2 | THE KINETIC THEORY OF GASES

Figure 2.1 A volcanic eruption releases tons of gas and dust into the atmosphere. Most of the gas is water vapor, but several other gases are common, including greenhouse gases such as carbon dioxide and acidic pollutants such as sulfur dioxide. However, the emission of volcanic gas is not all bad: Many geologists believe that in the earliest stages of Earth’s formation, volcanic emissions formed the early atmosphere. (credit: modification of work by “Boaworm”/Wikimedia Commons)

Chapter Outline

2.1 Molecular Model of an Ideal Gas
2.2 Pressure, Temperature, and RMS Speed
2.3 Heat Capacity and Equipartition of Energy
2.4 Distribution of Molecular Speeds

Introduction

Gases are literally all around us—the air that we breathe is a mixture of gases. Other gases include those that make breads and cakes soft, those that make drinks fizzy, and those that burn to heat many homes. Engines and refrigerators depend on the behaviors of gases, as we will see in later chapters.

As we discussed in the preceding chapter, the study of heat and temperature is part of an area of physics known as thermodynamics, in which we require a system to be *macroscopic*, that is, to consist of a huge number (such as 10^{23}) of molecules. We begin by considering some macroscopic properties of gases: volume, pressure, and temperature. The simple model of a hypothetical “ideal gas” describes these properties of a gas very accurately under many conditions. We move from the ideal gas model to a more widely applicable approximation, called the Van der Waals model.

To understand gases even better, we must also look at them on the *microscopic* scale of molecules. In gases, the molecules interact weakly, so the microscopic behavior of gases is relatively simple, and they serve as a good introduction to systems of many molecules. The molecular model of gases is called the kinetic theory of gases and is one of the classic examples of a molecular model that explains everyday behavior.

2.1 | Molecular Model of an Ideal Gas

Learning Objectives

By the end of this section, you will be able to:

- Apply the ideal gas law to situations involving the pressure, volume, temperature, and the number of molecules of a gas
- Use the unit of moles in relation to numbers of molecules, and molecular and macroscopic masses
- Explain the ideal gas law in terms of moles rather than numbers of molecules
- Apply the van der Waals gas law to situations where the ideal gas law is inadequate

In this section, we explore the thermal behavior of gases. Our word “gas” comes from the Flemish word meaning “chaos,” first used for vapors by the seventeenth-century chemist J. B. van Helmont. The term was more appropriate than he knew, because gases consist of molecules moving and colliding with each other at random. This randomness makes the connection between the microscopic and macroscopic domains simpler for gases than for liquids or solids.

How do gases differ from solids and liquids? Under ordinary conditions, such as those of the air around us, the difference is that the molecules of gases are much farther apart than those of solids and liquids. Because the typical distances between molecules are large compared to the size of a molecule, as illustrated in **Figure 2.2**, the forces between them are considered negligible, except when they come into contact with each other during collisions. Also, at temperatures well above the boiling temperature, the motion of molecules is fast, and the gases expand rapidly to occupy all of the accessible volume. In contrast, in liquids and solids, molecules are closer together, and the behavior of molecules in liquids and solids is highly constrained by the molecules’ interactions with one another. The macroscopic properties of such substances depend strongly on the forces between the molecules, and since many molecules are interacting, the resulting “many-body problems” can be extremely complicated (see **Condensed Matter Physics (http://cnx.org/content/m58591/latest/)**).

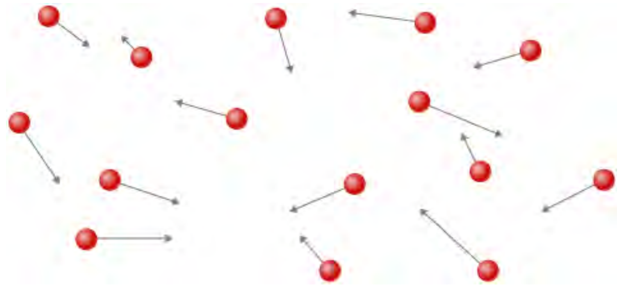

Figure 2.2 Atoms and molecules in a gas are typically widely separated. Because the forces between them are quite weak at these distances, the properties of a gas depend more on the number of atoms per unit volume and on temperature than on the type of atom.

The Gas Laws

In the previous chapter, we saw one consequence of the large intermolecular spacing in gases: Gases are easily compressed. **Table 1.2** shows that gases have larger coefficients of volume expansion than either solids or liquids. These large coefficients mean that gases expand and contract very rapidly with temperature changes. We also saw (in the section on thermal expansion) that most gases expand at the same rate or have the same coefficient of volume expansion, β. This raises a question: Why do all gases act in nearly the same way, when all the various liquids and solids have widely varying expansion rates?

To study how the pressure, temperature, and volume of a gas relate to one another, consider what happens when you pump air into a deflated car tire. The tire’s volume first increases in direct proportion to the amount of air injected, without much increase in the tire pressure. Once the tire has expanded to nearly its full size, the tire’s walls limit its volume expansion. If we continue to pump air into the tire, the pressure increases. When the car is driven and the tires flex, their temperature increases, and therefore the pressure increases even further (**Figure 2.3**).

