the angle AHB (or AHA) can deviate as much as 30° from linearity. Note that the O, N, and F atoms all possess at least one lone pair that can interact with the hydrogen atom in hydrogen bonding.

The average strength of a hydrogen bond is quite large for a dipole-dipole interaction (up to 40 kJ/mol). Thus, hydrogen bonds have a powerful effect on the structures and properties of many compounds. Figure 11.7 shows several examples of hydrogen bonding.

The strength of a hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom and the hydrogen nucleus. For example, fluorine is more electronegative than oxygen, and so we would expect

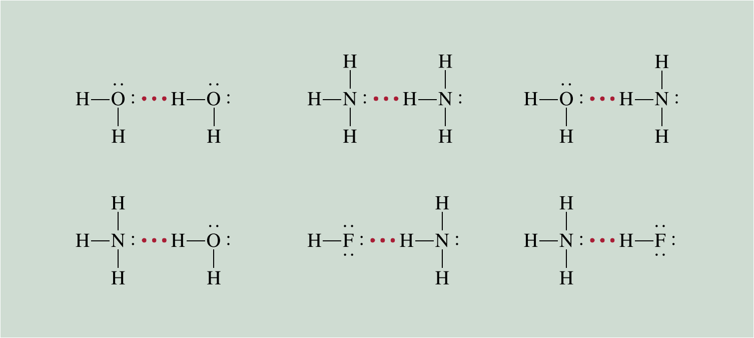
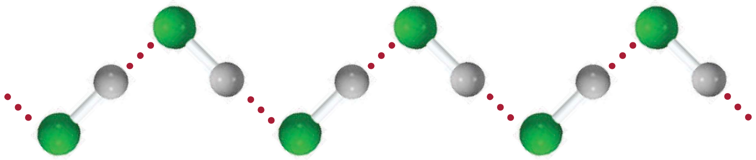
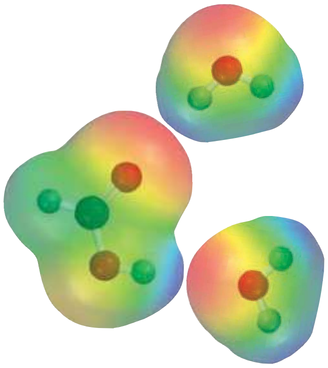


Figure 11.7 *Hydrogen bonding in water, ammonia, and hydrogen fluoride. Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.*

a stronger hydrogen bond to exist in liquid HF than in H_2O. In the liquid phase, the HF molecules form zigzag chains:



The boiling point of HF is lower than that of water because each H_2O takes part in *four* intermolecular hydrogen bonds. Therefore, the forces holding the molecules together are stronger in H_2O than in HF. We will return to this very important property of water in Section 11.3. Example 11.2 shows the type of species that can form hydrogen bonds with water.



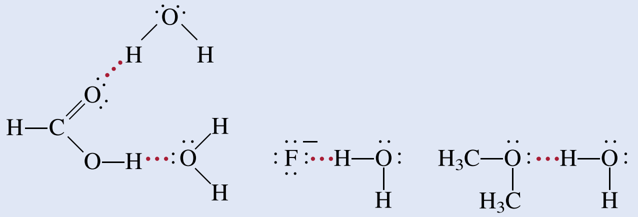
HCOOH forms hydrogen bonds with two H_2O molecules.

EXAMPLE 11.2

Which of the following can form hydrogen bonds with water? CH_3OCH_3, CH_4, F^-, HCOOH, Na^+.

Strategy A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has a H atom bonded to one of these three elements.

Solution There are no electronegative elements (F, O, or N) in either CH_4 or Na^+. Therefore, only CH_3OCH_3, F^-, and HCOOH can form hydrogen bonds with water.



Check Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.

Practice Exercise Which of the following species are capable of hydrogen bonding among themselves? (a) H_2S, (b) C_6H_6, (c) CH_3OH.

11.1 (a) Ionic and dispersion forces, (b) dispersion forces, (c) dipole-dipole and dispersion forces

The intermolecular forces discussed so far are all attractive in nature. Keep in mind, though, that molecules also exert repulsive forces on one another. Thus, when two molecules approach each other, the repulsion between the electrons and between the nuclei in the molecules comes into play. The magnitude of the repulsive force rises very steeply as the distance separating the molecules in a condensed phase decreases. This is the reason that liquids and solids are so hard to compress. In these phases, the molecules are already in close contact with one another, and so they greatly resist being compressed further.

11.3 Properties of Liquids

Intermolecular forces give rise to a number of structural features and properties of liquids. In this section we will look at two such phenomena associated with liquids in general: surface tension and viscosity. Then we will discuss the structure and properties of water.

The Structure and Properties of Water

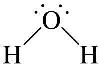
Water is so common a substance on Earth that we often overlook its unique nature. All life processes involve water. Water is an excellent solvent for many ionic compounds, as well as for other substances capable of forming hydrogen bonds with water.

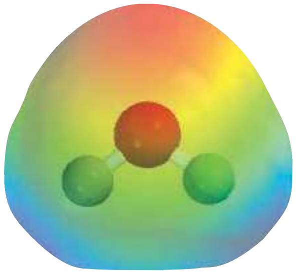
If water did not have the ability to form hydrogen bonds, it would be a gas at room temperature.

