

Atoms, Molecules, and Thermal Energy

So far we have treated thermal energy by observing matter—its temperature and its state—and then inventing concepts to describe what we see. Pizza sauce burns; crust at the same temperature does not. We invent the concept of specific heat capacity to describe differences in the amount of thermal energy transferred by the two materials. Ice at 0°C cools a glass of tea better than an equal amount of water at 0°C . We invent the concept of latent heats to describe the thermal energy transferred when substances undergo a change of state. Thermal energy can be transferred through empty space and through gases, liquids, and solids. Three processes, radiation-absorption, convection, and conduction, best summarize the differences we observe. Heat engines convert thermal energy into kinetic energy and thermal exhaust. Entropy explains the limits to the efficiencies of these devices. We could go on and on.

While you may have become pretty adept at using these concepts to describe a variety of interactions, lurking in the back of your mind may have

been the questions: How does it all really happen? What goes on inside matter? Physicists use the molecular model of matter to provide a more complete image of thermal processes in matter. By applying Newton's laws and the laws of conservation of energy and momentum to individual molecules, physicists have built a fairly detailed picture of how thermal energy arises at the molecular level. Such a picture allows us to see the concepts of thermal energy from a broader perspective.

In this chapter we examine the concepts introduced in the past three chapters in terms of the molecular model of matter. We use the concept of *restoring forces* to describe the different latent heats of fusion and vaporization. The *motion of individual molecules* is used to describe differences in specific heat capacities and the three thermal energy-transfer processes. Because of the billions of molecules found in each speck of matter, we cannot have absolute knowledge of the behavior of each molecule. We introduce a *probabilistic view of matter* that gives rise to the concept of entropy and the second law of thermodynamics.

INSIDE MATTER

In Chapter 10 we briefly described the molecular model of matter. Matter consists of molecules that interact with one another through electrical forces. These forces allow individual molecules to move about, yet restrict liquids and solids to a definite volume. To picture how electrical forces can allow motion and still restrain molecules to a definite volume, we introduce an analogy with springs. We use this analogy to describe the different states of matter and the thermal energy associated with changes in state.

Restoring Forces and Springs

The electrical interaction among atoms and molecules is the glue that holds matter together. As discussed in Chapter 8, these interactions result in forces that can be either attractive or repulsive, depending on the types of electrical charge involved. In matter, large numbers of both positive and negative electrical charges are present. Consequently, any given molecule will feel many, many forces—some attractive and some repulsive. We can replace this complex set of forces with a single force, called a *restoring force*.

A **restoring force** is a net force that always restores the molecule to some central location. One way to picture restoring forces in matter is to imagine that the molecules in matter are connected to one another by springs. If you push two molecules toward one another, you compress the spring connecting them. The spring pushes back, trying to restore the molecules to their original separation. If you pull the two molecules apart, the spring again resists your force, this time pulling the molecules back toward one another. No matter which way you move the molecules, the spring tries to restore them to their original location. The complex set of electrical interactions that act on individual molecules in matter combine to act like restoring forces.

The strength of the restoring force affects how far the molecules can move about their central location. A very strong restoring force, much like a tight spring, holds the molecules together tightly. It allows very small displacements as the molecules vibrate about their central location. A weaker force, like a very flexible spring, allows the molecules to move farther away but still binds them together. No restoring force at all allows the molecules to move about freely, bumping into whatever gets into their way. These three types of restoring forces characterize the three states of matter.

Solids, Liquids, and Gases

The molecules of a solid are held together by strong restoring forces. Their motion is analogous to a bunch of balls connected by springs, like those shown in Figure 13-1. Each ball has some energy and vibrates back and forth about an equilibrium position. But its energy is not sufficient to allow the molecule to overcome the restoring force exerted by the springs. This restricted motion leads to the definite shape and volume characteristic of solids.

Liquid molecules do not experience as strong a restoring force as solids. A liquid is more like a collection of balls with loosely attached springs, like those shown in Figure 13-2. The balls move about, collide with one another, and temporarily attach to one another via relatively weak springs. Inside the liquid, molecules feel forces in all directions. At the surface of the liquid, molecules feel forces back toward the other molecules. The weaker restoring forces in a liquid allow the molecules to move about more freely. This leads to the lack of shape characteristic of a liquid. The restoring forces are strong enough, however, to maintain relatively fixed average distances between molecules. A liquid does maintain a definite volume.

The weakest restoring forces are those among molecules in a gas. Molecules in a gas behave much like billiard balls moving about on a billiard table. They move about freely, bump into each other, and collide with the edges of the table. Each ball moves independently of the others. In a gas, molecules behave as though they were independent of one another. They move about freely, assuming the shape of their container. When placed in a larger container, the molecules simply move about farther before colliding with one another or with the walls of the container. Since the restoring forces are extremely weak, the molecules will move as far apart as the container allows. Gases have neither definite shapes nor definite volumes.

Changes in State

We can use the different restoring forces in solids, liquids, and gases to explain the thermal energy involved when matter changes state. The restoring force among molecules is greatest when the molecules form a solid, smaller when the molecules form a liquid, and essentially zero when the molecules form a gas. When an object changes state, the strength of its restoring force must change.

