Thermodynamics

PART

A bubble in one of the many mud pots in Yellowstone National Park is caught just at the moment of popping. A mud pot is a pool of bubbling hot mud that demonstrates the existence of thermodynamic processes below the Earth's surface. (© Adambooth/ Dreamstime.com)

We now direct our attention to the study of thermodynamics, which involves situations in which the temperature or state (solid, liquid, gas) of a system changes due to energy transfers. As we shall see, thermodynamics is very successful in explaining the bulk properties of matter and the correlation between these properties and the mechanics of atoms and molecules.

Historically, the development of thermodynamics paralleled the development of the atomic theory of matter. By the 1820s, chemical experiments had provided solid evidence for the existence of atoms. At that time, scientists recognized that a connection between thermodynamics and the structure of matter must exist. In 1827, botanist Robert Brown reported that grains of pollen suspended in a liquid move erratically from one place to another as if under constant agitation. In 1905, Albert Einstein used kinetic theory to explain the cause of this erratic motion, known today as *Brownian motion*. Einstein explained this phenomenon by assuming the grains are under constant bombardment by "invisible" molecules in the liquid, which themselves move erratically. This explanation gave scientists insight into the concept of molecular motion and gave credence to the idea that matter is made up of atoms. A connection was thus forged between the everyday world and the tiny, invisible building blocks that make up this world.

Thermodynamics also addresses more practical questions. Have you ever wondered how a refrigerator is able to cool its contents, or what types of transformations occur in a power plant or in the engine of your automobile, or what happens to the kinetic energy of a moving object when the object comes to rest? The laws of thermodynamics can be used to provide explanations for these and other phenomena.

CHAPTER 19

- 19.1 Temperature and the Zeroth Law of Thermodynamics
- **19.2** Thermometers and the Celsius Temperature Scale
- 19.3 The Constant-Volume Gas Thermometer and the Absolute Temperature Scale
- **19.4** Thermal Expansion of Solids and Liquids
- 19.5 Macroscopic Description of an Ideal Gas

Temperature



Why would someone designing a pipeline include these strange loops? Pipelines carrying liquids often contain such loops to allow for expansion and contraction as the temperature changes. We will study thermal expansion in this chapter. (© Lowell Georgia/CORBIS) In our study of mechanics, we carefully defined such concepts as *mass*, *force*, and *kinetic energy* to facilitate our quantitative approach. Likewise, a quantitative description of thermal phenomena requires careful definitions of such important terms as *temperature*, *heat*, and *internal energy*. This chapter begins with a discussion of temperature.

Next, when studying thermal phenomena, we consider the importance of the particular substance we are investigating. For example, gases expand appreciably when heated, whereas liquids and solids expand only slightly.

This chapter concludes with a study of ideal gases on the macroscopic scale. Here, we are concerned with the relationships among such quantities as pressure, volume, and temperature of a gas. In Chapter 21, we shall examine gases on a microscopic scale, using a model that represents the components of a gas as small particles.

19.1 Temperature and the Zeroth Law of Thermodynamics

We often associate the concept of temperature with how hot or cold an object feels when we touch it. In this way, our senses provide us with a qualitative indication of temperature. Our senses, however, are unreliable and often mislead us. For exam-

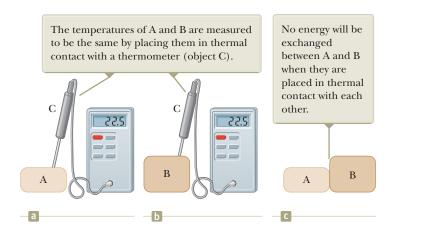


Figure 19.1 The zeroth law of thermodynamics.

ple, if you stand in bare feet with one foot on carpet and the other on an adjacent tile floor, the tile feels colder than the carpet *even though both are at the same temperature.* The two objects feel different because tile transfers energy by heat at a higher rate than carpet does. Your skin "measures" the rate of energy transfer by heat rather than the actual temperature. What we need is a reliable and reproducible method for measuring the relative hotness or coldness of objects rather than the rate of energy transfer. Scientists have developed a variety of thermometers for making such quantitative measurements.

Two objects at different initial temperatures eventually reach some intermediate temperature when placed in contact with each other. For example, when hot water and cold water are mixed in a bathtub, energy is transferred from the hot water to the cold water and the final temperature of the mixture is somewhere between the initial hot and cold temperatures.

Imagine that two objects are placed in an insulated container such that they interact with each other but not with the environment. If the objects are at different temperatures, energy is transferred between them, even if they are initially not in physical contact with each other. The energy-transfer mechanisms from Chapter 8 that we will focus on are heat and electromagnetic radiation. For purposes of this discussion, let's assume two objects are in **thermal contact** with each other if energy can be exchanged between them by these processes due to a temperature difference. **Thermal equilibrium** is a situation in which two objects would not exchange energy by heat or electromagnetic radiation if they were placed in thermal contact.

Let's consider two objects A and B, which are not in thermal contact, and a third object C, which is our thermometer. We wish to determine whether A and B are in thermal equilibrium with each other. The thermometer (object C) is first placed in thermal contact with object A until thermal equilibrium is reached¹ as shown in Figure 19.1a. From that moment on, the thermometer's reading remains constant and we record this reading. The thermometer is then removed from object A and placed in thermal contact with object B as shown in Figure 19.1b. The reading is again recorded after thermal equilibrium is reached. If the two readings are the same, we can conclude that object A and object B are in thermal equilibrium with each other. If they are placed in contact with each other as in Figure 19.1c, there is no exchange of energy between them.

¹We assume a negligible amount of energy transfers between the thermometer and object A in the time interval during which they are in thermal contact. Without this assumption, which is also made for the thermometer and object B, the measurement of the temperature of an object disturbs the system so that the measured temperature is different from the initial temperature of the object. In practice, whenever you measure a temperature with a thermometer, you measure the disturbed system, not the original system.

We can summarize these results in a statement known as the **zeroth law of ther-modynamics** (the law of equilibrium):

Zeroth law of thermodynamics If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

This statement can easily be proved experimentally and is very important because it enables us to define temperature. We can think of **temperature** as the property that determines whether an object is in thermal equilibrium with other objects. Two objects in thermal equilibrium with each other are at the same temperature. Conversely, if two objects have different temperatures, they are not in thermal equilibrium with each other. We now know that temperature is something that determines whether or not energy will transfer between two objects in thermal contact. In Chapter 21, we will relate temperature to the mechanical behavior of molecules.

O uick Quiz 19.1 Two objects, with different sizes, masses, and temperatures, are placed in thermal contact. In which direction does the energy travel? (a) Energy travels from the larger object to the smaller object. (b) Energy travels from the object with more mass to the one with less mass. (c) Energy travels from the

object at higher temperature to the object at lower temperature.

19.2 Thermometers and the Celsius Temperature Scale

Thermometers are devices used to measure the temperature of a system. All thermometers are based on the principle that some physical property of a system changes as the system's temperature changes. Some physical properties that change with temperature are (1) the volume of a liquid, (2) the dimensions of a solid, (3) the pressure of a gas at constant volume, (4) the volume of a gas at constant pressure, (5) the electric resistance of a conductor, and (6) the color of an object.

A common thermometer in everyday use consists of a mass of liquid—usually mercury or alcohol—that expands into a glass capillary tube when heated (Fig. 19.2). In this case, the physical property that changes is the volume of a liquid. Any temperature change in the range of the thermometer can be defined as being proportional to the change in length of the liquid column. The thermometer can be calibrated by placing it in thermal contact with a natural system that remains

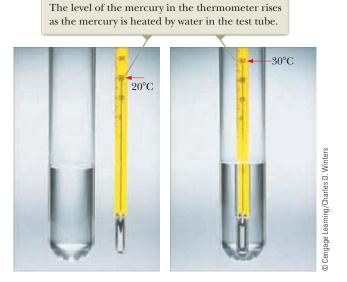


Figure 19.2 A mercury thermometer before and after increasing its temperature.

at constant temperature. One such system is a mixture of water and ice in thermal equilibrium at atmospheric pressure. On the **Celsius temperature scale**, this mixture is defined to have a temperature of zero degrees Celsius, which is written as 0°C; this temperature is called the *ice point* of water. Another commonly used system is a mixture of water and steam in thermal equilibrium at atmospheric pressure; its temperature is defined as 100°C, which is the *steam point* of water. Once the liquid levels in the thermometer have been established at these two points, the length of the liquid column between the two points is divided into 100 equal segments to create the Celsius scale. Therefore, each segment denotes a change in temperature of one Celsius degree.

Thermometers calibrated in this way present problems when extremely accurate readings are needed. For instance, the readings given by an alcohol thermometer calibrated at the ice and steam points of water might agree with those given by a mercury thermometer only at the calibration points. Because mercury and alcohol have different thermal expansion properties, when one thermometer reads a temperature of, for example, 50°C, the other may indicate a slightly different value. The discrepancies between thermometers are especially large when the temperatures to be measured are far from the calibration points.²

An additional practical problem of any thermometer is the limited range of temperatures over which it can be used. A mercury thermometer, for example, cannot be used below the freezing point of mercury, which is -39° C, and an alcohol thermometer is not useful for measuring temperatures above 85°C, the boiling point of alcohol. To surmount this problem, we need a universal thermometer whose readings are independent of the substance used in it. The gas thermometer, discussed in the next section, approaches this requirement.

19.3 The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

One version of a gas thermometer is the constant-volume apparatus shown in Figure 19.3. The physical change exploited in this device is the variation of pressure of a fixed volume of gas with temperature. The flask is immersed in an ice-water bath, and mercury reservoir *B* is raised or lowered until the top of the mercury in column *A* is at the zero point on the scale. The height *h*, the difference between the mercury levels in reservoir *B* and column *A*, indicates the pressure in the flask at 0° C by means of Equation 14.4, $P = P_0 + \rho gh$.

The flask is then immersed in water at the steam point. Reservoir *B* is readjusted until the top of the mercury in column *A* is again at zero on the scale, which ensures that the gas's volume is the same as it was when the flask was in the ice bath (hence the designation "constant-volume"). This adjustment of reservoir *B* gives a value for the gas pressure at 100°C. These two pressure and temperature values are then plotted as shown in Figure 19.4. The line connecting the two points serves as a calibration curve for unknown temperatures. (Other experiments show that a linear relationship between pressure and temperature is a very good assumption.) To measure the temperature of a substance, the gas flask of Figure 19.3 is placed in thermal contact with the substance and the height of reservoir *B* is adjusted until the top of the mercury column in *A* is at zero on the scale. The height of the mercury column in *B* indicates the pressure of the gas; knowing the pressure, the temperature of the substance is found using the graph in Figure 19.4.

Now suppose temperatures of different gases at different initial pressures are measured with gas thermometers. Experiments show that the thermometer readings are nearly independent of the type of gas used as long as the gas pressure is low and the temperature is well above the point at which the gas liquefies

²Two thermometers that use the same liquid may also give different readings, due in part to difficulties in constructing uniform-bore glass capillary tubes. The volume of gas in the flask is kept constant by raising or lowering reservoir *B* to keep the mercury level in column *A* constant.

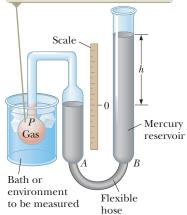


Figure 19.3 A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath.

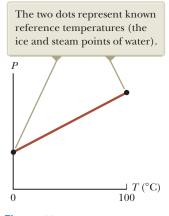


Figure 19.4 A typical graph of pressure versus temperature taken with a constant-volume gas thermometer.

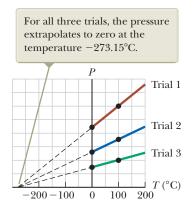


Figure 19.5 Pressure versus temperature for experimental trials in which gases have different pressures in a constant-volume gas thermometer.

Pitfall Prevention 19.1

A Matter of Degree Notations for temperatures in the Kelvin scale do not use the degree sign. The unit for a Kelvin temperature is simply "kelvins" and not "degrees Kelvin."

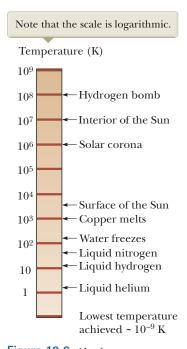


Figure 19.6 Absolute temperatures at which various physical processes occur.

(Fig. 19.5). The agreement among thermometers using various gases improves as the pressure is reduced.

If we extend the straight lines in Figure 19.5 toward negative temperatures, we find a remarkable result: in every case, the pressure is zero when the temperature is -273.15° C! This finding suggests some special role that this particular temperature must play. It is used as the basis for the **absolute temperature scale**, which sets -273.15° C as its zero point. This temperature is often referred to as **absolute zero**. It is indicated as a zero because at a lower temperature, the pressure of the gas would become negative, which is meaningless. The size of one degree on the absolute temperature scale is chosen to be identical to the size of one degree on the Celsius scale. Therefore, the conversion between these temperatures is

$$T_{\rm C} = T - 273.15$$
 (19.1)

where $T_{\rm C}$ is the Celsius temperature and T is the absolute temperature.

Because the ice and steam points are experimentally difficult to duplicate and depend on atmospheric pressure, an absolute temperature scale based on two new fixed points was adopted in 1954 by the International Committee on Weights and Measures. The first point is absolute zero. The second reference temperature for this new scale was chosen as the **triple point of water**, which is the single combination of temperature and pressure at which liquid water, gaseous water, and ice (solid water) coexist in equilibrium. This triple point occurs at a temperature of 0.01°C and a pressure of 4.58 mm of mercury. On the new scale, which uses the unit *kelvin*, the temperature of water at the triple point was set at 273.16 kelvins, abbreviated 273.16 K. This choice was made so that the old absolute temperature scale based on the ice and steam points would agree closely with the new scale based on the triple point. This new absolute temperature, the **kelvin**, which is defined to be 1/273.16 of the difference between absolute zero and the temperature of the triple point of water.

Figure 19.6 gives the absolute temperature for various physical processes and structures. The temperature of absolute zero (0 K) cannot be achieved, although laboratory experiments have come very close, reaching temperatures of less than one nanokelvin.

The Celsius, Fahrenheit, and Kelvin Temperature Scales³

Equation 19.1 shows that the Celsius temperature $T_{\rm C}$ is shifted from the absolute (Kelvin) temperature T by 273.15°. Because the size of one degree is the same on the two scales, a temperature difference of 5°C is equal to a temperature difference of 5 K. The two scales differ only in the choice of the zero point. Therefore, the ice-point temperature on the Kelvin scale, 273.15 K, corresponds to 0.00°C, and the Kelvin-scale steam point, 373.15 K, is equivalent to 100.00°C.

A common temperature scale in everyday use in the United States is the **Fahrenheit scale**. This scale sets the temperature of the ice point at 32°F and the temperature of the steam point at 212°F. The relationship between the Celsius and Fahrenheit temperature scales is

$$T_{\rm F} = \frac{9}{5}T_{\rm C} + 32^{\circ}{\rm F}$$
 (19.2)

We can use Equations 19.1 and 19.2 to find a relationship between changes in temperature on the Celsius, Kelvin, and Fahrenheit scales:

$$\Delta T_{\rm C} = \Delta T = \frac{5}{9} \Delta T_{\rm F} \tag{19.3}$$

Of these three temperature scales, only the Kelvin scale is based on a true zero value of temperature. The Celsius and Fahrenheit scales are based on an arbitrary zero associated with one particular substance, water, on one particular planet, the

³Named after Anders Celsius (1701–1744), Daniel Gabriel Fahrenheit (1686–1736), and William Thomson, Lord Kelvin (1824–1907), respectively.

Earth. Therefore, if you encounter an equation that calls for a temperature T or that involves a ratio of temperatures, you *must* convert all temperatures to kelvins. If the equation contains a change in temperature ΔT , using Celsius temperatures will give you the correct answer, in light of Equation 19.3, but it is always *safest* to convert temperatures to the Kelvin scale.

() uick Quiz 19.2 Consider the following pairs of materials. Which pair represents two materials, one of which is twice as hot as the other? (a) boiling water at 100°C, a glass of water at 50°C (b) boiling water at 100°C, frozen methane at

- -50° C (c) an ice cube at -20° C, flames from a circus fire-eater at 233° C
- (d) none of those pairs

Example 19.1 Converting Temperatures

On a day when the temperature reaches 50°F, what is the temperature in degrees Celsius and in kelvins?

SOLUTION

Conceptualize In the United States, a temperature of 50°F is well understood. In many other parts of the world, however, this temperature might be meaningless because people are familiar with the Celsius temperature scale.

Categorize This example is a simple substitution problem.

Solve Equation 19.2 for the Celsius temperature and substitute numerical values:

Use Equation 19.1 to find the Kelvin temperature:

 $T = T_{\rm C} + 273.15 = 10^{\circ}{\rm C} + 273.15 = 283 {\rm K}$

 $T_{\rm C} = \frac{5}{9}(T_{\rm F} - 32) = \frac{5}{9}(50 - 32) = 10^{\circ}{\rm C}$

A convenient set of weather-related temperature equivalents to keep in mind is that 0°C is (literally) freezing at 32°F, 10°C is cool at 50°F, 20°C is room temperature, 30°C is warm at 86°F, and 40°C is a hot day at 104°F.

19.4 Thermal Expansion of Solids and Liquids

Our discussion of the liquid thermometer makes use of one of the best-known changes in a substance: as its temperature increases, its volume increases. This phenomenon, known as **thermal expansion**, plays an important role in numerous engineering applications. For example, thermal-expansion joints such as those shown in Figure 19.7 must be included in buildings, concrete highways, railroad tracks,

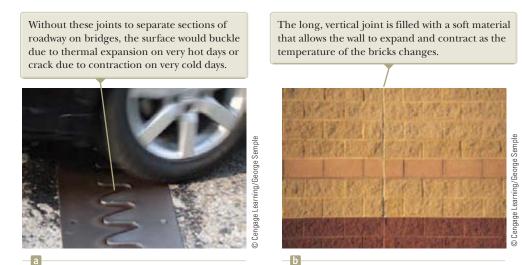


Figure 19.7 Thermal-expansion joints in (a) bridges and (b) walls.

brick walls, and bridges to compensate for dimensional changes that occur as the temperature changes.

Thermal expansion is a consequence of the change in the *average* separation between the atoms in an object. To understand this concept, let's model the atoms as being connected by stiff springs as discussed in Section 15.3 and shown in Figure 15.11b. At ordinary temperatures, the atoms in a solid oscillate about their equilibrium positions with an amplitude of approximately 10^{-11} m and a frequency of approximately 10^{13} Hz. The average spacing between the atoms is about 10^{-10} m. As the temperature of the solid increases, the atoms oscillate with greater amplitudes; as a result, the average separation between them increases.⁴ Consequently, the object expands.

If thermal expansion is sufficiently small relative to an object's initial dimensions, the change in any dimension is, to a good approximation, proportional to the first power of the temperature change. Suppose an object has an initial length L_i along some direction at some temperature and the length changes by an amount ΔL for a change in temperature ΔT . Because it is convenient to consider the fractional change in length per degree of temperature change, we define the **average coefficient of linear expansion** as

$$\alpha \equiv \frac{\Delta L/L_i}{\Delta T}$$

Experiments show that α is constant for small changes in temperature. For purposes of calculation, this equation is usually rewritten as

 $\Delta L = \alpha L_i \Delta T \tag{19.4}$

Thermal expansion in one dimension

or as

Pitfall Prevention 19.2

Do Holes Become Larger or Smaller? When an object's temperature is raised, every linear dimension increases in size. That includes any holes in the material, which expand in the same way as if the hole were filled with the material as shown in Figure 19.8.

> Thermal expansion in three dimensions

$$L_f - L_i = \alpha L_i (T_f - T_i)$$
(19.5)

where L_f is the final length, T_i and T_f are the initial and final temperatures, respectively, and the proportionality constant α is the average coefficient of linear expansion for a given material and has units of (°C)⁻¹. Equation 19.4 can be used for both thermal expansion, when the temperature of the material increases, and thermal contraction, when its temperature decreases.

It may be helpful to think of thermal expansion as an effective magnification or as a photographic enlargement of an object. For example, as a metal washer is heated (Fig. 19.8), all dimensions, including the radius of the hole, increase according to Equation 19.4. A cavity in a piece of material expands in the same way as if the cavity were filled with the material.

Table 19.1 lists the average coefficients of linear expansion for various materials. For these materials, α is positive, indicating an increase in length with increasing temperature. That is not always the case, however. Some substances—calcite (CaCO₃) is one example—expand along one dimension (positive α) and contract along another (negative α) as their temperatures are increased.

Because the linear dimensions of an object change with temperature, it follows that surface area and volume change as well. The change in volume is proportional to the initial volume V_i and to the change in temperature according to the relationship

$$\Delta V = \beta V_i \, \Delta T \tag{19.6}$$

where β is the **average coefficient of volume expansion.** To find the relationship between β and α , assume the average coefficient of linear expansion of the solid is the same in all directions; that is, assume the material is *isotropic*. Consider a solid box of dimensions ℓ , w, and h. Its volume at some temperature T_i is $V_i = \ell wh$. If the

⁴More precisely, thermal expansion arises from the *asymmetrical* nature of the potential energy curve for the atoms in a solid as shown in Figure 15.11a. If the oscillators were truly harmonic, the average atomic separations would not change regardless of the amplitude of vibration.

for Some Materials Near Room Temperature			
Material (Solids)	Average Linear Expansion Coefficient $(\alpha)(^{\circ}C)^{-1}$	Material (Liquids and Gases)	Average Volume Expansion Coefficient $(\beta)(^{\circ}C)^{-1}$
Aluminum	24×10^{-6}	Acetone	$1.5 imes10^{-4}$
Brass and bronze	$19 imes 10^{-6}$	Alcohol, ethyl	$1.12 imes 10^{-4}$
Concrete	$12 imes 10^{-6}$	Benzene	$1.24 imes 10^{-4}$
Copper	$17 imes 10^{-6}$	Gasoline	$9.6 imes10^{-4}$
Glass (ordinary)	$9 imes 10^{-6}$	Glycerin	$4.85 imes10^{-4}$
Glass (Pyrex)	$3.2 imes 10^{-6}$	Mercury	$1.82 imes 10^{-4}$
Invar (Ni–Fe alloy)	$0.9 imes 10^{-6}$	Turpentine	$9.0 imes 10^{-4}$
Lead	$29 imes 10^{-6}$	Air ^a at 0°C	$3.67 imes10^{-3}$
Steel	11×10^{-6}	Helium ^a	$3.665 imes10^{-3}$

Average Expansion Coefficients

Table 19.1

^aGases do not have a specific value for the volume expansion coefficient because the amount of expansion depends on the type of process through which the gas is taken. The values given here assume the gas undergoes an expansion at constant pressure.

temperature changes to $T_i + \Delta T$, its volume changes to $V_i + \Delta V$, where each dimension changes according to Equation 19.4. Therefore,

$$V_i + \Delta V = (\ell + \Delta \ell)(w + \Delta w)(h + \Delta h)$$

= $(\ell + \alpha \ell \Delta T)(w + \alpha w \Delta T)(h + \alpha h \Delta T)$
= $\ell w h (1 + \alpha \Delta T)^3$
= $V_i [1 + 3\alpha \Delta T + 3(\alpha \Delta T)^2 + (\alpha \Delta T)^3]$

Dividing both sides by V_i and isolating the term $\Delta V/V_i$, we obtain the fractional change in volume:

$$\frac{\Delta V}{V_i} = 3\alpha \,\Delta T + 3(\alpha \,\Delta T)^2 + (\alpha \,\Delta T)^3$$

Because $\alpha \Delta T \ll 1$ for typical values of $\Delta T \ll 100^{\circ}$ C), we can neglect the terms $3(\alpha \Delta T)^2$ and $(\alpha \Delta T)^3$. Upon making this approximation, we see that

$$\frac{\Delta V}{V_i} = 3\alpha \,\Delta T \quad \rightarrow \quad \Delta V = (3\alpha) V_i \,\Delta T$$

Comparing this expression to Equation 19.6 shows that

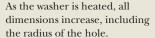
$$\beta = 3\alpha$$

In a similar way, you can show that the change in area of a rectangular plate is given by $\Delta A = 2\alpha A_i \Delta T$ (see Problem 61).

A simple mechanism called a *bimetallic strip*, found in practical devices such as mechanical thermostats, uses the difference in coefficients of expansion for different materials. It consists of two thin strips of dissimilar metals bonded together. As the temperature of the strip increases, the two metals expand by different amounts and the strip bends as shown in Figure 19.9.

uick Quiz 19.3 If you are asked to make a very sensitive glass thermometer,
 which of the following working liquids would you choose? (a) mercury (b) alcohol (c) gasoline (d) glycerin

uick Quiz 19.4 Two spheres are made of the same metal and have the same radius, but one is hollow and the other is solid. The spheres are taken through the same temperature increase. Which sphere expands more? (a) The solid sphere expands more. (b) The hollow sphere expands more. (c) They expand by
 the same amount. (d) There is not enough information to say.



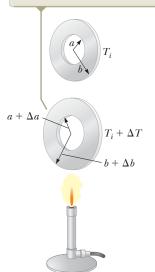


Figure 19.8 Thermal expansion of a homogeneous metal washer. (The expansion is exaggerated in this figure.)

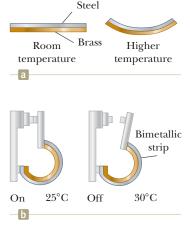


Figure 19.9 (a) A bimetallic strip bends as the temperature changes because the two metals have different expansion coefficients. (b) A bimetallic strip used in a thermostat to break or make electrical contact.

Example 19.2 Expansion of a Railroad Track

A segment of steel railroad track has a length of 30.000 m when the temperature is 0.0°C.

(A) What is its length when the temperature is 40.0° C?

SOLUTION

Conceptualize Because the rail is relatively long, we expect to obtain a measurable increase in length for a 40°C temperature increase.

Categorize We will evaluate a length increase using the discussion of this section, so this part of the example is a substitution problem.

Use Equation 19.4 and the value of the coefficient of linear expansion from Table 19.1:

 $\Delta L = \alpha L_i \Delta T = [11 \times 10^{-6} (^{\circ}\text{C})^{-1}](30.000 \text{ m})(40.0^{\circ}\text{C}) = 0.013 \text{ m}$

Find the new length of the track:

 $L_f = 30.000 \text{ m} + 0.013 \text{ m} = 30.013 \text{ m}$

(B) Suppose the ends of the rail are rigidly clamped at 0.0°C so that expansion is prevented. What is the thermal stress set up in the rail if its temperature is raised to 40.0°C?

SOLUTION

Categorize This part of the example is an analysis problem because we need to use concepts from another chapter.

Analyze The thermal stress is the same as the tensile stress in the situation in which the rail expands freely and is then compressed with a mechanical force F back to its original length.

Find the tensile stress from Equation 12.6 using Young's modulus for steel from Table 12.1:

Tensile stress $= \frac{F}{A} = Y \frac{\Delta L}{L_i}$	
$\frac{F}{A} = (20 \times 10^{10} \mathrm{N/m^2}) \left(\frac{0.013 \mathrm{m}}{30.000 \mathrm{m}}\right) = 8.7 \times 10^7 \mathrm{N/m^2}$	

Finalize The expansion in part (A) is 1.3 cm. This expansion is indeed measurable as predicted in the Conceptualize step. The thermal stress in part (B) can be avoided by leaving small expansion gaps between the rails.

WHAT IF? What if the temperature drops to -40.0° C? What is the length of the unclamped segment?

Answer The expression for the change in length in Equation 19.4 is the same whether the temperature increases or decreases. Therefore, if there is an increase in length of 0.013 m when the temperature increases by 40°C, there is a decrease in length of 0.013 m when the temperature decreases by 40°C. (We assume α is constant over the entire range of temperatures.) The new length at the colder temperature is 30.000 m - 0.013 m = 29.987 m.

Example 19.3 The Thermal Electrical Short

A poorly designed electronic device has two bolts attached to different parts of the device that almost touch each other in its interior as in Figure 19.10. The steel and brass bolts are at different electric potentials, and if they touch, a short circuit will develop, damaging the device. (We will study electric potential in Chapter 25.) The initial gap between the ends of the bolts is $d = 5.0 \ \mu \text{m}$ at 27°C. At what temperature will the bolts touch? Assume the distance between the walls of the device is not affected by the temperature change.



SOLUTION

Conceptualize Imagine the ends of both bolts expanding into the gap between them as the temperature rises.

19.3 continued

Categorize We categorize this example as a thermal expansion problem in which the *sum* of the changes in length of the two bolts must equal the length of the initial gap between the ends.

Analyze Set the sum of the length changes equal to the width of the gap:	$\Delta L_{\rm br} + \Delta L_{\rm st} = \alpha_{\rm br} L_{i,\rm br} \Delta T + \alpha_{\rm st} L_{i,\rm st} \Delta T = d$
Solve for ΔT :	$\Delta T = \frac{d}{\alpha_{\rm br} L_{i,\rm br} + \alpha_{\rm st} L_{i,\rm st}}$
Substitute numerical values:	$\Delta T = \frac{5.0 \times 10^{-6} \text{ m}}{[19 \times 10^{-6} (^{\circ}\text{C})^{-1}](0.030 \text{ m}) + [11 \times 10^{-6} (^{\circ}\text{C})^{-1}](0.010 \text{ m})} = 7.4^{\circ}\text{C}$
Find the temperature at which the bolts touch:	$T = 27^{\circ}C + 7.4^{\circ}C = 34^{\circ}C$
Finalize This temperature is possible if the	he air conditioning in the building housing the device fails for a long period

on a very hot summer day.

The Unusual Behavior of Water

Liquids generally increase in volume with increasing temperature and have average coefficients of volume expansion about ten times greater than those of solids. Cold water is an exception to this rule as you can see from its density-versus-temperature curve shown in Figure 19.11. As the temperature increases from 0°C to 4°C, water contracts and its density therefore increases. Above 4°C, water expands with increasing temperature and so its density decreases. Therefore, the density of water reaches a maximum value of 1.000 g/cm³ at 4°C.

We can use this unusual thermal-expansion behavior of water to explain why a pond begins freezing at the surface rather than at the bottom. When the air temperature drops from, for example, 7°C to 6°C, the surface water also cools and consequently decreases in volume. The surface water is denser than the water below it, which has not cooled and decreased in volume. As a result, the surface water sinks, and warmer water from below moves to the surface. When the air temperature is between 4°C and 0°C, however, the surface water expands as it cools, becoming less dense than the water below it. The mixing process stops, and eventually the surface water freezes. As the water freezes, the ice remains on the surface because ice is less dense than water. The ice continues to build up at the surface, while water near the

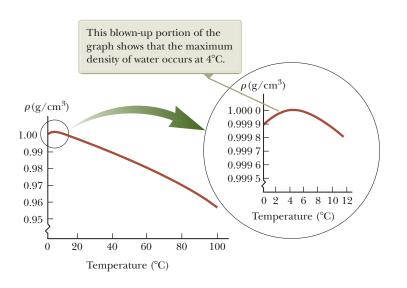


Figure 19.11 The variation in the density of water at atmospheric pressure with temperature.

bottom remains at 4°C. If that were not the case, fish and other forms of marine life would not survive.

19.5 Macroscopic Description of an Ideal Gas

The volume expansion equation $\Delta V = \beta V_i \Delta T$ is based on the assumption that the material has an initial volume V_i before the temperature change occurs. Such is the case for solids and liquids because they have a fixed volume at a given temperature.

The case for gases is completely different. The interatomic forces within gases are very weak, and, in many cases, we can imagine these forces to be nonexistent and still make very good approximations. Therefore, *there is no equilibrium separation* for the atoms and no "standard" volume at a given temperature; the volume depends on the size of the container. As a result, we cannot express changes in volume ΔV in a process on a gas with Equation 19.6 because we have no defined volume V_i at the beginning of the process. Equations involving gases contain the volume V, rather than a *change* in the volume from an initial value, as a variable.

For a gas, it is useful to know how the quantities volume V, pressure P, and temperature T are related for a sample of gas of mass m. In general, the equation that interrelates these quantities, called the *equation of state*, is very complicated. If the gas is maintained at a very low pressure (or low density), however, the equation of state is quite simple and can be determined from experimental results. Such a low-density gas is commonly referred to as an **ideal gas.**⁵ We can use the **ideal gas model** to make predictions that are adequate to describe the behavior of real gases at low pressures.

It is convenient to express the amount of gas in a given volume in terms of the number of moles *n*. One **mole** of any substance is that amount of the substance that contains **Avogadro's number** $N_{\rm A} = 6.022 \times 10^{23}$ of constituent particles (atoms or molecules). The number of moles *n* of a substance is related to its mass *m* through the expression

$$n = \frac{m}{M}$$
(19.7)

where M is the molar mass of the substance. The molar mass of each chemical element is the atomic mass (from the periodic table; see Appendix C) expressed in grams per mole. For example, the mass of one He atom is 4.00 u (atomic mass units), so the molar mass of He is 4.00 g/mol.

Now suppose an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston as in Figure 19.12. If we assume the cylinder does not leak, the mass (or the number of moles) of the gas remains constant. For such a system, experiments provide the following information:

- When the gas is kept at a constant temperature, its pressure is inversely proportional to the volume. (This behavior is described historically as Boyle's law.)
- When the pressure of the gas is kept constant, the volume is directly proportional to the temperature. (This behavior is described historically as Charles's law.)
- When the volume of the gas is kept constant, the pressure is directly proportional to the temperature. (This behavior is described historically as Gay– Lussac's law.)

These observations are summarized by the equation of state for an ideal gas:

Equation of state for an ideal gas PV = nRT

(19.8)

⁵To be more specific, the assumptions here are that the temperature of the gas must not be too low (the gas must not condense into a liquid) or too high and that the pressure must be low. The concept of an ideal gas implies that the gas molecules do not interact except upon collision and that the molecular volume is negligible compared with the volume of the container. In reality, an ideal gas does not exist. The concept of an ideal gas is nonetheless very useful because real gases at low pressures are well-modeled as ideal gases.



Figure 19.12 An ideal gas confined to a cylinder whose volume can be varied by means of a movable piston.

In this expression, also known as the **ideal gas law**, *n* is the number of moles of gas in the sample and R is a constant. Experiments on numerous gases show that as the $\frac{1}{2}$ pressure approaches zero, the quantity PV/nT approaches the same value R for all gases. For this reason, R is called the universal gas constant. In SI units, in which $\frac{8}{5}$ pressure is expressed in pascals (1 Pa = 1 N/m²) and volume in cubic meters, the group product *PV* has units of newton \cdot meters, or joules, and *R* has the value $R = 8.314 \text{ J/mol} \cdot \text{K}$ (19.9)

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$
 (19.9)

If the pressure is expressed in atmospheres and the volume in liters (1 L = $10^{3} \text{ cm}^{3} = 10^{-3} \text{ m}^{3}$), then *R* has the value

$$R = 0.082\ 06\ \text{L} \cdot \text{atm/mol} \cdot \text{K}$$

Using this value of R and Equation 19.8 shows that the volume occupied by 1 mol of any gas at atmospheric pressure and at 0°C (273 K) is 22.4 L.

The ideal gas law states that if the volume and temperature of a fixed amount of gas do not change, the pressure also remains constant. Consider a bottle of champagne that is shaken and then spews liquid when opened as shown in Figure 19.13. A common misconception is that the pressure inside the bottle is increased when the bottle is shaken. On the contrary, because the temperature of the bottle and its contents remains constant as long as the bottle is sealed, so does the pressure, as can be shown by replacing the cork with a pressure gauge. The correct explanation is as follows. Carbon dioxide gas resides in the volume between the liquid surface and the cork. The pressure of the gas in this volume is set higher than atmospheric pressure in the bottling process. Shaking the bottle displaces some of the carbon dioxide gas into the liquid, where it forms bubbles, and these bubbles become attached to the inside of the bottle. (No new gas is generated by shaking.) When the bottle is opened, the pressure is reduced to atmospheric pressure, which causes the volume of the bubbles to increase suddenly. If the bubbles are attached to the bottle (beneath the liquid surface), their rapid expansion expels liquid from the bottle. If the sides and bottom of the bottle are first tapped until no bubbles remain beneath the surface, however, the drop in pressure does not force liquid from the bottle when the champagne is opened.

The ideal gas law is often expressed in terms of the total number of molecules N. Because the number of moles n equals the ratio of the total number of molecules and Avogadro's number N_A , we can write Equation 19.8 as

$$PV = nRT = \frac{N}{N_{\rm A}}RT$$

$$PV = Nk_{\rm B}T$$
(19.10)

where $k_{\rm B}$ is **Boltzmann's constant**, which has the value

$$k_{\rm B} = \frac{R}{N_{\rm A}} = 1.38 \times 10^{-23} \,{\rm J/K}$$
 (19.11)

It is common to call quantities such as P, V, and T the **thermodynamic variables** of an ideal gas. If the equation of state is known, one of the variables can always be expressed as some function of the other two.

(Quick Quiz 19.5 A common material for cushioning objects in packages is made by trapping bubbles of air between sheets of plastic. Is this material more effective at keeping the contents of the package from moving around inside the package on (a) a hot day, (b) a cold day, or (c) either hot or cold days?

Ouick Quiz 19.6 On a winter day, you turn on your furnace and the temperature of the air inside your home increases. Assume your home has the normal amount of leakage between inside air and outside air. Is the number of moles of air in your room at the higher temperature (a) larger than before, (b) smaller • than before, or (c) the same as before?



pagne is shaken and opened. Liquid spews out of the opening. A common misconception is that the pressure inside the bottle is increased by the shaking.

Pitfall Prevention 19.3

So Many ks There are a variety of physical quantities for which the letter k is used. Two we have seen previously are the force constant for a spring (Chapter 15) and the wave number for a mechanical wave (Chapter 16). Boltzmann's constant is another k, and we will see k used for thermal conductivity in Chapter 20 and for an electrical constant in Chapter 23. To make some sense of this confusing state of affairs, we use a subscript B for Boltzmann's constant to help us recognize it. In this book, you will see Boltzmann's constant as $k_{\rm B}$, but you may see Boltzmann's constant in other resources as simply k.