As Table 6.2 shows, water has a high specific heat. The reason is that to raise the temperature of water (that is, to increase the average kinetic energy of water molecules), we must first break the many intermolecular hydrogen bonds. Thus, water can absorb a substantial amount of heat while its temperature rises only slightly. The converse is also true: Water can give off much heat with only a slight decrease in its temperature. For this reason, the huge quantities of water that are present in our lakes and oceans can effectively moderate the climate of adjacent land areas by absorbing heat in the summer and giving off heat in the winter, with only small changes in the temperature of the body of water.

The most striking property of water is that its solid form is less dense than its liquid form: ice floats at the surface of liquid water. The density of almost all other substances is greater in the solid state than in the liquid state (Figure 11.11).

To understand why water is different, we have to examine the electronic structure of the H_2O molecule. As we saw in Chapter 9, there are two pairs of nonbonding electrons, or two lone pairs, on the oxygen atom:





Electrostatic potential map of water.

Although many compounds can form intermolecular hydrogen bonds, the difference between H_2O and other polar molecules, such as NH_3 and HF, is that each oxygen atom can form *two* hydrogen bonds, the same as the number of lone electron pairs

Figure 11.11 *Left: Ice cubes float on water. Right: Solid benzene sinks to the bottom of liquid benzene.*

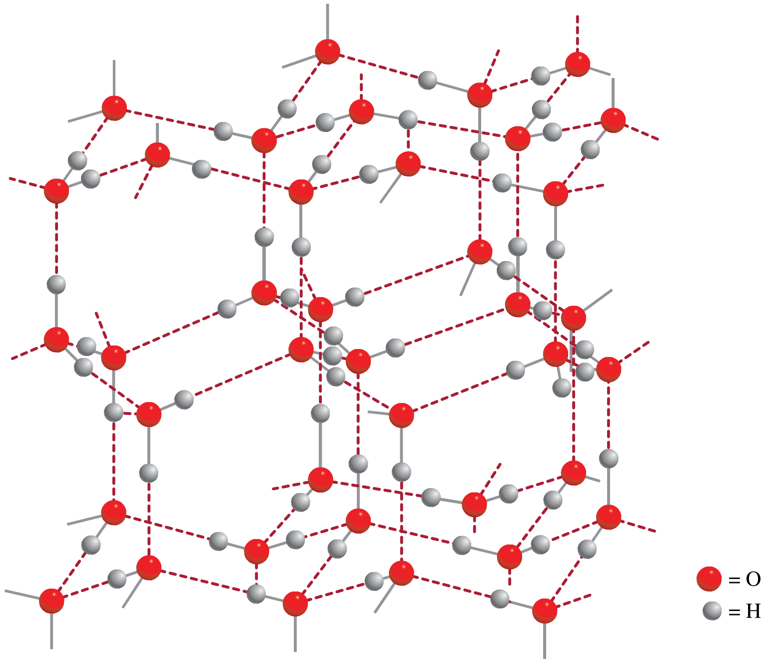


Figure 11.12 *The three-dimensional structure of ice. Each O atom is bonded to four H atoms. The covalent bonds are shown by short solid lines and the weaker hydrogen bonds by long dotted lines between O and H. The empty space in the structure accounts for the low density of ice.*

on the oxygen atom. Thus, water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is approximately tetrahedrally bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This equality in the number of hydrogen atoms and lone pairs is not characteristic of NH_3 or HF or, for that matter, of any other molecule capable of forming hydrogen bonds. Consequently, these other molecules can form rings or chains, but not three-dimensional structures.

The highly ordered three-dimensional structure of ice (Figure 11.12) prevents the molecules from getting too close to one another. But consider what happens when ice melts. At the melting point, a number of water molecules have enough kinetic energy to break free of the intermolecular hydrogen bonds. These molecules become trapped in the cavities of the three-dimensional structure, which is broken down into smaller clusters. As a result, there are more molecules per unit volume in liquid water than in ice. Thus, because density = mass/volume, the density of water is greater than that of ice. With further heating, more water molecules are released from intermolecular hydrogen bonding, so that the density of water tends to increase with rising temperature just above the melting point. Of course, at the same time, water expands as it is being heated so that its density is decreased. These two processes—the trapping of free water molecules in cavities and thermal expansion—act in opposite directions. From 0°C to 4°C, the trapping prevails and water becomes progressively denser. Beyond 4°C, however, thermal expansion predominates and the density of water decreases with increasing temperature (Figure 11.13).

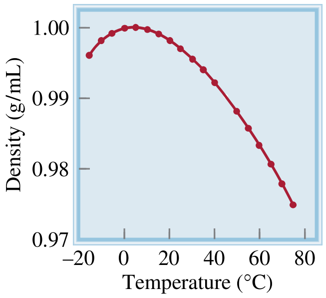


Figure 11.13 *Plot of density versus temperature for liquid water. The maximum density of water is reached at 4°C. The density of ice at 0°C is about 0.92 g/cm^3.*

11.4 Crystal Structure

Solids can be divided into two categories: crystalline and amorphous. Ice is a ***crystalline solid,*** which *possesses rigid and long-range order; its atoms, molecules, or ions occupy specific positions.* T