The spring analogy provides us with a convenient way to imagine how the strength of these restoring forces can change. When we change a solid

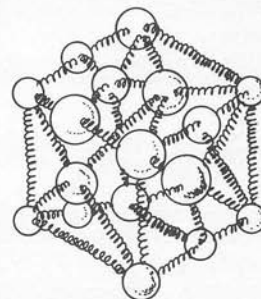


Figure 13-1

In solids, molecules are held in relatively fixed locations by strong restoring forces, represented as tight springs in this drawing.

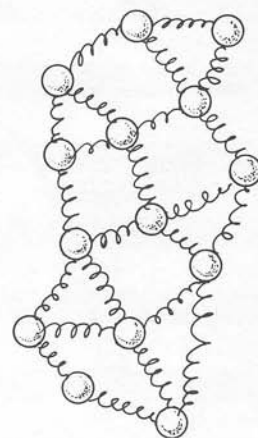
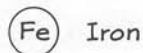


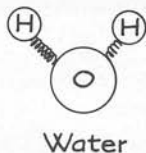
Figure 13-2

In liquids, molecules are free to move about more. Weaker restoring forces, represented here as loose springs, allow a liquid to change shape.

One-atom molecules

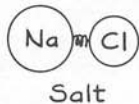


Three-atom molecules



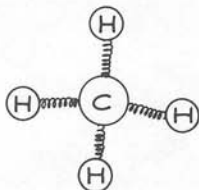
Carbon dioxide

Two-atom molecules



Carbon monoxide

Four-atom molecules



Methane

Figure 13-3

Molecules consisting of one, two, three, and four atoms.

into a liquid, we stretch the springs connecting the molecules until they are stretched out of shape. Longer and weaker, the springs allow the molecules to stay farther apart and move about more. Changing a liquid into a gas is like stretching the springs even farther—until they break completely. Broken springs allow the molecules to move freely about, much as the molecules in a gas move independently of one another.

Energy is required to stretch the springs and eventually break them. The **latent heat of fusion** and the **latent heat of vaporization** are the thermal equivalents of this energy. The latent heat of fusion describes the amount of energy needed to stretch the springs permanently. The latent heat of vaporization describes the amount of energy required to break the springs connecting the molecules. Since all substances differ in the strength of the restoring force holding their molecules together, each substance has unique latent heats of fusion and vaporization. The thermal energy needed to actually “break the springs” is much greater than that needed to “stretch the springs.” Consequently, the latent heat of vaporization of a substance is always greater than its latent heat of fusion.

SELF-CHECK 13A

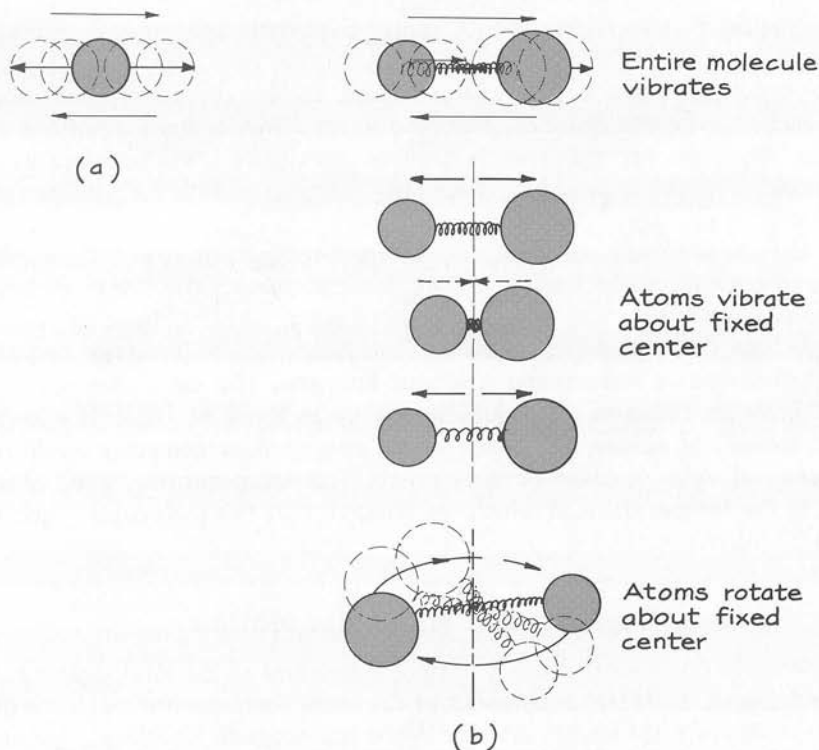
The latent heat of fusion of water (320 kilojoules per kilogram (kJ/kg)) is nearly three times that of alcohol (104 kJ/kg). Use the spring analogy to describe the difference in restoring forces present in the two substances.

INSIDE THE MOLECULE

In Chapter 10 we defined temperature as a measure of the average kinetic energy of the molecules in a material. Two substances at the same temperature have molecules with the same average kinetic energy. The pizza example suggests that different substances need different amounts of thermal energy to reach the same temperature. In order to understand both temperature and specific heat capacity at a molecular level, we need to look inside the molecule.