Boltzmann's constant

Example 19.4 Heating a Spray Can

A spray can containing a propellant gas at twice atmospheric pressure (202 kPa) and having a volume of 125.00 cm³ is at 22°C. It is then tossed into an open fire. (*Warning:* Do not do this experiment; it is very dangerous.) When the temperature of the gas in the can reaches 195°C, what is the pressure inside the can? Assume any change in the volume of the can is negligible.

SOLUTION

Conceptualize Intuitively, you should expect that the pressure of the gas in the container increases because of the increasing temperature.

(1) $\frac{PV}{T} = nR$

(2) $\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$

(3) $\frac{P_i}{T_i} = \frac{P_f}{T_f}$

 $\Delta V = \beta V_i \, \Delta T = 3 \alpha V_i \, \Delta T$

 $P_f = \left(\frac{T_f}{T_i}\right) \left(\frac{V_i}{V_f}\right) P_i$

Categorize We model the gas in the can as ideal and use the ideal gas law to calculate the new pressure.

Analyze Rearrange Equation 19.8:

No air escapes during the compression, so n, and therefore nR, remains constant. Hence, set the initial value of the left side of Equation (1) equal to the final value:

Because the initial and final volumes of the gas are assumed to be equal, cancel the volumes:

Solve for P_f :

 $P_f = \left(\frac{T_f}{T_i}\right) P_i = \left(\frac{468 \text{ K}}{295 \text{ K}}\right) (202 \text{ kPa}) = 320 \text{ kPa}$

 $= 3[11 \times 10^{-6} (^{\circ}C)^{-1}](125.00 \text{ cm}^{3})(173^{\circ}C) = 0.71 \text{ cm}^{3}$

 $\frac{V_i}{V_f} = \frac{125.00 \text{ cm}^3}{(125.00 \text{ cm}^3 + 0.71 \text{ cm}^3)} = 0.994 = 99.4\%$

Finalize The higher the temperature, the higher the pressure exerted by the trapped gas as expected. If the pressure increases sufficiently, the can may explode. Because of this possibility, you should never dispose of spray cans in a fire.

WHAT IF? Suppose we include a volume change due to thermal expansion of the steel can as the temperature increases. Does that alter our answer for the final pressure significantly?

Answer Because the thermal expansion coefficient of steel is very small, we do not expect much of an effect on our final answer.

Find the change in the volume of the can using Equation 19.6 and the value for α for steel from Table 19.1:

Start from Equation (2) again and find an equation for the final pressure:

This result differs from Equation (3) only in the factor V_i/V_f . Evaluate this factor:

Therefore, the final pressure will differ by only 0.6% from the value calculated without considering the thermal expansion of the can. Taking 99.4% of the previous final pressure, the final pressure including thermal expansion is 318 kPa.

Summary

Definitions

Two objects are in thermal equilibrium with each other if they do not exchange energy when in thermal contact.

Temperature is the property that determines whether an object is in thermal equilibrium with other objects. Two objects in thermal equilibrium with each other are at the same temperature. The SI unit of absolute temperature is the **kelvin**, which is defined to be 1/273.16 of the difference between absolute zero and the temperature of the triple point of water.

Concepts and Principles

The zeroth law of thermodynamics states that if objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other. When the temperature of an object is changed by an amount ΔT , its length changes by an amount ΔL that is proportional to ΔT and to its initial length L_i :

$$\Delta L = \alpha L_i \,\Delta T \tag{19.4}$$

where the constant α is the **average coefficient of linear expansion.** The **average coefficient of volume expansion** β for a solid is approximately equal to 3α .

An ideal gas is one for which *PV/nT* is constant. An ideal gas is described by the equation of state,

$$PV = nRT$$

where *n* equals the number of moles of the gas, *P* is its pressure, *V* is its volume, *R* is the universal gas constant (8.314 J/mol \cdot K), and *T* is the absolute temperature of the gas. A real gas behaves approximately as an ideal gas if it has a low density.

Objective Questions

1. denotes answer available in *Student Solutions Manual/Study Guide*

- 1. Markings to indicate length are placed on a steel tape in a room that is at a temperature of 22°C. Measurements are then made with the same tape on a day when the temperature is 27°C. Assume the objects you are measuring have a smaller coefficient of linear expansion than steel. Are the measurements (a) too long, (b) too short, or (c) accurate?
- 2. When a certain gas under a pressure of 5.00×10^6 Pa at 25.0°C is allowed to expand to 3.00 times its original volume, its final pressure is 1.07×10^6 Pa. What is its final temperature? (a) 450 K (b) 233 K (c) 212 K (d) 191 K (e) 115 K
- **3.** If the volume of an ideal gas is doubled while its temperature is quadrupled, does the pressure (a) remain the same, (b) decrease by a factor of 2, (c) decrease by a factor of 4, (d) increase by a factor of 2, or (e) increase by a factor of 4
- **4.** The pendulum of a certain pendulum clock is made of brass. When the temperature increases, what happens to the period of the clock? (a) It increases. (b) It decreases. (c) It remains the same.
- 5. A temperature of 162°F is equivalent to what temperature in kelvins? (a) 373 K (b) 288 K (c) 345 K (d) 201 K (e) 308 K
- **6.** A cylinder with a piston holds 0.50 m³ of oxygen at an absolute pressure of 4.0 atm. The piston is pulled outward, increasing the volume of the gas until the pressure drops to 1.0 atm. If the temperature stays con-

stant, what new volume does the gas occupy? (a) 1.0 m^3 (b) 1.5 m^3 (c) 2.0 m^3 (d) 0.12 m^3 (e) 2.5 m^3

- 7. What would happen if the glass of a thermometer expanded more on warming than did the liquid in the tube? (a) The thermometer would break. (b) It could be used only for temperatures below room temperature. (c) You would have to hold it with the bulb on top. (d) The scale on the thermometer is reversed so that higher temperature values would be found closer to the bulb. (e) The numbers would not be evenly spaced.
- 8. A cylinder with a piston contains a sample of a thin gas. The kind of gas and the sample size can be changed. The cylinder can be placed in different constant-temperature baths, and the piston can be held in different positions. Rank the following cases according to the pressure of the gas from the highest to the lowest, displaying any cases of equality. (a) A 0.002-mol sample of oxygen is held at 300 K in a 100-cm³ container. (b) A 0.002-mol sample of oxygen is held at 600 K in a 200-cm³ container. (c) A 0.002-mol sample of oxygen is held at 600 K in a 200-cm³ container. (d) A 0.004-mol sample of helium is held at 300 K in a 200-cm³ container. (e) A 0.004-mol sample of helium is held at 250 K in a 200-cm³ container.
- 9. Two cylinders A and B at the same temperature contain the same quantity of the same kind of gas. Cylinder A has three times the volume of cylinder B. What can you conclude about the pressures the gases exert?(a) We can conclude nothing about the pressures.

(19.8)

(b) The pressure in A is three times the pressure in B.(c) The pressures must be equal. (d) The pressure in A must be one-third the pressure in B.

- **10.** A rubber balloon is filled with 1 L of air at 1 atm and 300 K and is then put into a cryogenic refrigerator at 100 K. The rubber remains flexible as it cools. (i) What happens to the volume of the balloon? (a) It decreases to $\frac{1}{3}$ L. (b) It decreases to $1/\sqrt{3}$ L. (c) It is constant. (d) It increases to $\sqrt{3}$ L. (e) It increases to 3 L. (ii) What happens to the pressure of the air in the balloon? (a) It decreases to $\frac{1}{3}$ atm. (b) It decreases to $1/\sqrt{3}$ atm. (c) It is constant. (d) It increases to $\sqrt{3}$ atm. (e) It increases to 3 atm.
- 11. The average coefficient of linear expansion of copper is 17 × 10⁻⁶ (°C)⁻¹. The Statue of Liberty is 93 m tall on a summer morning when the temperature is 25°C. Assume the copper plates covering the statue are mounted edge to edge without expansion joints and do not buckle or bind on the framework supporting them as the day grows hot. What is the order of magnitude of the statue's increase in height? (a) 0.1 mm (b) 1 mm (c) 1 cm (d) 10 cm (e) 1 m
- 12. Suppose you empty a tray of ice cubes into a bowl partly full of water and cover the bowl. After one-half hour, the contents of the bowl come to thermal equilibrium, with more liquid water and less ice than you started with. Which of the following is true? (a) The temperature of the liquid water is higher than the temperature of the remaining ice. (b) The temperature of the liquid water is the same as that of the ice. (c) The temperature of the liquid water is less than that of the ice. (d) The comparative temperatures of the liquid water and ice depend on the amounts present.
- 13. A hole is drilled in a metal plate. When the metal is raised to a higher temperature, what happens to the diameter of the hole? (a) It decreases. (b) It increases. (c) It remains the same. (d) The answer depends on the initial temperature of the metal. (e) None of those answers is correct.
- 14. On a very cold day in upstate New York, the temperature is -25° C, which is equivalent to what Fahrenheit temperature? (a) -46° F (b) -77° F (c) 18° F (d) -25° F (e) -13° F

Conceptual Questions

1. denotes answer available in Student Solutions Manual/Study Guide

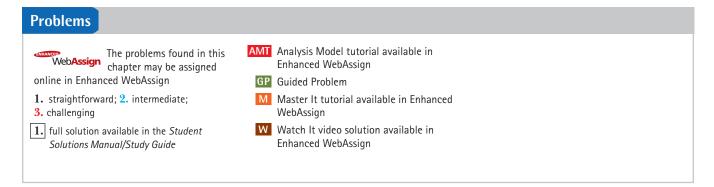
- 1. Common thermometers are made of a mercury column in a glass tube. Based on the operation of these thermometers, which has the larger coefficient of linear expansion, glass or mercury? (Don't answer the question by looking in a table.)
- 2. A piece of copper is dropped into a beaker of water. (a) If the water's temperature rises, what happens to the temperature of the copper? (b) Under what conditions are the water and copper in thermal equilibrium?
- **3.** (a) What does the ideal gas law predict about the volume of a sample of gas at absolute zero? (b) Why is this prediction incorrect?
- **4.** Some picnickers stop at a convenience store to buy some food, including bags of potato chips. They then drive up into the mountains to their picnic site. When they unload the food, they notice that the bags of chips are puffed up like balloons. Why did that happen?
- 5. In describing his upcoming trip to the Moon, and as portrayed in the movie *Apollo 13* (Universal, 1995), astronaut Jim Lovell said, "I'll be walking in a place where there's a 400-degree difference between sunlight and shadow." Suppose an astronaut standing on the Moon holds a thermometer in his gloved hand. (a) Is the thermometer reading the temperature of the vacuum at the Moon's surface? (b) Does it read any temperature? If so, what object or substance has that temperature?
- **6.** Metal lids on glass jars can often be loosened by running hot water over them. Why does that work?

- 7. An automobile radiator is filled to the brim with water when the engine is cool. (a) What happens to the water when the engine is running and the water has been raised to a high temperature? (b) What do modern automobiles have in their cooling systems to prevent the loss of coolants?
- 8. When the metal ring and metal sphere in Figure CQ19.8 are both at room temperature, the sphere can barely be passed through the ring. (a) After the sphere is warmed in a flame, it cannot be passed through the ring. Explain. (b) What If? What if the ring is warmed and the sphere is left at room temperature? Does the sphere pass through the ring?



Figure CQ19.8

- **9.** Is it possible for two objects to be in thermal equilibrium if they are not in contact with each other? Explain.
- 10. Use a periodic table of the elements (see Appendix C) to determine the number of grams in one mole of (a) hydrogen, which has diatomic molecules; (b) helium; and (c) carbon monoxide.



Section 19.2 Thermometers and the Celsius Temperature Scale Section 19.3 The Constant-Volume Gas Thermometer

and the Absolute Temperature Scale 1. A nurse measures the temperature of a patient to be 41.5°C. (a) What is this temperature on the Fahrenheit scale? (b) Do you think the patient is seriously ill? Explain.

- 2. The temperature difference between the inside and the outside of a home on a cold winter day is 57.0°F. Express this difference on (a) the Celsius scale and (b) the Kelvin scale.
- **3.** Convert the following temperatures to their values on the Fahrenheit and Kelvin scales: (a) the sublimation point of dry ice, -78.5°C; (b) human body temperature, 37.0°C.
- **4.** The boiling point of liquid hydrogen is 20.3 K at atmospheric pressure. What is this temperature on (a) the Celsius scale and (b) the Fahrenheit scale?
- **5.** Liquid nitrogen has a boiling point of -195.81°C at atmospheric pressure. Express this temperature (a) in degrees Fahrenheit and (b) in kelvins.
- 6. Death Valley holds the record for the highest recorded temperature in the United States. On July 10, 1913, at a place called Furnace Creek Ranch, the temperature rose to 134°F. The lowest U.S. temperature ever recorded occurred at Prospect Creek Camp in Alaska on January 23, 1971, when the temperature plummeted to -79.8° F. (a) Convert these temperatures to the Celsius scale. (b) Convert the Celsius temperatures to Kelvin.
- 7. In a student experiment, a constant-volume gas thermometer is calibrated in dry ice (-78.5°C) and in boiling ethyl alcohol (78.0°C). The separate pressures are 0.900 atm and 1.635 atm. (a) What value of absolute zero in degrees Celsius does the calibration yield? What pressures would be found at (b) the freezing and (c) the boiling points of water? *Hint:* Use the linear relationship P = A + BT, where A and B are constants.

Section 19.4 Thermal Expansion of Solids and Liquids

Note: Table 19.1 is available for use in solving problems in this section.

8. The concrete sections of a certain superhighway are W designed to have a length of 25.0 m. The sections are poured and cured at 10.0°C. What minimum spacing should the engineer leave between the sections to eliminate buckling if the concrete is to reach a temperature of 50.0° C?

- **9.** The active element of a certain laser
- M is made of a glass rod 30.0 cm long and 1.50 cm in diameter. Assume the average coefficient of linear expansion of the glass is equal to $9.00 \times 10^{-6} (^{\circ}\text{C})^{-1}$. If the temperature of the rod increases by 65.0°C, what is the increase in (a) its length, (b) its diameter, and (c) its volume?



10. Review. Inside the wall of a house, an L-shaped section of hot-water pipe consists of three parts: a straight, horizontal piece h = 28.0 cm long; an elbow; and a straight, vertical piece

Figure P19.10

 $\ell = 134$ cm long (Fig. P19.10). A stud and a secondstory floorboard hold the ends of this section of copper pipe stationary. Find the magnitude and direction of the displacement of the pipe elbow when the water flow is turned on, raising the temperature of the pipe from 18.0°C to 46.5°C.

- **11.** A copper telephone wire has essentially no sag between
- M poles 35.0 m apart on a winter day when the temperature is -20.0°C. How much longer is the wire on a summer day when the temperature is 35.0°C?
- 12. A pair of eyeglass frames is made of epoxy plastic. At room temperature (20.0°C), the frames have circular lens holes 2.20 cm in radius. To what temperature must the frames be heated if lenses 2.21 cm in radius are to be inserted in them? The average coefficient of linear expansion for epoxy is 1.30×10^{-4} (°C)⁻¹.
- **13.** The Trans-Alaska pipeline is 1 300 km long, reaching from Prudhoe Bay to the port of Valdez. It experiences temperatures from -73°C to +35°C. How much does the steel pipeline expand because of the difference in temperature? How can this expansion be compensated for?
- 14. Each year thousands of children are badly burned by hot tap water. Figure P19.14 (page 584) shows a crosssectional view of an antiscalding faucet attachment designed to prevent such accidents. Within the device, a spring made of material with a high coefficient of thermal expansion controls a movable plunger. When the

water temperature rises above a preset safe value, the expansion of the spring causes the plunger to shut off the water flow. Assuming that the initial length L of the unstressed spring is 2.40 cm and its coefficient of linear expansion is $22.0 \times 10^{-6} (^{\circ}C)^{-1}$, determine the increase in length of the spring when the water temperature rises by 30.0°C. (You will find the increase in length to be small. Therefore, to provide a greater variation in valve opening for the temperature change anticipated, actual

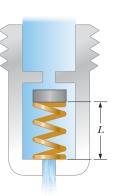


Figure P19.14

devices have a more complicated mechanical design.)

- **15.** A square hole 8.00 cm along each side is cut in a sheet of copper. (a) Calculate the change in the area of this hole resulting when the temperature of the sheet is increased by 50.0 K. (b) Does this change represent an increase or a decrease in the area enclosed by the hole?
- **16.** The average coefficient of volume expansion for carbon tetrachloride is $5.81 \times 10^{-4} (^{\circ}\text{C})^{-1}$. If a 50.0-gal steel container is filled completely with carbon tetrachloride when the temperature is 10.0°C , how much will spill over when the temperature rises to 30.0°C ?

17. At 20.0°C, an aluminum ring has an inner diameter of

- 5.000 0 cm and a brass rod has a diameter of 5.050 0 cm. (a) If only the ring is warmed, what temperature must it reach so that it will just slip over the rod? (b) What If? If both the ring and the rod are warmed together, what temperature must they both reach so that the ring barely slips over the rod? (c) Would this latter process work? Explain. *Hint*: Consult Table 20.2 in the next chapter.
- 18. Why is the following situation impossible? A thin brass
 w ring has an inner diameter 10.00 cm at 20.0°C. A solid aluminum cylinder has diameter 10.02 cm at 20.0°C. Assume the average coefficients of linear expansion of the two metals are constant. Both metals are cooled together to a temperature at which the ring can be slipped over the end of the cylinder.
- 19. A volumetric flask made of Pyrex is calibrated at 20.0°C. It is filled to the 100-mL mark with 35.0°C acetone. After the flask is filled, the acetone cools and the flask warms so that the combination of acetone and flask reaches a uniform temperature of 32.0°C. The combination is then cooled back to 20.0°C. (a) What is the volume of the acetone when it cools to 20.0°C? (b) At the temperature of 32.0°C, does the level of acetone lie above or below the 100-mL mark on the flask? Explain.
- 20. Review. On a day that the temperature is 20.0°C, a concrete walk is poured in such a way that the ends of the walk are unable to move. Take Young's modulus for concrete to be 7.00 × 10⁹ N/m² and the compressive strength to be 2.00 × 10⁹ N/m². (a) What is the stress in the cement on a hot day of 50.0°C? (b) Does the concrete fracture?

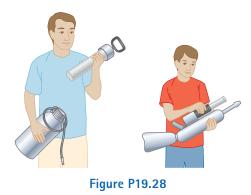
- 21. A hollow aluminum cylinder 20.0 cm deep has an internal capacity of 2.000 L at 20.0°C. It is completely filled with turpentine at 20.0°C. The turpentine and the aluminum cylinder are then slowly warmed together to 80.0°C. (a) How much turpentine overflows? (b) What is the volume of turpentine remaining in the cylinder at 80.0°C? (c) If the combination with this amount of turpentine is then cooled back to 20.0°C, how far below the cylinder's rim does the turpentine's surface recede?
- 22. Review. The Golden Gate Bridge in San Francisco has a main span of length 1.28 km, one of the longest in the world. Imagine that a steel wire with this length and a cross-sectional area of 4.00 \times $10^{-6}~{\rm m^2}$ is laid in a straight line on the bridge deck with its ends attached to the towers of the bridge. On a summer day the temperature of the wire is 35.0°C. (a) When winter arrives, the towers stay the same distance apart and the bridge deck keeps the same shape as its expansion joints open. When the temperature drops to -10.0° C, what is the tension in the wire? Take Young's modulus for steel to be $20.0 \times 10^{10} \text{ N/m}^2$. (b) Permanent deformation occurs if the stress in the steel exceeds its elastic limit of $3.00 \times 10^8 \text{ N/m}^2$. At what temperature would the wire reach its elastic limit? (c) What If? Explain how your answers to parts (a) and (b) would change if the Golden Gate Bridge were twice as long.
- 23. A sample of lead has a mass of 20.0 kg and a density of 11.3 × 10³ kg/m³ at 0°C. (a) What is the density of lead at 90.0°C? (b) What is the mass of the sample of lead at 90.0°C?
- 24. A sample of a solid substance has a mass *m* and a density ρ₀ at a temperature T₀. (a) Find the density of the substance if its temperature is increased by an amount ΔT in terms of the coefficient of volume expansion β. (b) What is the mass of the sample if the temperature is raised by an amount ΔT?
- 25. An underground gasoline tank can hold 1.00×10^3 gal-M lons of gasoline at 52.0°F. Suppose the tank is being filled on a day when the outdoor temperature (and the temperature of the gasoline in a tanker truck) is 95.0°F. When the underground tank registers that it is full, how many gallons have been transferred from the truck, according to a non-temperature-compensated gauge on the truck? Assume the temperature of the gasoline quickly cools from 95.0°F to 52.0°F upon entering the tank.

Section 19.5 Macroscopic Description of an Ideal Gas

- **26.** A rigid tank contains 1.50 moles of an ideal gas. Determine the number of moles of gas that must be withdrawn from the tank to lower the pressure of the gas from 25.0 atm to 5.00 atm. Assume the volume of the tank and the temperature of the gas remain constant during this operation.
- **27.** Gas is confined in a tank at a pressure of 11.0 atm and a temperature of 25.0°C. If two-thirds of the gas

is withdrawn and the temperature is raised to 75.0°C, what is the pressure of the gas remaining in the tank?

28. Your father and your younger brother are confronted with the same puzzle. Your father's garden sprayer and your brother's water cannon both have tanks with a capacity of 5.00 L (Fig. P19.28). Your father puts a negligible amount of concentrated fertilizer into his tank. They both pour in 4.00 L of water and seal up their tanks, so the tanks also contain air at atmospheric pressure. Next, each uses a hand-operated pump to inject more air until the absolute pressure in the tank reaches 2.40 atm. Now each uses his device to spray out water-not air-until the stream becomes feeble, which it does when the pressure in the tank reaches 1.20 atm. To accomplish spraying out all the water, each finds he must pump up the tank three times. Here is the puzzle: most of the water sprays out after the second pumping. The first and the third pumpingup processes seem just as difficult as the second but result in a much smaller amount of water coming out. Account for this phenomenon.



- 29. Gas is contained in an 8.00-L vessel at a temperature of
 20.0°C and a pressure of 9.00 atm. (a) Determine the number of moles of gas in the vessel. (b) How many molecules are in the vessel?
- 30. A container in the shape of a cube 10.0 cm on each edge contains air (with equivalent molar mass 28.9 g/mol) at atmospheric pressure and temperature 300 K. Find (a) the mass of the gas, (b) the gravitational force exerted on it, and (c) the force it exerts on each face of the cube. (d) Why does such a small sample exert such a great force?
- 31. An auditorium has dimensions 10.0 m × 20.0 m ×
 M 30.0 m. How many molecules of air fill the auditorium at 20.0°C and a pressure of 101 kPa (1.00 atm)?
- 32. The pressure gauge on a tank registers the gauge pressure, which is the difference between the interior pressure and exterior pressure. When the tank is full of oxygen (O₂), it contains 12.0 kg of the gas at a gauge pressure of 40.0 atm. Determine the mass of oxygen that has been withdrawn from the tank when the pressure reading is 25.0 atm. Assume the temperature of the tank remains constant.
- 33. (a) Find the number of moles in one cubic meter of an ideal gas at 20.0°C and atmospheric pressure. (b) For

air, Avogadro's number of molecules has mass 28.9 g. Calculate the mass of one cubic meter of air. (c) State how this result compares with the tabulated density of air at 20.0°C.

- **34.** Use the definition of Avogadro's number to find the mass of a helium atom.
- **35.** A popular brand of cola contains 6.50 g of carbon dioxide dissolved in 1.00 L of soft drink. If the evaporating carbon dioxide is trapped in a cylinder at 1.00 atm and 20.0°C, what volume does the gas occupy?

36. In state-of-the-art vacuum systems, pressures as low as

- 1.00×10^{-9} Pa are being attained. Calculate the number of molecules in a 1.00-m³ vessel at this pressure and a temperature of 27.0°C.
- 37. An automobile tire is inflated with air originally at 10.0°C and normal atmospheric pressure. During the process, the air is compressed to 28.0% of its original volume and the temperature is increased to 40.0°C.
 (a) What is the tire pressure? (b) After the car is driven at high speed, the tire's air temperature rises to 85.0°C and the tire's interior volume increases by 2.00%. What is the new tire pressure (absolute)?
- **38. Review.** To measure how far below the ocean surface a bird dives to catch a fish, a scientist uses a method originated by Lord Kelvin. He dusts the interiors of plastic tubes with powdered sugar and then seals one end of each tube. He captures the bird at nighttime in its nest and attaches a tube to its back. He then catches the same bird the next night and removes the tube. In one trial, using a tube 6.50 cm long, water washes away the sugar over a distance of 2.70 cm from the open end of the tube. Find the greatest depth to which the bird dived, assuming the air in the tube stayed at constant temperature.

39. Review. The mass of a hot-air balloon and its cargo **AMT** (not including the air inside) is 200 kg. The air outside

- M is at 10.0°C and 101 kPa. The volume of the balloon is 400 m³. To what temperature must the air in the balloon be warmed before the balloon will lift off? (Air density at 10.0°C is 1.244 kg/m³.)
- **40.** A room of volume V contains air having equivalent molar mass M (in g/mol). If the temperature of the room is raised from T_1 to T_2 , what mass of air will leave the room? Assume that the air pressure in the room is maintained at P_0 .
- **41. Review.** At 25.0 m below the surface of the sea, where the temperature is 5.00°C, a diver exhales an air bubble having a volume of 1.00 cm³. If the surface temperature of the sea is 20.0°C, what is the volume of the bubble just before it breaks the surface?
- **42.** Estimate the mass of the air in your bedroom. State the quantities you take as data and the value you measure or estimate for each.

43. A cook puts 9.00 g of water in a 2.00-L pressure cooker W that is then warmed to 500°C. What is the pressure inside the container?

44. The pressure gauge on a cylinder of gas registers the gauge pressure, which is the difference between the

interior pressure and the exterior pressure P_0 . Let's call the gauge pressure P_g . When the cylinder is full, the mass of the gas in it is m_i at a gauge pressure of P_{gi} . Assuming the temperature of the cylinder remains constant, show that the mass of the gas *remaining* in the cylinder when the pressure reading is P_{gf} is given by

$$m_f = m_i \left(\frac{P_{gf} + P_0}{P_{gi} + P_0} \right)$$

Additional Problems

- **45.** Long-term space missions require reclamation of the oxygen in the carbon dioxide exhaled by the crew. In one method of reclamation, 1.00 mol of carbon dioxide produces 1.00 mol of oxygen and 1.00 mol of methane as a byproduct. The methane is stored in a tank under pressure and is available to control the attitude of the spacecraft by controlled venting. A single astronaut exhales 1.09 kg of carbon dioxide each day. If the methane generated in the respiration recycling of three astronauts during one week of flight is stored in an originally empty 150-L tank at −45.0°C, what is the final pressure in the tank?
- **46.** A steel beam being used in the construction of a skyscraper has a length of 35.000 m when delivered on a cold day at a temperature of 15.000°F. What is the length of the beam when it is being installed later on a warm day when the temperature is 90.000°F?
- **47.** A spherical steel ball bearing has a diameter of 2.540 cm at 25.00°C. (a) What is its diameter when its temperature is raised to 100.0°C? (b) What temperature change is required to increase its volume by 1.000%?
- **48.** A bicycle tire is inflated to a gauge pressure of 2.50 atm when the temperature is 15.0°C. While a man rides the bicycle, the temperature of the tire rises to 45.0°C. Assuming the volume of the tire does not change, find the gauge pressure in the tire at the higher temperature.
- **49.** In a chemical processing plant, a reaction chamber of fixed volume V_0 is connected to a reservoir chamber of fixed volume $4V_0$ by a passage containing a thermally insulating porous plug. The plug permits the chambers to be at different temperatures. The plug allows gas to pass from either chamber to the other, ensuring that the pressure is the same in both. At one point in the processing, both chambers contain gas at a pressure of 1.00 atm and a temperature of 27.0°C. Intake and exhaust valves to the pair of chambers are closed. The reservoir is maintained at 27.0°C while the reaction chamber is heated to 400°C. What is the pressure in both chambers after that is done?
- **50.** Why is the following situation impossible? An apparatus is designed so that steam initially at T = 150°C, P = 1.00 atm, and V = 0.500 m³ in a piston–cylinder apparatus undergoes a process in which (1) the volume remains constant and the pressure drops to 0.870 atm, followed by (2) an expansion in which the pressure remains constant and the volume increases to 1.00 m³, followed by (3) a return to the initial conditions. It is

important that the pressure of the gas never fall below 0.850 atm so that the piston will support a delicate and very expensive part of the apparatus. Without such support, the delicate apparatus can be severely damaged and rendered useless. When the design is turned into a working prototype, it operates perfectly.

51. A mercury thermometer
M is constructed as shown in Figure P19.51. The Pyrex glass capillary tube has a diameter of 0.004 00 cm, and the bulb has a diameter of 0.250 cm. Find the change in height of the mercury column that occurs with a temperature change of 30.0°C.

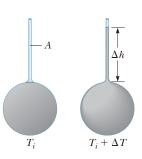


Figure P19.51

Problems 51 and 52.

52. A liquid with a coefficient of volume expansion β

just fills a spherical shell of volume *V* (Fig. P19.51). The shell and the open capillary of area *A* projecting from the top of the sphere are made of a material with an average coefficient of linear expansion α . The liquid is free to expand into the capillary. Assuming the temperature increases by ΔT , find the distance Δh the liquid rises in the capillary.

- 53. Review. An aluminum pipe is open at both ends and AMT used as a flute. The pipe is cooled to 5.00°C, at which its length is 0.655 m. As soon as you start to play it, the pipe fills with air at 20.0°C. After that, by how much does its fundamental frequency change as the metal rises in temperature to 20.0°C?
- 54. Two metal bars are made of invar and a third bar is made of aluminum. At 0°C, each of the three bars is drilled with two holes 40.0 cm apart. Pins are put through the holes to assemble the bars into an equilateral triangle as in Figure P19.54. (a) First ignore the expansion of the invar. Find



the angle between the invar bars as a function of Celsius temperature. (b) Is your answer accurate for negative as well as positive temperatures? (c) Is it accurate for 0°C? (d) Solve the problem again, including the expansion of the invar. Aluminum melts at 660°C and invar at 1 427°C. Assume the tabulated expansion coefficients are constant. What are (e) the greatest and (f) the smallest attainable angles between the invar bars?

- **55.** A student measures the length of a brass rod with a steel tape at 20.0°C. The reading is 95.00 cm. What will the tape indicate for the length of the rod when the rod and the tape are at (a) -15.0°C and (b) 55.0°C?
- 56. The density of gasoline is 730 kg/m³ at 0°C. Its average coefficient of volume expansion is 9.60 × 10⁻⁴ (°C)⁻¹. Assume 1.00 gal of gasoline occupies 0.003 80 m³.

How many extra kilograms of gasoline would you receive if you bought 10.0 gal of gasoline at 0°C rather than at 20.0°C from a pump that is not temperature compensated?

- 57. A liquid has a density ρ . (a) Show that the fractional change in density for a change in temperature ΔT is $\Delta \rho / \rho = -\beta \Delta T$. (b) What does the negative sign signify? (c) Fresh water has a maximum density of 1.000 0 g/cm³ at 4.0°C. At 10.0°C, its density is 0.999 7 g/cm³. What is β for water over this temperature interval? (d) At 0°C, the density of water is 0.999 9 g/cm³. What is the value for β over the temperature range 0°C to 4.00°C?
- **58.** (a) Take the definition of the coefficient of volume expansion to be

$$\beta = \frac{1}{V} \left. \frac{dV}{dT} \right|_{P = \text{constant}} = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_{P = \text{constant}}$$

Use the equation of state for an ideal gas to show that the coefficient of volume expansion for an ideal gas at constant pressure is given by $\beta = 1/T$, where *T* is the absolute temperature. (b) What value does this expression predict for β at 0°C? State how this result compares with the experimental values for (c) helium and (d) air in Table 19.1. *Note*: These values are much larger than the coefficients of volume expansion for most liquids and solids.

- 59. Review. A clock with a brass pendulum has a period of 1.000 s at 20.0°C. If the temperature increases to 30.0°C, (a) by how much does the period change and (b) how much time does the clock gain or lose in one week?
- **60.** A bimetallic strip of length *L* is made of two ribbons of different metals bonded together. (a) First assume the strip is originally straight. As the strip is warmed, the metal with the greater average coefficient of expansion expands more than the other, forcing the strip into an arc with the outer radius having a greater circumference (Fig. P19.60). Derive

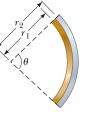


Figure P19.60

an expression for the angle of bending θ as a function of the initial length of the strips, their average coefficients of linear expansion, the change in temperature, and the separation of the centers of the strips ($\Delta r = r_2 - r_1$). (b) Show that the angle of bending decreases to zero when ΔT decreases to zero and also when the two average coefficients of expansion become equal. (c) What If? What happens if the strip is cooled?

61. The rectangular plate shown in Figure P19.61 has an area A_i equal to ℓw . If the temperature increases by ΔT ,

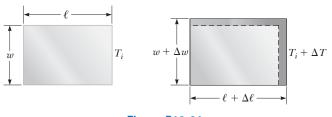


Figure P19.61

each dimension increases according to Equation 19.4, where α is the average coefficient of linear expansion. (a) Show that the increase in area is $\Delta A = 2\alpha A_i \Delta T$. (b) What approximation does this expression assume?

62. The measurement of the average coefficient of volume expansion β for a liquid is complicated because the container also changes size with temperature. Figure P19.62 shows a simple means for measuring β despite the expansion of the container. With this apparatus, one arm of a U-tube is maintained at 0°C in a water-ice bath, and the other arm is maintained at a different temperature $T_{\rm C}$ in a constant-temperature bath. The

connecting tube is horizontal. A difference in the length or diameter of the tube between the two arms of the U-tube has no effect on the pressure balance at the bottom of the tube because the pressure depends only on the depth of the liquid. Derive an expression for β for the liquid in terms of h_0 , h_r , and T_c .

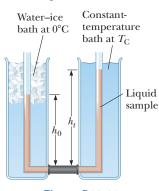


Figure P19.62

63. A copper rod and a steel rod are different in length by 5.00 cm at 0°C. The rods are warmed and cooled together. (a) Is it possible that the length difference remains constant at all temperatures? Explain. (b) If so, describe the lengths at 0°C as precisely as you can. Can you tell which rod is longer? Can you tell the lengths of the rods?

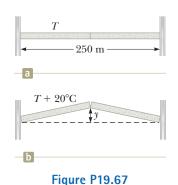
64. A vertical cylinder of cross-AMT sectional area A is fitted with a GP tight-fitting, frictionless piston of mass m (Fig. P19.64). The piston is not restricted in its motion in any way and is supported by the gas at pressure Pbelow it. Atmospheric pressure is P_0 . We wish to find the height h in Figure P19.64. (a) What analysis model is appropriate to describe the piston? (b) Write an appropriate force equation for the piston from this analysis model in terms of $P, P_0, m,$ A, and g. (c) Suppose n moles of



an ideal gas are in the cylinder at a temperature of T. Substitute for P in your answer to part (b) to find the height h of the piston above the bottom of the cylinder.

65. Review. Consider an object with any one of the shapes displayed in Table 10.2. What is the percentage increase in the moment of inertia of the object when it is warmed from 0°C to 100°C if it is composed of (a) copper or (b) aluminum? Assume the average linear expansion coefficients shown in Table 19.1 do not vary between 0°C and 100°C. (c) Why are the answers for parts (a) and (b) the same for all the shapes?

- **66.** (a) Show that the density of an ideal gas occupying a volume *V* is given by $\rho = PM/RT$, where *M* is the molar mass. (b) Determine the density of oxygen gas at atmospheric pressure and 20.0°C.
- 67. Two concrete spans of a 250-m-long bridge are placed end to end so that no room is allowed for expansion (Fig. P19.67a). If a temperature increase of 20.0°C occurs, what is the height yto which the spans rise when they buckle (Fig. P19.67b)?



Problems 67 and 68.

68. Two concrete spans that form a bridge

of length L are placed end to end so that no room is allowed for expansion (Fig. P19.67a). If a temperature increase of ΔT occurs, what is the height y to which the spans rise when they buckle (Fig. P19.67b)?

69. Review. (a) Derive an expression for the buoyant force on a spherical balloon, submerged in water, as a function of the depth *h* below the surface, the volume V_i of the balloon at the surface, the pressure P_0 at the surface, and the density ρ_{iv} of the water. Assume the water temperature does not change with depth. (b) Does the *buoyant* force increase or decrease as the balloon is submerged? (c) At what depth is the buoyant force one-half the surface value?

70. Review. Following a collision in outer space, a copper AMI disk at 850°C is rotating about its axis with an angular speed of 25.0 rad/s. As the disk radiates infrared light, its temperature falls to 20.0°C. No external torque acts on the disk. (a) Does the angular speed change as the disk cools? Explain how it changes or why it does not. (b) What is its angular speed at the lower temperature?

71. Starting with Equation 19.10, show that the total pressure P in a container filled with a mixture of several ideal gases is $P = P_1 + P_2 + P_3 + \cdots$, where P_1, P_2, \cdots are the pressures that each gas would exert if it alone filled the container. (These individual pressures are called the *partial pressures* of the respective gases.) This result is known as *Dalton's law of partial pressures*.

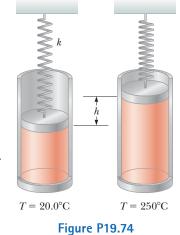
Challenge Problems

72. Review. A steel wire and a copper wire, each of diameter 2.000 mm, are joined end to end. At 40.0°C, each has an unstretched length of 2.000 m. The wires are connected between two fixed supports 4.000 m apart on a tabletop. The steel wire extends from x = -2.000 m to x = 0, the copper wire extends from x = 0 to x = 2.000 m, and the tension is negligible. The temperature is then lowered to 20.0°C. Assume the average coefficient of linear expansion of steel is 11.0×10^{-6} (°C)⁻¹ and that of copper is 17.0×10^{-6} (°C)⁻¹. Take Young's modulus for steel to be 20.0×10^{10} N/m² and that for

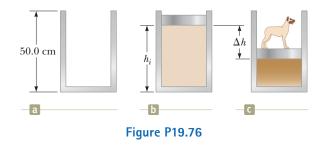
copper to be 11.0×10^{10} N/m². At this lower temperature, find (a) the tension in the wire and (b) the *x* coordinate of the junction between the wires.