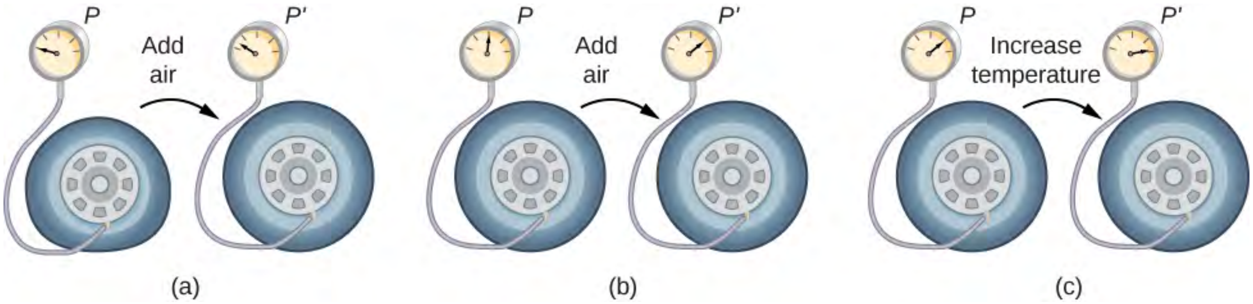

Figure 2.3 (a) When air is pumped into a deflated tire, its volume first increases without much increase in pressure. (b) When the tire is filled to a certain point, the tire walls resist further expansion, and the pressure increases with more air. (c) Once the tire is inflated, its pressure increases with temperature.

Figure 2.4 shows data from the experiments of Robert Boyle (1627–1691), illustrating what is now called Boyle's law: At constant temperature and number of molecules, the absolute pressure of a gas and its volume are inversely proportional. (Recall from **Fluid Mechanics (http://cnx.org/content/m58624/latest/)** that the absolute pressure is the true pressure and the gauge pressure is the absolute pressure minus the ambient pressure, typically atmospheric pressure.) The graph in **Figure 2.4** displays this relationship as an inverse proportionality of volume to pressure.

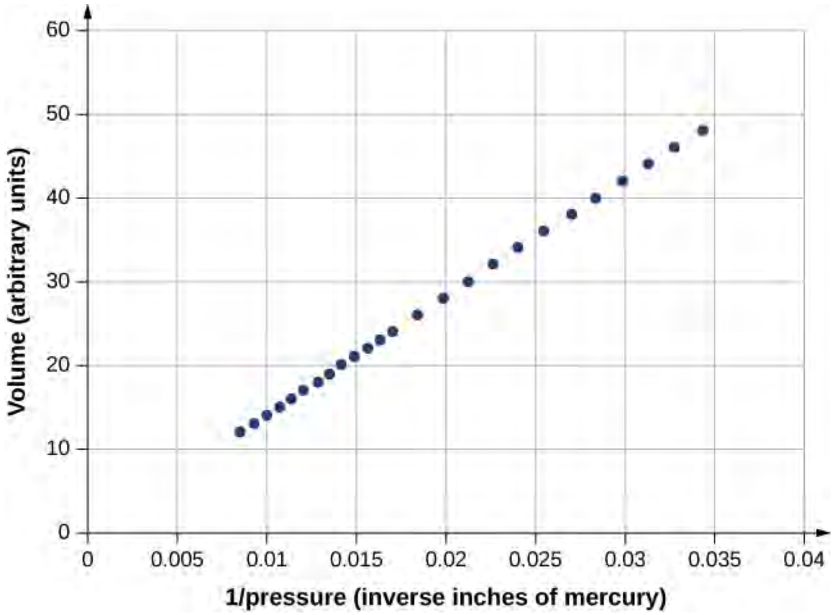

Figure 2.4 Robert Boyle and his assistant found that volume and pressure are inversely proportional. Here their data are plotted as V versus $1/p$; the linearity of the graph shows the inverse proportionality. The number shown as the volume is actually the height in inches of air in a cylindrical glass tube. The actual volume was that height multiplied by the cross-sectional area of the tube, which Boyle did not publish. The data are from Boyle's book *A Defence of the Doctrine Touching the Spring and Weight of the Air*…, p. 60.[1]

Figure 2.5 shows experimental data illustrating what is called Charles's law, after Jacques Charles (1746–1823). Charles's law states that at constant pressure and number of molecules, the volume of a gas is proportional to its absolute temperature.

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[1] http://bvpb.mcu.es/en/consulta/registro.cmd?id=406806

