I:n Chapter 19 we discussed the properties of an ideal gas, using such macroscopic variables as pressure, volume, and temperature. We shall now show that such large-scale properties can be described on a microscopic scale, where matter is treated as a collection of molecules. Newton's laws of motion applied in a statistical manner to a collection of particles provide a reasonable description of thermodynamic processes. To keep the mathematics relatively simple, we shall consider molecular behavior of gases only, because in gases the interactions between molecules are much weaker than they are in liquids or solids. In the current view of gas behavior, called the kinetic theory, gas molecules move about in a random fashion, colliding with the walls of their container and with each other. Perhaps the most important feature of this theory is that it demonstrates that the kinetic energy of molecular motion and the internal energy of a gas system are equivalent. Furthermore, the kinetic theory provides us with a physical basis for our understanding of the concept of temperature.

In the simplest model of a gas, each molecule is considered to be a hard sphere that collides elastically with other molecules and with the container's walls. The hard-sphere model assumes that the molecules do not interact with each other except during collisions and that they are not deformed by collisions. This description is adequate only for monatomic gases, for which the energy is entirely translational kinetic energy. One must modify the theory for more complex molecules, such as oxygen $\left(\mathrm{O}_{2}\right)$ and carbon dioxide $\left(\mathrm{CO}_{2}\right)$, to include the internal energy associated with rotations and vibrations of the molecules.

### 21.1 MOLECULAR MODEL OF AN IDEAL GAS

We begin this chapter by developing a microscopic model of an ideal gas. The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls. As we shall see, the model is consistent with the macroscopic description of Chapter 19. In developing this model, we make the following assumptions:- The number of molecules is large, and the average separation between molecules is great compared with their dimensions. This means that the volume of the molecules is negligible when compared with the volume of the container.
- The molecules obey Newton's laws of motion, but as a whole they move randomly. By "randomly" we mean that any molecule can move in any direction with equal probability. We also assume that the distribution of speeds does not change in time, despite the collisions between molecules. That is, at any given moment, a certain percentage of molecules move at high speeds, a certain percentage move at low speeds, and a certain percentage move at speeds intermediate between high and low.
- The molecules undergo elastic collisions with each other and with the walls of the container. Thus, in the collisions, both kinetic energy and momentum are constant.
- The forces between molecules are negligible except during a collision. The forces between molecules are short-range, so the molecules interact with each other only during collisions.
- The gas under consideration is a pure substance. That is, all of its molecules are identical.

Although we often picture an ideal gas as consisting of single atoms, we can assume that the behavior of molecular gases approximates that of ideal gases rather

Assumptions of the molecular model of an ideal gas


Figure 21.1 A cubical box with sides of length $d$ containing an ideal gas. The molecule shown moves with velocity $\mathbf{v}$.


Figure 21.2 A molecule makes an elastic collision with the wall of the container. Its $x$ component of momentum is reversed, while its $y$ component remains unchanged. In this construction, we assume that the molecule moves in the $x y$ plane.
well at low pressures. Molecular rotations or vibrations have no effect, on the average, on the motions that we considered here.

Now let us derive an expression for the pressure of an ideal gas consisting of $N$ molecules in a container of volume $V$. The container is a cube with edges of length $d$ (Fig. 21.1). Consider the collision of one molecule moving with a velocity $\mathbf{v}$ toward the right-hand face of the box. The molecule has velocity components $v_{x}, v_{y}$, and $v_{z}$. Previously, we used $m$ to represent the mass of a sample, but throughout this chapter we shall use $m$ to represent the mass of one molecule. As the molecule collides with the wall elastically, its $x$ component of velocity is reversed, while its $y$ and $z$ components of velocity remain unaltered (Fig. 21.2). Because the $x$ component of the momentum of the molecule is $m v_{x}$ before the collision and $-m v_{x}$ after the collision, the change in momentum of the molecule is

$$
\Delta p_{x}=-m v_{x}-\left(m v_{x}\right)=-2 m v_{x}
$$

Applying the impulse-momentum theorem (Eq. 9.9) to the molecule gives

$$
F_{1} \Delta t=\Delta p_{x}=-2 m v_{x}
$$

where $F_{1}$ is the magnitude of the average force exerted by the wall on the molecule in the time $\Delta t$. The subscript 1 indicates that we are currently considering only one molecule. For the molecule to collide twice with the same wall, it must travel a distance $2 d$ in the $x$ direction. Therefore, the time interval between two collisions with the same wall is $\Delta t=2 d / v_{x}$. Over a time interval that is long compared with $\Delta t$, the average force exerted on the molecule for each collision is

$$
\begin{equation*}
F_{1}=\frac{-2 m v_{x}}{\Delta t}=\frac{-2 m v_{x}}{2 d / v_{x}}=\frac{-m v_{x}^{2}}{d} \tag{21.1}
\end{equation*}
$$

