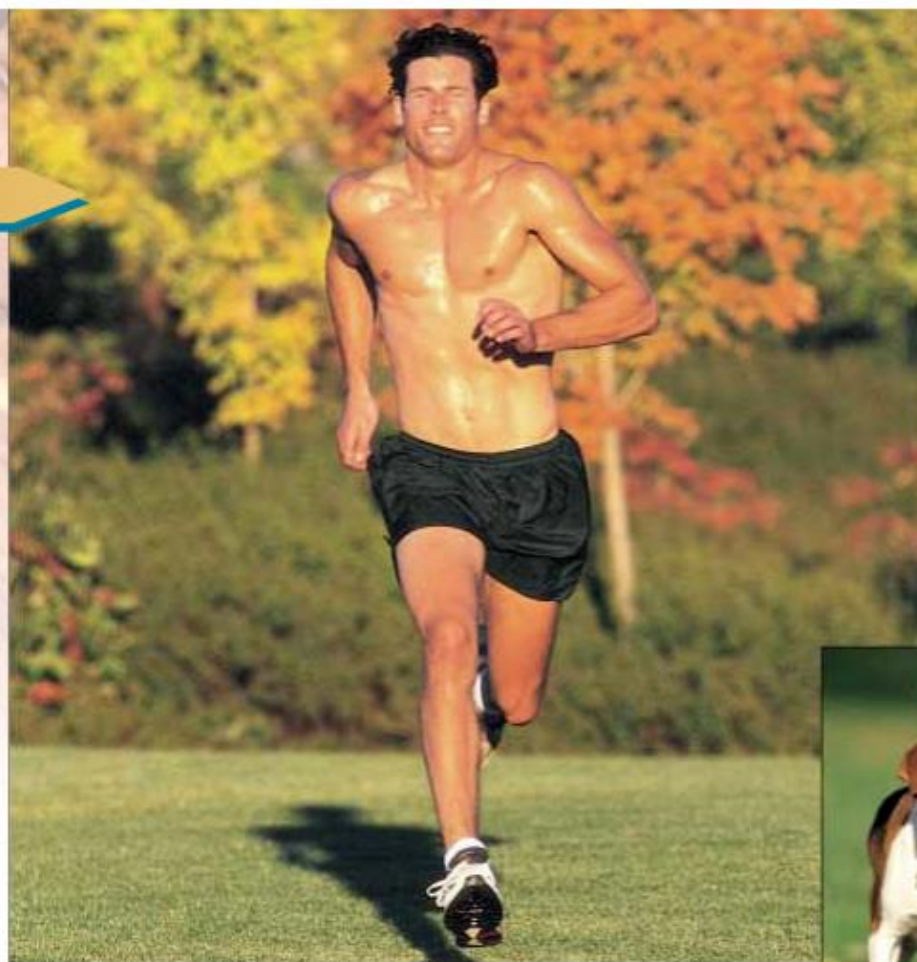


PUZZLER

During periods of strenuous exertion, our bodies generate excess internal energy that must be released into our surroundings. To facilitate this release, humans perspire. Dogs and other animals pant to accomplish the same goal. Both actions involve the evaporation of a liquid. How does this process help cool the body?

(Photograph of runner by Jim Cummins/FPG International; photograph of beagle by Renee Lynn/Photo Researchers, Inc.)



chapter

21

The Kinetic Theory of Gases


Chapter Outline

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| 21.2 Molar Specific Heat of an Ideal Gas | 21.7 (Optional) Mean Free Path |
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In 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 (O_2) and carbon dioxide (CO_2), 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.

Assumptions of the molecular model of an ideal gas

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

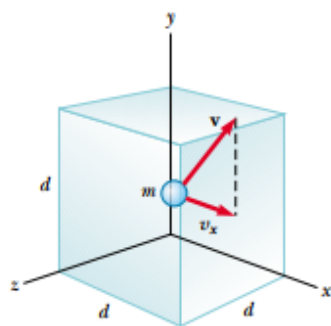


Figure 21.1 A cubical box with sides of length d containing an ideal gas. The molecule shown moves with velocity \mathbf{v} .

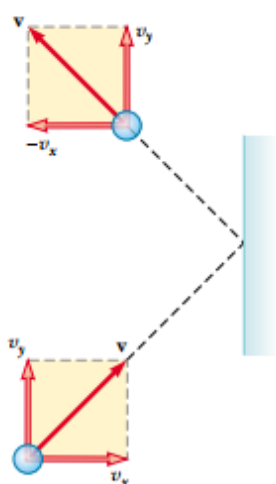


Figure 21.2 A molecule makes an elastic collision with the wall of the container. Its x component of momentum is reversed, while its y component remains unchanged. In this construction, we assume that the molecule moves in the xy plane.

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 mv_x before the collision and $-mv_x$ after the collision, the change in momentum of the molecule is

$$\Delta p_x = -mv_x - (mv_x) = -2mv_x$$

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

$$F_1 \Delta t = \Delta p_x = -2mv_x$$

where F_1 is the magnitude of the average force exerted by the wall on the molecule in the time Δt . 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 $2d$ in the x direction. Therefore, the time interval between two collisions with the same wall is $\Delta t = 2d/v_x$. Over a time interval that is long compared with Δt , the average force exerted on the molecule for each collision is

$$F_1 = \frac{-2mv_x}{\Delta t} = \frac{-2mv_x}{2d/v_x} = \frac{-mv_x^2}{d} \quad (21.1)$$

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:

$$F_{1, \text{ on wall}} = -F_1 = -\left(\frac{-mv_x^2}{d}\right) = \frac{mv_x^2}{d}$$

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:

$$F = \frac{m}{d} (v_{x1}^2 + v_{x2}^2 + \cdots)$$

In this equation, v_{x1} is the x component of velocity of molecule 1, v_{x2} 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