Atoms, Molecules, and Springs

A molecule can be composed of from one to hundreds of atoms. Like molecules bound together to form matter, atoms are glued together to form molecules by electrical restoring forces. Once again we can imagine the atoms within a molecule to be spherical balls held in place by springs. Figure 13-3 shows models for one-, two-, three-, and four-atom molecules. Since the restoring force holding atoms together in molecules is much greater than that hold-

**Figure 13-4**

How a molecule moves depends on the number of atoms it has. **(a)** The one-atom molecule can only move back and forth. **(b)** The two-atom molecule can move back and forth or the atoms within it can vibrate and rotate while the center of the molecule remains stationary.

ing molecules in solids and liquids, we rarely see molecules fall apart during thermal interactions. Instead we see changes in state.

As shown in Figure 13-4, the number of different ways a molecule can move depends on the number of atoms from which it is built. The one-atom molecule in (a) can move about only in straight lines as it vibrates about its central location. Two-atom molecules (Figure 13-4(b)) can move in three possible ways. The entire molecule can move back and forth in a straight line, as did the one-atom molecule. Additionally, the two-atom molecule can remain in a fixed location while its atoms rotate or vibrate about its center. A three-atom molecule has even more possibilities. As the number of atoms in a molecule increases, the number of possible ways that the molecule can move increases.

The total kinetic energy of the molecule depends upon all of the different ways in which it can move. In the one-atom molecule, the total kinetic energy of the molecule depends simply on its back-and-forth motion. In the two-atom molecule, its kinetic energy depends on all three motions—the back-and-forth motion of the molecule, as well as the rotation and vibration of the atoms within the molecule. The more complex the molecule, the more complex the distribution of kinetic energy among the different ways in which the molecule can move.

Temperature and Kinetic Energy

The simplest way to measure the temperature of a substance is to place a thermometer in it. The molecules in the substance collide with the molecules in the bulb of the thermometer. These collisions are similar to the interactions

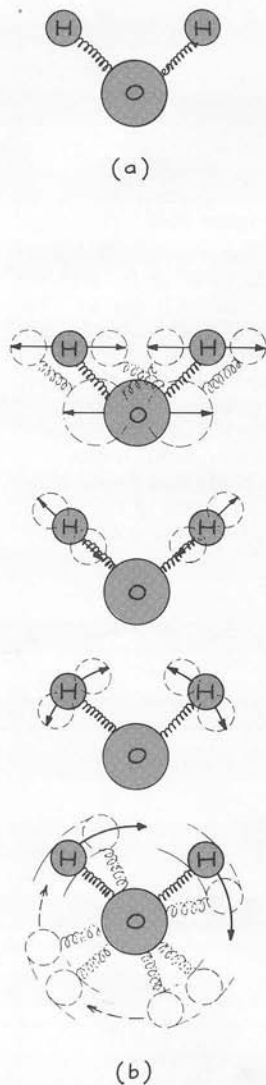


Figure 13-5

Water molecules consist of three atoms. Because of the number of different ways its atoms can move, water has a high specific heat capacity.

among billiard balls discussed in Chapter 5. Kinetic energy and momentum are transferred from the molecules in the substance to the molecules inside the thermometer. In collisions of this nature, the kinetic energy and momentum exchanged come primarily from the straight-line, or linear, motions of the atoms. When we say that two substances are at the same temperature, we are saying that the average kinetic energy associated with their linear motion is equal.

On any temperature scale, two different temperatures provide a qualitative comparison of the kinetic energy associated with the linear motions of molecules in a substance. The molecules of water at 60°C have more kinetic energy than those of water at 10°C . The Kelvin scale, however, provides a direct quantitative comparison of kinetic energies. The molecules of water at 60 K have six times as much kinetic energy as those at 10 K. If a material could actually be cooled to 0 K, the kinetic energy of its molecules would reach the smallest value it could possibly reach. This temperature, called absolute zero, is the temperature at which we imagine that the molecules reach minimum vibrations.

Specific Heat Capacity and Molecular Motion

Temperature does not provide a complete measure of the total kinetic energy of a substance. Different substances at the same temperature can have different amounts of total kinetic energy. While the average kinetic energy associated with their linear motions is the same, the energy associated with other motions can differ. **Specific heat capacities** describe these differences.

Complex molecules can do it all—move linearly, rotate, and vibrate—all simultaneously. Substances with high specific heat capacities consist of complex molecules that can vibrate and rotate in a variety of ways. Those with low specific heat capacities consist of much simpler molecules. For example, water consists of two hydrogen atoms and one oxygen atom, arranged as shown in Figure 13-5. Since its molecules can rotate and vibrate in a number of different ways, water has a high specific heat capacity. By contrast, helium consists of a one-atom molecule. All its thermal energy goes into the linear vibrations of the atom and consequently helium has an extremely low specific heat capacity.