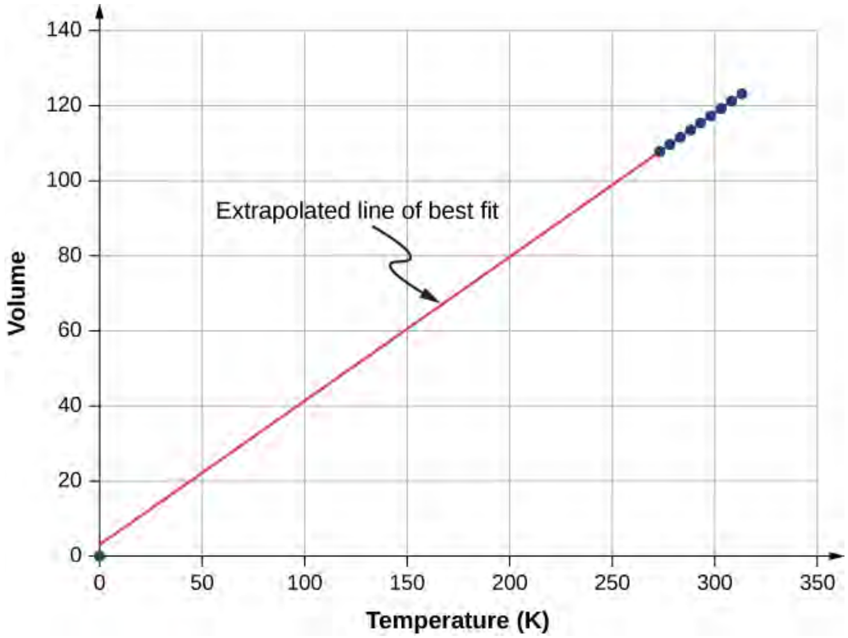

Figure 2.5 Experimental data showing that at constant pressure, volume is approximately proportional to temperature. The best-fit line passes approximately through the origin.[2]

Similar is Amonton's or Gay-Lussac's law, which states that at constant volume and number of molecules, the pressure is proportional to the temperature. That law is the basis of the constant-volume gas thermometer, discussed in the previous chapter. (The histories of these laws and the appropriate credit for them are more complicated than can be discussed here.)

It is known experimentally that for gases at low density (such that their molecules occupy a negligible fraction of the total volume) and at temperatures well above the boiling point, these proportionalities hold to a good approximation. Not surprisingly, with the other quantities held constant, either pressure or volume is proportional to the number of molecules. More surprisingly, when the proportionalities are combined into a single equation, the constant of proportionality is independent of the composition of the gas. The resulting equation for all gases applies in the limit of low density and high temperature; it's the same for oxygen as for helium or uranium hexafluoride. A gas at that limit is called an **ideal gas**; it obeys the **ideal gas law**, which is also called the equation of state of an ideal gas.

Ideal Gas Law

The ideal gas law states that

$$pV = Nk_B T, \tag{2.1}$$

where p is the absolute pressure of a gas, V is the volume it occupies, N is the number of molecules in the gas, and T is its absolute temperature.

The constant k_B is called the **Boltzmann constant** in honor of the Austrian physicist Ludwig Boltzmann (1844–1906) and has the value

$$k_B = 1.38 \times 10^{-23} \text{ J/K}.$$

The ideal gas law describes the behavior of any real gas when its density is low enough or its temperature high enough that it is far from liquefaction. This encompasses many practical situations. In the next section, we'll see why it's independent of the type of gas.

In many situations, the ideal gas law is applied to a sample of gas with a constant number of molecules; for instance, the gas may be in a sealed container. If N is constant, then solving for N shows that pV/T is constant. We can write that fact in a convenient form:

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[2] http://chemed.chem.purdue.edu/genchem/history/charles.html

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}, \tag{2.2}$$

where the subscripts 1 and 2 refer to any two states of the gas at different times. Again, the temperature must be expressed in kelvin and the pressure must be absolute pressure, which is the sum of gauge pressure and atmospheric pressure.

Example 2.1

Calculating Pressure Changes Due to Temperature Changes

Suppose your bicycle tire is fully inflated, with an absolute pressure of 7.00×10^5 Pa (a gauge pressure of just under 90.0 lb/in.^2) at a temperature of $18.0\,°\text{C}$. What is the pressure after its temperature has risen to $35.0\,°\text{C}$ on a hot day? Assume there are no appreciable leaks or changes in volume.

Strategy

The pressure in the tire is changing only because of changes in temperature. We know the initial pressure $p_0 = 7.00 \times 10^5$ Pa, the initial temperature $T_0 = 18.0\,°\text{C}$, and the final temperature $T_\text{f} = 35.0\,°\text{C}$. We must find the final pressure p_f. Since the number of molecules is constant, we can use the equation

$$\frac{p_\text{f} V_\text{f}}{T_\text{f}} = \frac{p_0 V_0}{T_0}.$$

Since the volume is constant, V_f and V_0 are the same and they divide out. Therefore,

$$\frac{p_\text{f}}{T_\text{f}} = \frac{p_0}{T_0}.$$

We can then rearrange this to solve for p_f :

$$p_\text{f} = p_0 \frac{T_\text{f}}{T_0},$$

where the temperature must be in kelvin.

Solution

1. Convert temperatures from degrees Celsius to kelvin

$$T_0 = (18.0 + 273)\text{K} = 291 \text{ K},$$

$$T_\text{f} = (35.0 + 273)\text{K} = 308 \text{ K}.$$

2. Substitute the known values into the equation,

$$p_\text{f} = p_0 \frac{T_\text{f}}{T_0} = 7.00 \times 10^5 \text{ Pa} \left(\frac{308 \text{ K}}{291 \text{ K}}\right) = 7.41 \times 10^5 \text{ Pa}.$$

Significance

The final temperature is about 6% greater than the original temperature, so the final pressure is about 6% greater as well. Note that *absolute pressure* (see **Fluid Mechanics (http://cnx.org/content/m58624/latest/)**) and *absolute temperature* (see **Temperature and Heat**) must be used in the ideal gas law.