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2}{N}$$

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

$$F = \frac{Nm}{d} \overline{v_x^2}$$

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:

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

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 quantity—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 Equation 21.2 in the more familiar form

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

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

$$PV = Nk_B T$$



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

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

Temperature is proportional to average kinetic energy

$$T = \frac{2}{3k_B} \left(\frac{1}{2} m \overline{v^2} \right) \quad (21.3)$$

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:

Average kinetic energy per molecule

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad (21.4)$$

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

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T \quad (21.5)$$

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

$$\frac{1}{2} m \overline{v_y^2} = \frac{1}{2} k_B T \quad \text{and} \quad \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} k_B T$$

Thus, each translational degree of freedom contributes an equal amount of energy to the gas, namely, $\frac{1}{2} k_B T$. (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

Theorem of equipartition of energy

each degree of freedom contributes $\frac{1}{2} k_B T$ 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:

Total translational kinetic energy of N molecules

$$E_{\text{trans}} = N \left(\frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (21.6)$$

where we have used $k_B = R/N_A$ for Boltzmann’s constant and $n = N/N_A$ 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 (g/mol)	v_{rms} at 20°C (m/s)
H ₂	2.02	1904
He	4.00	1352
H ₂ O	18.0	637
Ne	20.2	602
N ₂ or CO	28.0	511
NO	30.0	494
CO ₂	44.0	408
SO ₂	64.1	338

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,

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \quad (21.7)$$

Root-mean-square speed

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 2×10^{-3} kg/mol, have an average speed four times that of oxygen molecules, whose molar mass is 32×10^{-3} kg/mol. Table 21.1 lists the rms speeds for various molecules at 20°C.

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 . 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 $n = 2.00 \text{ mol}$ and $T = 293 \text{ K}$, we find that

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

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

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

$$\begin{aligned} \frac{1}{2} m \overline{v^2} &= \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K}) (293 \text{ K}) \\ &= 6.07 \times 10^{-21} \text{ J} \end{aligned}$$

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

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

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 depends 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 ΔT is the same for each path, the change in internal energy ΔE_{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.

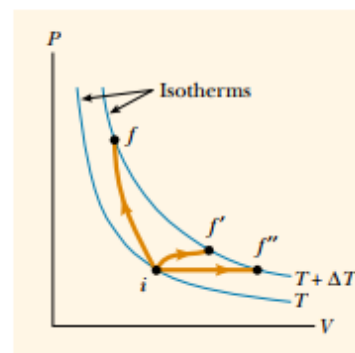


Figure 21.3 An ideal gas is taken from one isotherm at temperature T to another at temperature $T + \Delta T$ along three different paths.

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:

$$Q = nC_V\Delta T \quad (\text{constant volume}) \quad (21.8)$$

$$Q = nC_P\Delta T \quad (\text{constant pressure}) \quad (21.9)$$

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 $Q_{\text{constant } P}$ 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_{int} of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\text{int}} = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \quad (21.10)$$

Note that for a monatomic ideal gas, E_{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.

Internal energy of an ideal monatomic gas is proportional to its temperature

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_{int} increases. (b) E_{int} decreases. (c) E_{int} stays the same. (d) There is not enough information to determine ΔE_{int} .

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

$$Q = \Delta E_{\text{int}} \quad (21.11)$$

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 ΔT is the temperature difference between the two isotherms. Substituting the expression for Q given by Equation 21.8 into

Equation 21.11, we obtain

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (21.12)$$

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

$$E_{\text{int}} = nC_V T$$

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

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} \quad (21.13)$$

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

$$C_V = \frac{3}{2}R \quad (21.14)$$

This expression predicts a value of $C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K}$ 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 $i \rightarrow f'$ 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 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

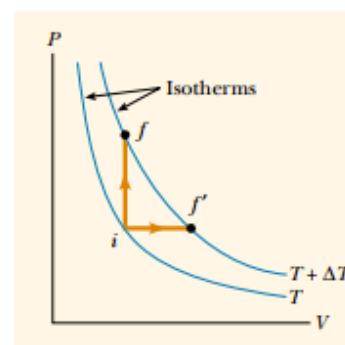


Figure 21.4 Energy is transferred by heat to an ideal gas in two ways. For the constant-volume path $i \rightarrow f$, all the energy goes into increasing the internal energy of the gas because no work is done. Along the constant-pressure path $i \rightarrow f'$, part of the energy transferred in by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

TABLE 21.2 Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol · K) ^a			
	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	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 ₂ O	35.4	27.0	8.37	1.30
CH ₄	35.5	27.1	8.41	1.31

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

the first law to this process, we have

$$\Delta E_{\text{int}} = Q - W = nC_p \Delta T - P\Delta V \quad (21.15)$$

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 $i \rightarrow f'$ is equal to that for the process $i \rightarrow f$ because E_{int} depends only on temperature for an ideal gas and because ΔT is the same for both processes. In addition, because $PV = nRT$, we note that for a constant-pressure process, $P\Delta V = nR\Delta T$. Substituting this value for $P\Delta V$ into Equation 21.15 with $\Delta E_{\text{int}} = nC_V \Delta T$ (Eq. 21.12) gives

$$\begin{aligned} nC_V \Delta T &= nC_p \Delta T - nR\Delta T \\ C_p - C_V &= R \end{aligned} \quad (21.16)$$

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 $8.31 \text{ J/mol} \cdot \text{K}$). 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 $C_p = \frac{5}{2}R = 20.8 \text{ J/mol} \cdot \text{K}$ for the molar specific heat of a monatomic gas at constant pressure. The ratio of these heat capacities is a dimensionless quantity γ (Greek letter gamma):

$$\gamma = \frac{C_p}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.67 \quad (21.17)$$

Ratio of molar specific heats for a monatomic ideal gas

Theoretical values of 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). 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 energy—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

$$Q_1 = nC_V \Delta T$$

Because $C_V = 12.5 \text{ J/mol} \cdot \text{K}$ for helium and $\Delta T = 200 \text{ K}$, we

obtain

$$Q_1 = (3.00 \text{ mol})(12.5 \text{ J/mol} \cdot \text{K})(200 \text{ K}) = 7.50 \times 10^3 \text{ J}$$

$$Q_2 = nC_p \Delta T = (3.00 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(200 \text{ K})$$

$$= 12.5 \times 10^3 \text{ J}$$

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

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

Solution Making use of Table 21.2, we obtain

Answer $W = Q_2 - Q_1 = 5.00 \times 10^3 \text{ J}.$

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.