According to Newton's third law, the average force exerted by the molecule on the wall is equal in magnitude and opposite in direction to the force in Equation 21.1:

$$
F_{1, \text { on wall }}=-F_{1}=-\left(\frac{-m v_{x}^{2}}{d}\right)=\frac{m v_{x}^{2}}{d}
$$

Each molecule of the gas exerts a force $F_{1}$ on the wall. We find the total force $F$ exerted by all the molecules on the wall by adding the forces exerted by the individual molecules:

$$
F=\frac{m}{d}\left(v_{x 1}^{2}+v_{x 2}^{2}+\cdots\right)
$$

In this equation, $v_{x 1}$ is the $x$ component of velocity of molecule $1, v_{x 2}$ is the $x$ component of velocity of molecule 2 , and so on. The summation terminates when we reach $N$ molecules because there are $N$ molecules in the container.

To proceed further, we must note that the average value of the square of the velocity in the $x$ direction for $N$ molecules is

$$
\overline{v_{x}^{2}}=\frac{v_{x 1}^{2}+v_{x 2}^{2}+\cdots+v_{x N}{ }^{2}}{N}
$$

Thus, the total force exerted on the wall can be written

$$
F=\frac{N m}{d} \overline{v_{x}^{2}}
$$

Now let us focus on one molecule in the container whose velocity components are $v_{x}, v_{y}$, and $v_{z}$. The Pythagorean theorem relates the square of the speed of this
molecule to the squares of these components:

$$
v^{2}=v_{x}^{2}+v_{y}^{2}+v_{z}^{2}
$$

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

$$
\overline{v^{2}}=\overline{v_{x}^{2}}+\overline{v_{y}^{2}}+\overline{v_{z}^{2}}
$$

Because the motion is completely random, the average values $\overline{v_{x}{ }^{2}}, \overline{v_{y}^{2}}$, and $\overline{v_{z}{ }^{2}}$ are equal to each other. Using this fact and the previous equation, we find that

$$
\overline{v^{2}}=3 \overline{v_{x}^{2}}
$$

Thus, the total force exerted on the wall is

$$
F=\frac{N}{3}\left(\frac{m \overline{v^{2}}}{d}\right)
$$

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

$$
\begin{gather*}
P=\frac{F}{A}=\frac{F}{d^{2}}=\frac{1}{3}\left(\frac{N}{d^{3}} m \overline{v^{2}}\right)=\frac{1}{3}\left(\frac{N}{V}\right) m \overline{v^{2}} \\
P=\frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2} m \overline{v^{2}}\right) \tag{21.2}
\end{gather*}
$$

This result indicates that the pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecules, $\frac{1}{2} m \overline{v^{2}}$. In deriving this simplified model of an ideal gas, we obtain an important result that relates the large-scale quantity of pressure to an atomic quan-tity- the average value of the square of the molecular speed. Thus, we have established a key link between the atomic world and the large-scale world.

You should note that Equation 21.2 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 in the container. This is what you do when you add air to a tire. The pressure in the tire can also be increased by increasing the average translational kinetic energy of the air molecules in the tire. As we shall soon see, this can be accomplished by increasing the temperature of that air. It is for this reason that the pressure inside a tire increases as the tire warms up during long trips. The continuous flexing of the tire as it moves along the surface of a road results in work done as parts of the tire distort and in 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.