Types of Crystals

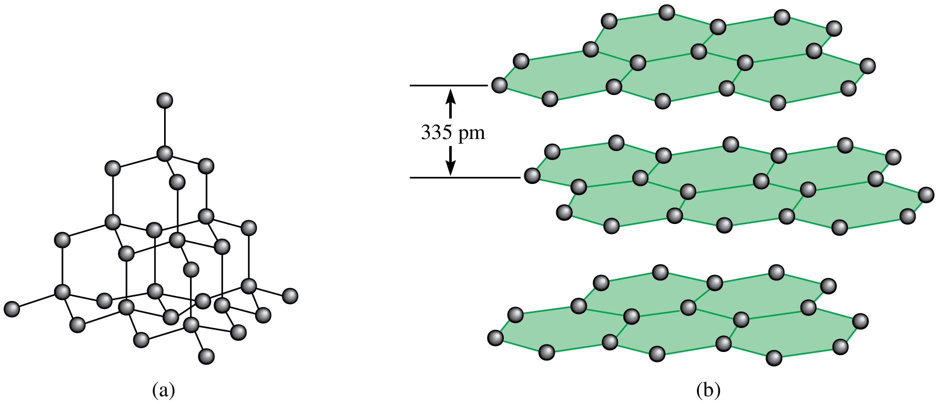
The structures and properties of crystals, such as melting point, density, and hardness, are determined by the kinds of forces that hold the particles together. We can classify any crystal as one of four types: ionic, covalent, molecular, or metallic.

Ionic Crystals

Ionic crystals have two important characteristics: (1) They are composed of charged species and (2) anions and cations are generally quite different in size. Knowing the radii of the ions is helpful in understanding the structure and stability of these compounds.

Most ionic crystals have high melting points, an indication of the strong cohesive forces holding the ions together. A measure of the stability of ionic crystals is the lattice energy (see Section 9.3); the higher the lattice energy, the more stable the solid.

These giant potassium dihydrogen phosphate crystals were grown in the laboratory. The largest one weighs 701 lb!



(a) (b)

Figure 11.28 *(a) The structure of diamond. Each carbon is tetrahedrally bonded to four other carbon atoms. (b) The structure of graphite. The distance between successive layers is 335 pm.*

These solids do not conduct electricity because the ions are fixed in position. However, in the molten state (that is, when melted) or dissolved in water, the ions are free to move and the resulting liquid is electrically conducting.

Covalent Crystals

In covalent crystals, atoms are held together in an extensive three-dimensional network entirely by covalent bonds. Well-known examples are the two allotropes of carbon: diamond and graphite (see Figure 8.17). In diamond, each carbon atom is sp^3-hybridized; it is bonded to four other atoms (Figure 11.28). The strong covalent bonds in three dimensions contribute to diamond's unusual hardness (it is the hardest material known) and very high melting point (3550°C). In graphite, carbon atoms are arranged in six-membered rings. The atoms are all sp^2-hybridized; each atom is covalently bonded to three other atoms. The remaining unhybridized $2p$ orbital is used in pi bonding. In fact, each layer of graphite has the kind of delocalized molecular orbital that is present in benzene (see Section 10.8). Because electrons are free to move around in this extensively delocalized molecular orbital, graphite is a good conductor of electricity in directions along the planes of carbon atoms. The layers are held together by weak van der Waals forces. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to the touch and is effective as a lubricant. It is also used in pencils and in ribbons made for computer printers and typewriters.

The central electrode in flashlight batteries is made of graphite.

Another covalent crystal is quartz (SiO_2). The arrangement of silicon atoms in quartz is similar to that of carbon in diamond, but in quartz there is an oxygen atom between each pair of Si atoms. Because Si and O have different electronegativities, the Si—O bond is polar. Nevertheless, SiO_2 is similar to diamond in many respects, such as hardness and high melting point (1610°C).

Quartz.

Molecular Crystals

In a molecular crystal, the lattice points are occupied by molecules, and the attractive forces between them are van der Waals forces and/or hydrogen bonding. An example of a molecular crystal is solid sulfur dioxide (SO_2), in which the predominant attractive force is a dipole-dipole interaction. Intermolecular hydrogen bonding is mainly responsible for maintaining the three-dimensional lattice of ice (see Figure 11.12). Other examples of molecular crystals are I_2, P_4, and S_8.

In general, except in ice, molecules in molecular crystals are packed together as closely as their size and shape allow. Because van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular

Sulfur.

crystals are more easily broken apart than ionic and covalent crystals. Indeed, most molecular crystals melt at temperatures below 100°C.

Metallic Crystals

In a sense, the structure of metallic crystals is the simplest because every lattice point in a crystal is occupied by an atom of the same metal.

The bonding in metals is quite different from that in other types of crystals. In a metal, the bonding electrons are delocalized over the entire crystal. In fact, metal atoms in a crystal can be imagined as an array of positive ions immersed in a sea of delocalized valence electrons (Figure 11.30). The great cohesive force resulting from delocalization is responsible for a metal's strength. The mobility of the delocalized electrons makes metals good conductors of heat and electricity.

Table 11.4 summarizes the properties of the four different types of crystals discussed.