Example 2.2

Calculating the Number of Molecules in a Cubic Meter of Gas

How many molecules are in a typical object, such as gas in a tire or water in a glass? This calculation can give us an idea of how large N typically is. Let's calculate the number of molecules in the air that a typical healthy young adult inhales in one breath, with a volume of 500 mL, at *standard temperature and pressure* (STP), which is defined as $0\,°\text{C}$ and atmospheric pressure. (Our young adult is apparently outside in winter.)

Strategy

Because pressure, volume, and temperature are all specified, we can use the ideal gas law, $pV = Nk_B T$, to find N.

Solution

1. Identify the knowns.

$$T = 0\,°\text{C} = 273\text{ K},\ \ p = 1.01\times 10^5\text{ Pa},\ \ V = 500\text{ mL} = 5\times 10^{-4}\ \text{m}^3,\ \ k_B = 1.38\times 10^{-23}\text{ J/K}$$

2. Substitute the known values into the equation and solve for N.

$$N = \frac{pV}{k_B T} = \frac{(1.01\times 10^5\text{ Pa})\,(5\times 10^{-4}\text{ m}^3)}{(1.38\times 10^{-23}\text{ J/K})\,(273\text{ K})} = 1.34\times 10^{22}\text{ molecules}$$

Significance

N is huge, even in small volumes. For example, 1 cm^3 of a gas at STP contains 2.68×10^{19} molecules. Once again, note that our result for N is the same for all types of gases, including mixtures.

As we observed in the chapter on fluid mechanics, pascals are N/m^2, so $\text{Pa}\cdot\text{m}^3 = \text{N}\cdot\text{m} = \text{J}$. Thus, our result for N is dimensionless, a pure number that could be obtained by counting (in principle) rather than measuring. As it is the number of molecules, we put "molecules" after the number, keeping in mind that it is an aid to communication rather than a unit.

Moles and Avogadro's Number

It is often convenient to measure the amount of substance with a unit on a more human scale than molecules. The SI unit for this purpose was developed by the Italian scientist Amedeo Avogadro (1776–1856). (He worked from the hypothesis that equal volumes of gas at equal pressure and temperature contain equal numbers of molecules, independent of the type of gas. As mentioned above, this hypothesis has been confirmed when the ideal gas approximation applies.) A **mole** (abbreviated mol) is defined as the amount of any substance that contains as many molecules as there are atoms in exactly 12 grams (0.012 kg) of carbon-12. (Technically, we should say "formula units," not "molecules," but this distinction is irrelevant for our purposes.) The number of molecules in one mole is called **Avogadro's number** (N_A), and the value of Avogadro's number is now known to be

$$N_A = 6.02\times 10^{23}\text{ mol}^{-1}.$$

We can now write $N = N_A n$, where n represents the number of moles of a substance.

Avogadro's number relates the mass of an amount of substance in grams to the number of protons and neutrons in an atom or molecule (12 for a carbon-12 atom), which roughly determine its mass. It's natural to define a unit of mass such that the mass of an atom is approximately equal to its number of neutrons and protons. The unit of that kind accepted for use with the SI is the *unified atomic mass unit* (u), also called the *dalton*. Specifically, a carbon-12 atom has a mass of exactly 12 u, so that its molar mass M in grams per mole is numerically equal to the mass of one carbon-12 atom in u. That equality holds for any substance. In other words, N_A is not only the conversion from numbers of molecules to moles, but it is also the conversion from u to grams: $6.02\times 10^{23}\text{ u} = 1\text{ g}$. See **Figure 2.6**.

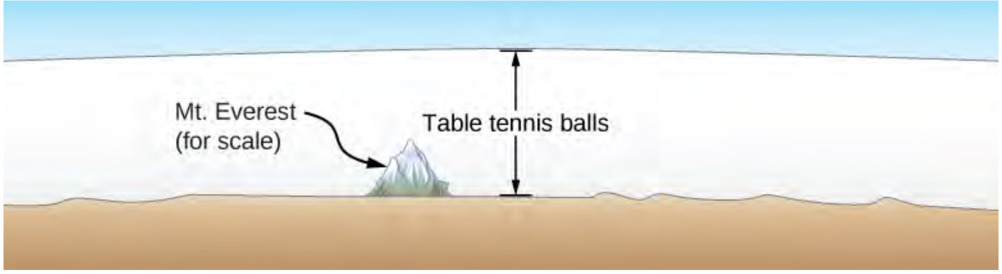


Figure 2.6 How big is a mole? On a macroscopic level, Avogadro's number of table tennis balls would cover Earth to a depth of about 40 km.

Now letting m_s stand for the mass of a sample of a substance, we have $m_s = nM$. Letting m stand for the mass of a molecule, we have $M = N_A m$.

2.1 Check Your Understanding The recommended daily amount of vitamin B_3 or niacin, $C_6NH_5O_2$, for women who are not pregnant or nursing, is 14 mg. Find the number of molecules of niacin in that amount.

2.2 Check Your Understanding The density of air in a classroom $(p = 1.00\,\text{atm}$ and $T = 20\,°\text{C})$ is $1.28\,\text{kg/m}^3$. At what pressure is the density $0.600\,\text{kg/m}^3$ if the temperature is kept constant?

The Ideal Gas Law Restated using Moles

A very common expression of the ideal gas law uses the number of moles in a sample, *n*, rather than the number of molecules, *N*. We start from the ideal gas law,

$$pV = Nk_B T,$$

and multiply and divide the right-hand side of the equation by Avogadro's number N_A. This gives us

$$pV = \frac{N}{N_A} N_A\, k_B T.$$

Note that $n = N/N_A$ is the number of moles. We define the **universal gas constant** as $R = N_A k_B$, and obtain the ideal gas law in terms of moles.