Definition of an adiabatic process

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 $PV = nRT$ is valid. As we shall soon see, the pressure and volume at any time during an adiabatic process are related by the expression

$$PV^\gamma = \text{constant} \quad (21.18)$$

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

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 $PV^\gamma = \text{constant}$ 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 dV and the infinitesimal change in temperature to be dT . The work done by 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 expansion is the same as that for an isovolumetric process between the same temperatures, $dE_{\text{int}} = nC_v dT$ (Eq. 21.12). Hence, the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, with $Q = 0$, becomes

$$dE_{\text{int}} = nC_v dT = -P dV$$

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

QuickLab

Rapidly pump up a bicycle tire and then feel the coupling at the end of the hose. Why is the coupling warm?

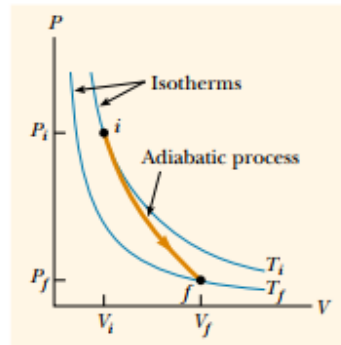


Figure 21.5 The PV diagram for an adiabatic expansion. Note that $T_f < T_i$ in this process.

see that

$$P dV + V dP = nR dT$$

Eliminating dT from these two equations, we find that

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

Substituting $R = C_P - C_V$ and dividing by PV , we obtain

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

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating this expression, we have

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

which is equivalent to Equation 21.18:

$$PV^\gamma = \text{constant}$$

The PV diagram for an adiabatic expansion is shown in Figure 21.5. Because $\gamma > 1$, the PV curve is steeper than it would be for an isothermal expansion. 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 (the gas does work, so its internal energy decreases) and so ΔT also is negative. Thus, we see that the gas cools ($T_f < T_i$) during an adiabatic expansion. Conversely, the temperature increases if the gas is compressed adiabatically. Applying Equation 21.18 to the initial and final states, we see that

Adiabatic process

$$P_i V_i^\gamma = P_f V_f^\gamma \quad (21.19)$$

Using the ideal gas law, we can express Equation 21.19 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (21.20)$$

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 that air behaves as an ideal gas with $\gamma = 1.40$ and that the compression is adiabatic. Find the final pressure and temperature of the air.

Solution Using Equation 21.19, we find that

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

$$= 37.6 \text{ atm}$$

Because $PV = nRT$ is valid during any process and because

no gas escapes from the cylinder,

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

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

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

The high compression in a diesel engine raises the temperature of the fuel enough to cause its combustion without the use of spark plugs.

21.4 THE EQUIPARTITION OF ENERGY

We have found that model predictions based on molar specific heat agree quite well with the behavior of monatomic gases but not with the behavior of complex gases (see Table 21.2). Furthermore, the value predicted by the model for the quantity $C_p - C_v = R$ is the same for all gases. This is not surprising because this difference is the result of the work done by 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 us first explain the origin of molar specific heat. So far, we have assumed that the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. However, the internal energy of a gas actually 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 the 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 $\frac{1}{2}k_B T$ of energy per molecule.

Let us consider a diatomic gas whose molecules have the shape of a dumbbell (Fig. 21.6). In this model, the center of mass of the molecule can translate in the x , y , and z directions (Fig. 21.6a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. 21.6b). We can neglect the rotation about the y axis because the moment of inertia I_y and the 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 taken to be point masses, then I_y is identically zero.) Thus, there are five degrees of freedom: three associated with the translational motion and two associated with the rotational motion. Because each degree of freedom contributes, on the average, $\frac{1}{2}k_B T$ of energy per molecule, the total internal energy for a sys-

tem of N molecules is

$$E_{\text{int}} = 3N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) = \frac{5}{2}Nk_B T = \frac{5}{2}nRT$$

We can use this result and Equation 21.13 to find the molar specific heat at constant volume:

$$C_v = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{5}{2} nRT \right) = \frac{5}{2} R$$

From Equations 21.16 and 21.17, we find that

$$C_p = C_v + R = \frac{7}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = 1.40$$

These results agree quite well with most of the data for diatomic molecules given in Table 21.2. This is rather surprising because we have not yet accounted for the possible vibrations of the molecule. In the vibratory model, the two atoms are joined by an imaginary spring (see Fig. 21.6c). 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, classical physics and the equipartition theorem predict an internal energy of

$$E_{\text{int}} = 3N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) = \frac{7}{2}Nk_B T = \frac{7}{2}nRT$$

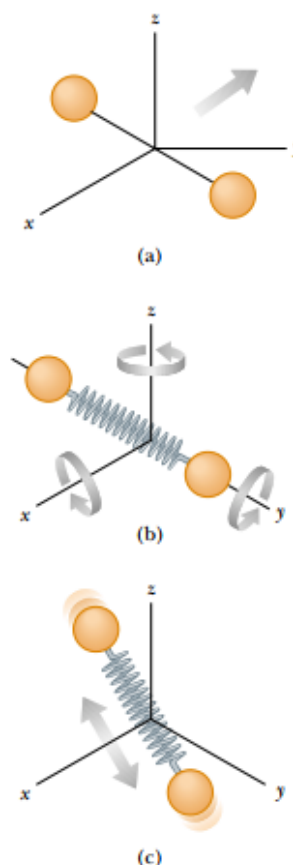


Figure 21.6 Possible motions of a diatomic molecule: (a) translational motion of the center of mass, (b) rotational motion about the various axes, and (c) vibrational motion along the molecular axis.