In order to see how specific heat capacities vary with the complexity of the molecule, we need to compare the thermal energy absorbed per degree temperature change for samples consisting of equal numbers of molecules instead of equal masses. Table 13-1 provides such a comparison for one-, two-, and three-atom molecules. Each sample contains 6×10^{23} molecules of the specific gas. If we compare the amount of thermal energy absorbed per degree temperature change for the two one-atom gases, we find them to be equal. The two-atom gases absorb a little less than twice as much thermal energy per degree change as the one-atom gases. They vary from one another by no more than 1 J/K. Three-atom molecules require even more thermal energy per degree temperature change than either the two-atom or one-atom molecules. Here the energies become more diverse because the arrangement of the three atoms within the molecule can be more varied. Those with higher specific heat capacities, like sulfur dioxide, have more different ways in which

their molecules can move. The specific heat capacity of a substance depends on the number of different ways the atoms within the molecules can move.

Table 13-1 Comparison of Specific Heat Capacities

Number of Atoms in Molecule	Name of Substance	Atoms	Thermal Energy Absorbed per 1 K (J)*
One	Helium	One helium	12.5
	Argon	One argon	12.5
Two	Hydrogen	Two hydrogen	20.4
	Nitrogen	Two nitrogen	20.8
	Oxygen	Two oxygen	21.1
	Carbon monoxide	One carbon One oxygen	20.9
Three	Carbon dioxide	One carbon Two oxygen	28.5
	Sulfur dioxide	One sulfur Two oxygen	31.4
	Hydrogen sulfide	Two hydrogen One sulfur	26.0
	Steam (water)	Two hydrogen One oxygen	28.8

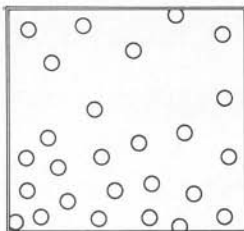
*Each sample of gas contained 6×10^{23} molecules.

SELF-CHECK 13B

The thermal energy absorbed by 6×10^{23} molecules of air per degree Kelvin is approximately 21 joules (J). Use Table 13-1 to determine whether air consists mostly of one-atom, two-atom, or three-atom molecules.

THERMAL ENERGY IN TRANSIT

The thermal energy in matter is stored in the electrical bonds and in the motions of the individual molecules. While restoring forces are important in holding



(a)



(b)

Figure 13-6

Gravitational forces produce an uneven distribution of molecules in the atmosphere. Faster-moving molecules will lose their energy more quickly near the bottom of a sample than near the top. Consequently, faster-moving molecules migrate upwards. Warmer air rises.

molecules together, the motion of the molecules is responsible for allowing thermal energy to be transferred from one substance to another or from one place to another. Let's consider the three transfer processes—convection, conduction, and radiation-absorption—in terms of the motions of individual molecules.

Convection

Convection is the primary process by which thermal energy is transferred in liquids and gases. Warmer samples of gas rise, taking thermal energy with them. The thermal energy is then transferred to other objects as the warmer samples cool. We can look at this process at the molecular level by considering the distribution of molecules in a fluid like air.

As shown in Figure 13-6, gravitational attraction between the earth and the air produces an uneven distribution of molecules. Each molecule is pulled downward toward the earth's surface. Collisions between molecules knock some of the molecules back upward, so that the air does not completely collapse. In spite of these collisions, more molecules are found near the bottom of the sample than near the top.

When we introduce thermal energy into this sample of gas, we are, in effect, adding rapidly moving molecules. These molecules will move in all directions, colliding with molecules in the air sample. Those that move downward run into a more dense layer of molecules than those that move upward. Consequently, the downward-moving molecules collide more frequently than the upward-moving molecules, losing energy with each collision. Within a relatively short time, only the energetic molecules that were initially moving upward are left. **Convection** occurs because the uneven molecular distribution created by gravitation favors upward rather than downward motion of the more energetic molecules.

SELF-CHECK 13C

In a gravity-free environment, such as Spacelab, the molecules in a sample of air will distribute themselves evenly throughout its volume. Use the molecular model to explain why convection will not occur in such an environment.

Conduction

The transfer of thermal energy by conduction occurs predominantly in a solid or at the interface between two substances—for example, air and the road. In solids, molecular motions are restricted by the large restoring forces between molecules. Consequently, thermal energy must be transferred within the aver-

age separation of molecules, rather than over the larger distances possible when molecules are actually free to move about.

If we heat one end of a solid, the average kinetic energy of the molecules near that end increases. Since the molecules in a solid are not free to move about, this increase in kinetic energy results in wider and more rapid vibrations of the molecules. Consequently, these molecules collide with their neighbors more often and transfer more thermal energy with each collision. The neighboring molecules then vibrate more rapidly, interacting with their neighboring molecules; and so on down the line. As with convection, the transfer of thermal energy by conduction is accomplished by molecular interactions. In conduction, however, the average position of each molecule remains fixed as the energy is transferred.

The **thermal resistivity** of a material, a measure of how effectively a material resists the transfer of thermal energy by conduction, depends on how easily the molecules transfer energy by interactions. This transfer, in turn, depends on the strength of the restoring force in the solid. Materials with a large resistivity have molecules with relatively weak restoring forces. The molecules tend to move about but interact only weakly with their neighbors. Materials with a small resistivity have molecules with large restoring forces. Since the molecules are so restricted in their motions, the transfer of thermal energy by interaction with their neighbors is much more efficient.