Ideal Gas Law (in terms of moles)

In terms of number of moles *n*, the ideal gas law is written as

$$pV = nRT. \tag{2.3}$$

In SI units,

$$R = N_A k_B = \left(6.02 \times 10^{23}\ \text{mol}^{-1}\right)\left(1.38 \times 10^{-23}\ \frac{\text{J}}{\text{K}}\right) = 8.31\ \frac{\text{J}}{\text{mol} \cdot \text{K}}.$$

In other units,

$$R = 1.99 \frac{\text{cal}}{\text{mol} \cdot \text{K}} = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}.$$

You can use whichever value of *R* is most convenient for a particular problem.

Example 2.3

Density of Air at STP and in a Hot Air Balloon

Calculate the density of dry air (a) under standard conditions and (b) in a hot air balloon at a temperature of $120\,°\text{C}$. Dry air is approximately $78\%\ \text{N}_2,\ 21\%\ \text{O}_2,$ and $1\%\ \text{Ar}$.

Strategy and Solution

a. We are asked to find the density, or mass per cubic meter. We can begin by finding the molar mass. If we have a hundred molecules, of which 78 are nitrogen, 21 are oxygen, and 1 is argon, the average molecular mass is $\frac{78\,m_{\text{N}_2} + 21\,m_{\text{O}_2} + m_{\text{Ar}}}{100}$, or the mass of each constituent multiplied by its percentage. The same applies to the molar mass, which therefore is

$$M = 0.78\,M_{\text{N}_2} + 0.21\,M_{\text{O}_2} + 0.01\,M_{\text{Ar}} = 29.0\ \text{g/mol}.$$

Now we can find the number of moles per cubic meter. We use the ideal gas law in terms of moles, $pV = nRT$, with $p = 1.00\ \text{atm}$, $T = 273\ \text{K}$, $V = 1\ \text{m}^3$, and $R = 8.31\ \text{J/mol} \cdot \text{K}$. The most convenient choice for R in this case is $R = 8.31\ \text{J/mol} \cdot \text{K}$ because the known quantities are in SI units:

$$n = \frac{pV}{RT} = \frac{(1.01 \times 10^5\ \text{Pa})\,(1\ \text{m}^3)}{(8.31\ \text{J/mol} \cdot \text{K})\,(273\ \text{K})} = 44.5\ \text{mol}.$$

Then, the mass m_s of that air is

$$m_\text{s} = nM = (44.5\ \text{mol})(29.0\ \text{g/mol}) = 1290\ \text{g} = 1.29\ \text{kg}.$$

Finally the density of air at STP is

$$\rho = \frac{m_\text{s}}{V} = \frac{1.29\ \text{kg}}{1\ \text{m}^3} = 1.29\ \text{kg/m}^3.$$

b. The air pressure inside the balloon is still 1 atm because the bottom of the balloon is open to the atmosphere. The calculation is the same except that we use a temperature of $120\,°\text{C}$, which is 393 K. We can repeat the calculation in (a), or simply observe that the density is proportional to the number of moles, which is inversely proportional to the temperature. Then using the subscripts 1 for air at STP and 2 for the hot air, we have

$$\rho_2 = \frac{T_1}{T_2}\rho_1 = \frac{273\ \text{K}}{393\ \text{K}}(1.29\ \text{kg/m}^3) = 0.896\ \text{kg/m}^3.$$

Significance

Using the methods of **Archimedes' Principle and Buoyancy (http://cnx.org/content/m58356/latest/)**, we can find that the net force on $2200\ \text{m}^3$ of air at $120\,°\text{C}$ is $F_b - F_g = \rho_{\text{atmosphere}} Vg - \rho_{\text{hot air}} Vg = 8.49 \times 10^3\ \text{N}$, or enough to lift about 867 kg. The mass density and molar density of air at STP, found above, are often useful numbers. From the molar density, we can easily determine another useful number, the volume of a mole of any ideal gas at STP, which is 22.4 L.

2.3 Check Your Understanding Liquids and solids have densities on the order of 1000 times greater than gases. Explain how this implies that the distances between molecules in gases are on the order of 10 times greater than the size of their molecules.

The ideal gas law is closely related to energy: The units on both sides of the equation are joules. The right-hand side of the ideal gas law equation is $Nk_\text{B}T$. This term is roughly the total translational kinetic energy (which, when discussing gases, refers to the energy of translation of a molecule, not that of vibration of its atoms or rotation) of N molecules at an absolute temperature *T*, as we will see formally in the next section. The left-hand side of the ideal gas law equation is *pV*. As mentioned in the example on the number of molecules in an ideal gas, pressure multiplied by volume has units of energy. The energy of a gas can be changed when the gas does work as it increases in volume, something we explored in the preceding chapter, and the amount of work is related to the pressure. This is the process that occurs in gasoline or steam engines and turbines, as we'll see in the next chapter.

Problem-Solving Strategy: The Ideal Gas Law

Step 1. Examine the situation to determine that an ideal gas is involved. Most gases are nearly ideal unless they are close to the boiling point or at pressures far above atmospheric pressure.