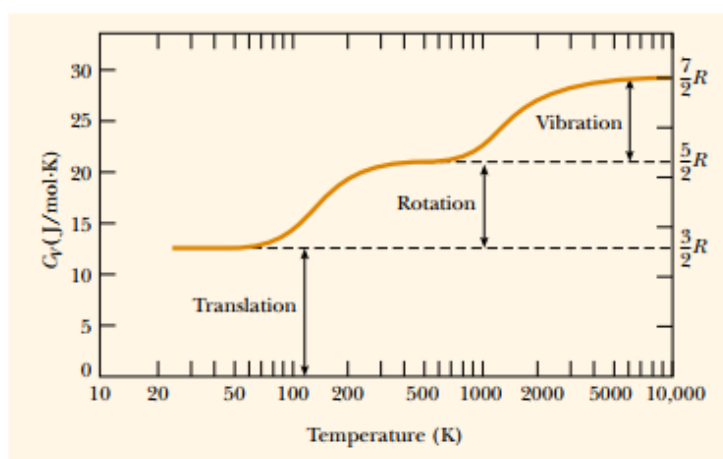


Figure 21.7 The molar specific heat of hydrogen as a function of temperature. The horizontal scale is logarithmic. Note that hydrogen liquefies at 20 K.

and a molar specific heat at constant volume of

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{7}{2} nRT \right) = \frac{7}{2} R$$

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.

For molecules consisting of more than two atoms, the number of degrees of freedom is even larger and the vibrations are more complex. This results in an even higher predicted molar specific heat, which is in qualitative agreement with experiment. The more degrees of freedom available to a molecule, the more “ways” it can store internal energy; this results in a higher molar specific heat.

We have seen that the equipartition theorem is successful in explaining some features of the molar specific heat of gas molecules with structure. However, the theorem does not account for the observed temperature variation in molar specific heats. As an example of such a temperature variation, C_V for H_2 is $\frac{5}{2}R$ from about 250 K to 750 K and then increases steadily to about $\frac{7}{2}R$ well above 750 K (Fig. 21.7). This suggests that much more significant vibrations occur at very high temperatures. At temperatures well below 250 K, C_V has a value of about $\frac{3}{2}R$, suggesting that the molecule has only translational energy at low temperatures.

A Hint of Energy Quantization

The failure of the equipartition theorem to explain such phenomena is due to the inadequacy of classical mechanics applied to molecular systems. For a more satisfactory description, it is necessary to use a quantum-mechanical model, in which the energy of an individual molecule is quantized. The energy separation between adjacent vibrational energy levels for a molecule such as H_2 is about ten times greater than the average kinetic energy of the molecule at room temperature. Consequently, collisions between molecules at low temperatures do not provide enough energy to change the vibrational state of the molecule. It is often stated that such degrees of freedom are “frozen out.” This explains why the vibrational energy does not contribute to the molar specific heats of molecules at low temperatures.

The rotational energy levels also are quantized, but their spacing at ordinary temperatures is small compared with $k_B T$. Because the spacing between quantized energy levels is small compared with the available energy, the system behaves in accordance with classical mechanics. However, at sufficiently low temperatures (typically less than 50 K), where $k_B T$ is small compared with the spacing between rotational levels, intermolecular collisions may not be sufficiently energetic to alter the rotational states. This explains why C_V reduces to $\frac{3}{2}R$ for H_2 in the range from 20 K to approximately 100 K.

The Molar Specific Heat of Solids

The molar specific heats of solids also demonstrate a marked temperature dependence. Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature and approach zero as the temperature approaches absolute zero. At high temperatures (usually above 300 K), the molar specific heats approach the value of $3R \approx 25 \text{ J/mol}\cdot\text{K}$, a result known as the *Dulong–Petit law*. The typical data shown in Figure 21.8 demonstrate the temperature dependence of the molar specific heats for two semiconducting solids, silicon and germanium.

We can explain the molar specific heat of a solid at high temperatures using the equipartition theorem. For small displacements of an atom from its equilibrium position, each atom executes simple harmonic motion in the x , y , and z directions. The energy associated with vibrational motion in the x direction is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2$$

The expressions for vibrational motions in the y and z directions are analogous. Therefore, each atom of the solid has six degrees of freedom. According to the equipartition theorem, this corresponds to an average vibrational energy of $6(\frac{1}{2}k_B T) = 3k_B T$ per atom. Therefore, the total internal energy of a solid consisting of N atoms is

$$E_{\text{int}} = 3Nk_B T = 3nRT \quad (21.21)$$

From this result, we find that the molar specific heat of a solid at constant volume is

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = 3R \quad (21.22)$$

This result is in agreement with the empirical Dulong–Petit law. The discrepancies between this model and the experimental data at low temperatures are again due to the inadequacy of classical physics in describing the microscopic world.

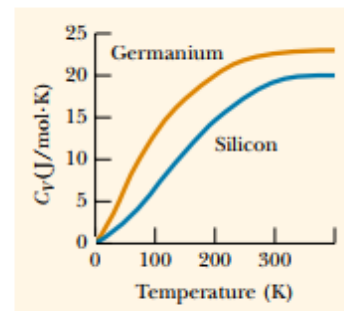


Figure 21.8 Molar specific heat of silicon and germanium. As T approaches zero, the molar specific heat also approaches zero. (From C. Kittel, *Introduction to Solid State Physics*, New York, Wiley, 1971.)