## Molecular Interpretation of Temperature

We can gain some insight into the meaning of temperature by first writing Equa-
10.3 tion 21.2 in the more familiar form

$$
P V=\frac{2}{3} N\left(\frac{1}{2} m \overline{v^{2}}\right)
$$

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

$$
P V=N k_{\mathrm{B}} T
$$



Ludwig Boltzmann Austrian theoretical 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. (Courtesy of AIP Niels Bohr Library, Lande Collection)

Relationship between pressure and molecular kinetic energy

Temperature is proportional to average kinetic energy

Average kinetic energy per molecule

Theorem of equipartition of energy

Total translational kinetic energy of $N$ molecules

Recall that the equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions, we find that

$$
\begin{equation*}
T=\frac{2}{3 k_{\mathrm{B}}}\left(\frac{1}{2} m \overline{v^{2}}\right) \tag{21.3}
\end{equation*}
$$

That is, temperature is a direct measure of average molecular kinetic energy.
By rearranging Equation 21.3, we can relate the translational molecular kinetic energy to the temperature:

$$
\begin{equation*}
\frac{1}{2} m \overline{v^{2}}=\frac{3}{2} k_{\mathrm{B}} T \tag{21.4}
\end{equation*}
$$

That is, the average translational kinetic energy per molecule is $\frac{3}{2} k_{\mathrm{B}} T$. Because $\overline{v_{x}{ }^{2}}=\frac{1}{3} \overline{v^{2}}$, it follows that

$$
\begin{equation*}
\frac{1}{2} m \overline{v_{x}^{2}}=\frac{1}{2} k_{\mathrm{B}} T \tag{21.5}
\end{equation*}
$$

In a similar manner, it follows that the motions in the $y$ and $z$ directions give us

$$
\frac{1}{2} m \overline{v_{y}^{2}}=\frac{1}{2} k_{\mathrm{B}} T \quad \text { and } \quad \frac{1}{2} m \overline{v_{z}^{2}}=\frac{1}{2} k_{\mathrm{B}} T
$$

Thus, each translational degree of freedom contributes an equal amount of energy to the gas, namely, $\frac{1}{2} k_{\mathrm{B}} T$. (In general, "degrees of freedom" refers to the number of independent means by which a molecule can possess energy.) A generalization of this result, known as the theorem of equipartition of energy, states that
each degree of freedom contributes $\frac{1}{2} k_{\mathrm{B}} T$ to the energy of a system.

The total translational kinetic energy of $N$ molecules of gas is simply $N$ times the average energy per molecule, which is given by Equation 21.4:

$$
\begin{equation*}
E_{\text {trans }}=N\left(\frac{1}{2} m \overline{v^{2}}\right)=\frac{3}{2} N k_{\mathrm{B}} T=\frac{3}{2} n R T \tag{21.6}
\end{equation*}
$$

where we have used $k_{\mathrm{B}}=R / N_{\mathrm{A}}$ for Boltzmann's constant and $n=N / N_{\mathrm{A}}$ for the number of moles of gas. If we consider a gas for which the only type of energy for the molecules is translational kinetic energy, we can use Equation 21.6 to express

| TABLE 21.1 | Some rms Speeds |  |
| :--- | :---: | :---: |
| Gas | Molar Mass <br> $(\mathbf{g} / \mathbf{m o l})$ | at $\mathbf{2 0}^{\circ} \mathbf{C}(\mathbf{m} / \mathbf{s})$ |
| $\mathrm{H}_{2}$ | 2.02 | 1904 |
| He | 4.00 | 1352 |
| $\mathrm{H}_{2} \mathrm{O}$ | 18.0 | 637 |
| Ne | 20.2 | 602 |
| $\mathrm{~N}_{2}$ or CO | 28.0 | 511 |
| $\mathrm{NO}^{\mathrm{CO}_{2}}$ | 30.0 | 494 |
| $\mathrm{SO}_{2}$ | 44.0 | 408 |

the internal energy of the gas. This result implies that the internal energy of an ideal gas depends only on the temperature.

The square root of $\overline{v^{2}}$ is called the root-mean-square ( rms ) speed of the molecules. From Equation 21.4 we obtain, for the rms speed,

$$
\begin{equation*}
v_{\mathrm{rms}}=\sqrt{v^{2}}=\sqrt{\frac{3 k_{\mathrm{B}} T}{m}}=\sqrt{\frac{3 R T}{M}} \tag{21.7}
\end{equation*}
$$

where $M$ is the molar mass in kilograms per mole. 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 $2 \times 10^{-3} \mathrm{~kg} / \mathrm{mol}$, have an average speed four times that of oxygen molecules, whose molar mass is $32 \times 10^{-3} \mathrm{~kg} / \mathrm{mol}$. Table 21.1 lists the rms speeds for various molecules at $20^{\circ} \mathrm{C}$.