73. Review. A steel guitar string with a diameter of 1.00 mm is stretched between supports 80.0 cm apart. The temperature is 0.0°C. (a) Find the mass per unit length of this string. (Use the value $7.86 \times 10^3 \text{ kg/m}^3$ for the density.) (b) The fundamental frequency of transverse oscillations of the string is 200 Hz. What is the tension in the string? Next, the temperature is raised to 30.0°C. Find the resulting values of (c) the tension and (d) the fundamental frequency. Assume both the Young's modulus of $20.0 \times 10^{10} \text{ N/m}^2$ and the average coefficient of expansion $\alpha = 11.0 \times 10^{-6} (^{\circ}\text{C})^{-1}$ have constant values between 0.0°C and 30.0°C.

74. A cylinder is closed by W a piston connected to a spring of constant 2.00×10^3 N/m (see Fig. P19.74). With the spring relaxed, the cylinder is filled with 5.00 L of gas at a pressure of 1.00 atm and a temperature of 20.0°C. (a) If the piston has a cross-sectional area of 0.010 0 m² and negligible mass, how high will it rise when the temperature is raised to 250° C? (b) What is the pressure of the gas at 250°C?



- **75.** Helium gas is sold in steel tanks that will rupture if subjected to tensile stress greater than its yield strength of 5×10^8 N/m². If the helium is used to inflate a balloon, could the balloon lift the spherical tank the helium came in? Justify your answer. *Suggestion:* You may consider a spherical steel shell of radius *r* and thickness *t* having the density of iron and on the verge of breaking apart into two hemispheres because it contains helium at high pressure.
- **76.** A cylinder that has a 40.0-cm radius and is 50.0 cm deep is filled with air at 20.0°C and 1.00 atm (Fig. P19.76a). A 20.0-kg piston is now lowered into the cylinder, compressing the air trapped inside as it takes equilibrium height h_i (Fig. P19.76b). Finally, a 25.0-kg dog stands on the piston, further compressing the air, which remains at 20°C (Fig. P19.76c). (a) How far down



 (Δh) does the piston move when the dog steps onto it? (b) To what temperature should the gas be warmed to raise the piston and dog back to h_i ?

- 77. The relationship $L = L_i + \alpha L_i \Delta T$ is a valid approximation when $\alpha \Delta T$ is small. If $\alpha \Delta T$ is large, one must integrate the relationship $dL = \alpha L dT$ to determine the final length. (a) Assuming the coefficient of linear expansion of a material is constant as L varies, determine a general expression for the final length of a rod made of the material. Given a rod of length 1.00 m and a temperature change of 100.0°C, determine the error caused by the approximation when (b) $\alpha = 2.00 \times 10^{-5} (^{\circ}C)^{-1}$ (a typical value for a metal) and (c) when $\alpha = 0.020 \ 0 \ (^{\circ}C)^{-1}$ (an unrealistically large value for comparison). (d) Using the equation from part (a), solve Problem 21 again to find more accurate results.
- **78. Review.** A house roof is a perfectly flat plane that makes an angle θ with the horizontal. When its temperature changes, between T_c before dawn each day and T_{h} in the middle of each afternoon, the roof expands and contracts uniformly with a coefficient of thermal expansion α_1 . Resting on the roof is a flat, rectangular metal plate with expansion coefficient α_2 , greater than α_1 . The length of the plate is L, measured along the slope of the roof. The component of the plate's weight perpendicular to the roof is supported by a normal force uniformly distributed over the area of the plate. The coefficient of kinetic friction between the plate and the roof is μ_k . The plate is always at the same temperature as the roof, so we assume its temperature is continuously changing. Because of the difference in expansion coefficients, each bit of the plate is moving relative to the roof below it, except for points along a certain horizontal line running across the plate called the stationary line. If the temperature is rising, parts

of the plate below the stationary line are moving down relative to the roof and feel a force of kinetic friction acting up the roof. Elements of area above the stationary line are sliding up the roof, and on them kinetic friction acts downward parallel to the roof. The stationary line occupies no area, so we assume no force of static friction acts on the plate while the temperature is changing. The plate as a whole is very nearly in equilibrium, so the net friction force on it must be equal to the component of its weight acting down the incline. (a) Prove that the stationary line is at a distance of

$$\frac{L}{2}\left(1-\frac{\tan\theta}{\mu_k}\right)$$

below the top edge of the plate. (b) Analyze the forces that act on the plate when the temperature is falling and prove that the stationary line is at that same distance above the bottom edge of the plate. (c) Show that the plate steps down the roof like an inchworm, moving each day by the distance

$$\frac{L}{\mu_k}(lpha_2-lpha_1)(T_h-T_c)\, an heta$$

(d) Evaluate the distance an aluminum plate moves each day if its length is 1.20 m, the temperature cycles between 4.00°C and 36.0°C, and if the roof has slope 18.5°, coefficient of linear expansion 1.50×10^{-5} (°C)⁻¹, and coefficient of friction 0.420 with the plate. (e) **What If?** What if the expansion coefficient of the plate is less than that of the roof? Will the plate creep up the roof?

79. A 1.00-km steel railroad rail is fastened securely at both ends when the temperature is 20.0° C. As the temperature increases, the rail buckles, taking the shape of an arc of a vertical circle. Find the height *h* of the center of the rail when the temperature is 25.0° C. (You will need to solve a transcendental equation.)

CHAPTER 20

The First Law of Thermodynamics



- 20.1 Heat and Internal Energy
- 20.2 Specific Heat and Calorimetry
- 20.3 Latent Heat
- 20.4 Work and Heat in Thermodynamic Processes
- 20.5 The First Law of Thermodynamics
- 20.6 Some Applications of the First Law of Thermodynamics
- 20.7 Energy Transfer Mechanisms in Thermal Processes

In this photograph of the Mt. Baker area near Bellingham, Washington, we see evidence of water in all three phases. In the lake is liquid water, and solid water in the form of snow appears on the ground. The clouds in the sky consist of liquid water droplets that have condensed from the gaseous water vapor in the air. Changes of a substance from one phase to another are a result of energy transfer. (©iStockphoto.com/ KingWu) Until about 1850, the fields of thermodynamics and mechanics were considered to be two distinct branches of science. The principle of conservation of energy seemed to describe only certain kinds of mechanical systems. Mid-19th-century experiments performed by Englishman James Joule and others, however, showed a strong connection between the transfer of energy by heat in thermal processes and the transfer of energy by work in mechanical processes. Today we know that mechanical energy can be transformed to internal energy, which is formally defined in this chapter. Once the concept of energy was generalized from mechanics to include internal energy, the principle of conservation of energy as discussed in Chapter 8 emerged as a universal law of nature.

This chapter focuses on the concept of internal energy, the first law of thermodynamics, and some important applications of the first law. The first law of thermodynamics describes systems in which the only energy change is that of internal energy and the transfers of energy are by heat and work. A major difference in our discussion of work in this chapter from that in most of the chapters on mechanics is that we will consider work done on *deformable* systems.

20.1 Heat and Internal Energy

At the outset, it is important to make a major distinction between internal energy and heat, terms that are often incorrectly used interchangeably in popular language. **Internal energy** is all the energy of a system that is associated with its microscopic components—atoms and molecules—when viewed from a reference frame at rest with respect to the center of mass of the system.

The last part of this sentence ensures that any bulk kinetic energy of the system due to its motion through space is not included in internal energy. Internal energy includes kinetic energy of random translational, rotational, and vibrational motion of molecules; vibrational potential energy associated with forces between atoms in molecules; and electric potential energy associated with forces between molecules. It is useful to relate internal energy to the temperature of an object, but this relationship is limited. We show in Section 20.3 that internal energy changes can also occur in the absence of temperature changes. In that discussion, we will investigate the internal energy of the system when there is a *physical change*, most often related to a phase change, such as melting or boiling. We assign energy associated with *chemical changes*, related to chemical reactions, to the potential energy term in Equation 8.2, not to internal energy. Therefore, we discuss the *chemical potential energy* in, for example, a human body (due to previous meals), the gas tank of a car (due to an earlier transfer of fuel), and a battery of an electric circuit (placed in the battery during its construction in the manufacturing process).

Heat is defined as a process of transferring energy across the boundary of a system because of a temperature difference between the system and its surroundings. It is also the amount of energy *Q* transferred by this process.

When you *heat* a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature. Such is the case, for example, when you place a pan of cold water on a stove burner. The burner is at a higher temperature than the water, and so the water gains energy by heat.

Read this definition of heat (Q in Eq. 8.2) very carefully. In particular, notice what heat is *not* in the following common quotes. (1) Heat is *not* energy in a hot substance. For example, "The boiling water has a lot of heat" is incorrect; the boiling water has *internal energy* E_{int} . (2) Heat is *not* radiation. For example, "It was so hot because the sidewalk was radiating heat" is incorrect; energy is leaving the sidewalk by *electromagnetic radiation*, T_{ER} in Equation 8.2. (3) Heat is *not* warmth of an environment. For example, "The heat in the air was so oppressive" is incorrect; on a hot day, the air has a high *temperature* T.

As an analogy to the distinction between heat and internal energy, consider the distinction between work and mechanical energy discussed in Chapter 7. The work done on a system is a measure of the amount of energy transferred to the system from its surroundings, whereas the mechanical energy (kinetic energy plus potential energy) of a system is a consequence of the motion and configuration of the system. Therefore, when a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work *of* a system; one can refer only to the work done *on* or *by* a system when some process has occurred in which energy has been transferred to or from the system. Likewise, it makes no sense to talk about the heat *of* a system; one can refer to heat only when energy has been transferred as a result of a temperature difference. Both heat and work are ways of transferring energy between a system and its surroundings.

Units of Heat

Early studies of heat focused on the resultant increase in temperature of a substance, which was often water. Initial notions of heat were based on a fluid called *caloric* that flowed from one substance to another and caused changes in temperature. From the name of this mythical fluid came an energy unit related to thermal processes, the **calorie (cal)**, which is defined as the amount of energy transfer

Pitfall Prevention 20.1

Internal Energy, Thermal Energy, and Bond Energy When reading other physics books, you may see terms such as *thermal energy* and *bond energy*. Thermal energy can be interpreted as that part of the internal energy associated with random motion of molecules and therefore related to temperature. Bond energy is the intermolecular potential energy. Therefore,

Internal energy =

thermal energy + bond energy

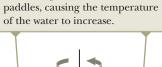
Although this breakdown is presented here for clarification with regard to other books, we will not use these terms because there is no need for them.

Pitfall Prevention 20.2

Heat, Temperature, and Internal Energy Are Different As you read the newspaper or explore the Internet, be alert for incorrectly used phrases including the word *heat* and think about the proper word to be used in place of *heat*. Incorrect examples include "As the truck braked to a stop, a large amount of heat was generated by friction" and "The heat of a hot summer day"



James Prescott Joule British physicist (1818–1889) Joule received some formal education in mathematics, philosophy, and chemistry from John Dalton but was in large part self-educated. Joule's research led to the establishment of the principle of conservation of energy. His study of the quantitative relationship among electrical, mechanical, and chemical effects of heat culminated in his announcement in 1843 of the amount of work required to produce a unit of energy, called the mechanical equivalent of heat.



The falling blocks rotate the

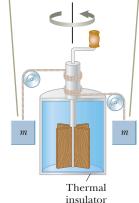


Figure 20.1 Joule's experiment for determining the mechanical equivalent of heat.

necessary to raise the temperature of 1 g of water from 14.5° C to 15.5° C.¹ (The "Calorie," written with a capital "C" and used in describing the energy content of foods, is actually a kilocalorie.) The unit of energy in the U.S. customary system is the **British thermal unit (Btu)**, which is defined as the amount of energy transfer required to raise the temperature of 1 lb of water from 63° F to 64° F.

Once the relationship between energy in thermal and mechanical processes became clear, there was no need for a separate unit related to thermal processes. The *joule* has already been defined as an energy unit based on mechanical processes. Scientists are increasingly turning away from the calorie and the Btu and are using the joule when describing thermal processes. In this textbook, heat, work, and internal energy are usually measured in joules.

The Mechanical Equivalent of Heat

In Chapters 7 and 8, we found that whenever friction is present in a mechanical system, the mechanical energy in the system decreases; in other words, mechanical energy is not conserved in the presence of nonconservative forces. Various experiments show that this mechanical energy does not simply disappear but is transformed into internal energy. You can perform such an experiment at home by hammering a nail into a scrap piece of wood. What happens to all the kinetic energy of the hammer once you have finished? Some of it is now in the nail as internal energy, as demonstrated by the nail being measurably warmer. Notice that there is *no* transfer of energy by heat in this process. For the nail and board as a nonisolated system, Equation 8.2 becomes $\Delta E_{int} = W + T_{MW}$, where *W* is the work done by the hammer on the nail and T_{MW} is the energy leaving the system by sound waves when the nail is struck. Although this connection between mechanical and internal energy was first suggested by Benjamin Thompson, it was James Prescott Joule who established the equivalence of the decrease in mechanical energy and the increase in internal energy.

A schematic diagram of Joule's most famous experiment is shown in Figure 20.1. The system of interest is the Earth, the two blocks, and the water in a thermally insulated container. Work is done within the system on the water by a rotating paddle wheel, which is driven by heavy blocks falling at a constant speed. If the energy transformed in the bearings and the energy passing through the walls by heat are neglected, the decrease in potential energy of the system as the blocks fall equals the work done by the paddle wheel on the water and, in turn, the increase in internal energy of the water. If the two blocks fall through a distance h, the decrease in potential energy of the system is 2mgh, where m is the mass of one block; this energy causes the temperature of the water to increase. By varying the conditions of the experiment, Joule found that the decrease in mechanical energy is proportional to the product of the mass of the water and the increase in water temperature. The proportionality constant was found to be approximately 4.18 $I/g \cdot {}^{\circ}C$. Hence, 4.18 J of mechanical energy raises the temperature of 1 g of water by 1°C. More precise measurements taken later demonstrated the proportionality to be 4.186 J/g \cdot °C when the temperature of the water was raised from 14.5°C to 15.5°C. We adopt this "15-degree calorie" value:

$$cal = 4.186 J$$
 (20.1)

This equality is known, for purely historical reasons, as the **mechanical equivalent of heat.** A more proper name would be *equivalence between mechanical energy and internal energy*, but the historical name is well entrenched in our language, despite the incorrect use of the word *heat*.

¹Originally, the calorie was defined as the energy transfer necessary to raise the temperature of 1 g of water by 1°C. Careful measurements, however, showed that the amount of energy required to produce a 1°C change depends somewhat on the initial temperature; hence, a more precise definition evolved.

Example 20.1 Losing Weight the Hard Way

A student eats a dinner rated at 2 000 Calories. He wishes to do an equivalent amount of work in the gymnasium by lifting a 50.0-kg barbell. How many times must he raise the barbell to expend this much energy? Assume he raises the barbell 2.00 m each time he lifts it and he regains no energy when he lowers the barbell.

AM

SOLUTION

Conceptualize Imagine the student raising the barbell. He is doing work on the system of the barbell and the Earth, so energy is leaving his body. The total amount of work that the student must do is 2 000 Calories.

Categorize We model the system of the barbell and the Earth as a *nonisolated system* for *energy*.

•••••••••••••••••••••••••••••••••••••••	
Analyze Reduce the conservation of energy equation, Equation 8.2, to the appropriate expression for the system of the barbell and the Earth:	(1) $\Delta U_{\text{total}} = W_{\text{total}}$
Express the change in gravitational potential energy of the system after the barbell is raised once:	$\Delta U = mgh$
Express the total amount of energy that must be transferred into the system by work for lifting the barbell n times, assuming energy is not regained when the barbell is lowered:	(2) $\Delta U_{\text{total}} = nmgh$
Substitute Equation (2) into Equation (1): nm	$gh = W_{\text{total}}$
Solve for <i>n</i> :	$n = rac{W_{ ext{total}}}{mgh}$
Substitute numerical values:	$n = \frac{(2\ 000\ \text{Cal})}{(50.0\ \text{kg})(9.80\ \text{m/s}^2)(2.00\ \text{m})} \left(\frac{1.00 \times 10^3\ \text{cal}}{\text{Calorie}}\right) \left(\frac{4.186\ \text{J}}{1\ \text{cal}}\right)$
	$= 8.54 \times 10^3 \text{ times}$

Finalize If the student is in good shape and lifts the barbell once every 5 s, it will take him about 12 h to perform this feat. Clearly, it is much easier for this student to lose weight by dieting.

In reality, the human body is not 100% efficient. Therefore, not all the energy transformed within the body from the dinner transfers out of the body by work done on the barbell. Some of this energy is used to pump blood and perform other functions within the body. Therefore, the 2 000 Calories can be worked off in less time than 12 h when these other energy processes are included.

20.2 Specific Heat and Calorimetry

When energy is added to a system and there is no change in the kinetic or potential energy of the system, the temperature of the system usually rises. (An exception to this statement is the case in which a system undergoes a change of state—also called a *phase transition*—as discussed in the next section.) If the system consists of a sample of a substance, we find that the quantity of energy required to raise the temperature of a given mass of the substance by some amount varies from one substance to another. For example, the quantity of energy required to raise the temperature of 1 kg of water by 1°C is 4 186 J, but the quantity of energy required to raise the temperature of 1 kg of copper by 1°C is only 387 J. In the discussion that follows, we shall use heat as our example of energy transfer, but keep in mind that the temperature of the system could be changed by means of any method of energy transfer.

The **heat capacity** *C* of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by 1°C. From this definition, we see that if energy *Q* produces a change ΔT in the temperature of a sample, then

Substance	Specific Heat (J/kg · °C)	Substance	Specific Heat (J/kg · °C)
Elemental solids		Other solids	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice $(-5^{\circ}C)$	2 0 9 0
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold Iron Lead Silicon	129 448 128 703	<i>Liquids</i> Alcohol (ethyl) Mercury	$\begin{array}{c} 2 \ 400 \\ 140 \end{array}$
	234	Water (15°C) <i>Gas</i> Steam (100°C)	4 186 2 010
Note: To convert values to	units of cal/g \cdot °C, divide by 4 1	186.	

Table 20.1	Specific Heats of Some Substances at 25°C
and Atmosp	heric Pressure

The **specific heat** c of a substance is the heat capacity per unit mass. Therefore, if energy Q transfers to a sample of a substance with mass m and the temperature of the sample changes by ΔT , the specific heat of the substance is

Specific heat >

Pitfall Prevention 20.3

An Unfortunate Choice of Terminology The name specific heat is an unfortunate holdover from the days when thermodynamics and mechanics developed separately. A better name would be specific energy transfer, but the existing term is too entrenched to be replaced.

Pitfall Prevention 20.4

Energy Can Be Transferred by Any Method The symbol Q represents the amount of energy transferred, but keep in mind that the energy transfer in Equation 20.4 could be by *any* of the methods introduced in Chapter 8; it does not have to be heat. For example, repeatedly bending a wire coat hanger raises the temperature at the bending point by *work*. $c = \frac{Q}{m\,\Delta T} \tag{20.3}$

Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular temperature change. Table 20.1 lists representative specific heats.

From this definition, we can relate the energy Q transferred between a sample of mass m of a material and its surroundings to a temperature change ΔT as

$$Q = mc \,\Delta T \tag{20.4}$$

For example, the energy required to raise the temperature of 0.500 kg of water by 3.00° C is $Q = (0.500 \text{ kg})(4 \ 186 \text{ J/kg} \cdot ^{\circ}\text{C})(3.00^{\circ}\text{C}) = 6.28 \times 10^{3} \text{ J}$. Notice that when the temperature increases, Q and ΔT are taken to be positive and energy transfers into the system. When the temperature decreases, Q and ΔT are negative and energy transfers out of the system.

We can identify $mc \Delta T$ as the change in internal energy of the system if we ignore any thermal expansion or contraction of the system. (Thermal expansion or contraction would result in a very small amount of work being done on the system by the surrounding air.) Then, Equation 20.4 is a reduced form of Equation 8.2: $\Delta E_{int} = Q$. The internal energy of the system can be changed by transferring energy into the system by any mechanism. For example, if the system is a baked potato in a microwave oven, Equation 8.2 reduces to the following analog to Equation 20.4: $\Delta E_{int} = T_{ER} = mc \Delta T$, where T_{ER} is the energy transferred to the potato from the microwave oven by electromagnetic radiation. If the system is the air in a bicycle pump, which becomes hot when the pump is operated, Equation 8.2 reduces to the following analog to Equation 20.4: $\Delta E_{int} = W = mc \Delta T$, where W is the work done on the pump by the operator. By identifying $mc \Delta T$ as ΔE_{int} , we have taken a step toward a better understanding of temperature: temperature is related to the energy of the molecules of a system. We will learn more details of this relationship in Chapter 21.

Specific heat varies with temperature. If, however, temperature intervals are not too great, the temperature variation can be ignored and c can be treated as a constant.²

²The definition given by Equation 20.4 assumes the specific heat does not vary with temperature over the interval $\Delta T = T_i - T_i$. In general, if *e* varies with temperature over the interval, the correct expression for Q is $Q = m \int_{T_i}^{T_i} c \, dT$.

For example, the specific heat of water varies by only about 1% from 0°C to 100°C at atmospheric pressure. Unless stated otherwise, we shall neglect such variations.

0 uick Quiz 20.1 Imagine you have 1 kg each of iron, glass, and water, and all

- three samples are at 10° C. (a) Rank the samples from highest to lowest tempera-
- ture after 100 J of energy is added to each sample. (b) Rank the samples from greatest to least amount of energy transferred by heat if each sample increases
- in temperature by 20°C.

Notice from Table 20.1 that water has the highest specific heat of common materials. This high specific heat is in part responsible for the moderate climates found near large bodies of water. As the temperature of a body of water decreases during the winter, energy is transferred from the cooling water to the air by heat, increasing the internal energy of the air. Because of the high specific heat of water, a relatively large amount of energy is transferred to the air for even modest temperature changes of the water. The prevailing winds on the West Coast of the United States are toward the land (eastward). Hence, the energy liberated by the Pacific Ocean as it cools keeps coastal areas much warmer than they would otherwise be. As a result, West Coast states generally have more favorable winter weather than East Coast states, where the prevailing winds do not tend to carry the energy toward land.

Calorimetry

One technique for measuring specific heat involves heating a sample to some known temperature T_x , placing it in a vessel containing water of known mass and temperature $T_w < T_x$, and measuring the temperature of the water after equilibrium has been reached. This technique is called **calorimetry**, and devices in which this energy transfer occurs are called **calorimeters**. Figure 20.2 shows the hot sample in the cold water and the resulting energy transfer by heat from the high-temperature part of the system to the low-temperature part. If the system of the sample and the water is isolated, the principle of conservation of energy requires that the amount of energy Q_{hot} that leaves the sample (of unknown specific heat) equal the amount of energy Q_{cold} that enters the water.³ Conservation of energy allows us to write the mathematical representation of this energy statement as

$$Q_{\rm cold} = -Q_{\rm hot} \tag{20.5}$$

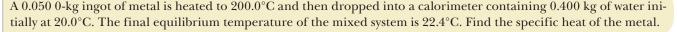
Suppose m_x is the mass of a sample of some substance whose specific heat we wish to determine. Let's call its specific heat c_x and its initial temperature T_x as shown in Figure 20.2. Likewise, let m_w , c_w , and T_w represent corresponding values for the water. If T_f is the final temperature after the system comes to equilibrium, Equation 20.4 shows that the energy transfer for the water is $m_w c_w (T_f - T_w)$, which is positive because $T_f > T_w$, and that the energy transfer for the sample of unknown specific heat is $m_x c_x (T_f - T_x)$, which is negative. Substituting these expressions into Equation 20.5 gives

$$m_w c_w (T_f - T_w) = -m_x c_x (T_f - T_x)$$

This equation can be solved for the unknown specific heat c_x .

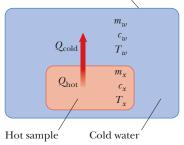
Example 20.2

Cooling a Hot Ingot



continued

³For precise measurements, the water container should be included in our calculations because it also exchanges energy with the sample. Doing so would require that we know the container's mass and composition, however. If the mass of the water is much greater than that of the container, we can neglect the effects of the container.



Isolated system boundary

Figure 20.2 In a calorimetry experiment, a hot sample whose specific heat is unknown is placed in cold water in a container that isolates the system from the environment.

Pitfall Prevention 20.5

Remember the Negative Sign It is *critical* to include the negative sign in Equation 20.5. The negative sign in the equation is necessary for consistency with our sign convention for energy transfer. The energy transfer Q_{hot} has a negative value because energy is leaving the hot substance. The negative sign in the equation ensures that the right side is a positive number, consistent with the left side, which is positive because energy is entering the cold water.

20.2 continued

SOLUTION

Conceptualize Imagine the process occurring in the isolated system of Figure 20.2. Energy leaves the hot ingot and goes into the cold water, so the ingot cools off and the water warms up. Once both are at the same temperature, the energy transfer stops.

Categorize We use an equation developed in this section, so we categorize this example as a substitution problem.

Use Equation 20.4 to evaluate each side of Equation 20.5:

Solve for c_x :

 $c_x = \frac{m_w c_w (T_f - T_w)}{m_x (T_x - T_f)}$

 $m_{w}c_{w}(T_{f}-T_{w}) = -m_{x}c_{x}(T_{f}-T_{x})$

Substitute numerical values:

 $c_x = \frac{(0.400 \text{ kg})(4 \text{ 186 J/kg} \cdot ^{\circ}\text{C})(22.4^{\circ}\text{C} - 20.0^{\circ}\text{C})}{(0.050 \text{ 0 kg})(200.0^{\circ}\text{C} - 22.4^{\circ}\text{C})}$

$= 453 \,\mathrm{J/kg} \cdot ^{\circ}\mathrm{C}$

The ingot is most likely iron as you can see by comparing this result with the data given in Table 20.1. The temperature of the ingot is initially above the steam point. Therefore, some of the water may vaporize when the ingot is dropped into the water. We assume the system is sealed and this steam cannot escape. Because the final equilibrium temperature is lower than the steam point, any steam that does result recondenses back into water.

WHAT IF? Suppose you are performing an experiment in the laboratory that uses this technique to determine the specific heat of a sample and you wish to decrease the overall uncertainty in your final result for c_{r} . Of the data given in this example, changing which value would be most effective in decreasing the uncertainty?

Answer The largest experimental uncertainty is associated with the small difference in temperature of 2.4°C for the water. For example, using the rules for propagation of uncertainty in Appendix Section B.8, an uncertainty of 0.1°C in each of T_f and T_w leads to an 8% uncertainty in their difference. For this temperature difference to be larger experimentally, the most effective change is to decrease the amount of water.

Fun Time for a Cowboy Example 20.3

A cowboy fires a silver bullet with a muzzle speed of 200 m/s into the pine wall of a saloon. Assume all the internal energy generated by the impact remains with the bullet. What is the temperature change of the bullet?

SOLUTION

Conceptualize Imagine similar experiences you may have had in which mechanical energy is transformed to internal energy when a moving object is stopped. For example, as mentioned in Section 20.1, a nail becomes warm after it is hit a few times with a hammer.

Categorize The bullet is modeled as an *isolated system*. No work is done on the system because the force from the wall moves through no displacement. This example is similar to the skateboarder pushing off a wall in Section 9.7. There, no work is done on the skateboarder by the wall, and potential energy stored in the body from previous meals is transformed to kinetic energy. Here, no work is done by the wall on the bullet, and kinetic energy is transformed to internal energy.

Analyze Reduce the conservation of energy equation,

Equation 8.2, to the appropriate expression for the system of the bullet:

The change in the bullet's internal energy is related to its change in temperature:

Substitute Equation (2) into Equation (1):

(1) $\Delta K + \Delta E_{int} = 0$

(2) $\Delta E_{\rm int} = mc \,\Delta T$

 $\left(0 - \frac{1}{2}mv^2\right) + mc\Delta T = 0$

20.3 continued

Solve for ΔT , using 234 J/kg \cdot °C as the specific heat of silver (see Table 20.1):

(3)
$$\Delta T = \frac{\frac{1}{2}mv^2}{mc} = \frac{v^2}{2c} = \frac{(200 \text{ m/s})^2}{2(234 \text{ J/kg} \cdot ^\circ\text{C})} = 85.5^\circ\text{C}$$

Finalize Notice that the result does not depend on the mass of the bullet.

WHAT IF? Suppose the cowboy runs out of silver bullets and fires a lead bullet at the same speed into the wall. Will the temperature change of the bullet be larger or smaller?

Answer Table 20.1 shows that the specific heat of lead is $128 \text{ J/kg} \cdot ^{\circ}\text{C}$, which is smaller than that for silver. Therefore, a given amount of energy input or transformation raises lead to a higher temperature than silver and the final temperature of the lead bullet will be larger. In Equation (3), let's substitute the new value for the specific heat:

$$\Delta T = \frac{v^2}{2c} = \frac{(200 \text{ m/s})^2}{2(128 \text{ J/kg} \cdot ^\circ\text{C})} = 156^\circ\text{C}$$

There is no requirement that the silver and lead bullets have the same mass to determine this change in temperature. The only requirement is that they have the same speed.

20.3 Latent Heat

As we have seen in the preceding section, a substance can undergo a change in temperature when energy is transferred between it and its surroundings. In some situations, however, the transfer of energy does not result in a change in temperature. That is the case whenever the physical characteristics of the substance change from one form to another; such a change is commonly referred to as a **phase change**. Two common phase changes are from solid to liquid (melting) and from liquid to gas (boiling); another is a change in the crystalline structure of a solid. All such phase changes involve a change in the system's internal energy but no change in its temperature. The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

As you might expect, different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangements vary. Also, the amount of energy transferred during a phase change depends on the amount of substance involved. (It takes less energy to melt an ice cube than it does to thaw a frozen lake.) When discussing two phases of a material, we will use the term *higher-phase material* to mean the material existing at the higher temperature. So, for example, if we discuss water and ice, water is the higher-phase material, whereas steam is the higher-phase material in a discussion of steam and water. Consider a system containing a substance in two phases in equilibrium such as water and ice. The initial amount of the higher-phase material, water, in the system is m_i . Now imagine that energy Q enters the system. As a result, the final amount of water is m_f due to the melting of some of the ice. Therefore, the amount of ice that melted, equal to the amount of *new* water, is $\Delta m = m_f - m_i$. We define the **latent heat** for this phase change as

$$L = \frac{Q}{\Delta m}$$
(20.6)

This parameter is called latent heat (literally, the "hidden" heat) because this added or removed energy does not result in a temperature change. The value of L for a substance depends on the nature of the phase change as well as on the properties of the substance. If the entire amount of the lower-phase material undergoes a phase change, the change in mass Δm of the higher-phase material is equal to the initial mass of the lower-phase material. For example, if an ice cube of mass m on a

Table 20.

Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
-272.2	5.23×10^{3}	-268.93	2.09×10^{4}
-218.79	$1.38 imes 10^4$	-182.97	$2.13 imes10^5$
-209.97	$2.55 imes 10^4$	-195.81	$2.01 imes 10^5$
-114	$1.04 imes 10^5$	78	$8.54 imes10^5$
0.00	$3.33 imes 10^5$	100.00	$2.26 imes10^6$
119	$3.81 imes 10^4$	444.60	$3.26 imes10^5$
327.3	$2.45 imes 10^4$	1 750	$8.70 imes10^5$
660	$3.97 imes10^5$	2450	$1.14 imes 10^7$
960.80	$8.82 imes 10^4$	2 193	$2.33 imes 10^6$
$1\ 063.00$	$6.44 imes 10^4$	2660	$1.58 imes10^6$
1 083	$1.34 imes 10^5$	1 187	$5.06 imes10^6$
	Point (°Č) -272.2 -218.79 -209.97 -114 0.00 119 327.3 660 960.80 1 063.00	$\begin{array}{c c} \mbox{Melting}\\ \mbox{Point (°C)} & \mbox{of Fusion}\\ \mbox{(J/kg)} \\ \hline \label{eq:J-2} \\ -272.2 & 5.23 \times 10^3 \\ -218.79 & 1.38 \times 10^4 \\ -209.97 & 2.55 \times 10^4 \\ -114 & 1.04 \times 10^5 \\ 0.00 & 3.33 \times 10^5 \\ 119 & 3.81 \times 10^4 \\ 327.3 & 2.45 \times 10^4 \\ 660 & 3.97 \times 10^5 \\ 960.80 & 8.82 \times 10^4 \\ 1063.00 & 6.44 \times 10^4 \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

2	Latent Heats	of Fusion a	and Vaporization
---	--------------	-------------	------------------

^aHelium does not solidify at atmospheric pressure. The melting point given here corresponds to a pressure of 2.5 MPa.

plate melts completely, the change in mass of the water is $m_f - 0 = m$, which is the mass of new water and is also equal to the initial mass of the ice cube.

From the definition of latent heat, and again choosing heat as our energy transfer mechanism, the energy required to change the phase of a pure substance is

$$Q = L \Delta m \tag{20.7}$$

where Δm is the change in mass of the higher-phase material.

Latent heat of fusion L_f is the term used when the phase change is from solid to liquid (to fuse means "to combine by melting"), and latent heat of vaporization L_v is the term used when the phase change is from liquid to gas (the liquid "vaporizes").⁴ The latent heats of various substances vary considerably as data in Table 20.2 show. When energy enters a system, causing melting or vaporization, the amount of the higher-phase material increases, so Δm is positive and Q is positive, consistent with our sign convention. When energy is extracted from a system, causing freezing or condensation, the amount of the higher-phase material decreases, so Δm is negative and Q is negative, again consistent with our sign convention. Keep in mind that Δm in Equation 20.7 always refers to the higher-phase material.

To understand the role of latent heat in phase changes, consider the energy required to convert a system consisting of a 1.00-g cube of ice at -30.0° C to steam at 120.0°C. Figure 20.3 indicates the experimental results obtained when energy is gradually added to the ice. The results are presented as a graph of temperature of the system versus energy added to the system. Let's examine each portion of the red-brown curve, which is divided into parts A through E.

Part A. On this portion of the curve, the temperature of the system changes from -30.0° C to 0.0° C. Equation 20.4 indicates that the temperature varies linearly with the energy added, so the experimental result is a straight line on the graph. Because the specific heat of ice is 2 090 J/kg \cdot °C, we can calculate the amount of energy added by using Equation 20.4:

$$Q = m_i c_i \Delta T = (1.00 \times 10^{-3} \text{ kg})(2.090 \text{ J/kg} \cdot ^{\circ}\text{C})(30.0^{\circ}\text{C}) = 62.7 \text{ J}$$

Part B. When the temperature of the system reaches 0.0°C, the ice–water mixture remains at this temperature—even though energy is being added—until all the ice melts. The energy required to melt 1.00 g of ice at 0.0°C is, from Equation 20.7,

$$Q = L_f \Delta m_w = L_f m_i = (3.33 \times 10^5 \,\text{J/kg})(1.00 \times 10^{-3} \,\text{kg}) = 333 \,\text{J}$$

Energy transferred to a substance during a phase change

Pitfall Prevention 20.6

Signs Are Critical Sign errors occur very often when students apply calorimetry equations. For phase changes, remember that Δm in Equation 20.7 is always the change in mass of the higherphase material. In Equation 20.4, be sure your ΔT is *always* the final temperature minus the initial temperature. In addition, you must *always* include the negative sign on the right side of Equation 20.5.

⁴When a gas cools, it eventually *condenses*; that is, it returns to the liquid phase. The energy given up per unit mass is called the *latent heat of condensation* and is numerically equal to the latent heat of vaporization. Likewise, when a liquid cools, it eventually solidifies, and the *latent heat of solidification* is numerically equal to the latent heat of fusion.

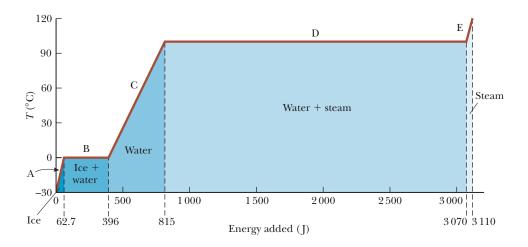


Figure 20.3 A plot of temperature versus energy added when a system initially consisting of 1.00 g of ice at -30.0° C is converted to steam at 120.0°C.

At this point, we have moved to the 396 J (= 62.7 J + 333 J) mark on the energy axis in Figure 20.3.

Part C. Between 0.0° C and 100.0° C, nothing surprising happens. No phase change occurs, and so all energy added to the system, which is now water, is used to increase its temperature. The amount of energy necessary to increase the temperature from 0.0° C to 100.0° C is

$$Q = m_w c_w \Delta T = (1.00 \times 10^{-3} \text{ kg})(4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C})(100.0^\circ\text{C}) = 419 \text{ J}$$

where m_w is the mass of the water in the system, which is the same as the mass m_i of the original ice.

Part D. At 100.0°C, another phase change occurs as the system changes from water at 100.0°C to steam at 100.0°C. Similar to the ice–water mixture in part B, the water–steam mixture remains at 100.0°C—even though energy is being added until all the liquid has been converted to steam. The energy required to convert 1.00 g of water to steam at 100.0°C is

$$Q = L_{y} \Delta m_{s} = L_{y} m_{y} = (2.26 \times 10^{6} \text{ J/kg})(1.00 \times 10^{-3} \text{ kg}) = 2.26 \times 10^{3} \text{ J}$$

Part E. On this portion of the curve, as in parts A and C, no phase change occurs; therefore, all energy added is used to increase the temperature of the system, which is now steam. The energy that must be added to raise the temperature of the steam from 100.0°C to 120.0°C is

$$Q = m_{\rm s}c_{\rm s}\Delta T = (1.00 \times 10^{-3} \,{\rm kg})(2.01 \times 10^{3} \,{\rm J/kg} \cdot {\rm ^{\circ}C})(20.0{\rm ^{\circ}C}) = 40.2 \,{\rm J}$$

The total amount of energy that must be added to the system to change 1 g of ice at -30.0° C to steam at 120.0° C is the sum of the results from all five parts of the curve, which is 3.11×10^{3} J. Conversely, to cool 1 g of steam at 120.0° C to ice at -30.0° C, we must remove 3.11×10^{3} J of energy.