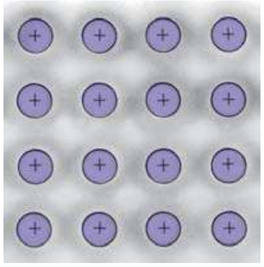


Figure 11.30 *A cross section of a metallic crystal. Each circled positive charge represents the nucleus and inner electrons of a metal atom. The gray area surrounding the positive metal ions indicates the mobile sea of valence electrons.*

TABLE 11.4 Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bond	Hard, high melting point	C (diamond),[†] SiO_2 (quartz)
Molecular*	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements; for example, Na, Mg, Fe, Cu

*Included in this category are crystals made up of individual atoms.

[†] Diamond is a good thermal conductor.

Amorphous Solids

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and may become locked in positions other than those of a regular crystal. The resulting solid is said to be *amorphous.* ***Amorphous solids,*** such as glass, *lack a regular three-dimensional arrangement of atoms.*

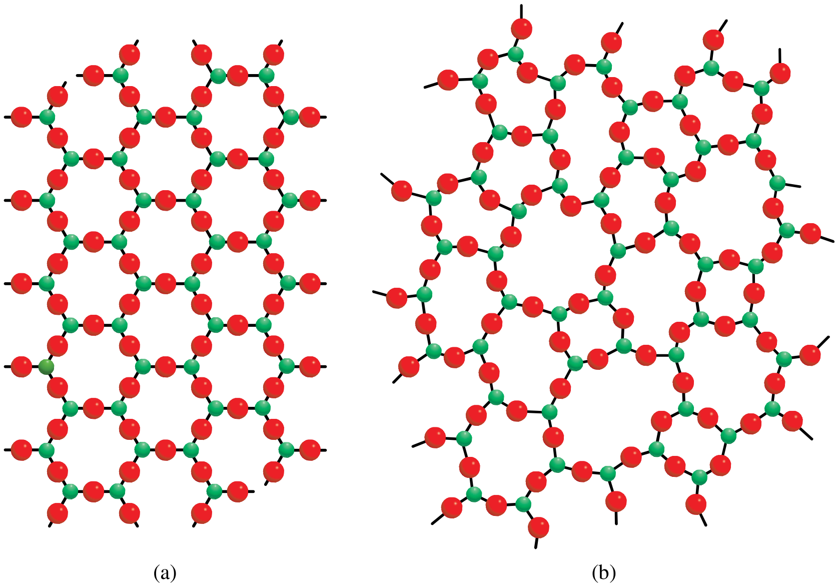


Figure 11.31 *Two-dimensional representation of (a) crystalline quartz and (b) noncrystalline quartz glass. The small spheres represent silicon. In reality, the structure of quartz is three-dimensional. Each Si atom is tetrahedrally bonded to four O atoms.*

11.8 Phase Changes

The discussions in Chapter 5 and in this chapter have given us an overview of the properties of the three phases of matter: gas, liquid, and solid. ***Phase changes,*** *transformations from one phase to another,* occur when energy (usually in the form of heat) is added or removed from a substance. Phase changes are physical changes characterized by changes in molecular order; molecules in the solid phase have the greatest order, and those in the gas phase have the greatest randomness. Keeping in mind the relationship between energy change and the increase or decrease in molecular order will help us understand the nature of these physical changes.

Liquid-Vapor Equilibrium

Molecules in a liquid are not fixed in a rigid lattice. Although they lack the total freedom of gaseous molecules, these molecules are in constant motion. Because liquids are denser than gases, the collision rate among molecules is much higher in the liquid phase than in the gas phase. When the molecules in a liquid have sufficient energy to escape from the surface a phase change occurs. ***Evaporation,*** or ***vaporization,*** is *the process in which a liquid is transformed into a gas.*

How does evaporation depend on temperature? Figure 11.32 shows the kinetic energy distribution of molecules in a liquid at two different temperatures. As we can see, the higher the temperature, the greater the kinetic energy, and hence more molecules leave the liquid.

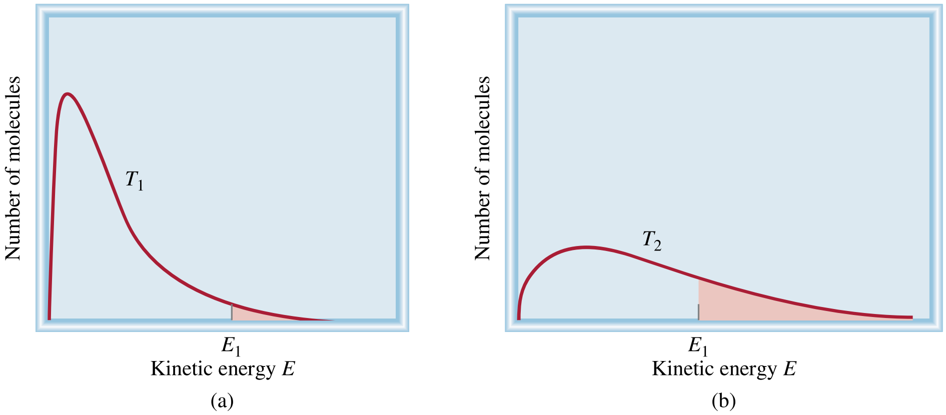


Figure 11.32 *Kinetic energy distribution curves for molecules in a liquid (a) at a temperature T_1 and (b) at a higher temperature T_2. Note that at the higher temperature, the curve flattens out. The shaded areas represent the number of molecules possessing kinetic energy equal to or greater than a certain kinetic energy E_1. The higher the temperature, the greater the number of molecules with high kinetic energy.*