## EXAMPLE 21.1 A Tank of Helium

A tank used for filling helium balloons has a volume of $0.300 \mathrm{~m}^{3}$ and contains 2.00 mol of helium gas at $20.0^{\circ} \mathrm{C}$. Assuming that the helium behaves like an ideal gas, (a) what is the total translational kinetic energy of the molecules of the gas?

Solution Using Equation 21.6 with $n=2.00 \mathrm{~mol}$ and $T=$ 293 K , we find that

$$
\begin{aligned}
E_{\text {trans }} & =\frac{3}{2} n R T=\frac{3}{2}(2.00 \mathrm{~mol})(8.31 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K})(293 \mathrm{~K}) \\
& =7.30 \times 10^{3} \mathrm{~J}
\end{aligned}
$$

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

Solution Using Equation 21.4, we find that the average kinetic energy per molecule is

$$
\begin{aligned}
\frac{1}{2} m \overline{v^{2}} & =\frac{3}{2} k_{\mathrm{B}} T=\frac{3}{2}\left(1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}\right)(293 \mathrm{~K}) \\
& =6.07 \times 10^{-21} \mathrm{~J}
\end{aligned}
$$

Exercise Using the fact that the molar mass of helium is $4.00 \times 10^{-3} \mathrm{~kg} / \mathrm{mol}$, determine the rms speed of the atoms at $20.0^{\circ} \mathrm{C}$.

Answer $1.35 \times 10^{3} \mathrm{~m} / \mathrm{s}$.

## Quick Quiz 21.1

At room temperature, the average speed of an air molecule is several hundred meters per second. A molecule traveling at this speed should travel across a room in a small fraction of a second. In view of this, why does it take the odor of perfume (or other smells) several minutes to travel across the room?

### 21.2 MOLAR SPECIFIC HEAT OF AN IDEAL GAS

- The energy required to raise the temperature of $n$ moles of gas from $T_{i}$ to $T_{f}$ de10.5 pends on the path taken between the initial and final states. To understand this, let us 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 by taking a variety of paths from one isotherm to another, as shown in Figure 21.3. Because $\Delta T$ is the same for each path, the change in internal energy $\Delta E_{\text {int }}$ is the same for all paths. However, we know from the first law, $Q=\Delta E_{\text {int }}+W$, that the heat $Q$ is different for each path because $W$ (the area under the curves) is different for each path. Thus, the heat associated with a given change in temperature does not have a unique value.


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 is proportional to its temperature

We can address this difficulty by defining specific heats for two processes that frequently occur: changes at constant volume and changes at constant pressure. Because the number of moles is a convenient measure of the amount of gas, we define the molar specific heats associated with these processes with the following equations:

$$
\begin{array}{ll}
Q=n C_{V} \Delta T & \text { (constant volume) } \\
Q=n C_{P} \Delta T & \text { (constant pressure) } \tag{21.9}
\end{array}
$$

where $C_{V}$ is the molar specific heat at constant volume and $C_{P}$ is the molar specific heat at constant pressure. When we heat a gas at constant pressure, not only does the internal energy of the gas increase, but the gas also does work because of the change in volume. Therefore, the heat $Q_{\text {constant } P \text { must account for }}$ both the increase in internal energy and the transfer of energy out of the system by work, and so $Q_{\text {constant } P}$ is greater than $Q_{\text {constant } V}$. Thus, $C_{P}$ 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. This should not be surprising because the simple kinetic theory model assumes a structureless molecule.

In view of this, let us 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 (by heating, for example), all of 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 21.6, we see that the total internal energy $E_{\text {int }}$ of $N$ molecules (or $n \mathrm{~mol}$ ) of an ideal monatomic gas is

$$
\begin{equation*}
E_{\mathrm{int}}=\frac{3}{2} N k_{\mathrm{B}} T=\frac{3}{2} n R T \tag{21.10}
\end{equation*}
$$

Note that for a monatomic ideal gas, $E_{\text {int }}$ is a function of $T$ only, and the functional relationship is given by Equation 21.10. In general, the internal energy of an ideal gas is a function of $T$ only, and the exact relationship depends on the type of gas, as we shall soon explore.