Notice in Figure 20.3 the relatively large amount of energy that is transferred into the water to vaporize it to steam. Imagine reversing this process, with a large amount of energy transferred out of steam to condense it into water. That is why a burn to your skin from steam at 100°C is much more damaging than exposure of your skin to water at 100°C. A very large amount of energy enters your skin from the steam, and the steam remains at 100°C for a long time while it condenses. Conversely, when your skin makes contact with water at 100°C, the water immediately begins to drop in temperature as energy transfers from the water to your skin.

If liquid water is held perfectly still in a very clean container, it is possible for the water to drop below 0°C without freezing into ice. This phenomenon, called **super-cooling**, arises because the water requires a disturbance of some sort for the molecules to move apart and start forming the large, open ice structure that makes the

density of ice lower than that of water as discussed in Section 19.4. If supercooled water is disturbed, it suddenly freezes. The system drops into the lower-energy configuration of bound molecules of the ice structure, and the energy released raises the temperature back to 0° C.

Commercial hand warmers consist of liquid sodium acetate in a sealed plastic pouch. The solution in the pouch is in a stable supercooled state. When a disk in the pouch is clicked by your fingers, the liquid solidifies and the temperature increases, just like the supercooled water just mentioned. In this case, however, the freezing point of the liquid is higher than body temperature, so the pouch feels warm to the touch. To reuse the hand warmer, the pouch must be boiled until the solid liquefies. Then, as it cools, it passes below its freezing point into the supercooled state.

It is also possible to create **superheating.** For example, clean water in a very clean cup placed in a microwave oven can sometimes rise in temperature beyond 100°C without boiling because the formation of a bubble of steam in the water requires scratches in the cup or some type of impurity in the water to serve as a nucleation site. When the cup is removed from the microwave oven, the superheated water can become explosive as bubbles form immediately and the hot water is forced upward out of the cup.

uick Quiz 20.2 Suppose the same process of adding energy to the ice cube is
performed as discussed above, but instead we graph the internal energy of the
system as a function of energy input. What would this graph look like?

Example 20.4 Cooling the Steam AM

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

SOLUTION

Conceptualize Imagine placing water and steam together in a closed insulated container. The system eventually reaches a uniform state of water with a final temperature of 50.0°C.

Categorize Based on our conceptualization of this situation, we categorize this example as one involving calorimetry in which a phase change occurs. The calorimeter is an *isolated system* for *energy*: energy transfers between the components of the system but does not cross the boundary between the system and the environment.

Analyze Write Equation 20.5 to describe the calo- (1) $Q_{cold} = -Q_{hot}$ rimetry process:

The steam undergoes three processes: first a decrease in temperature to 100°C, then condensation into liquid water, and finally a decrease in temperature of the water to 50.0°C. Find the energy transfer in the first process using the unknown mass m_s of the steam:

Find the energy transfer in the second process:

Find the energy transfer in the third process:

Add the energy transfers in these three stages:

The 20.0°C water and the glass undergo only one process, an increase in temperature to 50.0°C. Find the energy transfer in this process:

Substitute Equations (2) and (3) into Equation (1):

Solve for m_s :

$$Q_1 = m_s c_s \, \Delta T_s$$

 $Q_2 = L_v \Delta m_s = L_v (0 - m_s) = -m_s L_v$ $Q_3 = m_s c_w \Delta T_{\text{hot water}}$

(2) $Q_{\text{hot}} = Q_1 + Q_2 + Q_3 = m_s(c_s \Delta T_s - L_v + c_w \Delta T_{\text{hot water}})$

(3)
$$Q_{\text{cold}} = m_w c_w \Delta T_{\text{cold water}} + m_g c_g \Delta T_{\text{glass}}$$

$$\begin{split} m_w c_w \,\Delta T_{\rm cold\ water} + m_g c_g \,\Delta T_{\rm glass} &= -m_s (c_s \,\Delta T_s - L_v + c_w \,\Delta T_{\rm hot\ water}) \\ m_s &= -\frac{m_w c_w \,\Delta T_{\rm cold\ water} + m_g c_g \,\Delta T_{\rm glass}}{c_s \,\Delta T_s - L_v + c_w \,\Delta T_{\rm hot\ water}} \end{split}$$

20.4 continued

	Substitute	$m_{\rm c} = -\frac{(0.200 \text{ kg})(4186 \text{ J/kg} \cdot ^{\circ}\text{C})(50.0^{\circ}\text{C} - 20.0^{\circ}\text{C}) + (0.100 \text{ kg})(837 \text{ J/kg} \cdot ^{\circ}\text{C})(50.0^{\circ}\text{C} - 20.0^{\circ}\text{C})}{(6.000 \text{ kg})(4186 \text{ J/kg} \cdot ^{\circ}\text{C})(50.0^{\circ}\text{C} - 20.0^{\circ}\text{C}) + (0.100 \text{ kg})(837 \text{ J/kg} \cdot ^{\circ}\text{C})(50.0^{\circ}\text{C} - 20.0^{\circ}\text{C})}$
	numerical	$m_s = -\frac{1}{(2\ 010\ \text{J/kg} \cdot ^\circ\text{C})(100^\circ\text{C} - 130^\circ\text{C}) - (2.26 \times 10^6\ \text{J/kg}) + (4\ 186\ \text{J/kg} \cdot ^\circ\text{C})(50.0^\circ\text{C} - 100^\circ\text{C})}$
	values:	$= 1.09 \times 10^{-2} \text{ kg} = 10.9 \text{ g}$
1		

WHAT IF? What if the final state of the system is water at 100°C? Would we need more steam or less steam? How would the analysis above change?

Answer More steam would be needed to raise the temperature of the water and glass to 100°C instead of 50.0°C. There would be two major changes in the analysis. First, we would not have a term Q_3 for the steam because the water that condenses from the steam does not cool below 100°C. Second, in Q_{cold} , the temperature change would be 80.0°C instead of 30.0°C. For practice, show that the result is a required mass of steam of 31.8 g.

20.4 Work and Heat in Thermodynamic Processes

In thermodynamics, we describe the *state* of a system using such variables as pressure, volume, temperature, and internal energy. As a result, these quantities belong to a category called **state variables.** For any given configuration of the system, we can identify values of the state variables. (For mechanical systems, the state variables include kinetic energy K and potential energy U.) A state of a system can be specified only if the system is in thermal equilibrium internally. In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

A second category of variables in situations involving energy is **transfer variables**. These variables are those that appear on the right side of the conservation of energy equation, Equation 8.2. Such a variable has a nonzero value if a process occurs in which energy is transferred across the system's boundary. The transfer variable is positive or negative, depending on whether energy is entering or leaving the system. Because a transfer of energy across the boundary represents a change in the system, transfer variables are not associated with a given state of the system, but rather with a *change* in the state of the system.

In the previous sections, we discussed heat as a transfer variable. In this section, we study another important transfer variable for thermodynamic systems, work. Work performed on particles was studied extensively in Chapter 7, and here we investigate the work done on a deformable system, a gas. Consider a gas contained in a cylinder fitted with a movable piston (Fig. 20.4). At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A, the magnitude of the force exerted by the gas on the piston is F = PA. By Newton's third law, the magnitude of the force exerted by the piston on the gas is also PA. Now let's assume we push the piston inward and compress the gas **quasi-statically**, that is, slowly enough to allow the system to remain essentially in internal thermal equilibrium at all times. The point of application of the force on the gas is the bottom face of the piston. As the piston is pushed downward by an external force $\vec{F} = -F\hat{j}$ through a displacement of $d\vec{r} = dy\hat{j}$ (Fig. 20.4b), the work done on the gas is, according to our definition of work in Chapter 7,

$$dW = \vec{\mathbf{F}} \cdot d\vec{\mathbf{r}} = -F\hat{\mathbf{j}} \cdot dy\hat{\mathbf{j}} = -F\,dy = -PA\,dy$$

The mass of the piston is assumed to be negligible in this discussion. Because A dy is the change in volume of the gas dV, we can express the work done on the gas as

$$dW = -P \, dV \tag{20.8}$$

If the gas is compressed, dV is negative and the work done on the gas is positive. If the gas expands, dV is positive and the work done on the gas is negative. If the

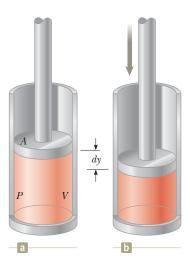


Figure 20.4 Work is done on a gas contained in a cylinder at a pressure *P* as the piston is pushed downward so that the gas is compressed.

volume remains constant, the work done on the gas is zero. The total work done on the gas as its volume changes from V_i to V_f is given by the integral of Equation 20.8:

Work done on a gas 🕨

The work done on a gas equals the negative of the area under the PV curve. The area is negative here because the volume is decreasing, resulting in positive work.

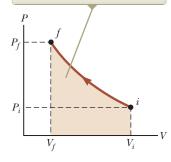


Figure 20.5 A gas is compressed quasi-statically (slowly) from state i to state f. An outside agent must do positive work on the gas to compress it.

$$W = -\int_{V_i}^{V_f} P \, dV$$
 (20.9)

To evaluate this integral, you must know how the pressure varies with volume during the process.

In general, the pressure is not constant during a process followed by a gas, but depends on the volume and temperature. If the pressure and volume are known at each step of the process, the state of the gas at each step can be plotted on an important graphical representation called a PV diagram as in Figure 20.5. This type of diagram allows us to visualize a process through which a gas is progressing. The curve on a *PV* diagram is called the *path* taken between the initial and final states.

Notice that the integral in Equation 20.9 is equal to the area under a curve on a PV diagram. Therefore, we can identify an important use for PV diagrams:

The work done on a gas in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on a PV diagram, evaluated between the initial and final states.

For the process of compressing a gas in a cylinder, the work done depends on the particular path taken between the initial and final states as Figure 20.5 suggests. To illustrate this important point, consider several different paths connecting i and f(Fig. 20.6). In the process depicted in Figure 20.6a, the volume of the gas is first reduced from V_i to V_f at constant pressure P_i and the pressure of the gas then increases from P_i to P_f by heating at constant volume V_f . The work done on the gas along this path is $-P_i(V_i - V_i)$. In Figure 20.6b, the pressure of the gas is increased from P_i to P_f at constant volume V_i and then the volume of the gas is reduced from V_i to V_f at constant pressure P_f . The work done on the gas is $-P_f(V_f - V_i)$. This value is greater than that for the process described in Figure 20.6a because the piston is moved through the same displacement by a larger force. Finally, for the process described in Figure 20.6c, where both P and V change continuously, the work done on the gas has some value between the values obtained in the first two processes. To evaluate the work in this case, the function P(V) must be known so that we can evaluate the integral in Equation 20.9.

The energy transfer Q into or out of a system by heat also depends on the process. Consider the situations depicted in Figure 20.7. In each case, the gas has the same initial volume, temperature, and pressure, and is assumed to be ideal. In Figure 20.7a, the gas is thermally insulated from its surroundings except at the bottom of the gas-filled region, where it is in thermal contact with an energy reservoir. An *energy* reservoir is a source of energy that is considered to be so great that a finite transfer of energy to or from the reservoir does not change its temperature. The piston is held

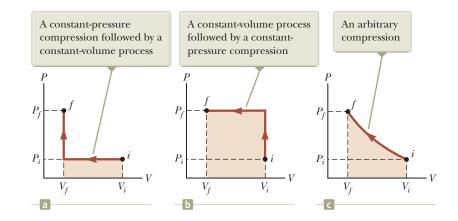


Figure 20.6 The work done on a gas as it is taken from an initial state to a final state depends on the path between these states.

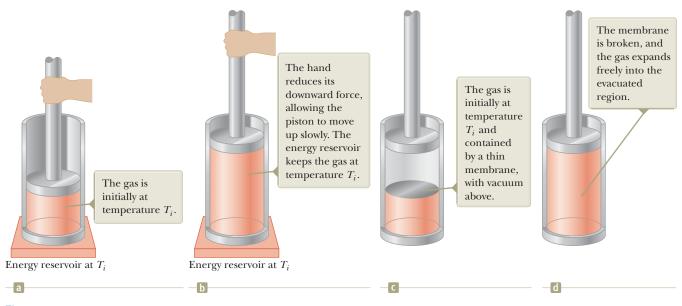


Figure 20.7 Gas in a cylinder. (a) The gas is in contact with an energy reservoir. The walls of the cylinder are perfectly insulating, but the base in contact with the reservoir is conducting. (b) The gas expands slowly to a larger volume. (c) The gas is contained by a membrane in half of a volume, with vacuum in the other half. The entire cylinder is perfectly insulating. (d) The gas expands freely into the larger volume.

at its initial position by an external agent such as a hand. When the force holding the piston is reduced slightly, the piston rises very slowly to its final position shown in Figure 20.7b. Because the piston is moving upward, the gas is doing work on the piston. During this expansion to the final volume V_j , just enough energy is transferred by heat from the reservoir to the gas to maintain a constant temperature T_j .

Now consider the completely thermally insulated system shown in Figure 20.7c. When the membrane is broken, the gas expands rapidly into the vacuum until it occupies a volume V_f and is at a pressure P_f . The final state of the gas is shown in Figure 20.7d. In this case, the gas does no work because it does not apply a force; no force is required to expand into a vacuum. Furthermore, no energy is transferred by heat through the insulating wall.

As we discuss in Section 20.5, experiments show that the temperature of the ideal gas does not change in the process indicated in Figures 20.7c and 20.7d. Therefore, the initial and final states of the ideal gas in Figures 20.7a and 20.7b are identical to the initial and final states in Figures 20.7c and 20.7d, but the paths are different. In the first case, the gas does work on the piston and energy is transferred slowly to the gas by heat. In the second case, no energy is transferred by heat and the value of the work done is zero. Therefore, energy transfer by heat, like work done, depends on the particular process occurring in the system. In other words, because heat and work both depend on the path followed on a PV diagram between the initial and final states, neither quantity is determined solely by the endpoints of a thermodynamic process.

20.5 The First Law of Thermodynamics

When we introduced the law of conservation of energy in Chapter 8, we stated that the change in the energy of a system is equal to the sum of all transfers of energy across the system's boundary (Eq. 8.2). The **first law of thermodynamics** is a special case of the law of conservation of energy that describes processes in which only the internal energy⁵ changes and the only energy transfers are by heat and work:

$$\Delta E_{\rm int} = Q + W$$

(20.10)

First law of thermodynamics

603

⁵It is an unfortunate accident of history that the traditional symbol for internal energy is U, which is also the traditional symbol for potential energy as introduced in Chapter 7. To avoid confusion between potential energy and internal energy, we use the symbol E_{int} for internal energy in this book. If you take an advanced course in thermodynamics, however, be prepared to see U used as the symbol for internal energy in the first law.

Pitfall Prevention 20.7

Dual Sign Conventions Some physics and engineering books present the first law as $\Delta E_{int} = Q - W$, with a minus sign between the heat and work. The reason is that work is defined in these treatments as the work done *by* the gas rather than *on* the gas, as in our treatment. The equivalent equation to Equation 20.9 in these treatments defines work as $W = \int_{V_i}^{V_i} P \, dV$. Therefore, if positive work is done by the gas, energy is leaving the system, leading to the negative sign in the first law.

In your studies in other chemistry or engineering courses, or in your reading of other physics books, be sure to note which sign convention is being used for the first law.

Pitfall Prevention 20.8

The First Law With our approach to energy in this book, the first law of thermodynamics is a special case of Equation 8.2. Some physicists argue that the first law is the general equation for energy conservation, equivalent to Equation 8.2. In this approach, the first law is applied to a closed system (so that there is no matter transfer), heat is interpreted so as to include electromagnetic radiation, and work is interpreted so as to include electrical transmission ("electrical work") and mechanical waves ("molecular work"). Keep that in mind if you run across the first law in your reading of other physics books.



Figure 20.8 The first law of thermodynamics equates the change in internal energy E_{int} in a system to the net energy transfer to the system by heat *Q* and work *W*. In the situation shown here, the internal energy of the gas increases.

Look back at Equation 8.2 to see that the first law of thermodynamics is contained within that more general equation.

Let us investigate some special cases in which the first law can be applied. First, consider an *isolated system*, that is, one that does not interact with its surroundings, as we have seen before. In this case, no energy transfer by heat takes place and the work done on the system is zero; hence, the internal energy remains constant. That is, because Q = W = 0, it follows that $\Delta E_{int} = 0$; therefore, $E_{int,i} = E_{int,f}$. We conclude that the internal energy E_{int} of an isolated system remains constant.

Next, consider the case of a system that can exchange energy with its surroundings and is taken through a **cyclic process**, that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero because E_{int} is a state variable; therefore, the energy Q added to the system must equal the negative of the work W done on the system during the cycle. That is, in a cyclic process,

$$\Delta E_{\text{int}} = 0$$
 and $Q = -W$ (cyclic process)

On a *PV* diagram for a gas, a cyclic process appears as a closed curve. (The processes described in Figure 20.6 are represented by open curves because the initial and final states differ.) It can be shown that in a cyclic process for a gas, the net work done on the system per cycle equals the area enclosed by the path representing the process on a *PV* diagram.

20.6 Some Applications of the First Law of Thermodynamics

In this section, we consider additional applications of the first law to processes through which a gas is taken. As a model, let's consider the sample of gas contained in the piston–cylinder apparatus in Figure 20.8. This figure shows work being done on the gas and energy transferring in by heat, so the internal energy of the gas is rising. In the following discussion of various processes, refer back to this figure and mentally alter the directions of the transfer of energy to reflect what is happening in the process.

Before we apply the first law of thermodynamics to specific systems, it is useful to first define some idealized thermodynamic processes. An **adiabatic process** is one during which no energy enters or leaves the system by heat; that is, Q = 0. An adiabatic process can be achieved either by thermally insulating the walls of the system or by performing the process rapidly so that there is negligible time for energy to transfer by heat. Applying the first law of thermodynamics to an adiabatic process gives

$$\Delta E_{\rm int} = W \quad \text{(adiabatic process)} \tag{20.11}$$

This result shows that if a gas is compressed adiabatically such that W is positive, then ΔE_{int} is positive and the temperature of the gas increases. Conversely, the temperature of a gas decreases when the gas expands adiabatically.

Adiabatic processes are very important in engineering practice. Some common examples are the expansion of hot gases in an internal combustion engine, the liquefaction of gases in a cooling system, and the compression stroke in a diesel engine.

The process described in Figures 20.7c and 20.7d, called an **adiabatic free** expansion, is unique. The process is adiabatic because it takes place in an insulated container. Because the gas expands into a vacuum, it does not apply a force on a piston as does the gas in Figures 20.7a and 20.7b, so no work is done on or by the gas. Therefore, in this adiabatic process, both Q = 0 and W = 0. As a result, $\Delta E_{int} =$ 0 for this process as can be seen from the first law. That is, the initial and final internal energies of a gas are equal in an adiabatic free expansion. As we shall see in Chapter 21, the internal energy of an ideal gas depends only on its temperature. Therefore, we expect no change in temperature during an adiabatic free expansion. This prediction is in accord with the results of experiments performed at low pressures. (Experiments performed at high pressures for real gases show a slight change in temperature after the expansion due to intermolecular interactions, which represent a deviation from the model of an ideal gas.)

A process that occurs at constant pressure is called an **isobaric process.** In Figure 20.8, an isobaric process could be established by allowing the piston to move freely so that it is always in equilibrium between the net force from the gas pushing upward and the weight of the piston plus the force due to atmospheric pressure pushing downward. The first process in Figure 20.6a and the second process in Figure 20.6b are both isobaric.

In such a process, the values of the heat and the work are both usually nonzero. The work done on the gas in an isobaric process is simply

$$W = -P(V_f - V_i) \quad \text{(isobaric process)} \tag{20.12}$$

where P is the constant pressure of the gas during the process.

A process that takes place at constant volume is called an **isovolumetric process.** In Figure 20.8, clamping the piston at a fixed position would ensure an isovolumetric process. The second process in Figure 20.6a and the first process in Figure 20.6b are both isovolumetric.

Because the volume of the gas does not change in such a process, the work given by Equation 20.9 is zero. Hence, from the first law we see that in an isovolumetric process, because W = 0,

$$\Delta E_{\rm int} = Q \quad \text{(isovolumetric process)} \tag{20.13}$$

This expression specifies that if energy is added by heat to a system kept at constant volume, all the transferred energy remains in the system as an increase in its internal energy. For example, when a can of spray paint is thrown into a fire, energy enters the system (the gas in the can) by heat through the metal walls of the can. Consequently, the temperature, and therefore the pressure, in the can increases until the can possibly explodes.

A process that occurs at constant temperature is called an **isothermal process**. This process can be established by immersing the cylinder in Figure 20.8 in an ice-water bath or by putting the cylinder in contact with some other constant-temperature reservoir. A plot of *P* versus *V* at constant temperature for an ideal gas yields a hyperbolic curve called an *isotherm*. The internal energy of an ideal gas is a function of temperature only. Hence, because the temperature does not change in an isothermal process involving an ideal gas, we must have $\Delta E_{int} = 0$. For an isothermal process, we conclude from the first law that the energy transfer *Q* must be equal to the negative of the work done on the gas; that is, Q = -W. Any energy that enters the system by heat is transferred out of the system by work; as a result, no change in the internal energy of the system occurs in an isothermal process.

Q uick Quiz 20.3 In the last three columns of the following table, fill in the boxes with the correct signs (-, +, or 0) for Q, W, and ΔE_{int} . For each situation, the system to be considered is identified.

Situation	System	Q	W	$\Delta E_{\rm int}$
(a) Rapidly pumping up a bicycle tire	Air in the pump			
(b) Pan of room-temperature water sitting on a hot stove	Water in the pan			
(c) Air quickly leaking out of a balloon	Air originally in the balloon			

Isobaric process

Isovolumetric process

Isothermal process

Pitfall Prevention 20.9

 $D \neq 0$ in an Isothermal Process Do not fall into the common trap of thinking there must be no transfer of energy by heat if the temperature does not change as is the case in an isothermal process. Because the cause of temperature change can be either heat *or* work, the temperature can remain constant even if energy enters the gas by heat, which can only happen if the energy entering the gas by heat leaves by work.

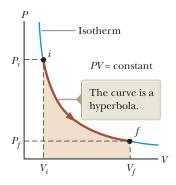


Figure 20.9 The *PV* diagram for an isothermal expansion of an ideal gas from an initial state to a final state.

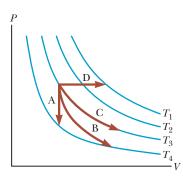


Figure 20.10 (Quick Quiz 20.4) Identify the nature of paths A, B, C, and D.

Isothermal Expansion of an Ideal Gas

Suppose an ideal gas is allowed to expand quasi-statically at constant temperature. This process is described by the *PV* diagram shown in Figure 20.9. The curve is a hyperbola (see Appendix B, Eq. B.23), and the ideal gas law (Eq. 19.8) with *T* constant indicates that the equation of this curve is PV = nRT = constant.

Let's calculate the work done on the gas in the expansion from state *i* to state *f*. The work done on the gas is given by Equation 20.9. Because the gas is ideal and the process is quasi-static, the ideal gas law is valid for each point on the path. Therefore,

$$W = -\int_{V_i}^{V_f} P \, dV = -\int_{V_i}^{V_f} \frac{nRT}{V} \, dV$$

Because T is constant in this case, it can be removed from the integral along with n and R:

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln V \Big|_{V_i}^{V_f}$$

To evaluate the integral, we used $\int (dx/x) = \ln x$. (See Appendix B.) Evaluating the result at the initial and final volumes gives

$$W = nRT \ln \left(\frac{V_i}{V_f}\right)$$
(20.14)

Numerically, this work Wequals the negative of the shaded area under the PV curve shown in Figure 20.9. Because the gas expands, $V_f > V_i$ and the value for the work done on the gas is negative as we expect. If the gas is compressed, then $V_f < V_i$ and the work done on the gas is positive.

uick Quiz 20.4 Characterize the paths in Figure 20.10 as isobaric, isovolumetiric, isothermal, or adiabatic. For path B, Q = 0. The blue curves are isotherms.

Example 20.5 An Isothermal Expansion

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 L to 10.0 L.

(A) How much work is done on the gas during the expansion?

SOLUTION

Conceptualize Run the process in your mind: the cylinder in Figure 20.8 is immersed in an ice-water bath, and the piston moves outward so that the volume of the gas increases. You can also use the graphical representation in Figure 20.9 to conceptualize the process.

Categorize We will evaluate parameters using equations developed in the preceding sections, so we categorize this example as a substitution problem. Because the temperature of the gas is fixed, the process is isothermal.

Substitute the given values into Equation 20.14:

$$W = nRT \ln \left(\frac{V_i}{V_f}\right)$$

= (1.0 mol)(8.31 J/mol · K)(273 K) ln $\left(\frac{3.0 L}{10.0 L}\right)$
= -2.7 × 10³ J

(B) How much energy transfer by heat occurs between the gas and its surroundings in this process?

SOLUTION

Find the heat from the first law:

$$\Delta E_{\text{int}} = Q + W$$

$$0 = Q + W$$

$$Q = -W = 2.7 \times 10^3 \text{ J}$$

20.5 continued

(C) If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas?

SOLUTION

Use Equation 20.12. The pressure is not given, so incorporate the ideal gas law:

$$W = -P(V_f - V_i) = -\frac{nRT_i}{V_i}(V_f - V_i)$$

= $-\frac{(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{10.0 \times 10^{-3} \text{ m}^3} (3.0 \times 10^{-3} \text{ m}^3 - 10.0 \times 10^{-3} \text{ m}^3)$
= $1.6 \times 10^3 \text{ J}$

We used the initial temperature and volume to calculate the work done because the final temperature was unknown. The work done on the gas is positive because the gas is being compressed.

Example 20.6 **Boiling Water**

Suppose 1.00 g of water vaporizes isobarically at atmospheric pressure $(1.013 \times 10^5 \text{ Pa})$. Its volume in the liquid state is $V_i = V_{\text{liquid}} = 1.00 \text{ cm}^3$, and its volume in the vapor state is $V_f = V_{\text{vapor}} = 1.671 \text{ cm}^3$. Find the work done in the expansion and the change in internal energy of the system. Ignore any mixing of the steam and the surrounding air; imagine that the steam simply pushes the surrounding air out of the way.

SOLUTION

Conceptualize Notice that the temperature of the system does not change. There is a phase change occurring as the water evaporates to steam.

Categorize Because the expansion takes place at constant pressure, we categorize the process as isobaric. We will use equations developed in the preceding sections, so we categorize this example as a substitution problem.

Use Equation 20.12 to find the work done on the sys- tem as the air is pushed out of the way:	$W = -P(V_f - V_i)$ = -(1.013 × 10 ⁵ Pa)(1 671 × 10 ⁻⁶ m ³ - 1.00 × 10 ⁻⁶ m ³) = -169 J
Use Equation 20.7 and the latent heat of vaporization for water to find the energy transferred into the system by heat:	$Q = L_v \Delta m_s = m_s L_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg})$ $= 2\ 260 \text{ J}$
Use the first law to find the change in internal energy	$\Delta E_{\rm int} = Q + W = 2\ 260\ \text{J} + (-169\ \text{J}) = 2.09\ \text{kJ}$

of the system:

The positive value for ΔE_{int} indicates that the internal energy of the system increases. The largest fraction of the energy (2 090 J/ 2260 J = 93%) transferred to the liquid goes into increasing the internal energy of the system. The remaining 7% of the energy transferred leaves the system by work done by the steam on the surrounding atmosphere.

Example 20.7 Heating a Solid

A 1.0-kg bar of copper is heated at atmospheric pressure so that its temperature increases from 20°C to 50°C.

(A) What is the work done on the copper bar by the surrounding atmosphere?

SOLUTION

Conceptualize This example involves a solid, whereas the preceding two examples involved liquids and gases. For a solid, the change in volume due to thermal expansion is very small.

Categorize Because the expansion takes place at constant at	mospheric pressure, we categorize the process as isobar
Analyze Find the work done on the copper bar using Equation 20.12:	$W = -P\Delta V$
Express the change in volume using Equation 19.6 and that $\beta = 3\alpha$:	$W = -P(\beta V_i \ \Delta T) = -P(3\alpha V_i \ \Delta T) = -3\alpha P V_i \ \Delta T$
Substitute for the volume in terms of the mass and den- sity of the copper:	$W = -3\alpha P\left(\frac{m}{\rho}\right)\Delta T$
Substitute numerical values: $W = -3[1.7 \times 10^{-5} (^{\circ}\text{C})]$	$^{-1}$](1.013 × 10 ⁵ N/m ²) $\left(\frac{1.0 \text{ kg}}{8.92 \times 10^3 \text{ kg/m}^3}\right)$ (50°C – 20°C
$= -1.7 \times 10^{-2} \text{ J}$	
Because this work is negative, work is done <i>by</i> the copper bar	on the atmosphere.
(B) How much energy is transferred to the copper bar by he	eat?
SOLUTION	
Use Equation 20.4 and the specific heat of copper from Table 20.1:	$Q = mc \Delta T = (1.0 \text{ kg})(387 \text{ J/kg} \cdot ^{\circ}\text{C})(50^{\circ}\text{C} - 20^{\circ}\text{C})$ $= 1.2 \times 10^{4} \text{ J}$
(C) What is the increase in internal energy of the copper ba	u;
SOLUTION	
Use the first law of thermodynamics:	$\Delta E_{\text{int}} = Q + W = 1.2 \times 10^4 \text{ J} + (-1.7 \times 10^{-2} \text{ J})$ $= 1.2 \times 10^4 \text{ J}$

Finalize Most of the energy transferred into the system by heat goes into increasing the internal energy of the copper bar. The fraction of energy used to do work on the surrounding atmosphere is only about 10^{-6} . Hence, when the thermal expansion of a solid or a liquid is analyzed, the small amount of work done on or by the system is usually ignored.

20.7 Energy Transfer Mechanisms in Thermal Processes

In Chapter 8, we introduced a global approach to the energy analysis of physical processes through Equation 8.1, $\Delta E_{\text{system}} = \Sigma T$, where *T* represents energy transfer, which can occur by several mechanisms. Earlier in this chapter, we discussed two of the terms on the right side of this equation, work *W* and heat *Q*. In this section, we explore more details about heat as a means of energy transfer and two other energy transfer methods often related to temperature changes: convection (a form of matter transfer T_{MT}) and electromagnetic radiation T_{ER} .

Thermal Conduction

The process of energy transfer by heat (Q in Eq. 8.2) can also be called **conduc**tion or thermal conduction. In this process, the transfer can be represented on an atomic scale as an exchange of kinetic energy between microscopic particles—molecules, atoms, and free electrons—in which less-energetic particles gain energy in collisions with more-energetic particles. For example, if you hold one end of a long metal bar and insert the other end into a flame, you will find that the temperature of the metal in your hand soon increases. The energy reaches your hand by means of conduction. Initially, before the rod is inserted into the flame, the microscopic particles in the metal are vibrating about their equilibrium positions. As the flame raises the temperature of the rod, the particles near the flame begin to vibrate with greater and greater amplitudes. These particles, in turn, collide with their neighbors and transfer some of their energy in the collisions. Slowly, the amplitudes of vibration of metal atoms and electrons farther and farther from the flame increase until eventually those in the metal near your hand are affected. This increased vibration is detected by an increase in the temperature of the metal and of your potentially burned hand.

The rate of thermal conduction depends on the properties of the substance being heated. For example, it is possible to hold a piece of asbestos in a flame indefinitely, which implies that very little energy is conducted through the asbestos. In general, metals are good thermal conductors and materials such as asbestos, cork, paper, and fiberglass are poor conductors. Gases also are poor conductors because the separation distance between the particles is so great. Metals are good thermal conductors because they contain large numbers of electrons that are relatively free to move through the metal and so can transport energy over large distances. Therefore, in a good conductor such as copper, conduction takes place by means of both the vibration of atoms and the motion of free electrons.

Conduction occurs only if there is a difference in temperature between two parts of the conducting medium. Consider a slab of material of thickness Δx and cross-sectional area A. One face of the slab is at a temperature T_c , and the other face is at a temperature $T_h > T_c$ (Fig. 20.11). Experimentally, it is found that energy Q transfers in a time interval Δt from the hotter face to the colder one. The rate $P = Q/\Delta t$ at which this energy transfer occurs is found to be proportional to the cross-sectional area and the temperature difference $\Delta T = T_h - T_c$ and inversely proportional to the thickness:

$$P = \frac{Q}{\Delta t} \propto A \frac{\Delta T}{\Delta x}$$

Notice that *P* has units of watts when *Q* is in joules and Δt is in seconds. That is not surprising because *P* is power, the rate of energy transfer by heat. For a slab of infinitesimal thickness *dx* and temperature difference *dT*, we can write the **law of thermal conduction** as

$$P = kA \left| \frac{dT}{dx} \right|$$
(20.15)

where the proportionality constant *k* is the **thermal conductivity** of the material and |dT/dx| is the **temperature gradient** (the rate at which temperature varies with position).

Substances that are good thermal conductors have large thermal conductivity values, whereas good thermal insulators have low thermal conductivity values. Table 20.3 lists thermal conductivities for various substances. Notice that metals are generally better thermal conductors than nonmetals.

Suppose a long, uniform rod of length L is thermally insulated so that energy cannot escape by heat from its surface except at the ends as shown in Figure 20.12 (page 610). One end is in thermal contact with an energy reservoir at temperature T_c , and the other end is in thermal contact with a reservoir at temperature $T_h > T_c$. When a steady state has been reached, the temperature at each point along the rod is constant in time. In this case, if we assume k is not a function of temperature, the temperature gradient is the same everywhere along the rod and is

$$\left|\frac{dT}{dx}\right| = \frac{T_h - T_c}{L}$$

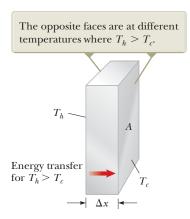


Figure 20.11 Energy transfer through a conducting slab with a cross-sectional area *A* and a thickness Δx .

Table 20.3

Thormal Conductivities

Thermal Conductivities		
Substance	Thermal Conductivity (W/m · °C)	
Metals (at 25°C)		
Aluminum	238	
Copper	397	
Gold	314	
Iron	79.5	
Lead	34.7	
Silver	427	
Nonmetals (approx	imate values)	
Asbestos	0.08	
Concrete	0.8	
Diamond	2 300	
Glass	0.8	
Ice	2	
Rubber	0.2	
Water	0.6	
Wood	0.08	
Gases (at 20°C)		
Air	0.023~4	
Helium	0.138	
Hydrogen	0.172	
Nitrogen	$0.023\ 4$	
Oxygen	$0.023\ 8$	

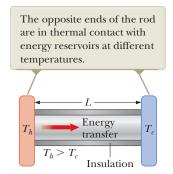


Figure 20.12 Conduction of energy through a uniform, insulated rod of length *L*.

Therefore, the rate of energy transfer by conduction through the rod is

$$P = kA\left(\frac{T_h - T_c}{L}\right)$$
(20.16)

For a compound slab containing several materials of thicknesses L_1, L_2, \ldots and thermal conductivities k_1, k_2, \ldots , the rate of energy transfer through the slab at steady state is

$$P = \frac{A(T_h - T_c)}{\sum (L_i / k_i)}$$
(20.17)

where T_h and T_c are the temperatures of the outer surfaces (which are held constant) and the summation is over all slabs. Example 20.8 shows how Equation 20.17 results from a consideration of two thicknesses of materials.

uick Quiz 20.5 You have two rods of the same length and diameter, but they are formed from different materials. The rods are used to connect two regions at different temperatures so that energy transfers through the rods by heat. They can be connected in series as in Figure 20.13a or in parallel as in Figure 20.13b. In which case is the rate of energy transfer by heat larger? (a) The rate is larger when the rods are in series. (b) The rate is larger when the rods are in parallel.
(c) The rate is the same in both cases.

Example 20.8 Energy Trai

Energy Transfer Through Two Slabs

Two slabs of thickness L_1 and L_2 and thermal conductivities k_1 and k_2 are in thermal contact with each other as shown in Figure 20.14. The temperatures of their outer surfaces are T_c and T_h , respectively, and $T_h > T_c$. Determine the temperature at the interface and the rate of energy transfer by conduction through an area A of the slabs in the steady-state condition.

SOLUTION

Conceptualize Notice the phrase "in the steady-state condition." We interpret this phrase to mean that energy transfers through the compound slab at the same rate at all points. Otherwise, energy would be building up or disappearing at some point. Furthermore, the temperature varies with position in the two slabs, most likely at different rates in each part of the compound slab. When the system is in steady state, the interface is at some fixed temperature *T*.

Categorize We categorize this example as a thermal conduction problem and impose the condition that the power is the same in both slabs of material.

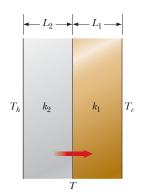


Figure 20.14 (Example 20.8) Energy transfer by conduction through two slabs in thermal contact with each other. At steady state, the rate of energy transfer through slab 1 equals the rate of energy transfer through slab 2.

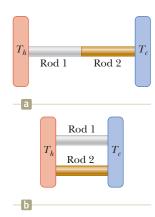


Figure 20.13 (Quick Quiz 20.5) In which case is the rate of energy transfer larger?

610

20.8 continued

Analyze Use Equation 20.16 to express the rate at which energy is transferred through an area *A* of slab 1:

Express the rate at which energy is transferred through the same area of slab 2:

Set these two rates equal to represent the steady-state situation:

Solve for *T*:

Substitute Equation (3) into either Equation (1) or Equation (2):

(1)
$$P_1 = k_1 A \left(\frac{T - T_c}{L_1} \right)$$

(2) $P_2 = k_2 A \left(\frac{T_h - T}{L_2} \right)$
 $k_1 A \left(\frac{T - T_c}{L_1} \right) = k_2 A \left(\frac{T_h - T}{L_2} \right)$
(3) $T = \frac{k_1 L_2 T_c + k_2 L_1 T_h}{k_1 L_2 + k_2 L_1}$

(4)
$$P = \frac{A(T_h - T_c)}{(L_1/k_1) + (L_2/k_2)}$$

Finalize Extension of this procedure to several slabs of materials leads to Equation 20.17.