SELF-CHECK 13D

In Chapter 11 we discussed the excellent insulating ability of trapped air. Compare the restoring force of a gas (such as air) with that in a solid. Why would you expect still air to have a high thermal resistivity?

Radiation-Absorption

Thermal energy transfer by **radiation-absorption** is accomplished directly by electromagnetic interactions. The process involves the motion of atoms and molecules at the beginning (radiation) and end (absorption) of the process, but not during the actual transfer through space. The transfer process itself is accomplished by electromagnetic waves.

Atoms and molecules have electrical charges capable of exerting forces on other electrical charges. When a molecule vibrates, it exerts a vibrating force on other electrical charges. Through interaction at a distance, this force is capable of causing a molecule in a different material to vibrate. Consequently, the thermal energy present in the vibrations of molecules in the energy source is eventually transferred to the thermal energy in the vibrations of molecules in the energy receiver. Electrical forces are responsible for the

entire process. The energy travels through space in the form of electromagnetic waves.

SECOND LAW OF THERMODYNAMICS

We know that thermal energy never spontaneously moves from a cold object to a warmer object, that heat engines must always exhaust some thermal energy, and that divers are never spontaneously thrown from the water back up to the diving board. We find that the preferred direction of energy transformations can be described in terms of increasing entropy, a measure of the disorder of the system. To understand entropy at the molecular level, we need to add the concept of probability to our molecular model of matter.

Thermal Energy and Chance

The molecules moving in a material do not prefer one direction over another; they move about randomly. When two of them happen to be at the same place at the same time, they collide. Since their motions are random, the collisions are accidental. However, some collisions are more likely to occur than others. For example, the probability for a collision is high when lots of molecules are around and low when few molecules are nearby. (More automobile collisions happen on congested freeways than on country roads.) Since collisions between molecules are responsible for the transfer of thermal energy, this **probability** argument can be used to explain why thermal energy is transferred from warmer objects to colder objects.

A warm substance and a cold substance can each be characterized as a collection of randomly moving molecules. The molecules in the warmer substance have a greater average kinetic energy than those in the cooler substance. When a container of warm water is brought into contact with a container of cold water, molecules in each strike the container walls. Each collision leads to the transfer of some thermal energy. Energy flows both ways—from cold to hot and from hot to cold. Since the molecules in the warm water are, on the average, moving faster, they collide with the walls more frequently (Figure 13-7). The probability of a warm-water molecule colliding with the container is greater than that of a cold-water molecule. Consequently, more thermal energy is transferred from hot to cold than from cold to hot. The net flow of thermal energy is from warmer objects to colder objects.

We can also apply the concept of probability to the high diver who converted her gravitational potential energy into thermal energy. Conservation of energy permits the reversal of this process—the transfer of thermal energy from the water back to the diver, pushing her out of the water and back to the top of the diving board. In order for this to occur, a huge number of water molecules would have to travel upward simultaneously, strike the diver, and transfer sufficient kinetic energy to her so that she flies out of the water. While not impossible, such an occurrence is extremely unlikely. Since molecules move about randomly, the probability that all the molecules in, for

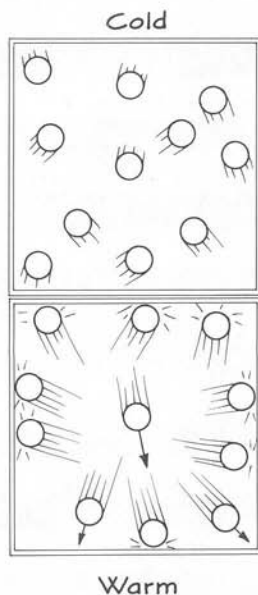
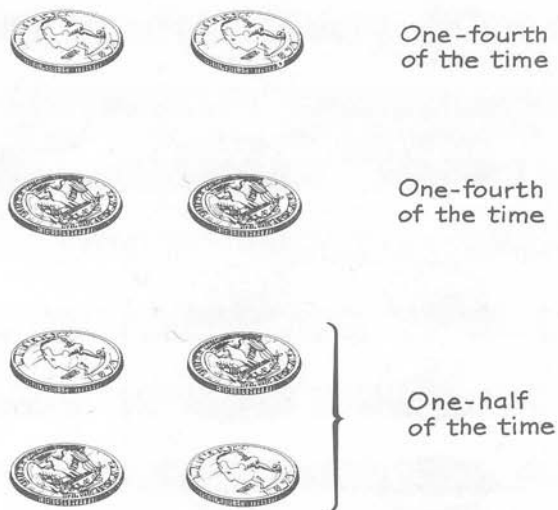


Figure 13-7

Because of their greater average speeds, molecules in warm water are more likely to hit the walls of their container than molecules in cold water. More thermal energy is transferred from warm to cold than from cold to warm.

**Figure 13-8**

We expect to get two heads one-fourth of the time, two tails one-fourth of the time, and one head and one tail one-half of the time.

example, a cubic meter of water move upward at the same time is exceedingly tiny.

Entropy and Chance

We have seen that entropy is a measure of the disorder of a system. Stacked poker chips represent a system with a relatively low entropy. Poker chips strewn about randomly represent a system with a higher entropy. Applied to the way in which energy is found in a system, entropy describes how orderly the energy is distributed. We can now examine the concept of entropy in terms of the probabilities of various molecular motions.