## Quick Quiz 21.2

How does the internal energy of a gas change as its pressure is decreased while its volume is increased in such a way that the process follows the isotherm labeled $T$ in Figure 21.4? (a) $E_{\text {int }}$ increases. (b) $E_{\text {int }}$ decreases. (c) $E_{\text {int }}$ stays the same. (d) There is not enough information to determine $\Delta E_{\text {int }}$.

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

$$
\begin{equation*}
Q=\Delta E_{\mathrm{int}} \tag{21.11}
\end{equation*}
$$

In other words, all of the energy transferred by heat goes into increasing the internal energy (and temperature) of the system. A constant-volume process from $i$ to $f$ is described in Figure 21.4, where $\Delta T$ is the temperature difference between the two isotherms. Substituting the expression for $Q$ given by Equation 21.8 into

Equation 21.11, we obtain

$$
\begin{equation*}
\Delta E_{\mathrm{int}}=n C_{V} \Delta T \tag{21.12}
\end{equation*}
$$

If the molar specific heat is constant, we can express the internal energy of a gas as

$$
E_{\mathrm{int}}=n C_{V} T
$$

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

In the limit of infinitesimal changes, we can use Equation 21.12 to express the molar specific heat at constant volume as

$$
\begin{equation*}
C_{V}=\frac{1}{n} \frac{d E_{\mathrm{int}}}{d T} \tag{21.13}
\end{equation*}
$$

Let us now apply the results of this discussion to the monatomic gas that we have been studying. Substituting the internal energy from Equation 21.10 into Equation 21.13, we find that

$$
\begin{equation*}
C_{V}=\frac{3}{2} R \tag{21.14}
\end{equation*}
$$

This expression predicts a value of $C_{V}=\frac{3}{2} R=12.5 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ for all monatomic gases. This 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).

Now suppose that the gas is taken along the constant-pressure path $i \rightarrow f^{\prime}$ shown in Figure 21.4. Along this path, the temperature again increases by $\Delta T$. The energy that must be transferred by heat to the gas in this process is $Q=n C_{P} \Delta T$. Because the volume increases in this process, the work done by the gas is $W=P \Delta V$, where $P$ is the constant pressure at which the process occurs. Applying


Figure 21.4 Energy is transferred by heat to an ideal gas in two ways. For the constant-volume path $i \rightarrow f$, all the energy goes into increasing the internal energy of the gas because no work is done. Along the constant-pressure path $i \rightarrow f^{\prime}$, part of the energy transferred in by heat is transferred out by work done by the gas.


[^0]Ratio of molar specific heats for a monatomic ideal gas
the first law to this process, we have

$$
\begin{equation*}
\Delta E_{\mathrm{int}}=Q-W=n C_{P} \Delta T-P \Delta V \tag{21.15}
\end{equation*}
$$

In this case, the energy added to the gas by heat is channeled as follows: Part of it does external work (that is, it goes into moving a piston), and the remainder increases the internal energy of the gas. But the change in internal energy for the process $i \rightarrow f^{\prime}$ is equal to that for the process $i \rightarrow f$ because $E_{\mathrm{int}}$ depends only on temperature for an ideal gas and because $\Delta T$ is the same for both processes. In addition, because $P V=n R T$, we note that for a constant-pressure process, $P \Delta V=n R \Delta T$. Substituting this value for $P \Delta V$ into Equation 21.15 with $\Delta E_{\mathrm{int}}=n C_{V} \Delta T$ (Eq. 21.12) gives

$$
\begin{align*}
n C_{V} \Delta T & =n C_{P} \Delta T-n R \Delta T \\
C_{P}-C_{V} & =R \tag{21.16}
\end{align*}
$$

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 $8.31 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K})$. This expression is applicable to real gases, as the data in Table 21.2 show.