WHAT IF? Suppose you are building an insulated container with two layers of insulation and the rate of energy transfer determined by Equation (4) turns out to be too high. You have enough room to increase the thickness of one of the two layers by 20%. How would you decide which layer to choose?

Answer To decrease the power as much as possible, you must increase the denominator in Equation (4) as much as possible. Whichever thickness you choose to increase, L_1 or L_2 , you increase the corresponding term L/k in the denominator by 20%. For this percentage change to represent the largest absolute change, you want to take 20% of the larger term. Therefore, you should increase the thickness of the layer that has the larger value of L/k.

Home Insulation

In engineering practice, the term L/k for a particular substance is referred to as the *R***-value** of the material. Therefore, Equation 20.17 reduces to

$$P = \frac{A(T_h - T_c)}{\sum_i R_i}$$
(20.18)

where $R_i = L_i/k_i$. The *R*-values for a few common building materials are given in Table 20.4. In the United States, the insulating properties of materials used in buildings are usually expressed in U.S. customary units, not SI units. Therefore, in

Table 20.4 R-Values for Some Common Building Materials		
Material	<i>R</i> -value ($ft^2 \cdot {}^\circ F \cdot h/Btu$)	
Hardwood siding (1 in. thick)	0.91	
Wood shingles (lapped)	0.87	
Brick (4 in. thick)	4.00	
Concrete block (filled cores)	1.93	
Fiberglass insulation (3.5 in. thick)	10.90	
Fiberglass insulation (6 in. thick)	18.80	
Fiberglass board (1 in. thick)	4.35	
Cellulose fiber (1 in. thick)	3.70	
Flat glass (0.125 in. thick)	0.89	
Insulating glass (0.25-in. space)	1.54	
Air space (3.5 in. thick)	1.01	
Stagnant air layer	0.17	
Drywall (0.5 in. thick)	0.45	
Sheathing (0.5 in. thick)	1.32	

Table 20.4, *R*-values are given as a combination of British thermal units, feet, hours, and degrees Fahrenheit.

At any vertical surface open to the air, a very thin stagnant layer of air adheres to the surface. One must consider this layer when determining the *R*-value for a wall. The thickness of this stagnant layer on an outside wall depends on the speed of the wind. Energy transfer through the walls of a house on a windy day is greater than that on a day when the air is calm. A representative *R*-value for this stagnant layer of air is given in Table 20.4.

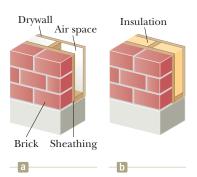
Example 20.9 The *R*-Value of a Typical Wall

Calculate the total *R*-value for a wall constructed as shown in Figure 20.15a. Starting outside the house (toward the front in the figure) and moving inward, the wall consists of 4 in. of brick, 0.5 in. of sheathing, an air space 3.5 in. thick, and 0.5 in. of drywall.

SOLUTION

Conceptualize Use Figure 20.15 to help conceptualize the structure of the wall. Do not forget the stagnant air layers inside and outside the house.

Figure 20.15 (Example 20.9) An exterior house wall containing (a) an air space and (b) insulation.



Categorize We will use specific equations developed in this section on home insulation, so we categorize this example as a substitution problem.

Use Table 20.4 to find the *R*-value of each layer:

$$\begin{split} R_1 \mbox{ (outside stagnant air layer)} &= 0.17 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \\ R_2 \mbox{ (brick)} &= 4.00 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \\ R_3 \mbox{ (sheathing)} &= 1.32 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \\ R_4 \mbox{ (air space)} &= 1.01 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \\ R_5 \mbox{ (drywall)} &= 0.45 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \\ R_6 \mbox{ (inside stagnant air layer)} &= 0.17 \mbox{ ft}^2 \cdot {}^\circ \mbox{F} \cdot \mbox{h}/\mbox{Btu} \end{split}$$

Add the *R*-values to obtain the total *R*-value for the wall:

$$R_{\text{total}} = R_1 + R_2 + R_3 + R_4 + R_5 + R_6 = 7.12 \text{ ft}^2 \cdot {}^\circ\text{F} \cdot \text{h/Btu}$$

WHAT IF? Suppose you are not happy with this total *R*-value for the wall. You cannot change the overall structure, but you can fill the air space as in Figure 20.15b. To *maximize* the total *R*-value, what material should you choose to fill the air space?

Answer Looking at Table 20.4, we see that 3.5 in. of fiberglass insulation is more than ten times as effective as 3.5 in. of air. Therefore, we should fill the air space with fiberglass insulation. The result is that we add 10.90 ft² · °F · h/Btu of *R*-value, and we lose 1.01 ft² · °F · h/Btu due to the air space we have replaced. The new total *R*-value is equal to 7.12 ft² · °F · h/Btu + 9.89 ft² · °F · h/Btu = 17.01 ft² · °F · h/Btu.

Convection

At one time or another, you probably have warmed your hands by holding them over an open flame. In this situation, the air directly above the flame is heated and expands. As a result, the density of this air decreases and the air rises. This hot air warms your hands as it flows by. Energy transferred by the movement of a warm substance is said to have been transferred by **convection**, which is a form of matter transfer, $T_{\rm MT}$ in Equation 8.2. When resulting from differences in density, as with air around a fire, the process is referred to as *natural convection*. Airflow at a beach

is an example of natural convection, as is the mixing that occurs as surface water in a lake cools and sinks (see Section 19.4). When the heated substance is forced to move by a fan or pump, as in some hot-air and hot-water heating systems, the process is called *forced convection*.

If it were not for convection currents, it would be very difficult to boil water. As water is heated in a teakettle, the lower layers are warmed first. This water expands and rises to the top because its density is lowered. At the same time, the denser, cool water at the surface sinks to the bottom of the kettle and is heated.

The same process occurs when a room is heated by a radiator. The hot radiator warms the air in the lower regions of the room. The warm air expands and rises to the ceiling because of its lower density. The denser, cooler air from above sinks, and the continuous air current pattern shown in Figure 20.16 is established.

Radiation

The third means of energy transfer we shall discuss is **thermal radiation**, T_{ER} in Equation 8.2. All objects radiate energy continuously in the form of electromagnetic waves (see Chapter 34) produced by thermal vibrations of the molecules. You are likely familiar with electromagnetic radiation in the form of the orange glow from an electric stove burner, an electric space heater, or the coils of a toaster.

The rate at which the surface of an object radiates energy is proportional to the fourth power of the absolute temperature of the surface. Known as **Stefan's law**, this behavior is expressed in equation form as

 $P = \sigma A e T^4$

where *P* is the power in watts of electromagnetic waves radiated from the surface of the object, σ is a constant equal to 5.669 6 × 10⁻⁸ W/m² · K⁴, *A* is the surface area of the object in square meters, *e* is the **emissivity**, and *T* is the surface temperature in kelvins. The value of *e* can vary between zero and unity depending on the properties of the surface of the object. The emissivity is equal to the **absorptivity**, which is the fraction of the incoming radiation that the surface absorbs. A mirror has very low absorptivity because it reflects almost all incident light. Therefore, a mirror surface also has a very low emissivity. At the other extreme, a black surface has high absorptivity and high emissivity. An **ideal absorber** is defined as an object that absorbs all the energy incident on it, and for such an object, *e* = 1. An object for which *e* = 1 is often referred to as a **black body**. We shall investigate experimental and theoretical approaches to radiation from a black body in Chapter 40.

Every second, approximately 1 370 J of electromagnetic radiation from the Sun passes perpendicularly through each 1 m^2 at the top of the Earth's atmosphere. This radiation is primarily visible and infrared light accompanied by a significant amount of ultraviolet radiation. We shall study these types of radiation in detail in Chapter 34. Enough energy arrives at the surface of the Earth each day to supply all our energy needs on this planet hundreds of times over, if only it could be captured and used efficiently. The growth in the number of solar energy–powered houses and proposals for solar energy "farms" in the United States reflects the increasing efforts being made to use this abundant energy.

What happens to the atmospheric temperature at night is another example of the effects of energy transfer by radiation. If there is a cloud cover above the Earth, the water vapor in the clouds absorbs part of the infrared radiation emitted by the Earth and re-emits it back to the surface. Consequently, temperature levels at the surface remain moderate. In the absence of this cloud cover, there is less in the way to prevent this radiation from escaping into space; therefore, the temperature decreases more on a clear night than on a cloudy one.

As an object radiates energy at a rate given by Equation 20.19, it also absorbs electromagnetic radiation from the surroundings, which consist of other objects

Radiator

Figure 20.16 Convection currents are set up in a room warmed by a radiator.



(20.19)

that radiate energy. If the latter process did not occur, an object would eventually radiate all its energy and its temperature would reach absolute zero. If an object is at a temperature T and its surroundings are at an average temperature T_0 , the net rate of energy gained or lost by the object as a result of radiation is

$$P_{\rm net} = \sigma A e (T^4 - T_0^4)$$
 (20.20)

When an object is in equilibrium with its surroundings, it radiates and absorbs energy at the same rate and its temperature remains constant. When an object is hotter than its surroundings, it radiates more energy than it absorbs and its temperature decreases.

The Dewar Flask

The *Dewar flask*⁶ is a container designed to minimize energy transfers by conduction, convection, and radiation. Such a container is used to store cold or hot liquids for long periods of time. (An insulated bottle, such as a Thermos, is a common household equivalent of a Dewar flask.) The standard construction (Fig. 20.17) consists of a double-walled Pyrex glass vessel with silvered walls. The space between the walls is evacuated to minimize energy transfer by conduction and convection. The silvered surfaces minimize energy transfer by radiation because silver is a very good reflector and has very low emissivity. A further reduction in energy loss is obtained by reducing the size of the neck. Dewar flasks are commonly used to store liquid nitrogen (boiling point 77 K) and liquid oxygen (boiling point 90 K).

To confine liquid helium (boiling point 4.2 K), which has a very low heat of vaporization, it is often necessary to use a double Dewar system in which the Dewar flask containing the liquid is surrounded by a second Dewar flask. The space between the two flasks is filled with liquid nitrogen.

Newer designs of storage containers use "superinsulation" that consists of many layers of reflecting material separated by fiberglass. All this material is in a vacuum, and no liquid nitrogen is needed with this design.

⁶Invented by Sir James Dewar (1842-1923).

Summary

Definitions

Internal energy is a system's energy associated with its temperature and its physical state (solid, liquid, gas). Internal energy includes kinetic energy of random translation, rotation, and vibration of molecules; vibrational potential energy within molecules; and potential energy between molecules.

Heat is the process of energy transfer across the boundary of a system resulting from a temperature difference between the system and its surroundings. The symbol Q represents the amount of energy transferred by this process. A **calorie** is the amount of energy necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

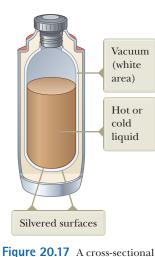
The **heat capacity** *C* of any sample is the amount of energy needed to raise the temperature of the sample by 1° C.

The **specific heat** *c* of a substance is the heat capacity per unit mass:

$$c \equiv \frac{Q}{m\,\Delta T} \tag{20.3}$$

The **latent heat** of a substance is defined as the ratio of the energy input to a substance to the change in mass of the higher-phase material:

$$L = \frac{Q}{\Delta m}$$
(20.6)



view of a Dewar flask, which is used to store hot or cold substances.

Concepts and Principles

The energy *Q* required to change the temperature of a mass *m* of a substance by an amount ΔT is

$$Q = mc \,\Delta T \tag{20.4}$$

where c is the specific heat of the substance.

The energy required to change the phase of a pure substance is

$$Q = L \Delta m \tag{20.7}$$

where *L* is the latent heat of the substance, which depends on the nature of the phase change and the substance, and Δm is the change in mass of the higher-phase material. The work done on a gas as its volume changes from some initial value V_i to some final value V_f is

$$W = -\int_{V_i}^{V_f} P \, dV \tag{20.9}$$

where *P* is the pressure of the gas, which may vary during the process. To evaluate *W*, the process must be fully specified; that is, *P* and *V* must be known during each step. The work done depends on the path taken between the initial and final states.

The **first law of thermodynamics** is a specific reduction of the conservation of energy equation (Eq. 8.2) and states that when a system undergoes a change from one state to another, the change in its internal energy is

$$E_{\rm int} = Q + W \tag{20.10}$$

where *Q* is the energy transferred into the system by heat and *W* is the work done on the system. Although *Q* and *W* both depend on the path taken from the initial state to the final state, the quantity ΔE_{int} does not depend on the path.

In a **cyclic process** (one that originates and terminates at the same state), $\Delta E_{int} = 0$ and therefore Q = -W. That is, the energy transferred into the system by heat equals the negative of the work done on the system during the process.

In an **adiabatic process**, no energy is transferred by heat between the system and its surroundings (Q = 0). In this case, the first law gives $\Delta E_{int} = W$. In the **adiabatic free expansion** of a gas, Q = 0 and W = 0, so $\Delta E_{int} = 0$. That is, the internal energy of the gas does not change in such a process. An **isobaric process** is one that occurs at constant pressure. The work done on a gas in such a process is $W = -P(V_f - V_i)$.

An **isovolumetric process** is one that occurs at constant volume. No work is done in such a process, so $\Delta E_{int} = Q$.

An **isothermal process** is one that occurs at constant temperature. The work done on an ideal gas during an isothermal process is

$$W = nRT \ln\left(\frac{V_i}{V_f}\right)$$
 (20.14)

In convection, a warm sub-

stance transfers energy from one

All objects emit thermal

 $P = \sigma A e T^4$

radiation in the form of electromagnetic waves at the rate

(20.19)

location to another.

Conduction can be viewed as an exchange of kinetic energy between colliding molecules or electrons. The rate of energy transfer by conduction through a slab of area *A* is

$$P = kA \left| \frac{dT}{dx} \right|$$
 (20.15)

where *k* is the **thermal conductivity** of the material from which the slab is made and |dT/dx| is the **temperature gradient.**

Objective Questions

1. denotes answer available in Student Solutions Manual/Study Guide

- 1. An ideal gas is compressed to half its initial volume by means of several possible processes. Which of the following processes results in the most work done on the gas? (a) isothermal (b) adiabatic (c) isobaric (d) The work done is independent of the process.
- A poker is a stiff, nonflammable rod used to push burning logs around in a fireplace. For safety and comfort of use, should the poker be made from a material with (a) high specific heat and high thermal conductivity, (b) low specific heat and low thermal conductivity,

(c) low specific heat and high thermal conductivity, or(d) high specific heat and low thermal conductivity?

- **3.** Assume you are measuring the specific heat of a sample of originally hot metal by using a calorimeter containing water. Because your calorimeter is not perfectly insulating, energy can transfer by heat between the contents of the calorimeter and the room. To obtain the most accurate result for the specific heat of the metal, you should use water with which initial temperature? (a) slightly lower than room temperature (b) the same as room temperature (c) slightly higher than room temperature (d) whatever you like because the initial temperature makes no difference
- 4. An amount of energy is added to ice, raising its temperature from -10°C to -5°C. A larger amount of energy is added to the same mass of water, raising its temperature from 15°C to 20°C. From these results, what would you conclude? (a) Overcoming the latent heat of fusion of ice requires an input of energy. (b) The latent heat of fusion of ice delivers some energy to the system. (c) The specific heat of ice is less than that of water. (d) The specific heat of ice is greater than that of water. (e) More information is needed to draw any conclusion.
- 5. How much energy is required to raise the temperature of 5.00 kg of lead from 20.0°C to its melting point of 327°C? The specific heat of lead is 128 J/kg · °C. (a) 4.04 × 10⁵ J (b) 1.07 × 10⁵ J (c) 8.15 × 10⁴ J (d) 2.13 × 10⁴ J (e) 1.96 × 10⁵ J
- 6. Ethyl alcohol has about one-half the specific heat of water. Assume equal amounts of energy are transferred by heat into equal-mass liquid samples of alcohol and water in separate insulated containers. The water rises in temperature by 25°C. How much will the alcohol rise in temperature? (a) It will rise by 12°C. (b) It will rise by 25°C. (c) It will rise by 50°C. (d) It depends on the rate of energy transfer. (e) It will not rise in temperature.
- 7. The specific heat of substance A is greater than that of substance B. Both A and B are at the same initial temperature when equal amounts of energy are added to them. Assuming no melting or vaporization occurs, which of the following can be concluded about the final temperature T_A of substance A and the final temperature T_B of substance B? (a) $T_A > T_B$ (b) $T_A < T_B$ (c) $T_A = T_B$ (d) More information is needed.
- 8. Beryllium has roughly one-half the specific heat of water (H_2O) . Rank the quantities of energy input required to produce the following changes from the

Conceptual Questions

1. denotes answer available in *Student Solutions Manual/Study Guide*

1. Rub the palm of your hand on a metal surface for about 30 seconds. Place the palm of your other hand on an unrubbed portion of the surface and then on the rubbed portion. The rubbed portion will feel warmer. Now repeat this process on a wood surface. Why does the temperature difference between the rubbed and unrubbed portions of the wood surface seem larger than for the metal surface?

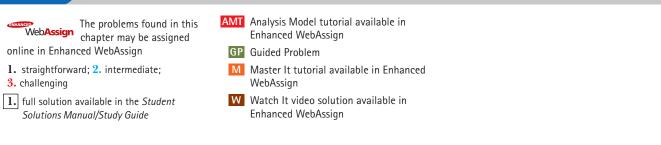
- largest to the smallest. In your ranking, note any cases of equality. (a) raising the temperature of 1 kg of H_2O from 20°C to 26°C (b) raising the temperature of 2 kg of H_2O from 20°C to 23°C (c) raising the temperature of 2 kg of H_2O from 1°C to 4°C (d) raising the temperature of 2 kg of beryllium from -1°C to 2°C (e) raising the temperature of 2 kg of H_2O from -1°C to 2°C
- **9.** A person shakes a sealed insulated bottle containing hot coffee for a few minutes. (i) What is the change in the temperature of the coffee? (a) a large decrease (b) a slight decrease (c) no change (d) a slight increase (e) a large increase (ii) What is the change in the internal energy of the coffee? Choose from the same possibilities.
- 10. A 100-g piece of copper, initially at 95.0°C, is dropped into 200 g of water contained in a 280-g aluminum can; the water and can are initially at 15.0°C. What is the final temperature of the system? (Specific heats of copper and aluminum are 0.092 and 0.215 cal/g · °C, respectively.) (a) 16°C (b) 18°C (c) 24°C (d) 26°C (e) none of those answers
- 11. Star A has twice the radius and twice the absolute surface temperature of star B. The emissivity of both stars can be assumed to be 1. What is the ratio of the power output of star A to that of star B? (a) 4 (b) 8 (c) 16 (d) 32 (e) 64
- If a gas is compressed isothermally, which of the following statements is true? (a) Energy is transferred into the gas by heat. (b) No work is done on the gas. (c) The temperature of the gas increases. (d) The internal energy of the gas remains constant. (e) None of those statements is true.
- 13. When a gas undergoes an adiabatic expansion, which of the following statements is true? (a) The temperature of the gas does not change. (b) No work is done by the gas. (c) No energy is transferred to the gas by heat. (d) The internal energy of the gas does not change. (e) The pressure increases.
- 14. If a gas undergoes an isobaric process, which of the following statements is true? (a) The temperature of the gas doesn't change. (b) Work is done on or by the gas. (c) No energy is transferred by heat to or from the gas. (d) The volume of the gas remains the same. (e) The pressure of the gas decreases uniformly.
- 15. How long would it take a 1 000 W heater to melt 1.00 kg of ice at -20.0°C, assuming all the energy from the heater is absorbed by the ice? (a) 4.18 s (b) 41.8 s (c) 5.55 min (d) 6.25 min (e) 38.4 min
- **2.** You need to pick up a very hot cooking pot in your kitchen. You have a pair of cotton oven mitts. To pick up the pot most comfortably, should you soak them in cold water or keep them dry?
- **3.** What is wrong with the following statement: "Given any two bodies, the one with the higher temperature contains more heat."

- **4.** Why is a person able to remove a piece of dry aluminum foil from a hot oven with bare fingers, whereas a burn results if there is moisture on the foil?
- **5.** Using the first law of thermodynamics, explain why the *total* energy of an isolated system is always constant.
- 6. In 1801, Humphry Davy rubbed together pieces of ice inside an icehouse. He made sure that nothing in the environment was at a higher temperature than the rubbed pieces. He observed the production of drops of liquid water. Make a table listing this and other experiments or processes to illustrate each of the following situations. (a) A system can absorb energy by heat, increase in internal energy, and increase in temperature. (b) A system can absorb energy by heat and increase in internal energy without an increase in temperature. (c) A system can absorb energy by heat without increasing in temperature or in internal energy. (d) A system can increase in internal energy and in temperature without absorbing energy by heat. (e) A system can increase in internal energy without absorbing energy by heat or increasing in temperature.
- **7.** It is the morning of a day that will become hot. You just purchased drinks for a picnic and are loading them, with ice, into a chest in the back of your car. (a) You

wrap a wool blanket around the chest. Does doing so help to keep the beverages cool, or should you expect the wool blanket to warm them up? Explain your answer. (b) Your younger sister suggests you wrap her up in another wool blanket to keep her cool on the hot day like the ice chest. Explain your response to her.

- 8. In usually warm climates that experience a hard freeze, fruit growers will spray the fruit trees with water, hoping that a layer of ice will form on the fruit. Why would such a layer be advantageous?
- **9.** Suppose you pour hot coffee for your guests, and one of them wants it with cream. He wants the coffee to be as warm as possible several minutes later when he drinks it. To have the warmest coffee, should the person add the cream just after the coffee is poured or just before drinking? Explain.
- **10.** When camping in a canyon on a still night, a camper notices that as soon as the sun strikes the surrounding peaks, a breeze begins to stir. What causes the breeze?
- **11.** Pioneers stored fruits and vegetables in underground cellars. In winter, why did the pioneers place an open barrel of water alongside their produce?
- **12.** Is it possible to convert internal energy to mechanical energy? Explain with examples.

Problems



Section 20.1 Heat and Internal Energy

1. A 55.0-kg woman eats a 540 Calorie (540 kcal) jelly doughnut for breakfast. (a) How many joules of energy are the equivalent of one jelly doughnut? (b) How many steps must the woman climb on a very tall stairway to change the gravitational potential energy of the woman–Earth system by a value equivalent to the food energy in one jelly doughnut? Assume the height of a single stair is 15.0 cm. (c) If the human body is only 25.0% efficient in converting chemical potential energy to mechanical energy, how many steps must the woman climb to work off her breakfast?

Section 20.2 Specific Heat and Calorimetry

2. Consider Joule's apparatus described in Figure 20.1.
AMT The mass of each of the two blocks is 1.50 kg, and the W insulated tank is filled with 200 g of water. What is the increase in the water's temperature after the blocks fall through a distance of 3.00 m?

- **3.** A combination of 0.250 kg of water at 20.0°C, 0.400 kg of aluminum at 26.0°C, and 0.100 kg of copper at 100°C is mixed in an insulated container and allowed to come to thermal equilibrium. Ignore any energy transfer to or from the container. What is the final temperature of the mixture?
- **4.** The highest waterfall in the world is the Salto Angel in Venezuela. Its longest single falls has a height of 807 m. If water at the top of the falls is at 15.0°C, what is the maximum temperature of the water at the bottom of the falls? Assume all the kinetic energy of the water as it reaches the bottom goes into raising its temperature.
- **5.** What mass of water at 25.0°C must be allowed to come to thermal equilibrium with a 1.85-kg cube of aluminum initially at 150°C to lower the temperature of the aluminum to 65.0°C? Assume any water turned to steam subsequently condenses.
- **6.** The temperature of a silver bar rises by 10.0°C when it **M** absorbs 1.23 kJ of energy by heat. The mass of the bar is

525 g. Determine the specific heat of silver from these data.

- 7. In cold climates, including the northern United States, a house can be built with very large windows facing south to take advantage of solar heating. Sunlight shining in during the daytime is absorbed by the floor, interior walls, and objects in the room, raising their temperature to 38.0°C. If the house is well insulated, you may model it as losing energy by heat steadily at the rate 6 000 W on a day in April when the average exterior temperature is 4°C and when the conventional heating system is not used at all. During the period between 5:00 p.m. and 7:00 a.m., the temperature of the house drops and a sufficiently large "thermal mass" is required to keep it from dropping too far. The thermal mass can be a large quantity of stone (with specific heat 850 J/kg \cdot °C) in the floor and the interior walls exposed to sunlight. What mass of stone is required if the temperature is not to drop below 18.0°C overnight?
- **8.** A 50.0-g sample of copper is at 25.0°C. If 1 200 J of energy is added to it by heat, what is the final temperature of the copper?
- 9. An aluminum cup of mass 200 g contains 800 g of water in thermal equilibrium at 80.0°C. The combination of cup and water is cooled uniformly so that the temperature decreases by 1.50°C per minute. At what rate is energy being removed by heat? Express your answer in watts.
- 10. If water with a mass m_h at temperature T_h is poured into an aluminum cup of mass m_{A1} containing mass m_c of water at T_c , where $T_h > T_c$, what is the equilibrium temperature of the system?
- A 1.50-kg iron horseshoe initially at 600°C is dropped
 M into a bucket containing 20.0 kg of water at 25.0°C.
 What is the final temperature of the water-horseshoe system? Ignore the heat capacity of the container and assume a negligible amount of water boils away.
- **12.** An electric drill with a steel drill bit of mass m = 27.0 g and diameter 0.635 cm is used to drill into a cubical steel block of mass M = 240 g. Assume steel has the same properties as iron. The cutting process can be modeled as happening at one point on the circumference of the bit. This point moves in a helix at constant tangential speed 40.0 m/s and exerts a force of constant magnitude 3.20 N on the block. As shown in Figure P20.12, a groove in the bit carries the chips up to the top of the block, where they form a pile around the hole. The drill is turned on and drills into the block for a time interval of 15.0 s. Let's assume this time interval is long enough for conduction within the steel to bring it all to a uniform temperature. Furthermore, assume the steel objects lose a negligible amount of energy by conduction, convection, and radiation into their environment. (a) Suppose the drill bit cuts three-quarters of the way through the block during 15.0 s. Find the temperature change of the whole quantity of steel. (b) What If? Now suppose the drill bit is dull and cuts only one-eighth of the way through the block in 15.0 s. Identify the temperature change of the whole quantity

of steel in this case. (c) What pieces of data, if any, are unnecessary for the solution? Explain.

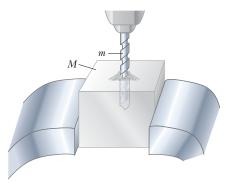


Figure P20.12

- 13. An aluminum calorimeter with a mass of 100 g conwater tains 250 g of water. The calorimeter and water are in thermal equilibrium at 10.0°C. Two metallic blocks are placed into the water. One is a 50.0-g piece of copper at 80.0°C. The other has a mass of 70.0 g and is originally at a temperature of 100°C. The entire system stabilizes at a final temperature of 20.0°C. (a) Determine the specific heat of the unknown sample. (b) Using the data in Table 20.1, can you make a positive identification of the unknown material? Can you identify a possible material? (c) Explain your answers for part (b).
- 14. A 3.00-g copper coin at 25.0°C drops 50.0 m to the ground. (a) Assuming 60.0% of the change in gravitational potential energy of the coin–Earth system goes into increasing the internal energy of the coin, determine the coin's final temperature. (b) What If? Does the result depend on the mass of the coin? Explain.
- **15.** Two thermally insulated vessels are connected by a narrow tube fitted with a valve that is initially closed as shown in Figure P20.15. One vessel of volume 16.8 L contains oxygen at a temperature of 300 K and a pressure of 1.75 atm. The other vessel of volume 22.4 L contains oxygen at a temperature of 450 K and a pressure of 2.25 atm. When the valve is opened, the gases in the two vessels mix and the temperature and pressure become uniform throughout. (a) What is the final temperature? (b) What is the final pressure?

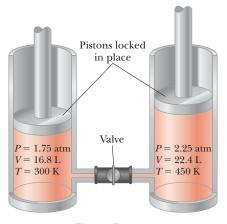


Figure P20.15

Section 20.3 Latent Heat

- **16.** A 50.0-g copper calorimeter contains 250 g of water at 20.0°C. How much steam at 100°C must be condensed into the water if the final temperature of the system is to reach 50.0°C?
- 17. A 75.0-kg cross-country
 M skier glides over snow as in Figure P20.17. The coefficient of friction between skis and snow is 0.200. Assume all the snow beneath his skis is at 0°C and that all the internal energy generated by friction is added to snow, which sticks to his skis until it melts. How far would he have to ski to melt 1.00 kg of snow?



Figure P20.17

- **18.** How much energy is required to change a 40.0-g ice **W** cube from ice at -10.0°C to steam at 110°C?
- **19.** A 75.0-g ice cube at 0°C is placed in 825 g of water at 25.0°C. What is the final temperature of the mixture?
- 20. A 3.00-g lead bullet at 30.0°C is fired at a speed of
 AMT 240 m/s into a large block of ice at 0°C, in which it
 M becomes embedded. What quantity of ice melts?
- 21. Steam at 100°C is added to ice at 0°C. (a) Find the amount of ice melted and the final temperature when the mass of steam is 10.0 g and the mass of ice is 50.0 g.
 (b) What If? Repeat when the mass of steam is 1.00 g and the mass of ice is 50.0 g.
- 22. A 1.00-kg block of copper at 20.0°C is dropped into
- W a large vessel of liquid nitrogen at 77.3 K. How many kilograms of nitrogen boil away by the time the copper reaches 77.3 K? (The specific heat of copper is 0.092 0 cal/g · °C, and the latent heat of vaporization of nitrogen is 48.0 cal/g.)
- 23. In an insulated vessel, 250 g of ice at 0°C is added to 600 g of water at 18.0°C. (a) What is the final temperature of the system? (b) How much ice remains when the system reaches equilibrium?
- 24. An automobile has a mass of 1 500 kg, and its aluminum brakes have an overall mass of 6.00 kg. (a) Assume all the mechanical energy that transforms into internal energy when the car stops is deposited in the brakes and no energy is transferred out of the brakes by heat. The brakes are originally at 20.0°C. How many times can the car be stopped from 25.0 m/s before the brakes start to melt? (b) Identify some effects ignored in part (a) that are important in a more realistic assessment of the warming of the brakes.

Section 20.4 Work and Heat in Thermodynamic Processes

25. An ideal gas is enclosed in a cylinder with a movable piston on top of it. The piston has a mass of 8 000 g and an area of 5.00 cm^2 and is free to slide up and

down, keeping the pressure of the gas constant. How much work is done on the gas as the temperature of 0.200 mol of the gas is raised from 20.0°C to 300°C?

- **26.** An ideal gas is enclosed in a cylinder that has a movable piston on top. The piston has a mass *m* and an area *A* and is free to slide up and down, keeping the pressure of the gas constant. How much work is done on the gas as the temperature of *n* mol of the gas is raised from T_1 to T_2 ?
- 27. One mole of an ideal gas is warmed slowly so that it goes from the *PV* state (P_i, V_i) to $(3P_i, 3V_i)$ in such a way that the pressure of the gas is directly proportional to the volume. (a) How much work is done on the gas in the process? (b) How is the temperature of the gas related to its volume during this process?
- 28. (a) Determine the work done on a gas that expandsW from *i* to *f* as indicated in Figure P20.28. (b) What If? How much work is done on the gas if it is compressed from *f* to *i* along the same path?

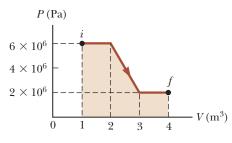


Figure P20.28

29. An ideal gas is taken through a quasi-static process described by $P = \alpha V^2$, with $\alpha = 5.00$ atm/m⁶, as shown in Figure P20.29. The gas is expanded to twice its original volume of 1.00 m³. How much work is done on the expanding gas in this process?

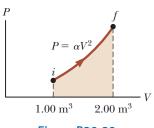
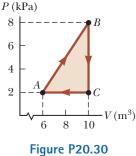


Figure P20.29

Section 20.5 The First Law of Thermodynamics

30. A gas is taken through the vyclic process described in Figure P20.30. (a) Find the net energy transferred to the system by heat during one complete cycle. (b) What If? If the cycle is reversed—that is, the process follows the path ACBA—what is the net energy input per cycle by heat?

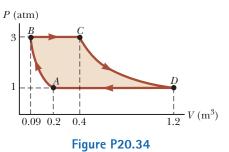


Problems 30 and 31.

- **31.** Consider the cyclic process depicted in Figure P20.30. If *Q* is negative for the process *BC* and ΔE_{int} is negative for the process *CA*, what are the signs of *Q*, *W*, and ΔE_{int} that are associated with each of the three processes?
- **32.** Why is the following situation impossible? An ideal gas undergoes a process with the following parameters: Q = 10.0 J, W = 12.0 J, and $\Delta T = -2.00$ °C.
- **33.** A thermodynamic system undergoes a process in which its internal energy decreases by 500 J. Over the same time interval, 220 J of work is done on the system. Find the energy transferred from it by heat.

34. A sample of an ideal gas goes through the process

w shown in Figure P20.34. From *A* to *B*, the process is adiabatic; from *B* to *C*, it is isobaric with 345 kJ of energy entering the system by heat; from *C* to *D*, the process is isothermal; and from *D* to *A*, it is isobaric with 371 kJ of energy leaving the system by heat. Determine the difference in internal energy $E_{int,B} - E_{int,A}$.



Section 20.6 Some Applications of the First Law of Thermodynamics

- **35.** A 2.00-mol sample of helium gas initially at 300 K, and
- M 0.400 atm is compressed isothermally to 1.20 atm. Noting that the helium behaves as an ideal gas, find (a) the final volume of the gas, (b) the work done on the gas, and (c) the energy transferred by heat.
- **36.** (a) How much work is done on the steam when 1.00 mol of water at 100°C boils and becomes 1.00 mol of steam at 100°C at 1.00 atm pressure? Assume the steam to behave as an ideal gas. (b) Determine the change in internal energy of the system of the water and steam as the water vaporizes.
- [37.] An ideal gas initially at 300 K undergoes an isobaric
 M expansion at 2.50 kPa. If the volume increases from 1.00 m³ to 3.00 m³ and 12.5 kJ is transferred to the gas by heat, what are (a) the change in its internal energy and (b) its final temperature?
- 38. One mole of an ideal gas does 3 000 J of work on its
- W surroundings as it expands isothermally to a final pressure of 1.00 atm and volume of 25.0 L. Determine (a) the initial volume and (b) the temperature of the gas.
- 39. A 1.00-kg block of aluminum is warmed at atmospheric pressure so that its temperature increases from 22.0°C to 40.0°C. Find (a) the work done on the aluminum, (b) the energy added to it by heat, and (c) the change in its internal energy.

40. In Figure P20.40, the change in internal energy of a gas that is taken from A to C along the blue path is +800 J. The work done on the gas along the red path ABC is -500 J.
(a) How much energy must be added to the system by heat as it goes from A through B to C? (b) If the pressure at point A is five times that of point C, what is the work

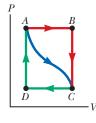
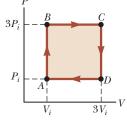


Figure P20.40

done on the system in going from C to D? (c) What is the energy exchanged with the surroundings by heat as the gas goes from C to A along the green path? (d) If the change in internal energy in going from point D to point A is +500 J, how much energy must be added to the system by heat as it goes from point C to point D?

41. An ideal gas initially at P_i,
W V_i, and T_i is taken through a cycle as shown in Figure P20.41. (a) Find the net work done on the gas per cycle for 1.00 mol of gas initially at 0°C. (b) What is the net energy added by heat to the gas per cycle?



42. An ideal gas initially at P_i , V_i , and T_i is taken through a cycle as shown in Figure

Figure P20.41 Problems 41 and 42.

P20.41. (a) Find the net work done on the gas per cycle.(b) What is the net energy added by heat to the system per cycle?

Section 20.7 Energy Transfer Mechanisms in Thermal Processes

- 43. A glass windowpane in a home is 0.620 cm thick and has dimensions of 1.00 m × 2.00 m. On a certain day, the temperature of the interior surface of the glass is 25.0°C and the exterior surface temperature is 0°C.
 (a) What is the rate at which energy is transferred by heat through the glass? (b) How much energy is transferred through the window in one day, assuming the temperatures on the surfaces remain constant?
- **44.** A concrete slab is 12.0 cm thick and has an area of 5.00 m². Electric heating coils are installed under the slab to melt the ice on the surface in the winter months. What minimum power must be supplied to the coils to maintain a temperature difference of 20.0°C between the bottom of the slab and its surface? Assume all the energy transferred is through the slab.
- **45.** A student is trying to decide what to wear. His bedroom is at 20.0°C. His skin temperature is 35.0°C. The area of his exposed skin is 1.50 m². People all over the world have skin that is dark in the infrared, with emissivity about 0.900. Find the net energy transfer from his body by radiation in 10.0 min.
- **46.** The surface of the Sun has a temperature of about 5 800 K. The radius of the Sun is 6.96×10^8 m. Calculate the total energy radiated by the Sun each second. Assume the emissivity of the Sun is 0.986.