Total internal energy of a solid

Molar specific heat of a solid at constant volume

21.5 THE BOLTZMANN DISTRIBUTION LAW

Thus far we have neglected the fact that not all molecules in a gas have the same speed and energy. In reality, their motion is extremely chaotic. Any individual molecule is colliding 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. From Equation 21.7, we see that average molecular speeds increase with increasing temperature. What we would like to know now is the relative number of molecules that possess some characteristic, such as a certain percentage of the total energy or speed. 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.

The Exponential Atmosphere

We begin by considering the distribution of molecules in our atmosphere. Let us determine how the number of molecules per unit volume varies with altitude. Our model assumes that the atmosphere is at a constant temperature T . (This assumption is not entirely correct because the temperature of our atmosphere decreases by about 2°C for every 300-m increase in altitude. However, the model does illustrate the basic features of the distribution.)

According to the ideal gas law, a gas containing N molecules in thermal equilibrium obeys the relationship $PV = Nk_B T$. It is convenient to rewrite this equation in terms of the **number density** $n_V = N/V$, which represents the number of molecules per unit volume of gas. This quantity is important because it can vary from one point to another. In fact, our goal is to determine how n_V changes in our atmosphere. We can express the ideal gas law in terms of n_V as $P = n_V k_B T$. Thus, if the number density n_V is known, we can find the pressure, and vice versa. The pressure in the atmosphere decreases with increasing altitude because a given layer of air must support the weight of all the atmosphere above it—that is, the greater the altitude, the less the weight of the air above that layer, and the lower

the pressure.

To determine the variation in pressure with altitude, let us consider an atmospheric layer of thickness dy and cross-sectional area A , as shown in Figure 21.9. Because the air is in static equilibrium, the magnitude PA of the upward force exerted on the bottom of this layer must exceed the magnitude of the downward force on the top of the layer, $(P + dP)A$, by an amount equal to the weight of gas in this thin layer. If the mass of a gas molecule in the layer is m , and if a total of N molecules are in the layer, then the weight of the layer is given by $mgN = mgn_V V = mgn_V A dy$. Thus, we see that

$$PA - (P + dP)A = mgn_V A dy$$

This expression reduces to

$$dP = -mgn_V dy$$

Because $P = n_V k_B T$ and T is assumed to remain constant, we see that $dP = k_B T dn_V$. Substituting this result into the previous expression for dP and rearranging terms, we have

$$\frac{dn_V}{n_V} = -\frac{mg}{k_B T} dy$$

Integrating this expression, we find that

$$n_V(y) = n_0 e^{-mgy/k_B T} \quad (21.23)$$

where the constant n_0 is the number density at $y = 0$. This result is known as the **law of atmospheres**.

According to Equation 21.23, the number density decreases exponentially with increasing altitude when the temperature is constant. The number density of our atmosphere at sea level is about $n_0 = 2.69 \times 10^{25}$ molecules/ m^3 . Because the pressure is $P = n_V k_B T$, we see from Equation 21.23 that the pressure of our atmosphere varies with altitude according to the expression

$$P = P_0 e^{-mgy/k_B T} \quad (21.24)$$

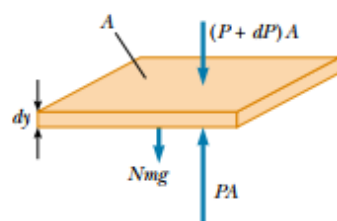


Figure 21.9 An atmospheric layer of gas in equilibrium.

where $P_0 = n_0 k_B T$. A comparison of this model with the actual atmospheric pressure as a function of altitude shows that the exponential form is a reasonable approximation to the Earth's atmosphere.

EXAMPLE 21.4 High-Flying Molecules

What is the number density of air at an altitude of 11.0 km (the cruising altitude of a commercial jetliner) compared with its number density at sea level? Assume that the air temperature at this height is the same as that at the ground, 20°C.

Solution The number density of our atmosphere decreases exponentially with altitude according to the law of atmospheres, Equation 21.23. We assume an average molecular mass of $28.9 \text{ u} = 4.80 \times 10^{-26} \text{ kg}$. Taking $y = 11.0 \text{ km}$, we calculate the power of the exponential in Equation 21.23 to be

$$\frac{mgy}{k_B T} = \frac{(4.80 \times 10^{-26} \text{ kg})(9.80 \text{ m/s}^2)(11\,000 \text{ m})}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} = 1.28$$

Thus, Equation 21.23 gives

$$n_V = n_0 e^{-mgy/k_B T} = n_0 e^{-1.28} = 0.278 n_0$$

That is, the number density of air at an altitude of 11.0 km is only 27.8% of the number density at sea level, if we assume constant temperature. Because the temperature actually decreases with altitude, the number density of air is less than this in reality.

The pressure at this height is reduced in the same manner. For this reason, high-flying aircraft must have pressurized cabins to ensure passenger comfort and safety.

Computing Average Values

The exponential function $e^{-mgy/k_B T}$ that appears in Equation 21.23 can be interpreted as a probability distribution that gives the relative probability of finding a gas molecule at some height y . Thus, the probability distribution $p(y)$ is proportional to the number density distribution $n_V(y)$. This concept enables us to determine many properties of the atmosphere, such as the fraction of molecules below a certain height or the average potential energy of a molecule.

As an example, let us determine the average height \bar{y} of a molecule in the atmosphere at temperature T . The expression for this average height is

$$\bar{y} = \frac{\int_0^\infty y n_V(y) dy}{\int_0^\infty n_V(y) dy} = \frac{\int_0^\infty y e^{-mgy/k_B T} dy}{\int_0^\infty e^{-mgy/k_B T} dy}$$

where the height of a molecule can range from 0 to ∞ . The numerator in this expression represents the sum of the heights of the molecules times their number, while the denominator is the sum of the number of molecules. That is, the denominator is the total number of molecules. After performing the indicated integrations, we find that

$$\bar{y} = \frac{(k_B T/mg)^2}{k_B T/mg} = \frac{k_B T}{mg}$$

This expression states that the average height of a molecule increases as T increases, as expected.