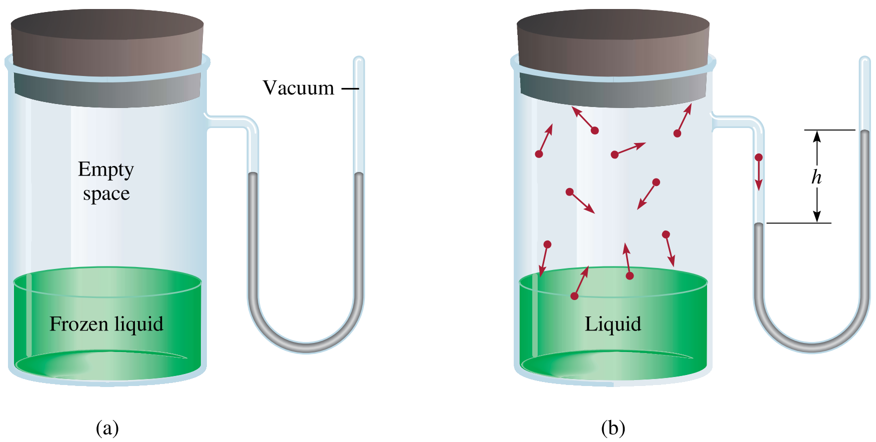


Figure 11.33 *Apparatus for measuring the vapor pressure of a liquid. (a) Initially the liquid is frozen so there are no molecules in the vapor phase. (b) On heating, a liquid phase is formed and evaporization begins. At equilibrium, the number of molecules leaving the liquid is equal to the number of molecules returning to the liquid. The difference in the mercury levels (h) gives the equilibrium vapor pressure of the liquid at the specified temperature.*

Vapor Pressure

The difference between a gas and a vapor is explained on p. 175.

When a liquid evaporates, its gaseous molecules exert a vapor pressure. Consider the apparatus shown in Figure 11.33. Before the evaporation process starts, the mercury levels in the U-shaped manometer tube are equal. As soon as some molecules leave the liquid, a vapor phase is established. The vapor pressure is measurable only when a fair amount of vapor is present. The process of evaporation does not continue indefinitely, however. Eventually, the mercury levels stabilize and no further changes are seen.

What happens at the molecular level during evaporation? In the beginning, the traffic is only one way: Molecules are moving from the liquid to the empty space. Soon the molecules in the space above the liquid establish a vapor phase. As the concentration of molecules in the vapor phase increases, some molecules *condense,* that is, they return to the liquid phase. ***Condensation,*** *the change from the gas phase to the liquid phase,* occurs because a molecule strikes the liquid surface and becomes trapped by intermolecular forces in the liquid.

The rate of evaporation is constant at any given temperature, and the rate of condensation increases with the increasing concentration of molecules in the vapor phase. A state of ***dynamic equilibrium,*** in which *the rate of a forward process is exactly balanced by the rate of the reverse process,* is reached when the rates of condensation and evaporation become equal (Figure 11.34). The ***equilibrium vapor pressure*** is *the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation.* We often use the simpler term "vapor pressure" when we talk about the equilibrium vapor pressure of a liquid. This practice is acceptable as long as we know the meaning of the abbreviated term.

It is important to note that the equilibrium vapor pressure is the *maximum* vapor pressure of a liquid at a given temperature and that it is constant at a constant temperature. (It is independent of the amount of liquid as long as there is some liquid present.) From the foregoing discussion we expect the vapor pressure of a liquid to increase with temperature. Plots of vapor pressure versus temperature for three different liquids in Figure 11.35 confirm this expectation.

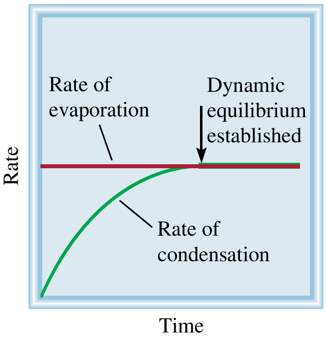


Figure 11.34 *Comparison of the rates of evaporation and condensation at constant temperature.*

Molar Heat of Vaporization and Boiling Point

A measure of the strength of intermolecular forces in a liquid is the ***molar heat of vaporization*** **(**ΔH_{vap}**),** defined as *the energy* (usually in kilojoules) *required to vaporize 1 mole of a liquid.* The molar heat of vaporization is directly related to the strength of intermolecular forces that exist in the liquid. If the intermolecular attraction is strong, it takes a lot of energy to free the molecules from the liquid phase and the molar heat of vaporization will be high. Such liquids will also have a low vapor pressure.