620

621

- **47.** The tungsten filament of a certain 100-W lightbulb radiates 2.00 W of light. (The other 98 W is carried away by convection and conduction.) The filament has a surface area of 0.250 mm² and an emissivity of 0.950. Find the filament's temperature. (The melting point of tungsten is 3 683 K.)
- **48.** At high noon, the Sun delivers 1 000 W to each square meter of a blacktop road. If the hot asphalt transfers energy only by radiation, what is its steady-state temperature?
- 49. Two lightbulbs have cylindrical filaments much greater in length than in diameter. The evacuated bulbs are identical except that one operates at a filament temperature of 2 100°C and the other operates at 2 000°C.(a) Find the ratio of the power emitted by the hotter lightbulb to that emitted by the cooler lightbulb.(b) With the bulbs operating at the same respective temperatures, the cooler lightbulb is to be altered by making its filament thicker so that it emits the same power as the hotter one. By what factor should the radius of this filament be increased?
- 50. The human body must maintain its core temperature inside a rather narrow range around 37°C. Metabolic processes, notably muscular exertion, convert chemical energy into internal energy deep in the interior. From the interior, energy must flow out to the skin or lungs to be expelled to the environment. During moderate exercise, an 80-kg man can metabolize food energy at the rate 300 kcal/h, do 60 kcal/h of mechanical work, and put out the remaining 240 kcal/h of energy by heat. Most of the energy is carried from the body interior out to the skin by forced convection (as a plumber would say), whereby blood is warmed in the interior and then cooled at the skin, which is a few degrees cooler than the body core. Without blood flow, living tissue is a good thermal insulator, with thermal conductivity about 0.210 W/m \cdot °C. Show that blood flow is essential to cool the man's body by calculating the rate of energy conduction in kcal/h through the tissue layer under his skin. Assume that its area is 1.40 m², its thickness is 2.50 cm, and it is maintained at 37.0°C on one side and at 34.0°C on the other side.
- 51. A copper rod and an aluminum rod of equal diameter
 M are joined end to end in good thermal contact. The temperature of the free end of the copper rod is held constant at 100°C and that of the far end of the aluminum rod is held at 0°C. If the copper rod is 0.150 m long, what must be the length of the aluminum rod so that the temperature at the junction is 50.0°C?
- **52.** A box with a total surface area of 1.20 m^2 and a wall thickness of 4.00 cm is made of an insulating material. A 10.0-W electric heater inside the box maintains the inside temperature at 15.0° C above the outside temperature. Find the thermal conductivity *k* of the insulating material.
- 53. (a) Calculate the *R*-value of a thermal window made of two single panes of glass each 0.125 in. thick and separated by a 0.250-in. air space. (b) By what factor is the transfer of energy by heat through the window reduced

by using the thermal window instead of the single-pane window? Include the contributions of inside and outside stagnant air layers.

- 54. At our distance from the Sun, the intensity of solar radiation is 1 370 W/m². The temperature of the Earth is affected by the *greenhouse effect* of the atmosphere. This phenomenon describes the effect of absorption of infrared light emitted by the surface so as to make the surface temperature of the Earth higher than if it were airless. For comparison, consider a spherical object of radius *r* with no atmosphere at the same distance from the Sun as the Earth. Assume its emissivity is the same for all kinds of electromagnetic waves and its temperature is uniform over its surface. (a) Explain why the projected area over which it radiates is $4\pi r^2$. (b) Compute its steady-state temperature. Is it chilly?
- 55. A bar of gold (Au) is in thermal contact with a bar of silver (Ag) of the same length and area (Fig. P20.55). One end of the compound bar is maintained at 80.0°C, and the opposite end is at 30.0°C. When the energy transfer reaches steady state, what is the temperature at the junction?
- **56.** For bacteriological testing of water supplies and in medical

clinics, samples must routinely be incubated for 24 h at 37°C. Peace Corps volunteer and MIT engineer Amy Smith invented a low-cost, low-maintenance incubator. The incubator consists of a foam-insulated box containing a waxy material that melts at 37.0°C interspersed among tubes, dishes, or bottles containing the test samples and growth medium (bacteria food). Outside the box, the waxy material is first melted by a stove or solar energy collector. Then the waxy material is put into the box to keep the test samples warm as the material solidifies. The heat of fusion of the phasechange material is 205 kJ/kg. Model the insulation as a panel with surface area 0.490 m², thickness 4.50 cm, and conductivity 0.012 0 W/m · °C. Assume the exterior temperature is 23.0°C for 12.0 h and 16.0°C for 12.0 h. (a) What mass of the waxy material is required to conduct the bacteriological test? (b) Explain why your calculation can be done without knowing the mass of the test samples or of the insulation.

57. A large, hot pizza floats in outer space after being jettisoned as refuse from a spacecraft. What is the order of magnitude (a) of its rate of energy loss and (b) of its rate of temperature change? List the quantities you estimate and the value you estimate for each.

Additional Problems

58. A gas expands from I to F in Figure P20.58 (page 622).

M The energy added to the gas by heat is 418 J when the gas goes from *I* to *F* along the diagonal path. (a) What is the change in internal energy of the gas? (b) How



Figure P20.55

much energy must be added to the gas by heat along the indirect path *IAF*?

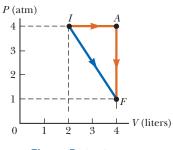


Figure P20.58

- 59. Gas in a container is at a pressure of 1.50 atm and a
 M volume of 4.00 m³. What is the work done on the gas
 (a) if it expands at constant pressure to twice its initial volume, and (b) if it is compressed at constant pressure to one-quarter its initial volume?
- **60.** Liquid nitrogen has a boiling point of 77.3 K and a latent heat of vaporization of 2.01×10^5 J/kg. A 25.0-W electric heating element is immersed in an insulated vessel containing 25.0 L of liquid nitrogen at its boiling point. How many kilograms of nitrogen are boiled away in a period of 4.00 h?
- 61. An aluminum rod 0.500 m in length and with a crossM sectional area of 2.50 cm² is inserted into a thermally insulated vessel containing liquid helium at 4.20 K. The rod is initially at 300 K. (a) If one-half of the rod is inserted into the helium, how many liters of helium boil off by the time the inserted half cools to 4.20 K? Assume the upper half does not yet cool. (b) If the circular surface of the upper end of the rod is maintained at 300 K, what is the approximate boil-off rate of liquid helium in liters per second after the lower half has reached 4.20 K? (Aluminum has thermal conductivity of 3 100 W/m ⋅ K at 4.20 K; ignore its temperature variation. The density of liquid helium is 125 kg/m³.)
- 62. Review. Two speeding lead bullets, one of mass 12.0 g AMT moving to the right at 300 m/s and one of mass 8.00 g GP moving to the left at 400 m/s, collide head-on, and all the material sticks together. Both bullets are originally at temperature 30.0°C. Assume the change in kinetic energy of the system appears entirely as increased internal energy. We would like to determine the temperature and phase of the bullets after the collision. (a) What two analysis models are appropriate for the system of two bullets for the time interval from before to after the collision? (b) From one of these models, what is the speed of the combined bullets after the collision? (c) How much of the initial kinetic energy has transformed to internal energy in the system after the collision? (d) Does all the lead melt due to the collision? (e) What is the temperature of the combined bullets after the collision? (f) What is the phase of the combined bullets after the collision?
- **63.** A *flow calorimeter* is an apparatus used to measure the specific heat of a liquid. The technique of flow calorimetry involves measuring the temperature difference between the input and output points of a flowing

stream of the liquid while energy is added by heat at a known rate. A liquid of density 900 kg/m³ flows through the calorimeter with volume flow rate of 2.00 L/min. At steady state, a temperature difference 3.50° C is established between the input and output points when energy is supplied at the rate of 200 W. What is the specific heat of the liquid?

- 64. A *flow calorimeter* is an apparatus used to measure the specific heat of a liquid. The technique of flow calorimetry involves measuring the temperature difference between the input and output points of a flowing stream of the liquid while energy is added by heat at a known rate. A liquid of density ρ flows through the calorimeter with volume flow rate R. At steady state, a temperature difference ΔT is established between the input and output points when energy is supplied at the rate P. What is the specific heat of the liquid?
- 65. Review. Following a collision between a large space-AMT craft and an asteroid, a copper disk of radius 28.0 m and thickness 1.20 m at a temperature of 850°C is floating in space, rotating about its symmetry axis with an angular speed of 25.0 rad/s. As the disk radiates infrared light, its temperature falls to 20.0°C. No external torque acts on the disk. (a) Find the change in kinetic energy of the disk. (b) Find the change in internal energy of the disk. (c) Find the amount of energy it radiates.
- 66. An ice-cube tray is filled with 75.0 g of water. After the filled tray reaches an equilibrium temperature of 20.0°C, it is placed in a freezer set at -8.00°C to make ice cubes. (a) Describe the processes that occur as energy is being removed from the water to make ice. (b) Calculate the energy that must be removed from the water to make ice cubes at -8.00°C.
- **67.** On a cold winter day, you buy roasted chestnuts from a street vendor. Into the pocket of your down parka you put the change he gives you: coins constituting 9.00 g of copper at -12.0°C. Your pocket already contains 14.0 g of silver coins at 30.0°C. A short time later the temperature of the copper coins is 4.00°C and is increasing at a rate of 0.500°C/s. At this time, (a) what is the temperature of the silver coins and (b) at what rate is it changing?
- **68.** The rate at which a resting person converts food energy is called one's basal metabolic rate (BMR). Assume that the resulting internal energy leaves a person's body by radiation and convection of dry air. When you jog, most of the food energy you burn above your BMR becomes internal energy that would raise your body temperature if it were not eliminated. Assume that evaporation of perspiration is the mechanism for eliminating this energy. Suppose a person is jogging for "maximum fat burning," converting food energy at the rate 400 kcal/h above his BMR, and putting out energy by work at the rate 60.0 W. Assume that the heat of evaporation of water at body temperature is equal to its heat of vaporization at 100° C. (a) Determine the hourly rate at which water must evaporate from his skin. (b) When you metabolize fat, the hydrogen atoms

in the fat molecule are transferred to oxygen to form water. Assume that metabolism of 1.00 g of fat generates 9.00 kcal of energy and produces 1.00 g of water. What fraction of the water the jogger needs is provided by fat metabolism?

- **69.** An iron plate is held against an iron wheel so that a kinetic friction force of 50.0 N acts between the two pieces of metal. The relative speed at which the two surfaces slide over each other is 40.0 m/s. (a) Calculate the rate at which mechanical energy is converted to internal energy. (b) The plate and the wheel each have a mass of 5.00 kg, and each receives 50.0% of the internal energy. If the system is run as described for 10.0 s and each object is then allowed to reach a uniform internal temperature, what is the resultant temperature increase?
- **70.** A resting adult of average size converts chemical energy in food into internal energy at the rate 120 W, called her basal metabolic rate. To stay at constant temperature, the body must put out energy at the same rate. Several processes exhaust energy from your body. Usually, the most important is thermal conduction into the air in contact with your exposed skin. If you are not wearing a hat, a convection current of warm air rises vertically from your head like a plume from a smokestack. Your body also loses energy by electromagnetic radiation, by your exhaling warm air, and by evaporation of perspiration. In this problem, consider still another pathway for energy loss: moisture in exhaled breath. Suppose you breathe out 22.0 breaths per minute, each with a volume of 0.600 L. Assume you inhale dry air and exhale air at 37.0°C containing water vapor with a vapor pressure of 3.20 kPa. The vapor came from evaporation of liquid water in your body. Model the water vapor as an ideal gas. Assume its latent heat of evaporation at 37.0°C is the same as its heat of vaporization at 100°C. Calculate the rate at which you lose energy by exhaling humid air.
- 71. A 40.0-g ice cube floats in 200 g of water in a 100-g
 M copper cup; all are at a temperature of 0°C. A piece of lead at 98.0°C is dropped into the cup, and the final equilibrium temperature is 12.0°C. What is the mass of the lead?
- 72. One mole of an ideal gas is contained in a cylinder with a movable piston. The initial pressure, volume, and temperature are P_i, V_i, and T_i, respectively. Find the work done on the gas in the following processes. In operational terms, describe how to carry out each process and show each process on a PV diagram. (a) an isobaric compression in which the final volume is one-half the initial volume (b) an isothermal compression in which the final pressure is four times the initial pressure (c) an isovolumetric process in which the final pressure is three times the initial pressure
- **73.** Review. A 670-kg meteoroid happens to be composed of aluminum. When it is far from the Earth, its temperature is -15.0°C and it moves at 14.0 km/s relative to the planet. As it crashes into the Earth, assume the internal energy transformed from the mechanical energy of the meteoroid–Earth system is shared equally between the meteoroid and the Earth and all the mate-

rial of the meteoroid rises momentarily to the same final temperature. Find this temperature. Assume the specific heat of liquid and of gaseous aluminum is $1 \ 170 \text{ J/kg} \cdot ^{\circ}\text{C}$.

74. Why is the following situation impossible? A group of campers arises at 8:30 a.m. and uses a solar cooker, which consists of a curved, reflecting surface that concentrates sunlight onto the object to be warmed (Fig. P20.74). During the day, the maximum solar intensity reaching the Earth's surface at the cooker's location is $I = 600 \text{ W/m}^2$. The cooker faces the Sun and has a face diameter of d = 0.600 m. Assume a fraction *f* of 40.0% of the incident energy is transferred to 1.50 L of water in an open container, initially at 20.0°C. The water comes to a boil, and the campers enjoy hot coffee for breakfast before hiking ten miles and returning by noon for lunch.



Figure P20.74

- 75. During periods of high activity, the Sun has more sunspots than usual. Sunspots are cooler than the rest of the luminous layer of the Sun's atmosphere (the photosphere). Paradoxically, the total power output of the active Sun is not lower than average but is the same or slightly higher than average. Work out the details of the following crude model of this phenomenon. Consider a patch of the photosphere with an area of 5.10×10^{14} m². Its emissivity is 0.965. (a) Find the power it radiates if its temperature is uniformly 5 800 K, corresponding to the quiet Sun. (b) To represent a sunspot, assume 10.0% of the patch area is at 4 800 K and the other 90.0% is at 5 890 K. Find the power output of the patch. (c) State how the answer to part (b) compares with the answer to part (a). (d) Find the average temperature of the patch. Note that this cooler temperature results in a higher power output.
- 76. (a) In air at 0°C, a 1.60-kg copper block at 0°C is set sliding at 2.50 m/s over a sheet of ice at 0°C. Friction brings the block to rest. Find the mass of the ice that melts. (b) As the block slows down, identify its energy input Q, its change in internal energy ΔE_{int}, and the change in mechanical energy for the block-ice system. (c) For the ice as a system, identify its energy input Q and its change in internal energy ΔE_{int}. (d) A 1.60-kg block of ice at 0°C. Friction brings the block to rest. Find the mass of the ice that melts. (e) Evaluate Q and ΔE_{int} for the block of ice as a system and ΔE_{mech} for the block-ice system. (f) Evaluate Q and ΔE_{int} for the metal

sheet as a system. (g) A thin, 1.60-kg slab of copper at 20°C is set sliding at 2.50 m/s over an identical stationary slab at the same temperature. Friction quickly stops the motion. Assuming no energy is transferred to the environment by heat, find the change in temperature of both objects. (h) Evaluate Q and ΔE_{int} for the sliding slab and ΔE_{mech} for the two-slab system. (i) Evaluate Q and ΔE_{int} for the stationary slab.

77. Water in an electric teakettle is boiling. The power
M absorbed by the water is 1.00 kW. Assuming the pressure of vapor in the kettle equals atmospheric pressure, determine the speed of effusion of vapor from the kettle's spout if the spout has a cross-sectional area of 2.00 cm². Model the steam as an ideal gas.

78. The average thermal conductivity of the walls (including the windows) and roof of the house depicted in Figure P20.78 is 0.480 W/m · °C, and their average thickness is 21.0 cm. The house is kept warm with natural gas having a heat of combustion (that is, the energy provided per cubic meter of gas burned) of 9 300 kcal/m³. How many cubic meters of gas must be burned each day to maintain an inside temperature of 25.0°C if the outside temperature is 0.0°C? Disregard radiation and the energy transferred by heat through the ground.



Figure P20.78

79. A cooking vessel on a slow burner contains 10.0 kg of water and an unknown mass of ice in equilibrium at 0°C at time t = 0. The temperature of the mixture is measured at various times, and the result is plotted in Figure P20.79. During the first 50.0 min, the mixture remains at 0°C. From 50.0 min to 60.0 min, the temperature increases to 2.00°C. Ignoring the heat capacity of the vessel, determine the initial mass of the ice.

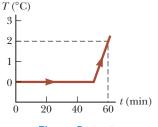


Figure P20.79

- **80.** A student measures the following data in a calorimetry experiment designed to determine the specific heat of aluminum:
 - Initial temperature of water and calorimeter: 70.0°C

Mass of water:	0.400 kg
Mass of calorimeter:	0.040 kg
Specific heat of calorimeter:	$0.63 \text{ kJ/kg} \cdot ^{\circ}\text{C}$
Initial temperature of aluminum:	27.0°C
Mass of aluminum:	0.200 kg
Final temperature of mixture:	66.3°C

(a) Use these data to determine the specific heat of aluminum. (b) Explain whether your result is within 15% of the value listed in Table 20.1.

Challenge Problems

81. Consider the pistoncylinder apparatus shown in Figure P20.81. The bottom of the cylinder contains 2.00 kg of water at just under 100.0° C. The cylinder has a radius of r = 7.50 cm. The piston of mass m = 3.00 kg sits on the surface of the water. An electric heater in the cylinder base transfers



Figure P20.81

energy into the water at a rate of 100 W. Assume the cylinder is much taller than shown in the figure, so we don't need to be concerned about the piston reaching the top of the cylinder. (a) Once the water begins boiling, how fast is the piston rising? Model the steam as an ideal gas. (b) After the water has completely turned to steam and the heater continues to transfer energy to the steam at the same rate, how fast is the piston rising?

82. A spherical shell has inner radius 3.00 cm and outer radius 7.00 cm. It is made of material with thermal conductivity k = 0.800 W/m · °C. The interior is maintained at temperature 5°C and the exterior at 40°C. After an interval of time, the shell reaches a steady state with the temperature at each point within it remaining constant in time. (a) Explain why the rate of energy transfer *P* must be the same through each spherical surface, of radius *r*, within the shell and must satisfy

$$\frac{dT}{dr} = \frac{P}{4\pi k r^2}$$

(b) Next, prove that

$$\int_{5}^{40} dT = \frac{P}{4\pi k} \int_{0.03}^{0.07} r^{-2} dr$$

where T is in degrees Celsius and r is in meters. (c) Find the rate of energy transfer through the shell. (d) Prove that

$$\int_{5}^{T} dT = 1.84 \int_{0.03}^{r} r^{-2} dr$$

where *T* is in degrees Celsius and *r* is in meters. (e) Find the temperature within the shell as a function of radius. (f) Find the temperature at r = 5.00 cm, halfway through the shell.

625

83. A pond of water at 0°C is covered with a layer of ice 4.00 cm thick. If the air temperature stays constant at -10.0°C, what time interval is required for the ice thickness to increase to 8.00 cm? *Suggestion:* Use Equation 20.16 in the form

$$\frac{dQ}{dt} = kA\frac{\Delta T}{x}$$

and note that the incremental energy dQ extracted from the water through the thickness *x* of ice is the amount required to freeze a thickness dx of ice. That is, $dQ = L_f \rho A \, dx$, where ρ is the density of the ice, *A* is the area, and L_f is the latent heat of fusion.

84. (a) The inside of a hollow cylinder is maintained at a temperature T_a , and the outside is at a lower temperature, T_b (Fig. P20.84). The wall of the cylinder has a thermal conductivity k. Ignoring end effects, show that the rate of energy conduction from the inner surface to the outer surface in the radial direction is

$$\frac{dQ}{dt} = 2\pi Lk \left[\frac{T_a - T_b}{\ln(b/a)} \right]$$

Suggestions: The temperature gradient is dT/dr. A radial energy current passes through a concentric cylinder of area $2\pi rL$. (b) The passenger section of a jet airliner is in the shape of a cylindrical tube with a length of 35.0 m and an inner radius of 2.50 m. Its walls are lined with an insulating material 6.00 cm in thickness and having a thermal conductivity of 4.00×10^{-5} cal/s \cdot cm \cdot °C. A heater must maintain the interior temperature at 25.0°C while the outside temperature is -35.0°C. What power must be supplied to the heater?

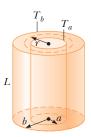
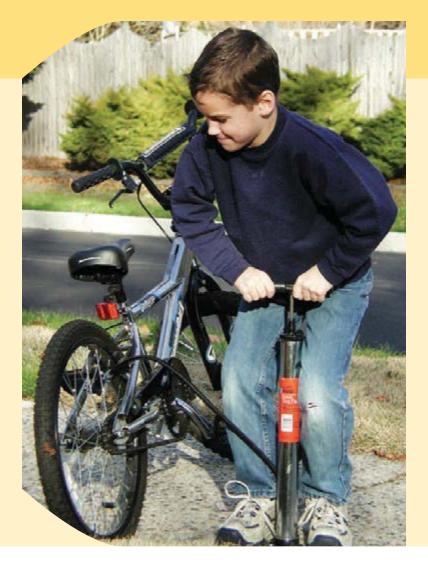


Figure P20.84

CHAPTER 21

The Kinetic Theory of Gases



- 21.1 Molecular Model of an Ideal Gas
- 21.2 Molar Specific Heat of an Ideal Gas
- 21.3 The Equipartition of Energy
- 21.4 Adiabatic Processes for an Ideal Gas
- 21.5 Distribution of Molecular Speeds

A boy inflates his bicycle tire with a hand-operated pump. Kinetic theory helps to describe the details of the air in the pump. (© Cengage Learning/ George Semple)

In Chapter 19, we discussed the properties of an ideal gas by using such macroscopic variables as pressure, volume, and temperature. Such large-scale properties can be related to a description on a microscopic scale, where matter is treated as a collection of molecules. Applying Newton's laws of motion in a statistical manner to a collection of particles provides a reasonable description of thermodynamic processes. To keep the mathematics relatively simple, we shall consider primarily the behavior of gases because in gases the interactions between molecules are much weaker than they are in liquids or solids.

We shall begin by relating pressure and temperature directly to the details of molecular motion in a sample of gas. Based on these results, we will make predictions of molar specific heats of gases. Some of these predictions will be correct and some will not. We will extend our model to explain those values that are not predicted correctly by the simpler model. Finally, we discuss the distribution of molecular speeds in a gas.

21.1 Molecular Model of an Ideal Gas

In this chapter, we will investigate a *structural model* for an ideal gas. A **structural model** is a theoretical construct designed to represent a system that cannot be observed directly because it is too large or too small. For example, we can only observe the solar system from the inside; we cannot travel outside the solar system and look back to see how it works. This restricted vantage point has led to different historical structural models of the solar system: the *geocentric model*, with the Earth at the center, and the *heliocentric model*, with the Sun at the center. Of course, the latter has been shown to be correct. An example of a system too small to observe directly is the hydrogen atom. Various structural models of this system have been developed, including the *Bohr model* (Section 42.3) and the *quantum model* (Section 42.4). Once a structural model is developed, various predictions are made for experimental observations. For example, the geocentric model of the solar system makes predictions of how the movement of Mars should appear from the Earth. It turns out that those predictions do not match the actual observations. When that occurs with a structural model, the model must be modified or replaced with another model.

The structural model that we will develop for an ideal gas is called **kinetic theory.** This model treats an ideal gas as a collection of molecules with the following properties:

1. Physical components:

The gas consists of a number of identical molecules within a cubic container of side length *d*. The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions. Therefore, the molecules occupy a negligible volume in the container. This assumption is consistent with the ideal gas model, in which we imagine the molecules to be point-like.

- 2. Behavior of the components:
 - (a) The molecules obey Newton's laws of motion, but as a whole their motion is isotropic: any molecule can move in any direction with any speed.
 - (b) The molecules interact only by short-range forces during elastic collisions. This assumption is consistent with the ideal gas model, in which the molecules exert no long-range forces on one another.
 - (c) The molecules make elastic collisions with the walls.

Although we often picture an ideal gas as consisting of single atoms, the behavior of molecular gases approximates that of ideal gases rather well at low pressures. Usually, molecular rotations or vibrations have no effect on the motions considered here.

For our first application of kinetic theory, let us relate the macroscope variable of pressure P to microscopic quantities. Consider a collection of N molecules of an ideal gas in a container of volume V. As indicated above, the container is a cube with edges of length d (Fig. 21.1). We shall first focus our attention on one of these molecules of mass m_0 and assume it is moving so that its component of velocity in the x direction is v_{xi} as in Figure 21.2. (The subscript *i* here refers to the *i*th molecule in the collection, not to an initial value. We will combine the effects of all the molecules shortly.) As the molecule collides elastically with any wall (property 2(c) above), its velocity component perpendicular to the wall is reversed because the mass of the wall is far greater than the mass of the molecule. The molecule is modeled as a nonisolated system for which the impulse from the wall causes a change in the molecule's momentum. Because the momentum component p_{xi} of the molecule is $m_0 v_{xi}$ before the collision and $-m_0 v_{xi}$ after the collision, the change in the x component of the momentum of the molecule is

$$\Delta p_{xi} = -m_0 v_{xi} - (m_0 v_{xi}) = -2m_0 v_{xi}$$

moves with velocity
$$\vec{v}$$
 on its way toward a collision with the wall.

One molecule of the gas

Figure 21.1 A cubical box with sides of length *d* containing an ideal gas.

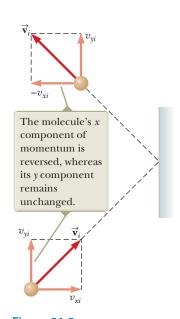


Figure 21.2 A molecule makes an elastic collision with the wall of the container. In this construction, we assume the molecule moves in the *xy* plane.

(21.1)

From the nonisolated system model for momentum, we can apply the impulsemomentum theorem (Eqs. 9.11 and 9.13) to the molecule to give

$$F_{i,\text{on molecule}} \Delta t_{\text{collision}} = \Delta p_{xi} = -2m_0 v_{xi}$$
(21.2)

where $F_{i,\text{on molecule}}$ is the *x* component of the average force¹ the wall exerts on the molecule during the collision and $\Delta t_{\text{collision}}$ is the duration of the collision. For the molecule to make another collision with the same wall after this first collision, it must travel a distance of 2d in the *x* direction (across the cube and back). Therefore, the time interval between two collisions with the same wall is

$$\Delta t = \frac{2d}{v_{xi}} \tag{21.3}$$

The force that causes the change in momentum of the molecule in the collision with the wall occurs only during the collision. We can, however, find the long-term average force for many back-and-forth trips across the cube by averaging the force in Equation 21.2 over the time interval for the molecule to move across the cube and back once, Equation 21.3. The average change in momentum per trip for the time interval for many trips is the same as that for the short duration of the collision. Therefore, we can rewrite Equation 21.2 as

$$\overline{F}_i \Delta t = -2m_0 v_{xi} \tag{21.4}$$

where $\overline{F_i}$ is the average force component over the time interval for the molecule to move across the cube and back. Because exactly one collision occurs for each such time interval, this result is also the long-term average force on the molecule over long time intervals containing any number of multiples of Δt .

Equation 21.3 and 21.4 enable us to express the *x* component of the long-term average force exerted by the wall on the molecule as

$$\bar{F}_{i} = -\frac{2m_{0}v_{xi}}{\Delta t} = -\frac{2m_{0}v_{xi}^{2}}{2d} = -\frac{m_{0}v_{xi}^{2}}{d}$$
(21.5)

Now, by Newton's third law, the *x* component of the long-term average force exerted by the *molecule* on the *wall* is equal in magnitude and opposite in direction:

$$\overline{F}_{i,\text{on wall}} = -\overline{F}_{i} = -\left(-\frac{m_{0}v_{xi}^{2}}{d}\right) = \frac{m_{0}v_{xi}^{2}}{d}$$
(21.6)

The total average force \overline{F} exerted by the gas on the wall is found by adding the average forces exerted by the individual molecules. Adding terms such as those in Equation 21.6 for all molecules gives

$$\bar{F} = \sum_{i=1}^{N} \frac{m_0 v_{xi}^2}{d} = \frac{m_0}{d} \sum_{i=1}^{N} v_{xi}^2$$
(21.7)

where we have factored out the length of the box and the mass m_0 because property 1 tells us that all the molecules are the same. We now impose an additional feature from property 1, that the number of molecules is large. For a small number of molecules, the actual force on the wall would vary with time. It would be nonzero during the short interval of a collision of a molecule with the wall and zero when no molecule happens to be hitting the wall. For a very large number of molecules such as Avogadro's number, however, these variations in force are smoothed out so that the average force given above is the same over *any* time interval. Therefore, the *constant* force *F* on the wall due to the molecular collisions is

$$F = \frac{m_0}{d} \sum_{i=1}^{N} v_{xi}^2$$
 (21.8)

¹For this discussion, we use a bar over a variable to represent the average value of the variable, such as \overline{F} for the average force, rather than the subscript "avg" that we have used before. This notation is to save confusion because we already have a number of subscripts on variables.

To proceed further, let's consider how to express the average value of the square of the *x* component of the velocity for N molecules. The traditional average of a set of values is the sum of the values over the number of values:

$$\overline{v_x^2} = \frac{\sum_{i=1}^{N} v_{xi}^2}{N} \to \sum_{i=1}^{N} v_{xi}^2 = N \overline{v_x^2}$$
(21.9)

Using Equation 21.9 to substitute for the sum in Equation 21.8 gives

$$F = \frac{m_0}{d} N \overline{v_x^2}$$
 (21.10)

Now let's focus again on one molecule with velocity components v_{xi} , v_{yi} , and v_{zi} . The Pythagorean theorem relates the square of the speed of the molecule to the squares of the velocity components:

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$
 (21.11)

Hence, the average value of v^2 for all the molecules in the container is related to the average values of v_x^2 , v_y^2 , and v_z^2 according to the expression

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$
(21.12)

Because the motion is isotropic (property 2(a) above), the average values v_x^2 , v_y^2 , and $\overline{v_z^2}$ are equal to one another. Using this fact and Equation 21.12, we find that

$$\overline{v^2} = 3\overline{v_x^2} \tag{21.13}$$

Therefore, from Equation 21.10, the total force exerted on the wall is

$$F = \frac{1}{3}N \,\frac{m_0 v^2}{d}$$
(21.14)

Using this expression, we can find the total pressure exerted on the wall:

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3}N \frac{m_0 \overline{v^2}}{d^3} = \frac{1}{3} \left(\frac{N}{V}\right) m_0 \overline{v^2}$$
$$P = \frac{2}{3} \left(\frac{N}{V}\right) (\frac{1}{2} m_0 \overline{v^2})$$
(21.15)

where we have recognized the volume V of the cube as d^3 .

Equation 21.15 indicates that the pressure of a gas is proportional to (1) the number of molecules per unit volume and (2) the average translational kinetic energy of the molecules, $\frac{1}{2}m_0v^2$. In analyzing this structural model of an ideal gas, we obtain an important result that relates the macroscopic quantity of pressure to a microscopic quantity, the average value of the square of the molecular speed. Therefore, a key link between the molecular world and the large-scale world has been established.

Notice that Equation 21.15 verifies some features of pressure with which you are probably familiar. One way to increase the pressure inside a container is to increase the number of molecules per unit volume N/V in the container. That is what you do when you add air to a tire. The pressure in the tire can also be raised by increasing the average translational kinetic energy of the air molecules in the tire. That can be accomplished by increasing the temperature of that air, which is why the pressure inside a tire increases as the tire warms up during long road trips. The continuous flexing of the tire as it moves along the road surface results in work done on the rubber as parts of the tire distort, causing an increase in internal energy of the rubber. The increased temperature of the rubber results in the transfer of energy by heat into the air inside the tire. This transfer increases the air's temperature, and this increase in temperature in turn produces an increase in pressure.

Relationship between pressure and molecular kinetic energy

Molecular Interpretation of Temperature

Let's now consider another macroscopic variable, the temperature T of the gas. We can gain some insight into the meaning of temperature by first writing Equation 21.15 in the form

$$PV = \frac{2}{3}N(\frac{1}{2}m_0v^2)$$
 (21.16)

Let's now compare this expression with the equation of state for an ideal gas (Eq. 19.10):

$$PV = Nk_{\rm B}T$$
 (21.17)

Equating the right sides of Equations 21.16 and 21.17 and solving for T gives

$$T = \frac{2}{3k_{\rm B}} \left(\frac{1}{2}m_0 \overline{v^2}\right)$$
(21.18)

This result tells us that temperature is a direct measure of average molecular kinetic energy. By rearranging Equation 21.18, we can relate the translational molecular kinetic energy to the temperature:

$$\frac{1}{2}m_0v^2 = \frac{3}{2}k_{\rm B}T$$
(21.19)

That is, the average translational kinetic energy per molecule is $\frac{3}{2}k_{\rm B}T$. Because $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$ (Eq. 21.13), it follows that

$$\frac{1}{2}m_0 v_x^2 = \frac{1}{2}k_{\rm B}T$$
(21.20)

In a similar manner, for the *y* and *z* directions,

$$\frac{1}{2}m_0v_y^2 = \frac{1}{2}k_BT$$
 and $\frac{1}{2}m_0v_z^2 = \frac{1}{2}k_BT$

Therefore, each translational degree of freedom contributes an equal amount of energy, $\frac{1}{2}k_{\rm B}T$, to the gas. (In general, a "degree of freedom" refers to an independent means by which a molecule can possess energy.) A generalization of this result, known as the **theorem of equipartition of energy**, is as follows:

Each degree of freedom contributes $\frac{1}{2}k_{\rm B}T$ to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules.

The total translational kinetic energy of N molecules of gas is simply N times the average energy per molecule, which is given by Equation 21.19:

$$K_{\text{tot trans}} = N(\frac{1}{2}m_0v^2) = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$$
 (21.21)

where we have used $k_{\rm B} = R/N_{\rm A}$ for Boltzmann's constant and $n = N/N_{\rm A}$ for the number of moles of gas. If the gas molecules possess only translational kinetic energy, Equation 21.21 represents the internal energy of the gas. This result implies that the internal energy of an ideal gas depends *only* on the temperature. We will follow up on this point in Section 21.2.

The square root of v^2 is called the **root-mean-square (rms) speed** of the molecules. From Equation 21.19, we find that the rms speed is

Root-mean-square speed >

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\rm B}T}{m_0}} = \sqrt{\frac{3RT}{M}}$$
 (21.22)

where *M* is the molar mass in kilograms per mole and is equal to m_0N_A . This expression shows that, at a given temperature, lighter molecules move faster, on the average, than do heavier molecules. For example, at a given temperature, hydrogen molecules, whose molar mass is 2.02×10^{-3} kg/mol, have an average speed approximately four times that of oxygen molecules, whose molar mass is 32.0×10^{-3} kg/mol. Table 21.1 lists the rms speeds for various molecules at 20° C.

Relationship between temperature and molecular kinetic energy

> Average kinetic energy per molecule

Theorem of equipartition >

Total translational kinetic energy of *N* molecules

of energy

	Some Root-Mean-Square (Tins) Speeds				
Gas	Molar Mass (g/mol)	v _{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	at 20°C (m/s)
H_2	2.02	1902	NO	30.0	494
He	4.00	1352	O_2	32.0	478
H_2O	18.0	637	CO_2	44.0	408
Ne	20.2	602	SO_2	64.1	338
N_2 or CO	28.0	511			

Table 21.1 Some Root-Mean-Square (rms) Speeds

• uick Quiz 21.1 Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A. (i) What is the average translational kinetic energy per molecule in container B? (a) twice that of container A (b) the same as that of container A (c) half that of container A (d) impossible to determine (ii) From

the same choices, describe the internal energy of the gas in container B.

Pitfall Prevention 21.1

The Square Root of the Square? Taking the square root of $\overline{v^2}$ does not "undo" the square because we have taken an average *between* squaring and taking the square root. Although the square root of $(\overline{v})^2$ is $\overline{v} = v_{avg}$ because the squaring is done after the averaging, the square root of $\overline{v^2}$ is *not* v_{avg} , but rather v_{rms} .

Example 21.1 A Tank of Helium

A tank used for filling helium balloons has a volume of 0.300 m^3 and contains 2.00 mol of helium gas at 20.0° C. Assume the helium behaves like an ideal gas.

(A) What is the total translational kinetic energy of the gas molecules?

SOLUTION

Conceptualize Imagine a microscopic model of a gas in which you can watch the molecules move about the container more rapidly as the temperature increases. Because the gas is monatomic, the total translational kinetic energy of the molecules is the internal energy of the gas.

Categorize We evaluate parameters with equations developed in the preceding discussion, so this example is a substitution problem.

Use Equation 21.21 with n = 2.00 mol and T = 293 K:

 $E_{\text{int}} = \frac{3}{2}nRT = \frac{3}{2}(2.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(293 \text{ K})$ $= 7.30 \times 10^3 \text{ J}$

(B) What is the average kinetic energy per molecule?

SOLUTION

Use Equation 21.19:

 $\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_BT = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})$ $= 6.07 \times 10^{-21} \text{ J}$

WHAT IF? What if the temperature is raised from 20.0°C to 40.0°C? Because 40.0 is twice as large as 20.0, is the total translational energy of the molecules of the gas twice as large at the higher temperature?

Answer The expression for the total translational energy depends on the temperature, and the value for the temperature must be expressed in kelvins, not in degrees Celsius. Therefore, the ratio of 40.0 to 20.0 is *not* the appropriate ratio. Converting the Celsius temperatures to kelvins, 20.0°C is 293 K and 40.0°C is 313 K. Therefore, the total translational energy increases by a factor of only 313 K/293 K = 1.07.

21.2 Molar Specific Heat of an Ideal Gas

Consider an ideal gas undergoing several processes such that the change in temperature is $\Delta T = T_f - T_i$ for all processes. The temperature change can be achieved

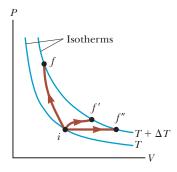


Figure 21.3 An ideal gas is taken from one isotherm at temperature *T* to another at temperature $T + \Delta T$ along three different paths.

Internal energy of an ideal monatomic gas by taking a variety of paths from one isotherm to another as shown in Figure 21.3. Because ΔT is the same for all paths, the change in internal energy ΔE_{int} is the same for all paths. The work *W* done on the gas (the negative of the area under the curves), however, is different for each path. Therefore, from the first law of thermodynamics, we can argue that the heat $Q = \Delta E_{int} - W$ associated with a given change in temperature does *not* have a unique value as discussed in Section 20.4.