Step 2. Make a list of what quantities are given or can be inferred from the problem as stated (identify the known quantities).

Step 3. Identify exactly what needs to be determined in the problem (identify the unknown quantities). A written list is useful.

Step 4. Determine whether the number of molecules or the number of moles is known or asked for to decide whether to use the ideal gas law as $pV = Nk_B T,$ where *N* is the number of molecules, or $pV = nRT,$ where *n* is the number of moles.

Step 5. Convert known values into proper SI units (K for temperature, Pa for pressure, m^3 for volume, molecules for *N*, and moles for *n*). If the units of the knowns are consistent with one of the non-SI values of *R*, you can leave them in those units. Be sure to use absolute temperature and absolute pressure.

Step 6. Solve the ideal gas law for the quantity to be determined (the unknown quantity). You may need to take a ratio of final states to initial states to eliminate the unknown quantities that are kept fixed.

Step 7. Substitute the known quantities, along with their units, into the appropriate equation and obtain numerical solutions complete with units.

Step 8. Check the answer to see if it is reasonable: Does it make sense?

The Van der Waals Equation of State

We have repeatedly noted that the ideal gas law is an approximation. How can it be improved upon? The **van der Waals equation of state** (named after the Dutch physicist Johannes van der Waals, 1837−1923) improves it by taking into account two factors. First, the attractive forces between molecules, which are stronger at higher density and reduce the pressure, are taken into account by adding to the pressure a term equal to the square of the molar density multiplied by a positive coefficient *a*. Second, the volume of the molecules is represented by a positive constant *b*, which can be thought of as the volume of a mole of molecules. This is subtracted from the total volume to give the remaining volume that the molecules can move in. The constants *a* and *b* are determined experimentally for each gas. The resulting equation is

$$\left[p + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT. \tag{2.4}$$

In the limit of low density (small *n*), the *a* and *b* terms are negligible, and we have the ideal gas law, as we should for low density. On the other hand, if $V - nb$ is small, meaning that the molecules are very close together, the pressure must be higher to give the same *nRT*, as we would expect in the situation of a highly compressed gas. However, the increase in pressure is less than that argument would suggest, because at high density the $(n/V)^2$ term is significant. Since it's positive, it causes a lower pressure to give the same *nRT*.

The van der Waals equation of state works well for most gases under a wide variety of conditions. As we'll see in the next module, it even predicts the gas-liquid transition.

pV Diagrams

We can examine aspects of the behavior of a substance by plotting a ***pV* diagram**, which is a graph of pressure versus volume. When the substance behaves like an ideal gas, the ideal gas law $pV = nRT$ describes the relationship between its pressure and volume. On a pV diagram, it's common to plot an *isotherm*, which is a curve showing p as a function of V with the number of molecules and the temperature fixed. Then, for an ideal gas, $pV = \text{constant}.$ For example, the volume of the gas decreases as the pressure increases. The resulting graph is a hyperbola.

However, if we assume the van der Waals equation of state, the isotherms become more interesting, as shown in Figure 2.7. At high temperatures, the curves are approximately hyperbolas, representing approximately ideal behavior at various fixed temperatures. At lower temperatures, the curves look less and less like hyperbolas—that is, the gas is not behaving ideally. There is a **critical temperature** T_c at which the curve has a point with zero slope. Below that temperature, the curves do not decrease monotonically; instead, they each have a "hump," meaning that for a certain range of volume, increasing the volume increases the pressure.