We can use a similar procedure to determine the average potential energy of a gas molecule. Because the gravitational potential energy of a molecule at height y is $U = mgy$, the average potential energy is equal to $m\bar{y}$. Because $\bar{y} = k_B T/mg$, we

see that $\bar{U} = mg(k_B T/mg) = k_B T$. This important result indicates that the average gravitational potential energy of a molecule depends only on temperature, and not on m or g .

The Boltzmann Distribution

Because the gravitational potential energy of a molecule at height y is $U = mgy$, we can express the law of atmospheres (Eq. 21.23) as

$$n_V = n_0 e^{-U/k_B T}$$

This means that gas molecules in thermal equilibrium are distributed in space with a probability that depends on gravitational potential energy according to the exponential factor $e^{-U/k_B T}$.

This exponential expression describing the distribution of molecules in the atmosphere is powerful and applies to any type of energy. In general, the number density of molecules having energy E is

Boltzmann distribution law

$$n_V(E) = n_0 e^{-E/k_B T} \quad (21.25)$$

This equation is known as the **Boltzmann distribution law** and 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 $k_B T$** . 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 21.5 Thermal Excitation of Atomic Energy Levels

As we discussed briefly in Section 8.10, 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 1.6×10^{-19} J (Fig. 21.10). Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

Solution Equation 21.25 gives the relative number of atoms in a given energy level. In this case, the atom has two possible energies, E_1 and E_2 , where E_1 is the lower energy level. Hence, the ratio of the number of atoms in the higher energy level to the number in the lower energy level is

$$\frac{n_V(E_2)}{n_V(E_1)} = \frac{n_0 e^{-E_2/k_B T}}{n_0 e^{-E_1/k_B T}} = e^{-(E_2 - E_1)/k_B T}$$

In this problem, $E_2 - E_1 = 1.50$ eV, and the denominator of the exponent is

$$\begin{aligned} k_B T &= (1.38 \times 10^{-23} \text{ J/K})(2\,500 \text{ K}) / 1.60 \times 10^{-19} \text{ J/eV} \\ &= 0.216 \text{ eV} \end{aligned}$$

Therefore, the required ratio is

$$\frac{n(E_2)}{n(E_1)} = e^{-1.50 \text{ eV} / 0.216 \text{ eV}} = e^{-6.94} = 9.64 \times 10^{-4}$$

This result indicates that at $T = 2\,500$ 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.

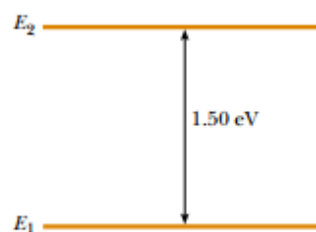


Figure 21.10 Energy level diagram for a gas whose atoms can occupy two energy levels.

21.6 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. However, about 60 years later, experiments were devised that confirmed Maxwell's predictions.

Let us 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 410 m/s. Intuitively, we expect that the speed distribution depends on temperature. Furthermore, we expect that the distribution peaks in the vicinity of v_{rms} . That is, few molecules are expected to have speeds much less than or much greater than v_{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 21.11. The quantity N_v , called the **Maxwell–Boltzmann distribution function**, is defined as follows: If N is the total number of molecules, then 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 21.11. 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 $v + dv$.

The fundamental expression that describes the distribution of speeds of N gas molecules is

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (21.26)$$

where m is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute temperature.¹ Observe the appearance of the Boltzmann factor $e^{-E/k_B T}$ with $E = \frac{1}{2}mv^2$.

As indicated in Figure 21.11, the average speed \bar{v} is somewhat lower than the rms speed. The *most probable speed* v_{mp} is the speed at which the distribution curve reaches a peak. Using Equation 21.26, one finds that

$$v_{\text{rms}} = \sqrt{v^2} = \sqrt{3k_B T/m} = 1.73 \sqrt{k_B T/m} \quad (21.27)$$

$$\bar{v} = \sqrt{8k_B T/\pi m} = 1.60 \sqrt{k_B T/m} \quad (21.28)$$

$$v_{\text{mp}} = \sqrt{2k_B T/m} = 1.41 \sqrt{k_B T/m} \quad (21.29)$$

The details of these calculations are left for the student (see Problems 41 and 62). From these equations, we see that

$$v_{\text{rms}} > \bar{v} > v_{\text{mp}}$$

Figure 21.12 represents speed distribution curves for N_2 . The curves were obtained by using Equation 21.26 to evaluate the distribution function at various speeds and at two temperatures. Note that the peak in the curve shifts to the right

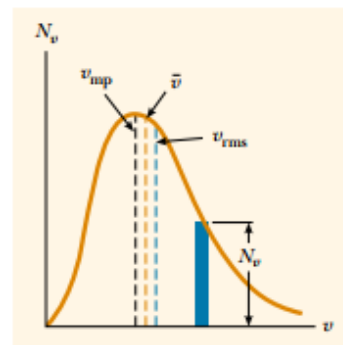


Figure 21.11 The speed distribution of gas molecules at some temperature. The number of molecules having speeds in the range dv is equal to the area of the shaded rectangle, $N_v dv$. The function N_v approaches zero as v approaches infinity.