We can address this difficulty by defining specific heats for two special processes that we have studied: isovolumetric and isobaric. Because the number of moles n is a convenient measure of the amount of gas, we define the **molar specific heats** associated with these processes as follows:

$$Q = nC_V \Delta T$$
 (constant volume) (21.23)

$$Q = nC_P \Delta T$$
 (constant pressure) (21.24)

where C_V is the **molar specific heat at constant volume** and C_P is the **molar specific heat at constant pressure.** When energy is added to a gas by heat at constant pressure, not only does the internal energy of the gas increase, but (negative) work is done on the gas because of the change in volume required to keep the pressure constant. Therefore, the heat Q in Equation 21.24 must account for both the increase in internal energy and the transfer of energy out of the system by work. For this reason, Q is greater in Equation 21.24 than in Equation 21.23 for given values of n and ΔT . Therefore, C_P is greater than C_V .

In the previous section, we found that the temperature of a gas is a measure of the average translational kinetic energy of the gas molecules. This kinetic energy is associated with the motion of the center of mass of each molecule. It does not include the energy associated with the internal motion of the molecule, namely, vibrations and rotations about the center of mass. That should not be surprising because the simple kinetic theory model assumes a structureless molecule.

So, let's first consider the simplest case of an ideal monatomic gas, that is, a gas containing one atom per molecule such as helium, neon, or argon. When energy is added to a monatomic gas in a container of fixed volume, all the added energy goes into increasing the translational kinetic energy of the atoms. There is no other way to store the energy in a monatomic gas. Therefore, from Equation 21.21, we see that the internal energy E_{int} of N molecules (or *n* mol) of an ideal monatomic gas is

$$E_{\rm int} = K_{\rm tot\,trans} = \frac{3}{2}Nk_{\rm B}T = \frac{3}{2}nRT$$
 (21.25)

For a monatomic ideal gas, E_{int} is a function of T only and the functional relationship is given by Equation 21.25. In general, the internal energy of any ideal gas is a function of T only and the exact relationship depends on the type of gas.

If energy is transferred by heat to a system at constant volume, no work is done on the system. That is, $W = -\int P \, dV = 0$ for a constant-volume process. Hence, from the first law of thermodynamics,

$$Q = \Delta E_{\rm int} \tag{21.26}$$

In other words, all the energy transferred by heat goes into increasing the internal energy of the system. A constant-volume process from *i* to *f* for an ideal gas is described in Figure 21.4, where ΔT is the temperature difference between the two isotherms. Substituting the expression for *Q* given by Equation 21.23 into Equation 21.26, we obtain

$$\Delta E_{\rm int} = nC_V \,\Delta T \tag{21.27}$$

This equation applies to all ideal gases, those gases having more than one atom per molecule as well as monatomic ideal gases.

In the limit of infinitesimal changes, we can use Equation 21.27 to express the molar specific heat at constant volume as

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT}$$
(21.28)

Let's now apply the results of this discussion to a monatomic gas. Substituting the internal energy from Equation 21.25 into Equation 21.28 gives

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K}$$
 (21.29)

This expression predicts a value of $C_V = \frac{3}{2}R$ for *all* monatomic gases. This prediction is in excellent agreement with measured values of molar specific heats for such gases as helium, neon, argon, and xenon over a wide range of temperatures (Table 21.2). Small variations in Table 21.2 from the predicted values are because real gases are not ideal gases. In real gases, weak intermolecular interactions occur, which are not addressed in our ideal gas model.

Now suppose the gas is taken along the constant-pressure path $i \rightarrow f'$ shown in Figure 21.4. Along this path, the temperature again increases by ΔT . The energy that must be transferred by heat to the gas in this process is $Q = nC_P \Delta T$. Because the volume changes in this process, the work done on the gas is $W = -P \Delta V$, where P is the constant pressure at which the process occurs. Applying the first law of thermodynamics to this process, we have

$$\Delta E_{\rm int} = Q + W = nC_P \Delta T + (-P\Delta V)$$
(21.30)

In this case, the energy added to the gas by heat is channeled as follows. Part of it leaves the system by work (that is, the gas moves a piston through a displacement), and the remainder appears as an increase in the internal energy of the gas. The change in internal energy for the process $i \rightarrow f'$, however, is equal to that for the process $i \rightarrow f$ because E_{int} depends only on temperature for an ideal gas and ΔT is the same for both processes. In addition, because PV = nRT, note that for a constant-pressure process, $P \Delta V = nR \Delta T$. Substituting this value for $P \Delta V$ into Equation 21.30 with $\Delta E_{int} = nC_V \Delta T$ (Eq. 21.27) gives

$$nC_V \Delta T = nC_P \Delta T - nR \Delta T$$

$$C_P - C_V = R$$
(21.31)

This expression applies to *any* ideal gas. It predicts that the molar specific heat of an ideal gas at constant pressure is greater than the molar specific heat at constant volume by an amount R, the universal gas constant (which has the value 8.31 J/mol \cdot K). This expression is applicable to real gases as the data in Table 21.2 show.

 Table 21.2
 Molar Specific Heats of Various Gases

	Molar S	Molar Specific Heat (J/mol · K) ^a			
Gas	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$	
Monatomic gases					
Не	20.8	12.5	8.33	1.67	
Ar	20.8	12.5	8.33	1.67	
Ne	20.8	12.7	8.12	1.64	
Kr	20.8	12.3	8.49	1.69	
Diatomic gases					
H ₂	28.8	20.4	8.33	1.41	
N ₂	29.1	20.8	8.33	1.40	
O_2	29.4	21.1	8.33	1.40	
CO	29.3	21.0	8.33	1.40	
Cl_2	34.7	25.7	8.96	1.35	
Polyatomic gases					
CO ₂	37.0	28.5	8.50	1.30	
SO ₂	40.4	31.4	9.00	1.29	
H_2O	35.4	27.0	8.37	1.30	
\tilde{CH}_4	35.5	27.1	8.41	1.31	

^a All values except that for water were obtained at 300 K.

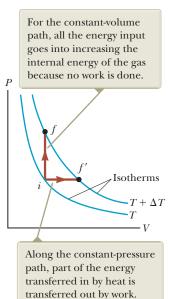


Figure 21.4 Energy is transferred by heat to an ideal gas in two ways.

Because $C_V = \frac{3}{2}R$ for a monatomic ideal gas, Equation 21.31 predicts a value $C_P = \frac{5}{2}R = 20.8 \text{ J/mol} \cdot \text{K}$ for the molar specific heat of a monatomic gas at constant pressure. The ratio of these molar specific heats is a dimensionless quantity γ (Greek letter gamma):

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3} = 1.67$$
(21.32)

Theoretical values of C_V , C_P , and γ are in excellent agreement with experimental values obtained for monatomic gases, but they are in serious disagreement with the values for the more complex gases (see Table 21.2). That is not surprising; the value $C_V = \frac{3}{2}R$ was derived for a monatomic ideal gas, and we expect some additional contribution to the molar specific heat from the internal structure of the more complex molecules. In Section 21.3, we describe the effect of molecular structure on the molar specific heat of a gas. The internal energy—and hence the molar specific heat—of a complex gas must include contributions from the rotational and the vibrational motions of the molecule.

In the case of solids and liquids heated at constant pressure, very little work is done during such a process because the thermal expansion is small. Consequently, C_P and C_V are approximately equal for solids and liquids.

Quiz 21.2 (i) How does the internal energy of an ideal gas change as it follows path *i*→ *f* in Figure 21.4? (a) E_{int} increases. (b) E_{int} decreases. (c) E_{int} stays the same. (d) There is not enough information to determine how E_{int} changes.
(ii) From the same choices, how does the internal energy of an ideal gas change
as it follows path *f*→ *f'* along the isotherm labeled *T* + Δ*T* in Figure 21.4?

Example 21.2 Heating a Cylinder of Helium

A cylinder contains 3.00 mol of helium gas at a temperature of 300 K.

(A) If the gas is heated at constant volume, how much energy must be transferred by heat to the gas for its temperature to increase to 500 K?

SOLUTION

Conceptualize Run the process in your mind with the help of the piston–cylinder arrangement in Figure 19.12. Imagine that the piston is clamped in position to maintain the constant volume of the gas.

Categorize We evaluate parameters with equations developed in the preceding discussion, so this example is a substitution problem.

Use Equation 21.23 to find the energy transfer:	$Q_1 = nC_V \Delta T$
Substitute the given values:	$Q_1 = (3.00 \text{ mol})(12.5 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K})$
	$= 7.50 \times 10^3 \text{ J}$

(B) How much energy must be transferred by heat to the gas at constant pressure to raise the temperature to 500 K?

SOLUTION

Use Equation 21.24 to find the energy transfer:	$Q_2 = nC_P \ \Delta T$
Substitute the given values:	$Q_2 = (3.00 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K})$
	$= 12.5 \times 10^{3} \text{ J}$

This value is larger than Q_1 because of the transfer of energy out of the gas by work to raise the piston in the constant pressure process.

Ratio of molar specific heats for a monatomic ideal gas

21.3 The Equipartition of Energy

Predictions based on our model for molar specific heat agree quite well with the behavior of monatomic gases, but not with the behavior of complex gases (see Table 21.2). The value predicted by the model for the quantity $C_P - C_V = R$, however, is the same for all gases. This similarity is not surprising because this difference is the result of the work done on the gas, which is independent of its molecular structure.

To clarify the variations in C_V and C_P in gases more complex than monatomic gases, let's explore further the origin of molar specific heat. So far, we have assumed the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. The internal energy of a gas, however, includes contributions from the translational, vibrational, and rotational motion of the molecules. The rotational and vibrational motions of molecules can be activated by collisions and therefore are "coupled" to the translational motion of the molecules. The branch of physics known as *statistical mechanics* has shown that, for a large number of particles obeying the laws of Newtonian mechanics, the available energy is, on average, shared equally by each independent degree of freedom. Recall from Section 21.1 that the equipartition theorem states that, at equilibrium, each degree of freedom contributes $\frac{1}{2}k_{\rm B}T$ of energy per molecule.

Let's consider a diatomic gas whose molecules have the shape of a dumbbell (Fig. 21.5). In this model, the center of mass of the molecule can translate in the *x*, *y*, and *z* directions (Fig. 21.5a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. 21.5b). The rotation about the *y* axis can be neglected because the molecule's moment of inertia I_y and its rotational energy $\frac{1}{2}I_y\omega^2$ about this axis are negligible compared with those associated with the *x* and *z* axes. (If the two atoms are modeled as particles, then I_y is identically zero.) Therefore, there are five degrees of freedom for translation and rotation: three associated with the translational motion and two associated with the rotational motion. Because each degree of freedom contributes, on average, $\frac{1}{2}k_BT$ of energy per molecule, the internal energy for a system of *N* molecules, ignoring vibration for now, is

$$E_{\rm int} = 3N(\frac{1}{2}k_{\rm B}T) + 2N(\frac{1}{2}k_{\rm B}T) = \frac{5}{2}Nk_{\rm B}T = \frac{5}{2}nRT$$

We can use this result and Equation 21.28 to find the molar specific heat at constant volume:

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} (\frac{5}{2}nRT) = \frac{5}{2}R = 20.8 \text{ J/mol} \cdot \text{K}$$
 (21.33)

From Equations 21.31 and 21.32, we find that

$$C_P = C_V + R = \frac{7}{2}R = 29.1 \text{ J/mol} \cdot \text{K}$$

 $\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.40$

These results agree quite well with most of the data for diatomic molecules given in Table 21.2. That is rather surprising because we have not yet accounted for the possible vibrations of the molecule.

In the model for vibration, the two atoms are joined by an imaginary spring (see Fig. 21.5c). The vibrational motion adds two more degrees of freedom, which correspond to the kinetic energy and the potential energy associated with vibrations along the length of the molecule. Hence, a model that includes all three types of motion predicts a total internal energy of

$$E_{\rm int} = 3N(\frac{1}{2}k_{\rm B}T) + 2N(\frac{1}{2}k_{\rm B}T) + 2N(\frac{1}{2}k_{\rm B}T) = \frac{7}{2}Nk_{\rm B}T = \frac{7}{2}nRT$$

and a molar specific heat at constant volume of

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} (\frac{7}{2}nRT) = \frac{7}{2}R = 29.1 \text{ J/mol} \cdot \text{K}$$
 (21.34)

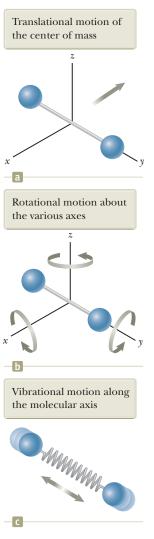
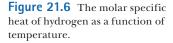
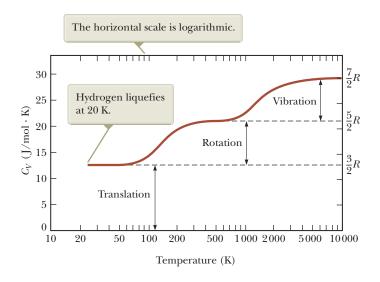


Figure 21.5 Possible motions of a diatomic molecule.





This value is inconsistent with experimental data for molecules such as H_2 and N_2 (see Table 21.2) and suggests a breakdown of our model based on classical physics.

It might seem that our model is a failure for predicting molar specific heats for diatomic gases. We can claim some success for our model, however, if measurements of molar specific heat are made over a wide temperature range rather than at the single temperature that gives us the values in Table 21.2. Figure 21.6 shows the molar specific heat of hydrogen as a function of temperature. The remarkable feature about the three plateaus in the graph's curve is that they are at the values of the molar specific heat predicted by Equations 21.29, 21.33, and 21.34! For low temperature, the diatomic hydrogen gas behaves like a monatomic gas. As the temperature rises to room temperature, its molar specific heat rises to a value for a diatomic gas, consistent with the inclusion of rotation but not vibration. For high temperatures, the molar specific heat is consistent with a model including all types of motion.

Before addressing the reason for this mysterious behavior, let's make some brief remarks about polyatomic gases. For molecules with more than two atoms, three axes of rotation are available. The vibrations are more complex than for diatomic molecules. Therefore, the number of degrees of freedom is even larger. The result is an even higher predicted molar specific heat, which is in qualitative agreement with experiment. The molar specific heats for the polyatomic gases in Table 21.2 are higher than those for diatomic gases. The more degrees of freedom available to a molecule, the more "ways" there are to store energy, resulting in a higher molar specific heat.

A Hint of Energy Quantization

Our model for molar specific heats has been based so far on purely classical notions. It predicts a value of the specific heat for a diatomic gas that, according to Figure 21.6, only agrees with experimental measurements made at high temperatures. To explain why this value is only true at high temperatures and why the plateaus in Figure 21.6 exist, we must go beyond classical physics and introduce some quantum physics into the model. In Chapter 18, we discussed quantization of frequency for vibrating strings and air columns; only certain frequencies of standing waves can exist. That is a natural result whenever waves are subject to boundary conditions.

Quantum physics (Chapters 40 through 43) shows that atoms and molecules can be described by the waves under boundary conditions analysis model. Consequently, these waves have quantized frequencies. Furthermore, in quantum physics, the energy of a system is proportional to the frequency of the wave representing the system. Hence, **the energies of atoms and molecules are quantized**.

For a molecule, quantum physics tells us that the rotational and vibrational energies are quantized. Figure 21.7 shows an **energy-level diagram** for the rotational and vibrational quantum states of a diatomic molecule. The lowest allowed state is called the **ground state**. The black lines show the energies allowed for the molecule. Notice that allowed vibrational states are separated by larger energy gaps than are rotational states.

At low temperatures, the energy a molecule gains in collisions with its neighbors is generally not large enough to raise it to the first excited state of either rotation or vibration. Therefore, even though rotation and vibration are allowed according to classical physics, they do not occur in reality at low temperatures. All molecules are in the ground state for rotation and vibration. The only contribution to the molecules' average energy is from translation, and the specific heat is that predicted by Equation 21.29.

As the temperature is raised, the average energy of the molecules increases. In some collisions, a molecule may have enough energy transferred to it from another molecule to excite the first rotational state. As the temperature is raised further, more molecules can be excited to this state. The result is that rotation begins to contribute to the internal energy, and the molar specific heat rises. At about room temperature in Figure 21.6, the second plateau has been reached and rotation contributes fully to the molar specific heat. The molar specific heat is now equal to the value predicted by Equation 21.33.

There is no contribution at room temperature from vibration because the molecules are still in the ground vibrational state. The temperature must be raised even further to excite the first vibrational state, which happens in Figure 21.6 between 1 000 K and 10 000 K. At 10 000 K on the right side of the figure, vibration is contributing fully to the internal energy and the molar specific heat has the value predicted by Equation 21.34.

The predictions of this model are supportive of the theorem of equipartition of energy. In addition, the inclusion in the model of energy quantization from quantum physics allows a full understanding of Figure 21.6.

uick Quiz 21.3 The molar specific heat of a diatomic gas is measured at constant volume and found to be 29.1 J/mol · K. What are the types of energy that are contributing to the molar specific heat? (a) translation only (b) translation and rotation only (c) translation and vibration only (d) translation, rotation, and vibration

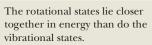
uick Quiz 21.4 The molar specific heat of a gas is measured at constant volume and found to be 11*R*/2. Is the gas most likely to be (a) monatomic, (b) diatomic,
or (c) polyatomic?

21.4 Adiabatic Processes for an Ideal Gas

As noted in Section 20.6, an **adiabatic process** is one in which no energy is transferred by heat between a system and its surroundings. For example, if a gas is compressed (or expanded) rapidly, very little energy is transferred out of (or into) the system by heat, so the process is nearly adiabatic. Such processes occur in the cycle of a gasoline engine, which is discussed in detail in Chapter 22. Another example of an adiabatic process is the slow expansion of a gas that is thermally insulated from its surroundings. All three variables in the ideal gas law—*P*, *V*, and *T*—change during an adiabatic process.

Let's imagine an adiabatic gas process involving an infinitesimal change in volume dV and an accompanying infinitesimal change in temperature dT. The work done on the gas is -P dV. Because the internal energy of an ideal gas depends only on temperature, the change in the internal energy in an adiabatic process is the same as that for an isovolumetric process between the same temperatures, $dE_{int} = nC_V dT$ (Eq. 21.27). Hence, the first law of thermodynamics, $\Delta E_{int} = Q + W$, with Q = 0, becomes the infinitesimal form

$$dE_{\rm int} = nC_V dT = -P \, dV \tag{21.35}$$



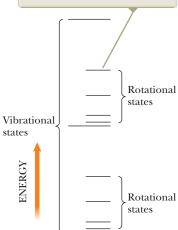


Figure 21.7 An energy-level diagram for vibrational and rotational states of a diatomic molecule.

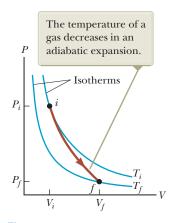


Figure 21.8 The *PV* diagram for an adiabatic expansion of an ideal gas.

Relationship between P and V > for an adiabatic process involving an ideal gas

Taking the total differential of the equation of state of an ideal gas, PV = nRT, gives

$$P \, dV + V \, dP = nR \, dT \tag{21.36}$$

Eliminating dT from Equations 21.35 and 21.36, we find that

$$P \, dV + V \, dP = -\frac{R}{C_V} P \, dV$$

Substituting $R = C_P - C_V$ and dividing by *PV* gives

$$\frac{dV}{V} + \frac{dP}{P} = -\left(\frac{C_P - C_V}{C_V}\right)\frac{dV}{V} = (1 - \gamma)\frac{dV}{V}$$
$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating this expression, we have

$$\ln P + \gamma \ln V = \text{constant}$$

which is equivalent to

$$PV^{\gamma} = \text{constant}$$
 (21.37)

The PV diagram for an adiabatic expansion is shown in Figure 21.8. Because $\gamma > 1$, the PV curve is steeper than it would be for an isothermal expansion, for which PV = constant. By the definition of an adiabatic process, no energy is transferred by heat into or out of the system. Hence, from the first law, we see that ΔE_{int} is negative (work is done by the gas, so its internal energy decreases) and so ΔT also is negative. Therefore, the temperature of the gas decreases $(T_f < T_i)$ during an adiabatic expansion.² Conversely, the temperature increases if the gas is compressed adiabatically. Applying Equation 21.37 to the initial and final states, we see that

 $TV^{\gamma-1} = \text{constant}$

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \tag{21.38}$$

(21.39)

Using the ideal gas law, we can express Equation 21.37 as

Relationship between T and $V \ge$ for an adiabatic process involving an ideal gas

Example 21.3 A Diesel Engine Cylinder

Air at 20.0°C in the cylinder of a diesel engine is compressed from an initial pressure of 1.00 atm and volume of 800.0 cm^3 to a volume of 60.0 cm^3 . Assume air behaves as an ideal gas with $\gamma = 1.40$ and the compression is adiabatic. Find the final pressure and temperature of the air.

SOLUTION

Conceptualize Imagine what happens if a gas is compressed into a smaller volume. Our discussion above and Figure 21.8 tell us that the pressure and temperature both increase.

Categorize We categorize this example as a problem involving an adiabatic process.

Analyze Use Equation 21.38 to find the final pressure:

Analyze Use Equation 21.38 to find the final pressure:

$$P_f = P_i \left(\frac{V_i}{V_f}\right)^{\gamma} = (1.00 \text{ atm}) \left(\frac{800.0 \text{ cm}^3}{60.0 \text{ cm}^3}\right)^{1.40}$$

$$= 37.6 \text{ atm}$$

²In the adiabatic free expansion discussed in Section 20.6, the temperature remains constant. In this unique process, no work is done because the gas expands into a vacuum. In general, the temperature decreases in an adiabatic expansion in which work is done.

21.3 continued

Use the ideal gas law to find the final temperature:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

$$T_f = \frac{P_f V_f}{P_i V_i} T_i = \frac{(37.6 \text{ atm})(60.0 \text{ cm}^3)}{(1.00 \text{ atm})(800.0 \text{ cm}^3)} (293 \text{ K})$$

$$= 826 \text{ K} = 553^{\circ}\text{C}$$

Finalize The temperature of the gas increases by a factor of 826 K/293 K = 2.82. The high compression in a diesel engine raises the temperature of the gas enough to cause the combustion of fuel without the use of spark plugs.

21.5 Distribution of Molecular Speeds

Thus far, we have considered only average values of the energies of all the molecules in a gas and have not addressed the distribution of energies among individual molecules. The motion of the molecules is extremely chaotic. Any individual molecule collides with others at an enormous rate, typically a billion times per second. Each collision results in a change in the speed and direction of motion of each of the participant molecules. Equation 21.22 shows that rms molecular speeds increase with increasing temperature. At a given time, what is the relative number of molecules that possess some characteristic such as energy within a certain range?

We shall address this question by considering the **number density** $n_V(E)$. This quantity, called a *distribution function*, is defined so that $n_V(E)$ *dE* is the number of molecules per unit volume with energy between *E* and *E* + *dE*. (The ratio of the number of molecules that have the desired characteristic to the total number of molecules is the probability that a particular molecule has that characteristic.) In general, the number density is found from statistical mechanics to be

$$n_{\rm V}(E) = n_0 e^{-E/k_{\rm B}T}$$
(21.40)

where n_0 is defined such that $n_0 dE$ is the number of molecules per unit volume having energy between E = 0 and E = dE. This equation, known as the **Boltzmann distribution law**, is important in describing the statistical mechanics of a large number of molecules. It states that the probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by k_BT . All the molecules would fall into the lowest energy level if the thermal agitation at a temperature *T* did not excite the molecules to higher energy levels.

Example 21.4 Thermal Excitation of Atomic Energy Levels

As discussed in Section 21.4, atoms can occupy only certain discrete energy levels. Consider a gas at a temperature of 2 500 K whose atoms can occupy only two energy levels separated by 1.50 eV, where 1 eV (electron volt) is an energy unit equal to 1.60×10^{-19} J (Fig. 21.9). Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

SOLUTION

Conceptualize In your mental representation of this example, remember that only two possible states are allowed for the system of the atom. Figure 21.9 helps you visualize the two states on an energy-level diagram. In this case, the atom has two possible energies, E_1 and E_2 , where $E_1 < E_2$.

Pitfall Prevention 21.2 The Distribution Function

The distribution function $n_V(E)$ is defined in terms of the number of molecules with energy in the range *E* to E + dE rather than in terms of the number of molecules with energy *E*. Because the number of molecules is finite and the number of possible values of the energy is infinite, the number of molecules with an *exact* energy *E* may be zero.

A Boltzmann distribution law

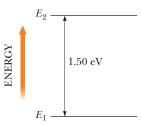


Figure 21.9 (Example 21.4) Energy-level diagram for a gas whose atoms can occupy two energy states.

continued

21.4 continued

Categorize We categorize this example as one in which we focus on particles in a two-state quantized system. We will apply the Boltzmann distribution law to this system.

(1) $\frac{n_V(E_2)}{n_V(E_1)} = \frac{n_0 e^{-E_2/k_{\rm B}T}}{n_0 e^{-E_1/k_{\rm B}T}} = e^{-(E_2 - E_1)/k_{\rm B}T}$

Analyze Set up the ratio of the number of atoms in the higher energy level to the number in the lower energy level and use Equation 21.40 to express each number:

Evaluate $k_{\rm B}T$ in the exponent:

Substitute this value into Equation (1):

$$k_{\rm B}T = (1.38 \times 10^{-23} \,\text{J/K})(2\,500 \,\text{K}) \left(\frac{1 \,\text{eV}}{1.60 \times 10^{-19} \,\text{J}}\right) = 0.216 \,\text{eV}$$
$$\frac{n_V(E_2)}{n_V(E_1)} = e^{-1.50 \,\text{eV}/0.216 \,\text{eV}} = e^{-6.96} = 9.52 \times 10^{-4}$$

Finalize This result indicates that at T = 2500 K, only a small fraction of the atoms are in the higher energy level. In fact, for every atom in the higher energy level, there are about 1 000 atoms in the lower level. The number of atoms in the higher level increases at even higher temperatures, but the distribution law specifies that at equilibrium there are always more atoms in the lower level than in the higher level.

WHAT IF? What if the energy levels in Figure 21.9 were closer together in energy? Would that increase or decrease the fraction of the atoms in the upper energy level?

Answer If the excited level is lower in energy than that in Figure 21.9, it would be easier for thermal agitation to excite atoms to this level and the fraction of atoms in this energy level would be larger, which we can see mathematically by expressing Equation (1) as

$$r_{\rm 2} = e^{-(E_2 - E_1)/k_{\rm B}T}$$

where r_2 is the ratio of atoms having energy E_2 to those with energy E_1 . Differentiating with respect to E_2 , we find

$$\frac{dr_2}{dE_2} = \frac{d}{dE_2} \left[e^{-(E_2 - E_1)/k_{\rm B}T} \right] = -\frac{1}{k_{\rm B}T} e^{-(E_2 - E_1)/k_{\rm B}T} < 0$$

Because the derivative has a negative value, as E_2 decreases, r_2 increases.



Ludwig Boltzmann

Austrian physicist (1844–1906) Boltzmann made many important contributions to the development of the kinetic theory of gases, electromagnetism, and thermodynamics. His pioneering work in the field of kinetic theory led to the branch of physics known as statistical mechanics. Now that we have discussed the distribution of energies among molecules in a gas, let's think about the distribution of molecular speeds. In 1860, James Clerk Maxwell (1831–1879) derived an expression that describes the distribution of molecular speeds in a very definite manner. His work and subsequent developments by other scientists were highly controversial because direct detection of molecules could not be achieved experimentally at that time. About 60 years later, however, experiments were devised that confirmed Maxwell's predictions.

Let's consider a container of gas whose molecules have some distribution of speeds. Suppose we want to determine how many gas molecules have a speed in the range from, for example, 400 to 401 m/s. Intuitively, we expect the speed distribution to depend on temperature. Furthermore, we expect the distribution to peak in the vicinity of $v_{\rm rms}$. That is, few molecules are expected to have speeds much less than or much greater than $v_{\rm rms}$ because these extreme speeds result only from an unlikely chain of collisions.

The observed speed distribution of gas molecules in thermal equilibrium is shown in Figure 21.10. The quantity N_v , called the **Maxwell–Boltzmann speed distribution function**, is defined as follows. If N is the total number of molecules, the number of molecules with speeds between v and v + dv is $dN = N_v dv$. This number is also equal to the area of the shaded rectangle in Figure 21.10. Furthermore, the fraction of molecules with speeds between v and v + dv is $(N_v dv)/N$. This fraction is also equal to the probability that a molecule has a speed in the range v to v + dv.

640

The fundamental expression that describes the distribution of speeds of N gas molecules is

$$N_{v} = 4\pi N \left(\frac{m_{0}}{2\pi k_{\rm B}T}\right)^{3/2} v^{2} e^{-m_{0}v^{2}/2k_{\rm B}T}$$
(21.41)

where m_0 is the mass of a gas molecule, $k_{\rm B}$ is Boltzmann's constant, and *T* is the absolute temperature.³ Observe the appearance of the Boltzmann factor $e^{-E/k_{\rm B}T}$ with $E = \frac{1}{2}m_0v^2$.

As indicated in Figure 21.10, the average speed is somewhat lower than the rms speed. The *most probable speed* $v_{\rm mp}$ is the speed at which the distribution curve reaches a peak. Using Equation 21.41, we find that

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\rm B}T}{m_0}} = 1.73\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.42)

$$v_{\rm avg} = \sqrt{\frac{8k_{\rm B}T}{\pi m_0}} = 1.60\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.43)

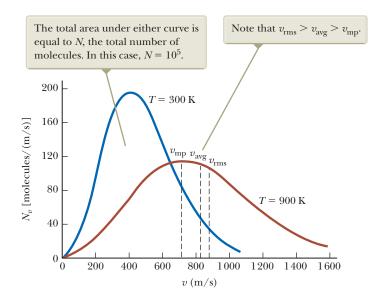
$$v_{\rm mp} = \sqrt{\frac{2k_{\rm B}T}{m_0}} = 1.41\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.44)

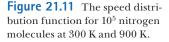
Equation 21.42 has previously appeared as Equation 21.22. The details of the derivations of these equations from Equation 21.41 are left for the end-of-chapter problems (see Problems 42 and 69). From these equations, we see that

 $v_{\rm rms} > v_{\rm avg} > v_{\rm mp}$

Figure 21.11 represents speed distribution curves for nitrogen, N_2 . The curves were obtained by using Equation 21.41 to evaluate the distribution function at various speeds and at two temperatures. Notice that the peak in each curve shifts to the right as *T* increases, indicating that the average speed increases with increasing temperature, as expected. Because the lowest speed possible is zero and the upper classical limit of the speed is infinity, the curves are asymmetrical. (In Chapter 39, we show that the actual upper limit is the speed of light.)

Equation 21.41 shows that the distribution of molecular speeds in a gas depends both on mass and on temperature. At a given temperature, the fraction of molecules with speeds exceeding a fixed value increases as the mass decreases. Hence,





The number of molecules having speeds ranging from vto v + dv equals the area of the tan rectangle, $N_v dv$.

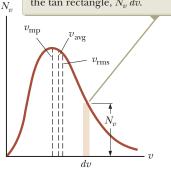


Figure 21.10 The speed distribution of gas molecules at some temperature. The function N_v approaches zero as *v* approaches infinity.

lighter molecules such as H_2 and He escape into space more readily from the Earth's atmosphere than do heavier molecules such as N_2 and O_2 . (See the discussion of escape speed in Chapter 13. Gas molecules escape even more readily from the Moon's surface than from the Earth's because the escape speed on the Moon is lower than that on the Earth.)

The speed distribution curves for molecules in a liquid are similar to those shown in Figure 21.11. We can understand the phenomenon of evaporation of a liquid from this distribution in speeds, given that some molecules in the liquid are more energetic than others. Some of the faster-moving molecules in the liquid penetrate the surface and even leave the liquid at temperatures well below the boiling point. The molecules that escape the liquid by evaporation are those that have sufficient energy to overcome the attractive forces of the molecules in the liquid phase. Consequently, the molecules left behind in the liquid phase have a lower average kinetic energy; as a result, the temperature of the liquid decreases. Hence, evaporation is a cooling process. For example, an alcohol-soaked cloth can be placed on a feverish head to cool and comfort a patient.

Example 21.5 A System of Nine Particles

Nine particles have speeds of 5.00, 8.00, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s.

(A) Find the particles' average speed.

SOLUTION

Conceptualize Imagine a small number of particles moving in random directions with the few speeds listed. This situation is not representative of the large number of molecules in a gas, so we should not expect the results to be consistent with those from statistical mechanics.

Categorize Because we are dealing with a small number of particles, we can calculate the average speed directly.

Analyze Find the average speed of the particles by dividing the sum of the speeds by the total number of particles: $v_{avg} = \frac{(5.00 + 8.00 + 12.0 + 12.0 + 12.0 + 14.0 + 14.0 + 17.0 + 20.0) \text{ m/s}}{9}$ = 12.7 m/s

(B) What is the rms speed of the particles?

SOLUTION

Find the average speed squared of the particles by dividing the sum of the speeds squared by the total number of particles:

$$\overline{v^2} = \frac{(5.00^2 + 8.00^2 + 12.0^2 + 12.0^2 + 12.0^2 + 14.0^2 + 14.0^2 + 17.0^2 + 20.0^2) \text{ m}^2/\text{s}^2}{9}$$
$$= 178 \text{ m}^2/\text{s}^2$$

Find the rms speed of the particles by taking the square root:

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{178 \, {\rm m^2/s^2}} = 13.3 \, {\rm m/s}$$

(C) What is the most probable speed of the particles?

SOLUTION

Three of the particles have a speed of 12.0 m/s, two have a speed of 14.0 m/s, and the remaining four have different speeds. Hence, the most probable speed $v_{\rm mp}$ is 12.0 m/s.

Finalize Compare this example, in which the number of particles is small and we know the individual particle speeds, with the next example.

Example 21.6 Molecular Speeds in a Hydrogen Gas

A 0.500-mol sample of hydrogen gas is at 300 K.

(A) Find the average speed, the rms speed, and the most probable speed of the hydrogen molecules.

SOLUTION

Conceptualize Imagine a huge number of particles in a real gas, all moving in random directions with different speeds.

Categorize We cannot calculate the averages as was done in Example 21.5 because the individual speeds of the particles are not known. We are dealing with a very large number of particles, however, so we can use the Maxwell-Boltzmann speed distribution function.

Analyze Use Equation 21.43 to find the average speed:

$$v_{\text{avg}} = 1.60 \sqrt{\frac{k_{\text{B}}T}{m_0}} = 1.60 \sqrt{\frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{2(1.67 \times 10^{-27} \text{ kg})}}$$
$$= 1.78 \times 10^3 \text{ m/s}$$

Use Equation 21.42 to find the rms speed:

$$v_{\rm rms} = 1.73 \sqrt{\frac{k_{\rm B}T}{m_0}} = 1.73 \sqrt{\frac{(1.38 \times 10^{-23} \,\text{J/K})(300 \,\text{K})}{2(1.67 \times 10^{-27} \,\text{kg})}}$$
$$= 1.93 \times 10^3 \,\text{m/s}$$

 $v_{\rm mp} = 1.41 \sqrt{\frac{k_{\rm B}T}{m_0}} = 1.41 \sqrt{\frac{(1.38 \times 10^{-23} \,\text{J/K})(300 \,\text{K})}{2(1.67 \times 10^{-27} \,\text{kg})}}$

Use Equation 21.44 to find the most probable speed:

(B) Find the number of molecules with speeds between 400 m/s and 401 m/s.

SOLUTION

Use Equation 21.41 to evaluate the number of molecules in a narrow speed range between v and v + dv:

(1)
$$N_v dv = 4\pi N \left(\frac{m_0}{2\pi k_{\rm B}T}\right)^{3/2} v^2 e^{-m_0 v^2/2k_{\rm B}T} dv$$

 $= 1.57 \times 10^3 \,\mathrm{m/s}$

Evaluate the constant in
$$4\pi N \left(\frac{m_0}{2\pi k_{\rm B}T}\right)^{3/2} = 4\pi n N_{\rm A} \left(\frac{m_0}{2\pi k_{\rm B}T}\right)^{3/2}$$

= $4\pi (0.500 \text{ mol}) (6.02 \times 10^{23} \text{ mol}^{-1}) \left[\frac{2(1.67 \times 10^{-27} \text{ kg})}{2\pi (1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}\right]^{3/2}$
= $1.74 \times 10^{14} \text{ s}^3/\text{m}^3$

Evaluate the exponent of *e* that appears in Equation (1):

$$\frac{m_0 v^2}{2k_B T} = -\frac{2(1.67 \times 10^{-27} \text{ kg})(400 \text{ m/s})^2}{2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = -0.064 \text{ 5}$$

Evaluate $N_v dv$ using these values in Equation (1):

$$N_v dv = (1.74 \times 10^{14} \text{ s}^3/\text{m}^3)(400 \text{ m/s})^2 e^{-0.0645} (1 \text{ m/s})$$
$$= 2.61 \times 10^{19} \text{ molecules}$$

Finalize In this evaluation, we could calculate the result without integration because dv = 1 m/s is much smaller than v = 400 m/s. Had we sought the number of particles between, say, 400 m/s and 500 m/s, we would need to integrate Equation (1) between these speed limits.

Summary

Concepts and Principles

The pressure of *N* molecules of an ideal gas contained in a volume *V* is

$$P = \frac{2}{3} \left(\frac{N}{V} \right) (\frac{1}{2} m_0 \overline{v^2})$$
 (21.15)

The average translational kinetic energy per molecule of a gas, $\frac{1}{2}m_0v^2$, is related to the temperature *T* of the gas through the expression

$$\frac{1}{2}m_0v^2 = \frac{3}{2}k_{\rm B}T$$
 (21.19)

where $k_{\rm B}$ is Boltzmann's constant. Each translational degree of freedom (*x*, *y*, or *z*) has $\frac{1}{2}k_{\rm B}T$ of energy associated with it.

The molar specific heat of an ideal monatomic gas at constant volume is $C_V = \frac{3}{2}R$; the molar specific heat at constant pressure is $C_P = \frac{5}{2}R$. The ratio of specific heats is given by $\gamma = C_P/C_V = \frac{5}{3}$.