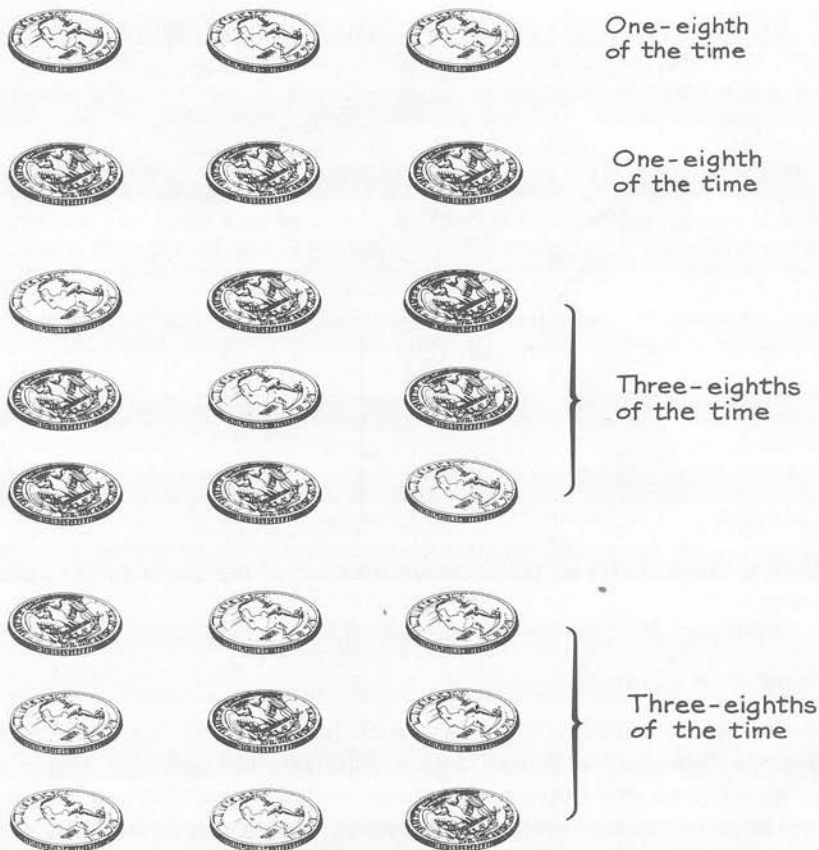
Consider a common example. Suppose you have a system of two identical coins. If you flip the two coins simultaneously, the outcomes possible for any given flip are shown in Figure 13-8. Since flipping coins is a random process, each outcome (HH, HT, TH, or TT) is equally likely. Out of a large number of flips, each combination will occur one-fourth of the time. Since we cannot distinguish between identical coins, the combinations of one head with one tail (HT or TH) are lumped together. We expect to get two heads one-fourth of the time, two tails one-fourth of the time and one head and one tail one-half of the time.

We can use the concept of entropy to describe the relative order of the various outcomes. The most ordered arrangement of the two coins is the two-head or two-tail outcome. The least ordered is one head and one tail. Consequently, a system in which both coins are heads or both coins are tails has a low entropy. A system with one head and one tail has a higher entropy.

If we compare our description of the entropy of each outcome with its probability of occurring, we see a pattern. The two most ordered arrangements (HH or TT) each occur only one-fourth of the time. The least ordered arrangement (HT or TH) occurs one-half of the time. This pattern becomes even more striking when we increase the number of coins to three, as shown

Figure 13-9

The arrangement with the most entropy (two heads and one tail or two tails and one head) are also the arrangements that are most likely to occur.



in Figure 13-9. The outcome with the most entropy is also the outcome most likely to occur.

SELF-CHECK 13E

Five outcomes are possible when we flip four coins: (a) all heads, (b) three heads and one tail, (c) two heads and two tails, (d) one head and three tails, or (e) all tails. Construct a figure like Figure 13-9 and use it to determine which outcome is the most probable one. Which outcome has the most entropy?

Second Law of Thermodynamics

The second law of thermodynamics states that in all processes the entropy of the system must increase. If we think of entropy in terms of high probabilities associated with high-entropy arrangements and low probabilities with low-entropy arrangements, the second law of thermodynamics states that systems move toward the most probable arrangement.

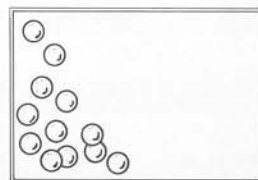
The distinction between spontaneous and nonspontaneous processes is one of probabilities. Spontaneous processes involve the transformation of a system from a less probable arrangement to a more probable arrangement. Nonspontaneous processes involve the reverse. While they can conceivably occur, nonspontaneous processes are highly improbable. The way in which we make them occur is to expand the system so that we include a spontaneous process. For example, thermal energy flows from hot to cold because a system in which thermal energy is evenly distributed is a more probable arrangement of molecules. We can make thermal energy flow from cold to hot but only by broadening our system to include entropy-increasing devices—electrical generating plants or refrigerators. Within a small section of the refrigerator, thermal energy flows from cold to hot. Within the entire kitchen, this energy is distributed over more molecules. The entropy of the entire system has increased.