Maxwell speed distribution function

rms speed

Average speed

Most probable speed

¹ For the derivation of this expression, see an advanced textbook on thermodynamics, such as that by R. P. Bauman, *Modern Thermodynamics with Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

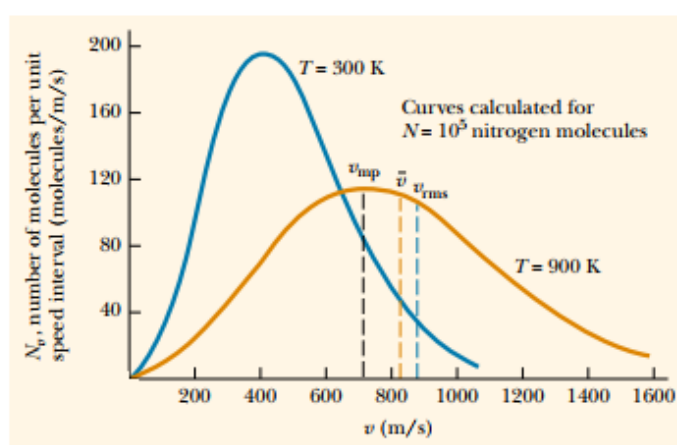


Figure 21.12 The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K. The total area under either curve is equal to the total number of molecules, which in this case equals 10^5 . Note that $v_{\text{rms}} > \bar{v} > v_{\text{mp}}$.

as T increases, indicating that the average speed increases with increasing temperature, as expected. The asymmetric shape of the curves is due to the fact that the lowest speed possible is zero while the upper classical limit of the speed is infinity.

Quick Quiz 21.3

Consider the two curves in Figure 21.12. What is represented by the area under each of the curves between the 800-m/s and 1 000-m/s marks on the horizontal axis?

QuickLab

Fill one glass with very hot tap water and another with very cold water. Put a single drop of food coloring in each glass. Which drop disperses faster? Why?

Equation 21.26 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. This explains why lighter molecules, such as H_2 and He , escape 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 14. 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 21.12. We can understand the phenomenon of evaporation of a liquid from this distribution in speeds, using the fact that some molecules in the liquid are more energetic than others. Some of the faster-moving molecules in the liquid penetrate the surface and leave the liquid even 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 often is placed on a feverish head to cool and comfort a patient.

The evaporation process

EXAMPLE 21.6 A System of Nine Particles

Nine particles have speeds of 5.00, 8.00, 12.0, 12.0, 12.0, 14.0, 17.0, and 20.0 m/s. (a) Find the particles' average speed.

Solution The average speed is the sum of the speeds divided by the total number of particles:

$$\bar{v} = \frac{(5.00 + 8.00 + 12.0 + 12.0 + 12.0 + 14.0 + 14.0 + 17.0 + 20.0) \text{ m/s}}{9} = 12.7 \text{ m/s}$$

(b) What is the rms speed?

Solution The average value of the square of the speed is

$$\overline{v^2} = \frac{(5.00^2 + 8.00^2 + 12.0^2 + 12.0^2 + 12.0^2 + 14.0^2 + 14.0^2 + 17.0^2 + 20.0^2) \text{ m}^2/\text{s}^2}{9} = 178 \text{ m}^2/\text{s}^2$$

Hence, the rms speed is

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{178 \text{ m}^2/\text{s}^2} = 13.3 \text{ m/s}$$

(c) What is the most probable speed of the particles?

Solution Three of the particles have a speed of 12 m/s, two have a speed of 14 m/s, and the remaining have different speeds. Hence, we see that the most probable speed v_{mp} is

$$12 \text{ m/s.}$$

*Optional Section***21.7 MEAN FREE PATH**

Most of us are familiar with the fact that the strong odor associated with a gas such as ammonia may take a fraction of a minute to diffuse throughout a room. However, because average molecular speeds are typically several hundred meters per second at room temperature, we might expect a diffusion time much less than 1 s. But, as we saw in Quick Quiz 21.1, molecules collide with one other because they are not geometrical points. Therefore, they do not travel from one side of a room to the other in a straight line. Between collisions, the molecules move with constant speed along straight lines. The average distance between collisions is called the **mean free path**. The path of an individual molecule is random and resembles that shown in Figure 21.13. As we would expect from this description, the mean free path is related to the diameter of the molecules and the density of the gas.

We now describe how to estimate the mean free path for a gas molecule. For this calculation, we assume that the molecules are spheres of diameter d . We see from Figure 21.14a that no two molecules collide unless their centers are less than a distance d apart as they approach each other. An equivalent way to describe the

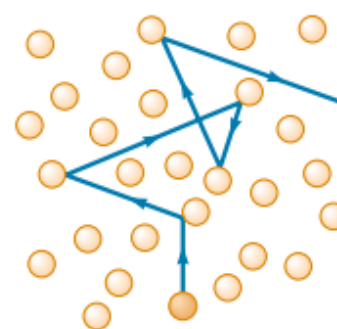


Figure 21.13 A molecule moving through a gas collides with other molecules in a random fashion. This behavior is sometimes referred to as a *random-walk process*. The mean free path increases as the number of molecules per unit volume decreases. Note that the motion is not limited to the plane of the paper.

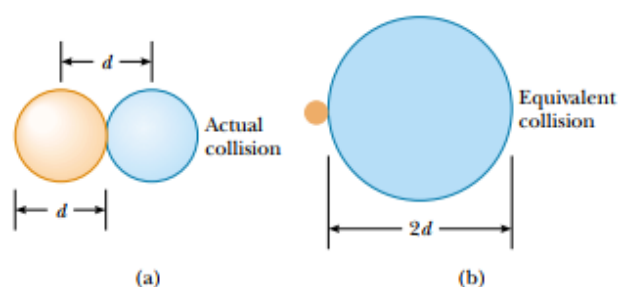


Figure 21.14 (a) Two spherical molecules, each of diameter d , collide if their centers are within a distance d of each other. (b) The collision between the two molecules is equivalent to a point molecule's colliding with a molecule having an effective diameter of $2d$.