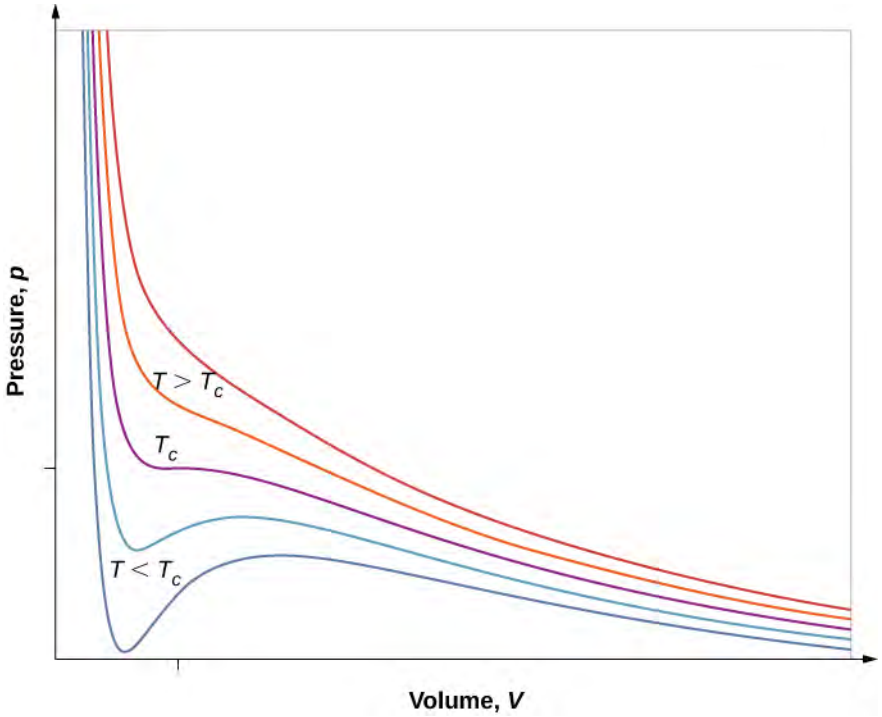
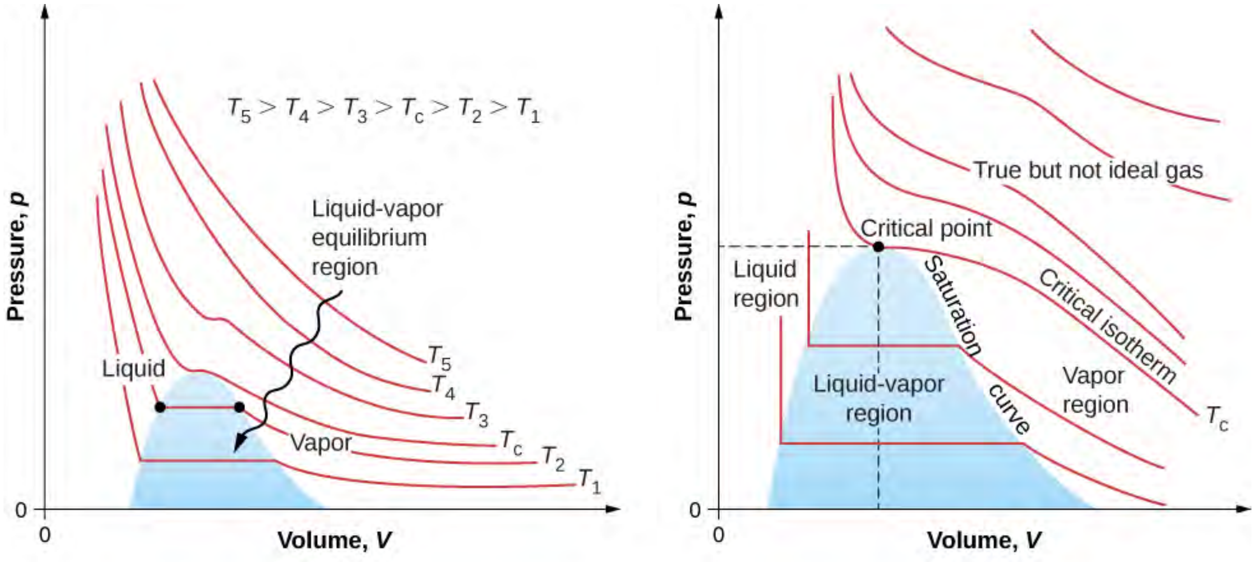


Figure 2.7 pV diagram for a Van der Waals gas at various temperatures. The red curves are calculated at temperatures above the critical temperature and the blue curves at temperatures below it. The blue curves have an oscillation in which volume (V) increases with increasing temperature (T), an impossible situation, so they must be corrected as in Figure 2.8. (credit: "Eman"/Wikimedia Commons)

Such behavior would be completely unphysical. Instead, the curves are understood as describing a liquid-gas phase transition. The oscillating part of the curve is replaced by a horizontal line, showing that as the volume increases at constant temperature, the pressure stays constant. That behavior corresponds to boiling and condensation; when a substance is at its boiling temperature for a particular pressure, it can increase in volume as some of the liquid turns to gas, or decrease as some of the gas turns to liquid, without any change in temperature or pressure.

Figure 2.8 shows similar isotherms that are more realistic than those based on the van der Waals equation. The steep parts of the curves to the left of the transition region show the liquid phase, which is almost incompressible—a slight decrease in volume requires a large increase in pressure. The flat parts show the liquid-gas transition; the blue regions that they define represent combinations of pressure and volume where liquid and gas can coexist.



(a) (b)

Figure 2.8 *pV* diagrams. (a) Each curve (isotherm) represents the relationship between *p* and *V* at a fixed temperature; the upper curves are at higher temperatures. The lower curves are not hyperbolas because the gas is no longer an ideal gas. (b) An expanded portion of the *pV* diagram for low temperatures, where the phase can change from a gas to a liquid. The term "vapor" refers to the gas phase when it exists at a temperature below the boiling temperature.

The isotherms above T_c do not go through the liquid-gas transition. Therefore, liquid cannot exist above that temperature, which is the critical temperature (described in the chapter on temperature and heat). At sufficiently low pressure above that temperature, the gas has the density of a liquid but will not condense; the gas is said to be **supercritical**. At higher pressure, it is solid. Carbon dioxide, for example, has no liquid phase at a temperature above $31.0\,°C$. The critical pressure is the maximum pressure at which the liquid can exist. The point on the *pV* diagram at the critical pressure and temperature is the critical point (which you learned about in the chapter on temperature and heat). **Table 2.1** lists representative critical temperatures and pressures.