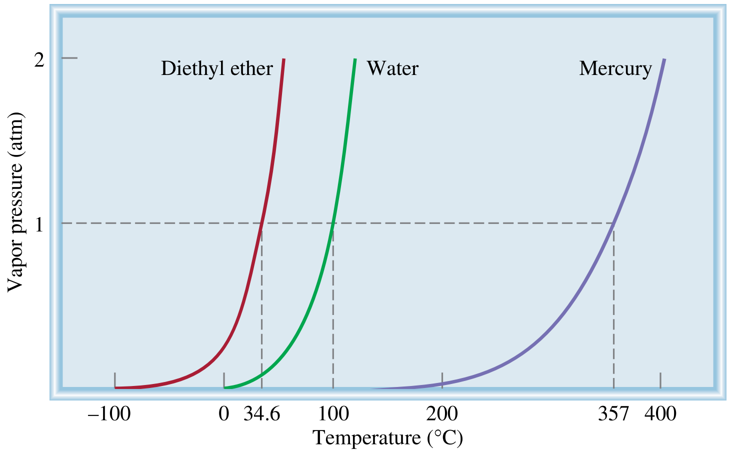


Figure 11.35 *The increase in vapor pressure with temperature for three liquids. The normal boiling points of the liquids (at 1 atm) are shown on the horizontal axis. The strong metallic bonding in mercury results in a much lower vapor pressure of the liquid at room temperature.*

The previous discussion predicts that the equilibrium vapor pressure (P) of a liquid should increase with increasing temperature, as shown in Figure 11.35.

TABLE 11.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Ethanol (C_2H_5OH)	78.3	39.3
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

*Measured at 1 atm.

A practical way to demonstrate the molar heat of vaporization is by rubbing an alcohol such as ethanol (C_2H_5OH) or isopropanol (C_3H_7OH), or rubbing alcohol, on your hands. These alcohols have a lower ΔH_{vap} than water, so that the heat from your hands is enough to increase the kinetic energy of the alcohol molecules and evaporate them. As a result of the loss of heat, your hands feel cool. This process is similar to perspiration, which is one of the means by which the human body maintains a constant temperature. Because of the strong intermolecular hydrogen bonding that exists in water, a considerable amount of energy is needed to vaporize the water in perspiration from the body's surface. This energy is supplied by the heat generated in various metabolic processes.

You have already seen that the vapor pressure of a liquid increases with temperature. Every liquid has a temperature at which it begins to boil. The ***boiling point*** is *the temperature at which the vapor pressure of a liquid is equal to the external pressure.* The *normal* boiling point of a liquid is the temperature at which it boils when the external pressure is 1 atm.

At the boiling point, bubbles form within the liquid. When a bubble forms, the liquid originally occupying that space is pushed aside, and the level of the liquid in the container is forced to rise. The pressure exerted *on* the bubble is largely atmospheric pressure, plus some *hydrostatic pressure* (that is, pressure due to the presence of liquid). The pressure *inside* the bubble is due solely to the vapor pressure of the liquid. When the vapor pressure becomes equal to the external pressure, the bubble rises to the surface of the liquid and bursts. If the vapor pressure in the bubble were lower than the external pressure, the bubble would collapse before it could rise. We can thus conclude that the boiling point of a liquid depends on the external pressure. (We usually ignore the small contribution due to the hydrostatic pressure.) For example, at 1 atm, water boils at 100°C, but if the pressure is reduced to 0.5 atm, water boils at only 82°C.

Because the boiling point is defined in terms of the vapor pressure of the liquid, we expect the boiling point to be related to the molar heat of vaporization: The higher ΔH_{vap}, the higher the boiling point. The data in Table 11.6 roughly confirm our prediction. Ultimately, both the boiling point and ΔH_{vap} are determined by the strength of intermolecular forces. For example, argon (Ar) and methane (CH_4), which have weak dispersion forces, have low boiling points and small molar heats of vaporization. Diethyl ether ($C_2H_5OC_2H_5$) has a dipole moment, and the dipole-dipole forces account for its moderately high boiling point and ΔH_{vap}. Both ethanol (C_2H_5OH) and water have strong hydrogen bonding, which accounts for their high boiling points and large ΔH_{vap} values. Strong metallic bonding causes mercury to have the highest boiling point and ΔH_{vap} of this group of liquids. Interestingly, the boiling point of benzene, which is nonpolar, is comparable to that of ethanol. Benzene has a high polarizability due to the distribution of its electrons in the delocalized pi molecular orbitals, and thedispersion forces among benzene molecules can be as strong as or even stronger than dipole-dipole forces and/or hydrogen bonds.

Liquid-Solid Equilibrium

The transformation of liquid to solid is called *freezing,* and the reverse process is called *melting,* or *fusion.* The ***melting point*** *of a solid or the* ***freezing point*** *of a liquid* is *the temperature at which solid and liquid phases coexist in equilibrium.* The *normal* melting (or freezing) point of a substance is the temperature at which a substance melts (or freezes) at 1 atm pressure. We generally omit the word "normal" when the pressure is at 1 atm.

The most familiar liquid-solid equilibrium is that of water and ice. At 0°C and 1 atm, the dynamic equilibrium is represented by

$$\text{ice} \rightleftharpoons \text{water}$$

A practical illustration of this dynamic equilibrium is provided by a glass of ice water. As the ice cubes melt to form water, some of the water between ice cubes may freeze, thus joining the cubes together. This is not a true dynamic equilibrium, however, because the glass is not kept at 0°C; thus, all the ice cubes will eventually melt away. Figure 11.38 shows how the temperature of a substance changes as it absorbs heat from its surroundings. We see that as a solid is heated, its temperature increases until it reaches its melting point. At this temperature, the average kinetic energy of the molecules has become sufficiently large to begin overcoming the intermolecular forces that hold the molecules together in the solid state. A transition from the solid to liquid phase begins in which the absorption of heat is used to break apart more and more of the molecules in the solid. It is important to note that during this transition ($A \longrightarrow B$) the average kinetic energy of the molecules does not change, so the temperature stays constant. Once the substance has completely melted, further absorption of heat increases