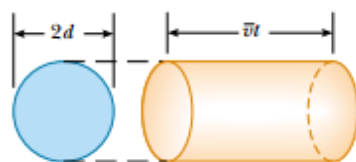


Figure 21.15 In a time t , a molecule of effective diameter $2d$ sweeps out a cylinder of length $\bar{v}t$, where \bar{v} is its average speed. In this time, it collides with every point molecule within this cylinder.

collisions is to imagine that one of the molecules has a diameter $2d$ and that the rest are geometrical points (Fig. 21.14b). Let us choose the large molecule to be one moving with the average speed \bar{v} . In a time t , this molecule travels a distance $\bar{v}t$. In this time interval, the molecule sweeps out a cylinder having a cross-sectional area πd^2 and a length $\bar{v}t$ (Fig. 21.15). Hence, the volume of the cylinder is $\pi d^2 \bar{v}t$. If n_V is the number of molecules per unit volume, then the number of point-size molecules in the cylinder is $(\pi d^2 \bar{v}t) n_V$. The molecule of equivalent diameter $2d$ collides with every molecule in this cylinder in the time t . Hence, the number of collisions in the time t is equal to the number of molecules in the cylinder, $(\pi d^2 \bar{v}t) n_V$.

The mean free path ℓ equals the average distance $\bar{v}t$ traveled in a time t divided by the number of collisions that occur in that time:

$$\ell = \frac{\bar{v}t}{(\pi d^2 \bar{v}t) n_V} = \frac{1}{\pi d^2 n_V}$$

Because the number of collisions in a time t is $(\pi d^2 \bar{v}t) n_V$, the number of collisions per unit time, or **collision frequency** f , is

$$f = \pi d^2 \bar{v} n_V$$

The inverse of the collision frequency is the average time between collisions, known as the **mean free time**.

Our analysis has assumed that molecules in the cylinder are stationary. When the motion of these molecules is included in the calculation, the correct results are

Mean free path

$$\ell = \frac{1}{\sqrt{2} \pi d^2 n_V} \quad (21.30)$$

Collision frequency

$$f = \sqrt{2} \pi d^2 \bar{v} n_V = \frac{\bar{v}}{\ell} \quad (21.31)$$

EXAMPLE 21.7 Bouncing Around in the Air

Approximate the air around you as a collection of nitrogen molecules, each of which has a diameter of 2.00×10^{-10} m. (a) How far does a typical molecule move before it collides with another molecule?

Solution Assuming that the gas is ideal, we can use the equation $PV = Nk_B T$ to obtain the number of molecules per unit volume under typical room conditions:

$$\begin{aligned} n_V &= \frac{N}{V} = \frac{P}{k_B T} = \frac{1.01 \times 10^5 \text{ N/m}^2}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} \\ &= 2.50 \times 10^{25} \text{ molecules/m}^3 \end{aligned}$$

Hence, the mean free path is

$$\begin{aligned} \ell &= \frac{1}{\sqrt{2} \pi d^2 n_V} \\ &= \frac{1}{\sqrt{2} \pi (2.00 \times 10^{-10} \text{ m})^2 (2.50 \times 10^{25} \text{ molecules/m}^3)} \\ &= 2.25 \times 10^{-7} \text{ m} \end{aligned}$$

This value is about 10^3 times greater than the molecular diameter.

(b) On average, how frequently does one molecule collide with another?

Solution Because the rms speed of a nitrogen molecule at 20.0°C is 511 m/s (see Table 21.1), we know from Equations 21.27 and 21.28 that $\bar{v} = (1.60/1.73)(511 \text{ m/s}) = 473 \text{ m/s}$. Therefore, the collision frequency is

$$f = \frac{\bar{v}}{\ell} = \frac{473 \text{ m/s}}{2.25 \times 10^{-7} \text{ m}} = 2.10 \times 10^9/\text{s}$$

The molecule collides with other molecules at the average rate of about two billion times each second!

The mean free path ℓ is *not* the same as the average separation between particles. In fact, the average separation d between particles is approximately $n_V^{-1/3}$. In this example, the average molecular separation is

$$d = \frac{1}{n_V^{1/3}} = \frac{1}{(2.5 \times 10^{25})^{1/3}} = 3.4 \times 10^{-9} \text{ m}$$

SUMMARY

The pressure of N molecules of an ideal gas contained in a volume V is

$$P = \frac{2}{3} \frac{N}{V} \left(\frac{1}{2} m \overline{v^2} \right) \quad (21.2)$$

The average translational kinetic energy per molecule of a gas, $\frac{1}{2} m \overline{v^2}$, is related to the temperature T of the gas through the expression

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad (21.4)$$

where k_B is Boltzmann's constant. Each translational degree of freedom (x , y , or z) has $\frac{1}{2} k_B T$ of energy associated with it.

The **theorem of equipartition of energy** states that the energy of a system in thermal equilibrium is equally divided among all degrees of freedom.

The total energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\text{int}} = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (21.10)$$

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature ΔT is

$$\Delta E_{\text{int}} = n C_V \Delta T \quad (21.12)$$

where C_V is the molar specific heat at constant volume.

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 $\gamma = C_P / C_V = \frac{5}{3}$.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$P V^\gamma = \text{constant} \quad (21.18)$$

The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy E is

$$n_V(E) = n_0 e^{-E/k_B T} \quad (21.25)$$

The **Maxwell-Boltzmann distribution function** describes the distribution of speeds of molecules in a gas:

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (21.26)$$

This expression enables us to calculate the **root-mean-square speed**, the **average speed**, and the **most probable speed**:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{3k_B T/m} = 1.73 \sqrt{k_B T/m} \quad (21.27)$$

$$\bar{v} = \sqrt{8k_B T/\pi m} = 1.60 \sqrt{k_B T/m} \quad (21.28)$$

$$v_{\text{mp}} = \sqrt{2k_B T/m} = 1.41 \sqrt{k_B T/m} \quad (21.29)$$