A PHILOSOPHICAL CONCLUSION— OR IS IT A BEGINNING?

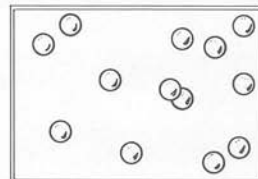
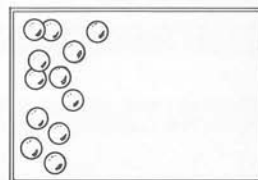
The most probable processes are those which move a system toward more disorder. Thermal energy represents the most disordered arrangement of energy within a system. The most probable state of any system, including the universe, is one in which all energy exists as thermal energy. The heat death of the universe discussed in Chapter 12 is our most probable end. Yet probabilities are not certainties; improbable events can and do occur.

Computer models based on our understanding of molecular motion enable us to investigate systems consisting of just a few molecules. Let's examine a simple system consisting of 10 molecules free to move about randomly in a room. We begin with a relatively ordered system—all 10 molecules are located in one-half of the room. As these molecules move about and collide with one another, they eventually distribute themselves throughout the entire room. However, as shown in Figure 13-10, eventually all the molecules once again find themselves in the same half of the room. While the system spends most of its time in the state in which the molecules are spread throughout the entire room, once every few minutes the molecules return briefly to a more ordered state. Given just 10 molecules, the system periodically experiences a spontaneous decrease in entropy.

If we increase the number of molecules in our room, the time during which the system remains in its disordered state increases to what seems to us to be eternity. One hundred molecules that begin on one side of the room spread out to fill the entire room in less than a minute. Then, for all practical purposes, they stay there! Very complicated calculations show that only once in every 1.5×10^{22} years will all 100 molecules return to one side of the room. Increasing the molecules in the room by a factor of 10 changes the frequency with which we observe the system decreasing its entropy from once every few minutes to once every 1.5×10^{22} years. If we calculated the probabilities for the actual number of molecules in the room (10^{30}), we would essentially never see the system spontaneously decrease its entropy.



Start

Less than
1 min. later

Still later

Figure 13-10

A computer simulation of ten molecules in a room shows that most of the time the molecules remain spread throughout the entire room. Periodically, however, they return briefly to just half the room.

One day our universe will reach its heat death. Then the bits and pieces of matter will bounce randomly about for billions and billions of years. During that time a probability—though exceedingly small—exists that these pieces of matter will again drift close enough to experience attractive forces and become more ordered. Atoms become molecules. Molecules become chemical elements. Chemical elements form the suns and the earths on which life can be sustained. A new universe comes into being. Will it happen after our universe has run down? Did it happen before our universe began?

CHAPTER SUMMARY

Matter is composed of atoms and molecules held together by restoring forces. A *restoring force* acts to return an atom or molecule to some central location. While the atom or molecule is free to move about to some extent, its average location appears fixed. Three types of restoring forces characterize the three states of matter. Solids experience the strongest restoring force, liquids have a somewhat weaker restoring force, and gases are characterized as having essentially no restoring force. The thermal energy required to break the restoring force characteristic of the state of matter is the *latent heat of fusion* (solids to liquids) and the *latent heat of vaporization* (liquids to gases).

Molecules can be composed of any number of atoms. The number of atoms in the molecule and the way in which these atoms are arranged determine the different ways in which a molecule can move. *Temperature* generally measures the average kinetic energy of a molecule as it moves along a straight line. Other molecular motions include vibrations and rotations of atoms within the molecule. *Specific heat capacity* depends upon these different motions. The higher the specific heat capacity of a substance, the more thermal energy is absorbed into motions other than the linear kinetic energy described by temperature.

Convection, conduction, and radiation-absorption can be described in terms of the motion of atoms and molecules. *Convection* arises from the uneven distribution of molecules in a fluid such as air or water, which is caused by the gravitational forces exerted by the earth. As thermal energy is added to the fluid, the more energetic molecules tend to drift upward because there are fewer molecules with which to collide. *Conduction* arises from collisions between neighboring atoms or molecules in the solid. The greater the restoring force, the lower the thermal resistivity of the substance. *Radiation-absorption* occurs when the vibration of electromagnetic waves is transferred to the vibration of atoms and molecules.

Entropy and the *second law of thermodynamics* arise from the application of the laws of probability to the motion and collisions between atoms and molecules. The most disorderly arrangement of energy within matter is also the most probable state of matter. Consequently, all processes lead to increasing disorder because disorderly states are the most probable states. Processes can proceed from disorder to order, but such processes are extremely rare.

ANSWERS TO SELF-CHECKS

- 13A.** The stronger the restoring force between molecules, the more difficult it is to stretch the springs permanently, allowing the solid to become a liquid. Since water has a higher latent heat of fusion than alcohol, the restoring force between water molecules must be greater than the restoring force between alcohol molecules.
- 13B.** A thermal energy of 21 J per 6×10^{23} molecules is approximately equal to those listed for two-atom molecules. Air must consist mostly of two-atom gases. (Air is roughly 78% nitrogen and 21% oxygen. Both exist as two-atom molecules.)
- 13C.** If the molecules in a sample of air are spread about evenly, then a more energetic molecule has the same likelihood of colliding with molecules in all directions. Consequently, more energetic molecules will not rise and convection will not occur.
- 13D.** Gases have extremely small restoring forces. Consequently, gas molecules will not transfer energy effectively through conduction.
- 13E.** The most probable arrangement is two heads and two tails. It will occur, on the average, 6 out of 16 trials. This arrangement also has the most entropy.