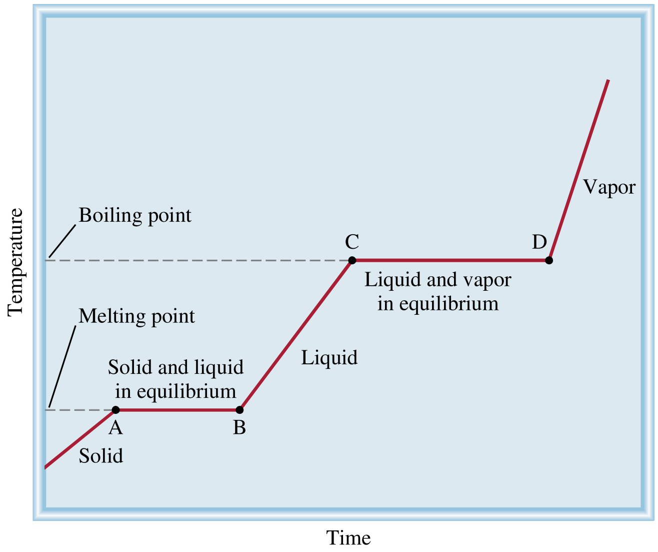


Figure 11.38 *A typical heating curve, from the solid phase through the liquid phase to the gas phase of a substance. Because ΔH_{fus} is smaller than ΔH_{vap}, a substance melts in less time than it takes to boil. This explains why AB is shorter than CD. The steepness of the solid, liquid, and vapor heating lines is determined by the specific heat of the substance in each state.*

its temperature until the boiling point is reached (B ⟶ C). Here, the transition from the liquid to the gaseous phase occurs (C ⟶ D) in which the absorbed heat is used to break the intermolecular forces holding the molecules in the liquid phase so the temperature again remains constant. Once this transition has been completed, the temperature of the gas increases on further heating.

Molar heat of fusion **(*ΔH_{fus}*)** is *the energy* (usually in kilojoules) *required to melt 1 mole of a solid.* Table 11.8 shows the molar heats of fusion for the substances listed in Table 11.6. A comparison of the data in the two tables shows that for each substance ΔH_{fus} is smaller than ΔH_{vap}. This is consistent with the fact that molecules in a liquid are still fairly closely packed together, so that some energy is needed to bring about the rearrangement from solid to liquid. On the other hand, when a liquid evaporates, its molecules become completely separated from one another and considerably more energy is required to overcome the attractive force.

As we would expect, *cooling* a substance has the opposite effect of heating it. If we remove heat from a gas sample at a steady rate, its temperature decreases. As the liquid is being formed, heat is given off by the system, because its potential energy is decreasing. For this reason, the temperature of the system remains constant over the condensation period (D ⟶ C). After all the vapor has condensed, the temperature of the liquid begins to drop. Continued cooling of the liquid finally leads to freezing (B ⟶ A).

TABLE 11.8 Molar Heats of Fusion for Selected Substances

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Ethanol (C_2H_5OH)	−117.3	7.61
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

*Measured at 1 atm.

The phenomenon known as ***supercooling*** refers to the situation in which *a liquid can be temporarily cooled to below its freezing point.* Supercooling occurs when heat is removed from a liquid so rapidly that the molecules literally have no time to assume the ordered structure of a solid. A supercooled liquid is unstable; gentle stirring or the addition to it of a small "seed" crystal of the same substance will cause it to solidify quickly.

Solid-Vapor Equilibrium

Solids, too, undergo evaporation and, therefore, possess a vapor pressure. Consider the following dynamic equilibrium:

$$\text{solid} \rightleftharpoons \text{vapor}$$

Sublimation is *the process in which molecules go directly from the solid into the vapor phase.* ***Deposition*** is the reverse process, that is, *molecules make the transition from vapor to solid directly.* Naphthalene, which is the substance used to make mothballs, has a fairly high (equilibrium) vapor pressure for a solid (1 mmHg at 53°C); thus, its pungent vapor quickly permeates an enclosed space. Iodine also sublimes. Above room temperature, the violet color of iodine vapor is easily visible in a closed container.

Because molecules are more tightly held in a solid, the vapor pressure of a solid is generally much less than that of the corresponding liquid. ***Molar heat of sublimation*** (ΔH_{sub}) of a substance is *the energy* (usually in kilojoules) *required to sublime 1 mole of a solid.* It is equal to the sum of the molar heats of fusion and vaporization:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \tag{11.6}$$

Solid iodine in equilibrium with its vapor.

Equation (11.6) is an illustration of Hess's law (see Section 6.6). The enthalpy, or heat change, for the overall process is the same whether the substance changes directly from the solid to the vapor form or from the solid to the liquid and then to the vapor. Note that Equation (11.6) holds only if all the phase changes occur at the *same* temperature. If not, the equation can be used only as an approximation.

Figure 11.39 summarizes the types of phase changes discussed in this section.

When a substance is heated, its temperature will rise and eventually it will undergo a phase transition. To calculate the total energy change for such a process we must include all of the steps, shown in Example 11.8.