The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy between *E* and E + dE is $n_V(E) dE$, where

$$n_V(E) = n_0 e^{-E/k_{\rm B}T}$$
 (21.40)

The **Maxwell–Boltzmann speed distribution function** describes the distribution of speeds of molecules in a gas:

$$N_{v} = 4\pi N \left(\frac{m_{0}}{2\pi k_{\rm B}T}\right)^{3/2} v^{2} e^{-m_{0}v^{2}/2k_{\rm B}T}$$
(21.41)

Objective Questions

1. denotes answer available in *Student Solutions Manual/Study Guide*

- Cylinder A contains oxygen (O₂) gas, and cylinder B contains nitrogen (N₂) gas. If the molecules in the two cylinders have the same rms speeds, which of the following statements is *false*? (a) The two gases have different temperatures. (b) The temperature of cylinder B is less than the temperature of cylinder A. (c) The temperature of cylinder B is greater than the temperature of cylinder A. (d) The average kinetic energy of the nitrogen molecules is less than the average kinetic energy of the oxygen molecules.
- 2. An ideal gas is maintained at constant pressure. If the temperature of the gas is increased from 200 K to 600 K, what happens to the rms speed of the molecules? (a) It increases by a factor of 3. (b) It remains the same. (c) It is one-third the original speed. (d) It is

The internal energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\rm int} = \frac{3}{2}Nk_{\rm B}T = \frac{3}{2}nRT$$
 (21.25)

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature ΔT is

$$\Delta E_{\rm int} = nC_V \Delta T \tag{21.27}$$

where C_V is the molar specific heat at constant volume.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$PV^{\gamma} = \text{constant}$$
 (21.37)

Equation 21.41 enables us to calculate the **rootmean-square speed**, the **average speed**, and the **most probable speed** of molecules in a gas:

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\rm B}T}{m_0}} = 1.73\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.42)

$$v_{\rm avg} = \sqrt{\frac{8k_{\rm B}T}{\pi m_0}} = 1.60 \sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.43)

$$v_{\rm mp} = \sqrt{\frac{2k_{\rm B}T}{m_0}} = 1.41\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.44)

 $\sqrt{3}$ times the original speed. (e) It increases by a factor of 6.

- **3.** Two samples of the same ideal gas have the same pressure and density. Sample B has twice the volume of sample A. What is the rms speed of the molecules in sample B? (a) twice that in sample A (b) equal to that in sample A (c) half that in sample A (d) impossible to determine
- **4.** A helium-filled latex balloon initially at room temperature is placed in a freezer. The latex remains flexible. (i) Does the balloon's volume (a) increase, (b) decrease, or (c) remain the same? (ii) Does the pressure of the helium gas (a) increase significantly, (b) decrease significantly, or (c) remain approximately the same?

645

- A gas is at 200 K. If we wish to double the rms speed of the molecules of the gas, to what value must we raise its temperature? (a) 283 K (b) 400 K (c) 566 K (d) 800 K (e) 1130 K
- **6.** Rank the following from largest to smallest, noting any cases of equality. (a) the average speed of molecules in a particular sample of ideal gas (b) the most probable speed (c) the root-mean-square speed (d) the average vector velocity of the molecules
- 7. A sample of gas with a thermometer immersed in the gas is held over a hot plate. A student is asked to give a step-by-step account of what makes our observation of the temperature of the gas increase. His response includes the following steps. (a) The molecules speed up. (b) Then the molecules collide with one another more often. (c) Internal friction makes the collisions inelastic. (d) Heat is produced in the collisions. (e) The molecules of the gas transfer more energy to the thermometer when they strike it, so we observe that the temperature has gone up. (f) The same process can take place without the use of a hot plate if you quickly push in the piston in an insulated cylinder containing the gas. (i) Which of the parts (a) through

(f) of this account are correct statements necessary for a clear and complete explanation? (ii) Which are correct statements that are not necessary to account for the higher thermometer reading? (iii) Which are incorrect statements?

- 8. An ideal gas is contained in a vessel at 300 K. The temperature of the gas is then increased to 900 K. (i) By what factor does the average kinetic energy of the molecules change, (a) a factor of 9, (b) a factor of 3, (c) a factor of √3, (d) a factor of 1, or (e) a factor of 1/3? Using the same choices as in part (i), by what factor does each of the following change: (ii) the rms molecular speed of the molecules, (iii) the average momentum change that one molecule undergoes in a collision with one particular wall, (iv) the rate of collisions of molecules with walls, and (v) the pressure of the gas.
- **9.** Which of the assumptions below is *not* made in the kinetic theory of gases? (a) The number of molecules is very large. (b) The molecules obey Newton's laws of motion. (c) The forces between molecules are long range. (d) The gas is a pure substance. (e) The average separation between molecules is large compared to their dimensions.

Conceptual Questions

1. denotes answer available in Student Solutions Manual/Study Guide

- 1. Hot air rises, so why does it generally become cooler as you climb a mountain? *Note:* Air has low thermal conductivity.
- **2.** Why does a diatomic gas have a greater energy content per mole than a monatomic gas at the same temperature?
- **3.** When alcohol is rubbed on your body, it lowers your skin temperature. Explain this effect.
- **4.** What happens to a helium-filled latex balloon released into the air? Does it expand or contract? Does it stop rising at some height?

- **5.** Which is denser, dry air or air saturated with water vapor? Explain.
- 6. One container is filled with helium gas and another with argon gas. Both containers are at the same temperature. Which molecules have the higher rms speed? Explain.
- 7. Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the pressures that each gas in the mixture would exert if it were alone in the container. Give a convincing argument for this law based on the kinetic theory of gases.

Problems



Section 21.1 Molecular Model of an Ideal Gas

Problem 30 in Chapter 19 can be assigned with this section.

1. (a) How many atoms of helium gas fill a spherical M balloon of diameter 30.0 cm at 20.0°C and 1.00 atm? (b) What is the average kinetic energy of the belium

(b) What is the average kinetic energy of the helium

atoms? (c) What is the rms speed of the helium atoms?

2. A cylinder contains a mixture of helium and argon gas
M in equilibrium at 150°C. (a) What is the average kinetic energy for each type of gas molecule? (b) What is the rms speed of each type of molecule?

- 3. In a 30.0-s interval, 500 hailstones strike a glass window of area 0.600 m² at an angle of 45.0° to the window surface. Each hailstone has a mass of 5.00 g and a speed of 8.00 m/s. Assuming the collisions are elastic, find (a) the average force and (b) the average pressure on the window during this interval.
- **4.** In an ultrahigh vacuum system (with typical pressures lower than 10^{-7} pascal), the pressure is measured to be 1.00×10^{-10} torr (where 1 torr = 133 Pa). Assuming the temperature is 300 K, find the number of molecules in a volume of 1.00 m³.
- 5. A spherical balloon of volume 4.00 × 10³ cm³ contains
 M helium at a pressure of 1.20 × 10⁵ Pa. How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is 3.60 × 10⁻²² J?
- **6.** A spherical balloon of volume *V* contains helium at a pressure *P*. How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is \overline{K} ?
- 7. A 2.00-mol sample of oxygen gas is confined to a 5.00-L
- W vessel at a pressure of 8.00 atm. Find the average translational kinetic energy of the oxygen molecules under these conditions.
- 8. Oxygen, modeled as an ideal gas, is in a container and has a temperature of 77.0°C. What is the rms-average magnitude of the momentum of the gas molecules in the container?
- **9.** Calculate the mass of an atom of (a) helium, (b) iron, and (c) lead. Give your answers in kilograms. The atomic masses of these atoms are 4.00 u, 55.9 u, and 207 u, respectively.
- 10. The rms speed of an oxygen molecule (O_2) in a container of oxygen gas is 625 m/s. What is the temperature of the gas?
- **11.** A 5.00-L vessel contains nitrogen gas at 27.0°C and 3.00 atm. Find (a) the total translational kinetic energy of the gas molecules and (b) the average kinetic energy per molecule.
- 12. A 7.00-L vessel contains 3.50 moles of gas at a pressure of 1.60 × 10⁶ Pa. Find (a) the temperature of the gas and (b) the average kinetic energy of the gas molecules in the vessel. (c) What additional information would you need if you were asked to find the average speed of the gas molecules?
- **13.** In a period of 1.00 s, 5.00×10^{23} nitrogen molecules **M** strike a wall with an area of 8.00 cm². Assume the mol-
- w ecules move with a speed of 300 m/s and strike the wall head-on in elastic collisions. What is the pressure exerted on the wall? *Note:* The mass of one N_2 molecule is 4.65×10^{-26} kg.

Section 21.2 Molar Specific Heat of an Ideal Gas

Note: You may use data in Table 21.2 about particular gases. Here we define a "monatomic ideal gas" to have molar specific heats $C_V = \frac{3}{2}R$ and $C_P = \frac{5}{2}R$, and a "diatomic ideal gas" to have $C_V = \frac{5}{2}R$ and $C_P = \frac{7}{2}R$.

- 14. In a constant-volume process, 209 J of energy is trans-W ferred by heat to 1.00 mol of an ideal monatomic gas initially at 300 K. Find (a) the work done on the gas, (b) the increase in internal energy of the gas, and (c) its final temperature.
- **15.** A sample of a diatomic ideal gas has pressure *P* and volume *V*. When the gas is warmed, its pressure triples and its volume doubles. This warming process includes two steps, the first at constant pressure and the second at constant volume. Determine the amount of energy transferred to the gas by heat.
- 16. Review. A house has well-insulated walls. It contains a volume of 100 m³ of air at 300 K. (a) Calculate the energy required to increase the temperature of this diatomic ideal gas by 1.00°C. (b) What If? If all this energy could be used to lift an object of mass m through a height of 2.00 m, what is the value of m?
- A 1.00-mol sample of hydrogen gas is heated at con M stant pressure from 300 K to 420 K. Calculate (a) the energy transferred to the gas by heat, (b) the increase in its internal energy, and (c) the work done on the gas.
- 18. A vertical cylinder with a heavy piston contains air at 300 K. The initial pressure is 2.00×10^5 Pa, and the initial volume is 0.350 m^3 . Take the molar mass of air as 28.9 g/mol and assume $C_V = \frac{5}{2}R$. (a) Find the specific heat of air at constant volume in units of J/kg \cdot °C. (b) Calculate the mass of the air in the cylinder. (c) Suppose the piston is held fixed. Find the energy input required to raise the temperature of the air to 700 K. (d) What If? Assume again the conditions of the initial state and assume the heavy piston is free to move. Find the energy input required to raise the temperature to 700 K.
- **19.** Calculate the change in internal energy of 3.00 mol of helium gas when its temperature is increased by 2.00 K.
- **20.** A 1.00-L insulated bottle is full of tea at 90.0°C. You pour out one cup of tea and immediately screw the stopper back on the bottle. Make an order-of-magnitude estimate of the change in temperature of the tea remaining in the bottle that results from the admission of air at room temperature. State the quantities you take as data and the values you measure or estimate for them.
- **21. Review.** This problem is a continuation of Problem 39 in Chapter 19. A hot-air balloon consists of an envelope of constant volume 400 m3. Not including the air inside, the balloon and cargo have mass 200 kg. The air outside and originally inside is a diatomic ideal gas at 10.0°C and 101 kPa, with density 1.25 kg/m³. A propane burner at the center of the spherical envelope injects energy into the air inside. The air inside stays at constant pressure. Hot air, at just the temperature required to make the balloon lift off, starts to fill the envelope at its closed top, rapidly enough so that negligible energy flows by heat to the cool air below it or out through the wall of the balloon. Air at 10°C leaves through an opening at the bottom of the envelope until the whole balloon is filled with hot air at uniform temperature. Then the burner is shut off and

the balloon rises from the ground. (a) Evaluate the quantity of energy the burner must transfer to the air in the balloon. (b) The "heat value" of propane—the internal energy released by burning each kilogram—is 50.3 MJ/kg. What mass of propane must be burned?

Section 21.3 The Equipartition of Energy

- **22.** A certain molecule has *f* degrees of freedom. Show that an ideal gas consisting of such molecules has the following properties: (a) its total internal energy is fnRT/2, (b) its molar specific heat at constant volume is fR/2, (c) its molar specific heat at constant pressure is (f + 2)R/2, and (d) its specific heat ratio is $\gamma = C_P/C_V = (f + 2)/f$.
- **23.** In a crude model (Fig. P21.23) of a rotating diatomic chlorine molecule (Cl₂), the two Cl atoms are 2.00 × 10^{-10} m apart and rotate about their center of mass with angular speed $\omega = 2.00 \times 10^{12}$ rad/s. What is the rotational kinetic energy of one molecule of Cl₂, which has a molar mass of 70.0 g/mol?



Figure P21.23

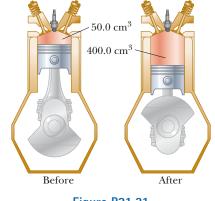
- 24. Why is the following situation impossible? A team of researchers discovers a new gas, which has a value of $\gamma = C_P/C_V$ of 1.75.
- 25. The relationship between the heat capacity of a samM ple and the specific heat of the sample material is discussed in Section 20.2. Consider a sample containing 2.00 mol of an ideal diatomic gas. Assuming the molecules rotate but do not vibrate, find (a) the total heat capacity of the sample at constant volume and (b) the total heat capacity at constant pressure. (c) What If? Repeat parts (a) and (b), assuming the molecules both rotate and vibrate.

Section 21.4 Adiabatic Processes for an Ideal Gas

- 26. A 2.00-mol sample of a diatomic ideal gas expands
 M slowly and adiabatically from a pressure of 5.00 atm and a volume of 12.0 L to a final volume of 30.0 L.
 (a) What is the final pressure of the gas? (b) What are the initial and final temperatures? Find (c) Q, (d) ΔE_{int}, and (e) W for the gas during this process.
- 27. During the compression stroke of a certain gasoline engine, the pressure increases from 1.00 atm to 20.0 atm. If the process is adiabatic and the air-fuel mixture behaves as a diatomic ideal gas, (a) by what factor does the volume change and (b) by what factor does the temperature change? Assuming the compression starts with 0.016 0 mol of gas at 27.0°C, find the values of (c) Q, (d) ΔE_{int} , and (e) W that characterize the process.
- **28.** How much work is required to compress 5.00 mol of **W** air at 20.0°C and 1.00 atm to one-tenth of the original volume (a) by an isothermal process? (b) **What If**?

How much work is required to produce the same compression in an adiabatic process? (c) What is the final pressure in part (a)? (d) What is the final pressure in part (b)?

- Air in a thundercloud expands as it rises. If its initial
 temperature is 300 K and no energy is lost by thermal conduction on expansion, what is its temperature when the initial volume has doubled?
- **30.** Why is the following situation impossible? A new diesel engine that increases fuel economy over previous models is designed. Automobiles fitted with this design become incredible best sellers. Two design features are responsible for the increased fuel economy: (1) the engine is made entirely of aluminum to reduce the weight of the automobile, and (2) the exhaust of the engine is used to prewarm the air to 50°C before it enters the cylinder to increase the final temperature of the compressed gas. The engine has a *compression ratio*—that is, the ratio of the initial volume of the air to its final volume after compression—of 14.5. The compression process is adiabatic, and the air behaves as a diatomic ideal gas with $\gamma = 1.40$.
- 31. During the power stroke in a four-stroke automobile engine, the piston is forced down as the mixture of combustion products and air undergoes an adiabatic expansion. Assume (1) the engine is running at 2 500 cycles/min; (2) the gauge pressure immediately before the expansion is 20.0 atm; (3) the volumes of the mixture immediately before and after the expansion are 50.0 cm³ and 400 cm³, respectively (Fig. P21.31); (4) the time interval for the expansion is one-fourth that of the total cycle; and (5) the mixture behaves like an ideal gas with specific heat ratio 1.40. Find the average power generated during the power stroke.





32. Air (a diatomic ideal gas) at 27.0°C and atmospheric
GP pressure is drawn into a bicycle pump (see the chapter-opening photo on page 626) that has a cylinder with an inner diameter of 2.50 cm and length 50.0 cm. The downstroke adiabatically compresses the air, which reaches a gauge pressure of 8.00 × 10⁵ Pa before entering the tire. We wish to investigate the temperature increase of the pump. (a) What is the initial volume of the air in the pump? (b) What is the absolute

pressure of the compressed air? (d) What is the volume of the compressed air? (e) What is the temperature of the compressed air? (f) What is the increase in internal energy of the gas during the compression? **What If?** The pump is made of steel that is 2.00 mm thick. Assume 4.00 cm of the cylinder's length is allowed to come to thermal equilibrium with the air. (g) What is the volume of steel in this 4.00-cm length? (h) What is the mass of steel in this 4.00-cm length? (i) Assume the pump is compressed once. After the adiabatic expansion, conduction results in the energy increase in part (f) being shared between the gas and the 4.00-cm length of steel. What will be the increase in temperature of the steel after one compression?

- 33. A 4.00-L sample of a diatomic ideal gas with specific heat ratio 1.40, confined to a cylinder, is carried through a closed cycle. The gas is initially at 1.00 atm and 300 K. First, its pressure is tripled under constant volume. Then, it expands adiabatically to its original pressure. Finally, the gas is compressed isobarically to its original volume. (a) Draw a *PV* diagram of this cycle. (b) Determine the volume of the gas at the end of the adiabatic expansion. (c) Find the temperature of the gas at the start of the adiabatic expansion. (d) Find the temperature at the end of the cycle. (e) What was the net work done on the gas for this cycle?
- 34. An ideal gas with specific heat ratio γ confined to a cylinder is put through a closed cycle. Initially, the gas is at P_i , V_i , and T_i . First, its pressure is tripled under constant volume. It then expands adiabatically to its original pressure and finally is compressed isobarically to its original volume. (a) Draw a *PV* diagram of this cycle. (b) Determine the volume at the end of the adiabatic expansion. Find (c) the temperature of the gas at the start of the adiabatic expansion and (d) the temperature at the end of the cycle. (e) What was the net work done on the gas for this cycle?

Section 21.5 Distribution of Molecular Speeds

- **35.** Helium gas is in thermal equilibrium with liquid helium at 4.20 K. Even though it is on the point of condensation, model the gas as ideal and determine the most probable speed of a helium atom (mass = 6.64×10^{-27} kg) in it.
- 36. Fifteen identical particles have various speeds: one has
 a speed of 2.00 m/s, two have speeds of 3.00 m/s, three have speeds of 5.00 m/s, four have speeds of 7.00 m/s, three have speeds of 9.00 m/s, and two have speeds of 12.0 m/s. Find (a) the average speed, (b) the rms speed, and (c) the most probable speed of these particles.

37. One cubic meter of atomic hydrogen at 0°C at atmo-

- Spheric pressure contains approximately 2.70×10^{25} atoms. The first excited state of the hydrogen atom has an energy of 10.2 eV above that of the lowest state, called the ground state. Use the Boltzmann factor to find the number of atoms in the first excited state (a) at 0°C and at (b) (1.00×10^4) °C.
- **38.** Two gases in a mixture diffuse through a filter at rates proportional to their rms speeds. (a) Find the ratio of

speeds for the two isotopes of chlorine, ³⁵Cl and ³⁷Cl, as they diffuse through the air. (b) Which isotope moves faster?

- 39. Review. At what temperature would the average speed of helium atoms equal (a) the escape speed from the Earth, 1.12 × 10⁴ m/s, and (b) the escape speed from the Moon, 2.37 × 10³ m/s? *Note:* The mass of a helium atom is 6.64 × 10⁻²⁷ kg.
- 40. Consider a container of nitrogen gas molecules at 900 K. Calculate (a) the most probable speed, (b) the average speed, and (c) the rms speed for the molecules. (d) State how your results compare with the values displayed in Figure 21.11.
- **41.** Assume the Earth's atmosphere has a uniform temperature of 20.0°C and uniform composition, with an effective molar mass of 28.9 g/mol. (a) Show that the number density of molecules depends on height *y* above sea level according to

$$n_V(\gamma) = n_0 e^{-m_0 g \gamma / k_{\rm B} T}$$

where n_0 is the number density at sea level (where y = 0). This result is called the *law of atmospheres*. (b) Commercial jetliners typically cruise at an altitude of 11.0 km. Find the ratio of the atmospheric density there to the density at sea level.

- **42.** From the Maxwell–Boltzmann speed distribution, show that the most probable speed of a gas molecule is given by Equation 21.44. *Note:* The most probable speed corresponds to the point at which the slope of the speed distribution curve dN_v/dv is zero.
- **43.** The law of atmospheres states that the number density of molecules in the atmosphere depends on height *y* above sea level according to

$$n_V(y) = n_0 e^{-m_0 g y/k_B T}$$

where n_0 is the number density at sea level (where y = 0). The average height of a molecule in the Earth's atmosphere is given by

$$y_{\text{avg}} = \frac{\int_{0}^{\infty} y n_V(y) \, dy}{\int_{0}^{\infty} n_V(y) \, dy} = \frac{\int_{0}^{\infty} y e^{-m_0 g y/k_{\text{B}}T} \, dy}{\int_{0}^{\infty} e^{-m_0 g y/k_{\text{B}}T} \, dy}$$

(a) Prove that this average height is equal to $k_{\rm B}T/m_0g$. (b) Evaluate the average height, assuming the temperature is 10.0°C and the molecular mass is 28.9 u, both uniform throughout the atmosphere.

Additional Problems

- **44.** Eight molecules have speeds of 3.00 km/s, 4.00 km/s, 5.80 km/s, 2.50 km/s, 3.60 km/s, 1.90 km/s, 3.80 km/s, and 6.60 km/s. Find (a) the average speed of the molecules and (b) the rms speed of the molecules.
- 45. A small oxygen tank at a gauge pressure of 125 atm has a volume of 6.88 L at 21.0°C. (a) If an athlete breathes oxygen from this tank at the rate of 8.50 L/min when measured at atmospheric pressure and the temperature remains at 21.0°C, how long will the tank last before it is empty? (b) At a particular moment during

this process, what is the ratio of the rms speed of the molecules remaining in the tank to the rms speed of those being released at atmospheric pressure?

- 46. The dimensions of a classroom are 4.20 m × 3.00 m × 2.50 m. (a) Find the number of molecules of air in the classroom at atmospheric pressure and 20.0°C. (b) Find the mass of this air, assuming the air consists of diatomic molecules with molar mass 28.9 g/mol. (c) Find the average kinetic energy of the molecules. (d) Find the rms molecular speed. (e) What If? Assume the molar specific heat of the air is independent of temperature. Find the change in internal energy of the air in the room as the temperature is raised to 25.0°C. (f) Explain how you could convince a fellow student that your answer to part (e) is correct, even though it sounds surprising.
- 47. The Earth's atmosphere consists primarily of oxygen (21%) and nitrogen (78%). The rms speed of oxygen molecules (O₂) in the atmosphere at a certain location is 535 m/s. (a) What is the temperature of the atmosphere at this location? (b) Would the rms speed of nitrogen molecules (N₂) at this location be higher, equal to, or lower than 535 m/s? Explain. (c) Determine the rms speed of N₂ at his location.
- **48.** The *mean free path* ℓ of a molecule is the average dis-**AMI** tance that a molecule travels before colliding with another molecule. It is given by

$$\ell = \frac{1}{\sqrt{2}\pi d^2 N_V}$$

where *d* is the diameter of the molecule and N_V is the number of molecules per unit volume. The number of collisions that a molecule makes with other molecules per unit time, or *collision frequency f*, is given by

$$f = \frac{v_{\text{avg}}}{\ell}$$

(a) If the diameter of an oxygen molecule is 2.00×10^{-10} m, find the mean free path of the molecules in a scuba tank that has a volume of 12.0 L and is filled with oxygen at a gauge pressure of 100 atm at a temperature of 25.0°C. (b) What is the average time interval between molecular collisions for a molecule of this gas?

49. An air rifle shoots a lead pellet by allowing high-**AMI** pressure air to expand, propelling the pellet down the rifle barrel. Because this process happens very quickly, no appreciable thermal conduction occurs and the expansion is essentially adiabatic. Suppose the rifle starts with 12.0 cm³ of compressed air, which behaves as an ideal gas with $\gamma = 1.40$. The expanding air pushes a 1.10-g pellet as a piston with cross-sectional area 0.030 0 cm² along the 50.0-cm-long gun barrel. What initial pressure is required to eject the pellet with a muzzle speed of 120 m/s? Ignore the effects of the air in front of the bullet and friction with the inside walls of the barrel.

50. In a sample of a solid metal, each atom is free to vibrate about some equilibrium position. The atom's energy consists of kinetic energy for motion in the *x*,

y, and z directions plus elastic potential energy associated with the Hooke's law forces exerted by neighboring atoms on it in the x, y, and z directions. According to the theorem of equipartition of energy, assume the average energy of each atom is $\frac{1}{2}k_{\rm B}T$ for each degree of freedom. (a) Prove that the molar specific heat of the solid is 3R. The *Dulong–Petit law* states that this result generally describes pure solids at sufficiently high temperatures. (You may ignore the difference between the specific heat at constant pressure and the specific heat at constant volume.) (b) Evaluate the specific heat *c* of iron. Explain how it compares with the value listed in Table 20.1. (c) Repeat the evaluation and comparison for gold.

- 51. A certain ideal gas has a molar specific heat of C_V = ⁷/₂R. A 2.00-mol sample of the gas always starts at pressure 1.00 × 10⁵ Pa and temperature 300 K. For each of the following processes, determine (a) the final pressure, (b) the final volume, (c) the final temperature, (d) the change in internal energy of the gas, (e) the energy added to the gas by heat, and (f) the work done on the gas. (i) The gas is heated at constant pressure to 400 K. (ii) The gas is heated at constant volume to 400 K. (iii) The gas is compressed at constant temperature to 1.20 × 10⁵ Pa. (iv) The gas is compressed adiabatically to 1.20 × 10⁵ Pa.
- **52.** The compressibility κ of a substance is defined as the fractional change in volume of that substance for a given change in pressure:

$$\kappa = -\frac{1}{V} \, \frac{dV}{dP}$$

(a) Explain why the negative sign in this expression ensures κ is always positive. (b) Show that if an ideal gas is compressed isothermally, its compressibility is given by $\kappa_1 = 1/P$. (c) **What If?** Show that if an ideal gas is compressed adiabatically, its compressibility is given by $\kappa_2 = 1/(\gamma P)$. Determine values for (d) κ_1 and (e) κ_2 for a monatomic ideal gas at a pressure of 2.00 atm.

- **53. Review.** Oxygen at pressures much greater than 1 atm is toxic to lung cells. Assume a deep-sea diver breathes a mixture of oxygen (O_2) and helium (He). By weight, what ratio of helium to oxygen must be used if the diver is at an ocean depth of 50.0 m?
- **54.** Examine the data for polyatomic gases in Table 21.2 and give a reason why sulfur dioxide has a higher specific heat at constant volume than the other polyatomic gases at 300 K.
- 55. Model air as a diatomic ideal gas with M = 28.9 g/mol. A cylinder with a piston contains 1.20 kg of air at 25.0°C and 2.00 × 10⁵ Pa. Energy is transferred by heat into the system as it is permitted to expand, with the pressure rising to 4.00×10^5 Pa. Throughout the expansion, the relationship between pressure and volume is given by

$$P = CV^{1/2}$$

where *C* is a constant. Find (a) the initial volume, (b) the final volume, (c) the final temperature, (d) the work done on the air, and (e) the energy transferred by heat.

56. Review. As a sound wave passes through a gas, the compressions are either so rapid or so far apart that thermal conduction is prevented by a negligible time interval or by effective thickness of insulation. The compressions and rarefactions are adiabatic. (a) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma RT}{M}}$$

where *M* is the molar mass. The speed of sound in a gas is given by Equation 17.8; use that equation and the definition of the bulk modulus from Section 12.4. (b) Compute the theoretical speed of sound in air at 20.0°C and state how it compares with the value in Table 17.1. Take M = 28.9 g/mol. (c) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma k_{\rm B} T}{m_0}}$$

where m_0 is the mass of one molecule. (d) State how the result in part (c) compares with the most probable, average, and rms molecular speeds.

- 57. Twenty particles, each of mass m_0 and confined to a volume *V*, have various speeds: two have speed *v*, three have speed 2v, five have speed 3v, four have speed 4v, three have speed 5v, two have speed 6v, and one has speed 7v. Find (a) the average speed, (b) the rms speed, (c) the most probable speed, (d) the average pressure the particles exert on the walls of the vessel, and (e) the average kinetic energy per particle.
- **58.** In a cylinder, a sample of an ideal gas with number of moles *n* undergoes an adiabatic process. (a) Starting with the expression $W = -\int P \, dV$ and using the condition PV^{γ} = constant, show that the work done on the gas is

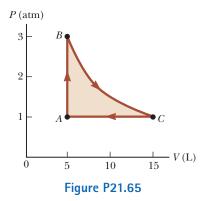
$$W = \left(\frac{1}{\gamma - 1}\right) (P_f V_f - P_i V_i)$$

(b) Starting with the first law of thermodynamics, show that the work done on the gas is equal to $nC_V(T_f - T_i)$. (c) Are these two results consistent with each other? Explain.

- **59.** As a 1.00-mol sample of a monatomic ideal gas expands adiabatically, the work done on it is -2.50×10^3 J. The initial temperature and pressure of the gas are 500 K and 3.60 atm. Calculate (a) the final temperature and (b) the final pressure.
- **60.** A sample consists of an amount n in moles of a monatomic ideal gas. The gas expands adiabatically, with work W done on it. (Work W is a negative number.) The initial temperature and pressure of the gas are T_i and P_i . Calculate (a) the final temperature and (b) the final pressure.
- **61.** When a small particle is suspended in a fluid, bombardment by molecules makes the particle jitter about at random. Robert Brown discovered this motion in 1827 while studying plant fertilization, and the motion has become known as *Brownian motion*. The particle's average kinetic energy can be taken as $\frac{3}{2}k_BT$, the same

as that of a molecule in an ideal gas. Consider a spherical particle of density 1.00×10^3 kg/m³ in water at 20.0°C. (a) For a particle of diameter *d*, evaluate the rms speed. (b) The particle's actual motion is a random walk, but imagine that it moves with constant velocity equal in magnitude to its rms speed. In what time interval would it move by a distance equal to its own diameter? (c) Evaluate the rms speed and the time interval for a particle of diameter 3.00 μ m. (d) Evaluate the rms speed and the time interval for a sphere of mass 70.0 kg, modeling your own body.

- 62. A vessel contains 1.00 × 10⁴ oxygen molecules at 500 K.
 (a) Make an accurate graph of the Maxwell speed distribution function versus speed with points at speed intervals of 100 m/s.
 (b) Determine the most probable speed from this graph.
 (c) Calculate the average and rms speeds for the molecules and label these points on your graph.
 (d) From the graph, estimate the fraction of molecules with speeds in the range 300 m/s to 600 m/s.
- **63.** A pitcher throws a 0.142-kg baseball at 47.2 m/s. As it **AMI** travels 16.8 m to home plate, the ball slows down to 42.5 m/s because of air resistance. Find the change in temperature of the air through which it passes. To find the greatest possible temperature change, you may make the following assumptions. Air has a molar specific heat of $C_P = \frac{7}{2}R$ and an equivalent molar mass of 28.9 g/mol. The process is so rapid that the cover of the baseball acts as thermal insulation and the temperature of the ball itself does not change. A change in temperature happens initially only for the air in a cylinder 16.8 m in length and 3.70 cm in radius. This air is initially at 20.0°C.
 - **64.** The latent heat of vaporization for water at room temperature is 2 430 J/g. Consider one particular molecule at the surface of a glass of liquid water, moving upward with sufficiently high speed that it will be the next molecule to join the vapor. (a) Find its translational kinetic energy. (b) Find its speed. Now consider a thin gas made only of molecules like that one. (c) What is its temperature? (d) Why are you not burned by water evaporating from a vessel at room temperature?
 - 65. A sample of a monatomic ideal gas occupies 5.00 L at atmospheric pressure and 300 K (point *A* in Fig. P21.65). It is warmed at constant volume to 3.00 atm (point *B*). Then it is allowed to expand isothermally to 1.00 atm (point *C*) and at last compressed isobarically to its original state. (a) Find the number of moles in the sample.

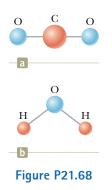


Find (b) the temperature at point *B*, (c) the temperature at point *C*, and (d) the volume at point *C*. (e) Now consider the processes $A \rightarrow B$, $B \rightarrow C$, and $C \rightarrow A$. Describe how to carry out each process experimentally. (f) Find *Q*, *W*, and ΔE_{int} for each of the processes. (g) For the whole cycle $A \rightarrow B \rightarrow C \rightarrow A$, find *Q*, *W*, and ΔE_{int} .

66. Consider the particles in a gas centrifuge, a device used to separate particles of different mass by whirling them in a circular path of radius *r* at angular speed ω . The force acting on a gas molecule toward the center of the centrifuge is $m_0\omega^2 r$. (a) Discuss how a gas centrifuge can be used to separate particles of different mass. (b) Suppose the centrifuge contains a gas of particles of identical mass. Show that the density of the particles as a function of *r* is

$$n(r) = n_0 e^{m_0 r^2 \omega^2 / 2k_{\rm B}T}$$

- 67. For a Maxwellian gas, use a computer or programmable calculator to find the numerical value of the ratio $N_v(v)/N_v(v_{\rm mp})$ for the following values of v: (a) $v = (v_{\rm mp}/50.0)$, (b) $(v_{\rm mp}/10.0)$, (c) $(v_{\rm mp}/2.00)$, (d) $v_{\rm mp}$, (e) $2.00v_{\rm mp}$, (f) $10.0v_{\rm mp}$, and (g) $50.0v_{\rm mp}$. Give your results to three significant figures.
- 68. A triatomic molecule can have a linear configuration, as does CO_9 (Fig. P21.68a), or it can be nonlinear, like $H_{2}O$ (Fig. P21.68b). Suppose the temperature of a gas of triatomic molecules is sufficiently low that vibrational motion is negligible. What is the molar specific heat at constant volume, expressed as a multiple of the universal gas constant, (a) if the molecules are linear and (b) if the molecules are nonlinear? At high temperatures, a triatomic molecule has two modes of vibration, and each contributes $\frac{1}{2}R$ to the molar specific heat for its kinetic energy and another $\frac{1}{2}R$ for its potential energy. Identify the high-temperature molar specific heat at constant volume for a triatomic ideal gas of (c) linear molecules and (d) nonlinear molecules. (e) Explain how specific heat data can be used to determine whether a triatomic molecule is linear or nonlinear. Are the data in Table 21.2 sufficient to make this determination?



69. Using the Maxwell–Boltzmann speed distribution function, verify Equations 21.42 and 21.43 for (a) the rms speed and (b) the average speed of the molecules of a gas at a temperature *T*. The average value of v^n is

$$\overline{v^n} = \frac{1}{N} \int_0^\infty v^n N_v \, dv$$

Use the table of integrals B.6 in Appendix B.

70. On the *PV* diagram for an ideal gas, one isothermal curve and one adiabatic curve pass through each point as shown in Figure P21.70. Prove that the slope of the adiabatic curve is steeper than the slope of the isotherm at that point by the factor γ .

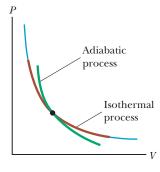


Figure P21.70

- 71. In Beijing, a restaurant keeps a pot of chicken broth simmering continuously. Every morning, it is topped up to contain 10.0 L of water along with a fresh chicken, vegetables, and spices. The molar mass of water is 18.0 g/mol. (a) Find the number of molecules of water in the pot. (b) During a certain month, 90.0% of the broth was served each day to people who then emigrated immediately. Of the water molecules in the pot on the first day of the month, when was the last one likely to have been ladled out of the pot? (c) The broth has been simmering for centuries, through wars, earthquakes, and stove repairs. Suppose the water that was in the pot long ago has thoroughly mixed into the Earth's hydrosphere, of mass 1.32×10^{21} kg. How many of the water molecules originally in the pot are likely to be present in it again today?
- 72. Review. (a) If it has enough kinetic energy, a molecule at the surface of the Earth can "escape the Earth's gravitation" in the sense that it can continue to move away from the Earth forever as discussed in Section 13.6. Using the principle of conservation of energy, show that the minimum kinetic energy needed for "escape" is m_0gR_E , where m_0 is the mass of the molecule, g is the free-fall acceleration at the surface, and R_E is the radius of the Earth. (b) Calculate the temperature for which the minimum escape kinetic energy is ten times the average kinetic energy of an oxygen molecule.
- **73.** Using multiple laser beams, physicists have been able to cool and trap sodium atoms in a small region. In one experiment, the temperature of the atoms was reduced to 0.240 mK. (a) Determine the rms speed of the sodium atoms at this temperature. The atoms can be trapped for about 1.00 s. The trap has a linear dimension of roughly 1.00 cm. (b) Over what approximate time interval would an atom wander out of the trap region if there were no trapping action?

Challenge Problems

74. Equations 21.42 and 21.43 show that $v_{\rm rms} > v_{\rm avg}$ for a collection of gas particles, which turns out to be true whenever the particles have a distribution of speeds. Let us explore this inequality for a two-particle gas.

Let the speed of one particle be $v_1 = av_{avg}$ and the other particle have speed $v_2 = (2 - a)v_{avg}$. (a) Show that the average of these two speeds is v_{avg} . (b) Show that

$$v_{\rm rms}^2 = v_{\rm avg}^2 \left(2 - 2a + a^2\right)$$

(c) Argue that the equation in part (b) proves that, in general, $v_{\rm rms} > v_{\rm avg}$. (d) Under what special condition will $v_{\rm rms} = v_{\rm avg}$ for the two-particle gas?

75. A cylinder is closed at both ends and has insulating MIT walls. It is divided into two compartments by an insulating piston that is perpendicular to the axis of the cylinder as shown in Figure P21.75a. Each compartment contains 1.00 mol of oxygen that behaves as an ideal gas with $\gamma = 1.40$. Initially, the two compartments have equal volumes and their temperatures are 550 K and 250 K. The piston is then allowed to move slowly parallel to the axis of the cylinder until it comes to rest at an equilibrium position (Fig. P21.75b). Find the final temperatures in the two compartments.