PROBLEMS AND QUESTIONS

A. Review of Chapter Material

- A1. What are the properties of a restoring force?
- A2. Rank the three states of matter in order of the strengths of their restoring forces. Use the strength of the restoring force to describe why a liquid has no definite shape and a gas has neither a definite shape nor a definite volume.
- A3. Use the spring analogy for molecular forces to describe why energy is needed to change states.
- A4. How do the possible motions of a two-atom molecule differ from those of a one-atom molecule?
- A5. To what molecular motion is temperature related?
- A6. Why does the specific heat capacity of a substance depend on the number of atoms per molecule?
- A7. Why is gravity important in convection?

- A8. How is the thermal resistivity of a solid related to the strength of the restoring force?
- A9. Use a probability argument to explain why entropy does not decrease.
- A10. State the second law of thermodynamics in terms of molecular motions and probabilities.

B. Using the Chapter Material

- B1. Use the molecular model to explain why more energy is needed to increase the temperature of 2 kg of water by 10°C than is needed to increase the temperature of 1 kg of water by 10°C .
- B2. Use the molecular model of matter to describe why the total energy required to change a state depends on the mass of the substance.
- B3. Listed below are the energies needed to increase the temperature of 6×10^{23} molecules of three gases by 1K. How many

atoms would you expect to be present in each? How did you reach your conclusion?

Mercury:	12.52 J
Nitric oxide:	20.7 J
Sodium:	12.5 J

B4. Smoke particles are more massive than air molecules, yet smoke rises. Use the molecular model of matter to explain why.

B5. Listed below are the thermal resistivities of three solids. Rank them in order from smallest to largest restoring force. Explain your ranking in terms of the molecular model of matter.

Silver:	$0.0023 \text{ m}^2 \cdot \text{s} \cdot ^\circ\text{C}/\text{J} \cdot \text{m}$
Gold:	$0.0030 \text{ m}^2 \cdot \text{s} \cdot ^\circ\text{C}/\text{J} \cdot \text{m}$
Iron:	$0.0125 \text{ m}^2 \cdot \text{s} \cdot ^\circ\text{C}/\text{J} \cdot \text{m}$

B6. We have seen that the R-value depends on the thickness of a substance. Explain why in terms of the number of molecules between the energy source and the energy receiver.

B7. A neutron is a small particle that has no electric charge. Can it absorb thermal energy by the radiation-absorption process?

B8. Suppose you mix 1 kg of water at 300 K with 1 kg of water at 350 K. We know that the final temperature will be 325 K. Use the molecular model of matter to explain how this final temperature comes about.

B9. Since air molecules are moving about continuously, they could all move away from you right now and leave you with no air to breathe. Why have you never heard of this occurring before?

B10. Suppose you put a red marble and a green marble on a vibrating table. The table's vibrations keep the marbles constantly moving. Would you expect the arrangement of red on the right half, green on the left half to occur reasonably often? If you place 50 red and 50 green marbles on the table, would the arrangement of all red on one side and all green on the other side occur very often?

C. Extensions to New Situations

C1. In 1827 a Scottish botanist, Robert Brown, observed that small particles of pollen were always moving and the direction in which they were moving frequently changed. This

motion is now called *Brownian motion* and was not explained adequately until the beginning of this century. How can Brownian motion be explained in terms of interactions between air molecules and pollen particles?

C2. Your brother walks into a room just after applying after-shave lotion. You notice it very quickly.

a. Describe what must happen at the molecular level in order for you to smell the lotion.

b. If the after-shave lotion were spread on a block of ice instead of your brother's face, would you smell it as rapidly?

C3. Evaporation occurs when molecules in a liquid break free from the liquid and move into the air.

a. Of all molecules in a liquid, which are most likely to overcome the restoring force—those with high kinetic energy or those with low kinetic energy? Why?

b. What will happen to the temperature of the remaining liquid?

c. Alcohol evaporates more rapidly than water at the same temperature. What does that tell you about the strength of the restoring forces acting on water compared to alcohol?

d. Use the molecular model to explain why evaporation of sweat cools your body.

C4. The temperature of a pot of boiling water remains at 100°C until all the water has turned to steam.

a. Which molecules are likely to become steam—high-energy or low-energy ones?

b. When a molecule has enough energy to become steam, what happens to it?

c. As molecules leave, where does the thermal energy that has been added to the water go?

d. In terms of molecular motion, why does the temperature remain constant during boiling?

C5. A metal rod has one end in a flame and the other end 3 meters (m) directly above the flame. If you place one hand at the top of the rod, you will feel heat conducted through the rod before you feel it transferred through the surrounding air by convection. Why?

C6. In general, solids expand as their tempera-