Because $C_{V}=\frac{3}{2} R$ for a monatomic ideal gas, Equation 21.16 predicts a value $C_{P}=\frac{5}{2} R=20.8 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ for the molar specific heat of a monatomic gas at constant pressure. The ratio of these heat capacities is a dimensionless quantity $\gamma$ (Greek letter gamma):

$$
\begin{equation*}
\gamma=\frac{C_{P}}{C_{V}}=\frac{(5 / 2) R}{(3 / 2) R}=\frac{5}{3}=1.67 \tag{21.17}
\end{equation*}
$$

Theoretical values of $C_{P}$ and $\gamma$ 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). This is not surprising because 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 21.4, we describe the effect of molecular structure on the molar specific heat of a gas. We shall find that the internal en-ergy-and, hence, the molar specific heat - of a complex gas must include contributions from the rotational and the vibrational motions of the molecule.

We have seen that the molar specific heats of gases at constant pressure are greater than the molar specific heats at constant volume. This difference is a consequence of the fact that in a constant-volume process, no work is done and all of the energy transferred by heat goes into increasing the internal energy (and temperature) of the gas, whereas in a constant-pressure process, some of the energy transferred by heat is transferred out as work done by the gas as it expands. In the case of solids and liquids heated at constant pressure, very little work is done because the thermal expansion is small. Consequently, $C_{P}$ and $C_{V}$ are approximately equal for solids and liquids.

## 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 For the constant-volume process, we have

$$
Q_{1}=n C_{V} \Delta T
$$

Because $C_{V}=12.5 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ for helium and $\Delta T=200 \mathrm{~K}$, we
obtain

$$
Q_{1}=(3.00 \mathrm{~mol})(12.5 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K})(200 \mathrm{~K})=7.50 \times 10^{3} \mathrm{~J}
$$

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

Solution Making use of Table 21.2, we obtain

$$
\begin{aligned}
Q_{2} & =n C_{P} \Delta T=(3.00 \mathrm{~mol})(20.8 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K})(200 \mathrm{~K}) \\
& =12.5 \times 10^{3} \mathrm{~J}
\end{aligned}
$$

Exercise What is the work done by the gas in this isobaric process?

Answer $W=Q_{2}-Q_{1}=5.00 \times 10^{3} \mathrm{~J}$.

### 21.3 ADIABATIC PROCESSES FOR AN IDEAL GAS

As we 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) very rapidly, very little energy is transferred out of (or into) the system by heat, and so the process is nearly adiabatic. (We must remember that the temperature of a system changes in an adiabatic process even though no energy is transferred by heat.) Such processes occur in the cycle of a gasoline engine, which we discuss in detail in the next chapter.

Another example of an adiabatic process is the very slow expansion of a gas that is thermally insulated from its surroundings. In general,
an adiabatic process is one in which no energy is exchanged by heat between a system and its surroundings.

Let us suppose that an ideal gas undergoes an adiabatic expansion. At any time during the process, we assume that the gas is in an equilibrium state, so that the equation of state $P V=n R T$ is valid. As we shall soon see, the pressure and volume at any time during an adiabatic process are related by the expression

$$
\begin{equation*}
P V^{\gamma}=\text { constant } \tag{21.18}
\end{equation*}
$$

where $\gamma=C_{P} / C_{V}$ is assumed to be constant during the process. Thus, we see that all three variables in the ideal gas law- $P, V$, and $T$-change during an adiabatic process.

## Proof That $P V^{\gamma}=$ constant for an Adiabatic Process

When a gas expands adiabatically in a thermally insulated cylinder, no energy is transferred by heat between the gas and its surroundings; thus, $Q=0$. Let us take the infinitesimal change in volume to be $d V$ and the infinitesimal change in temperature to be $d T$. The work done by the gas is $P d V$. Because the internal energy of an ideal gas depends only on temperature, the change in the internal energy in an adiabatic expansion is the same as that for an isovolumetric process between the same temperatures, $d E_{\text {int }}=n C_{V} d T$ (Eq. 21.12). Hence, the first law of thermodynamics, $\Delta E_{\mathrm{int}}=Q-W$, with $Q=0$, becomes

$$
d E_{\mathrm{int}}=n C_{V} d T=-P d V
$$

Taking the total differential of the equation of state of an ideal gas, $P V=n R T$, we

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


[^0]:    ${ }^{\text {a }}$ All values except that for water were obtained at 300 K .