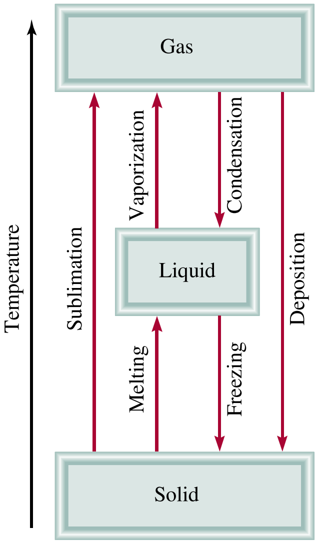


Figure 11.39 *The various phase changes that a substance can undergo.*

EXAMPLE 11.8

Calculate the amount of energy (in kilojoules) needed to heat 346 g of liquid water from 0°C to 182°C. Assume that the specific heat of water is 4.184 J/g · °C over the entire liquid range and that the specific heat of steam is 1.99 J/g · °C.

Strategy The heat change (q) at each stage is given by $q = ms\Delta t$, where m is the mass of water, s is the specific heat, and Δt is the temperature change. If there is a phase change, such as vaporization, then q is given by $n\Delta H_{\text{vap}}$, where n is the number of moles of water.

Solution The calculation can be broken down in three steps.

Step 1: Heating water from 0°C to 100°C
Using Equation (6.12) we write

$$\begin{aligned} q_1 &= ms\Delta t \\ &= (346\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C})(100^\circ\text{C} - 0^\circ\text{C}) \\ &= 1.45 \times 10^5\text{ J} \\ &= 145\text{ kJ} \end{aligned}$$

(Continued)

Step 2: Evaporating 346 g of water at 100°C (a phase change)
In Table 11.6 we see $\Delta H_{\text{vap}} = 40.79$ kJ/mol for water, so

$$\begin{aligned} q_2 &= 346\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.02\ \cancel{\text{g H}_2\text{O}}} \times \frac{40.79\ \text{kJ}}{1\ \cancel{\text{mol H}_2\text{O}}} \\ &= 783\ \text{kJ} \end{aligned}$$

Step 3: Heating steam from 100°C to 182°C

$$\begin{aligned} q_3 &= ms\Delta t \\ &= (346\ \text{g})(1.99\ \text{J/g}\cdot{}^\circ\text{C})(182^\circ\text{C} - 100^\circ\text{C}) \\ &= 5.65 \times 10^4\ \text{J} \\ &= 56.5\ \text{kJ} \end{aligned}$$

The overall energy required is given by

$$\begin{aligned} q_{\text{overall}} &= q_1 + q_2 + q_3 \\ &= 145\ \text{kJ} + 783\ \text{kJ} + 56.5\ \text{kJ} \\ &= 985\ \text{kJ} \end{aligned}$$

Check All the qs have a positive sign, which is consistent with the fact that heat is absorbed to raise the temperature from 0°C to 182°C. Also, as expected, much more heat is absorbed during phase transition.

Practice Exercise Calculate the heat released when 68.0 g of steam at 124°C is converted to water at 45°C.

Key Equations

$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$ (11.6)

Application of Hess's law.

Summary of Facts and Concepts

1. All substances exist in one of three states: gas, liquid, or solid. The major difference between the condensed state and the gaseous state is the distance separating molecules.
2. Intermolecular forces act between molecules or between molecules and ions. Generally, these attractive forces are much weaker than bonding forces.
3. Dipole-dipole forces and ion-dipole forces attract molecules with dipole moments to other polar molecules or ions.
4. Dispersion forces are the result of temporary dipole moments induced in ordinarily nonpolar molecules. The extent to which a dipole moment can be induced in a molecule is called its **polarizability**.
5. Hydrogen bonding is a relatively strong dipole-dipole interaction between a polar bond containing a hydrogen atom and an electronegative O, N, or F atom. Hydrogen bonds between water molecules are particularly strong.
6. Surface tension is the energy needed to ex-pand a liquid surface area; strong intermolecular forces lead to greater surface tension.
7. Viscosity is a measure of the resistance of a liquid to flow.
8. Water molecules in the solid state form a three-dimensional network in which each oxygen atom is covalently bonded to two hydrogen atoms and is hydrogen-bonded to two hydrogen atoms.
10. All solids are either crystalline (with a regular structure of atoms, ions, or molecules) or amorphous (without a regular structure). Glass is an example of an amorphous solid.
11. The four types of crystals and the forces that hold their particles together are
    ionic crystals, held to-gether by ionic bonding;

    network covalent crystals, covalent bonding;

    molecular crystals, held together by intemolecualr forces (dipoles, London foraes and/or hydrogen bonding);

    metallic crystals, metallic bonding (valence electron clouds).
12. A liquid in a closed vessel eventually establishes a dynamic equilibrium between evaporation and condensation. The vapor pressure over the liquid under these conditions is the equilibrium vapor pressure, which is often referred to simply as "vapor pressure."
13. At the boiling point, the vapor pressure of a liquid equals the external pressure. The molar heat of vaporization of a liquid is the energy required to vaporize one mole of the liquid. The molar heat of fusion of a solid is the energy required to melt one mole of the solid.
14. Not AP: The relationships among the phases of a single sub-stance are illustrated by a phase diagram, in which each region represents a pure phase and the boundaries be-tween the regions show the temperatures and pressures at which the two phases are in equilibrium. At the triple point, all three phases are in equilibrium.