Substance	Critical temperature		Critical pressure	
	K	°C	Pa	atm
Water	647.4	374.3	22.12×10^6	219.0
Sulfur dioxide	430.7	157.6	7.88×10^6	78.0
Ammonia	405.5	132.4	11.28×10^6	111.7
Carbon dioxide	304.2	31.1	7.39×10^6	73.2
Oxygen	154.8	–118.4	5.08×10^6	50.3
Nitrogen	126.2	–146.9	3.39×10^6	33.6
Hydrogen	33.3	–239.9	1.30×10^6	12.9
Helium	5.3	–267.9	0.229×10^6	2.27

Table 2.1 Critical Temperatures and Pressures for Various Substances

2.2 | Pressure, Temperature, and RMS Speed

Learning Objectives

By the end of this section, you will be able to:

- Explain the relations between microscopic and macroscopic quantities in a gas
- Solve problems involving mixtures of gases
- Solve problems involving the distance and time between a gas molecule's collisions

We have examined pressure and temperature based on their macroscopic definitions. Pressure is the force divided by the area on which the force is exerted, and temperature is measured with a thermometer. We can gain a better understanding of pressure and temperature from the **kinetic theory of gases**, the theory that relates the macroscopic properties of gases to the motion of the molecules they consist of. First, we make two assumptions about molecules in an ideal gas.

1. There is a very large number N of molecules, all identical and each having mass m.
2. The molecules obey Newton's laws and are in continuous motion, which is random and isotropic, that is, the same in all directions.

To derive the ideal gas law and the connection between microscopic quantities such as the energy of a typical molecule and macroscopic quantities such as temperature, we analyze a sample of an ideal gas in a rigid container, about which we make two further assumptions:

3. The molecules are much smaller than the average distance between them, so their total volume is much less than that of their container (which has volume V). In other words, we take the Van der Waals constant b, the volume of a mole of gas molecules, to be negligible compared to the volume of a mole of gas in the container.
4. The molecules make perfectly elastic collisions with the walls of the container and with each other. Other forces on them, including gravity and the attractions represented by the Van der Waals constant a, are negligible (as is necessary for the assumption of isotropy).

The collisions between molecules do not appear in the derivation of the ideal gas law. They do not disturb the derivation either, since collisions between molecules moving with random velocities give new random velocities. Furthermore, if the velocities of gas molecules in a container are initially not random and isotropic, molecular collisions are what make them random and isotropic.

We make still further assumptions that simplify the calculations but do not affect the result. First, we let the container be a rectangular box. Second, we begin by considering *monatomic* gases, those whose molecules consist of single atoms, such as helium. Then, we can assume that the atoms have no energy except their translational kinetic energy; for instance, they have neither rotational nor vibrational energy. (Later, we discuss the validity of this assumption for real monatomic gases and dispense with it to consider diatomic and polyatomic gases.)

Figure 2.9 shows a collision of a gas molecule with the wall of a container, so that it exerts a force on the wall (by Newton's third law). These collisions are the source of pressure in a gas. As the number of molecules increases, the number of collisions, and thus the pressure, increases. Similarly, if the average velocity of the molecules is higher, the gas pressure is higher.

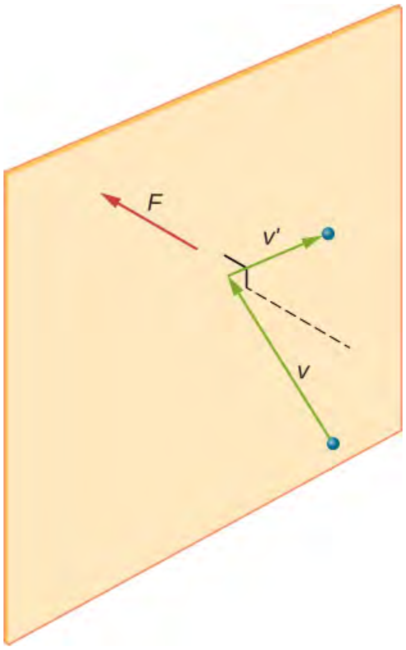


Figure 2.9 When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

In a sample of gas in a container, the randomness of the molecular motion causes the number of collisions of molecules with any part of the wall in a given time to fluctuate. However, because a huge number of molecules collide with the wall in a short time, the number of collisions on the scales of time and space we measure fluctuates by only a tiny, usually unobservable fraction from the average. We can compare this situation to that of a casino, where the outcomes of the bets are random and the casino's takings fluctuate by the minute and the hour. However, over long times such as a year, the casino's takings are very close to the averages expected from the odds. A tank of gas has enormously more molecules than a casino has bettors in a year, and the molecules make enormously more collisions in a second than a casino has bets.

A calculation of the average force exerted by molecules on the walls of the box leads us to the ideal gas law and to the connection between temperature and molecular kinetic energy. (In fact, we will take two averages: one over time to get the average force exerted by one molecule with a given velocity, and then another average over molecules with different velocities.) This approach was developed by Daniel Bernoulli (1700–1782), who is best known in physics for his work on fluid flow (hydrodynamics). Remarkably, Bernoulli did this work before Dalton established the view of matter as consisting of atoms.

Figure 2.10 shows a container full of gas and an expanded view of an elastic collision of a gas molecule with a wall of the container, broken down into components. We have assumed that a molecule is small compared with the separation of molecules in the gas, and that its interaction with other molecules can be ignored. Under these conditions, the ideal gas law is experimentally valid. Because we have also assumed the wall is rigid and the particles are points, the collision is elastic (by conservation of energy—there's nowhere for a particle's kinetic energy to go). Therefore, the molecule's kinetic energy remains constant, and hence, its speed and the magnitude of its momentum remain constant as well. This assumption is not always valid, but the results in the rest of this module are also obtained in models that let the molecules exchange energy and momentum with the wall.

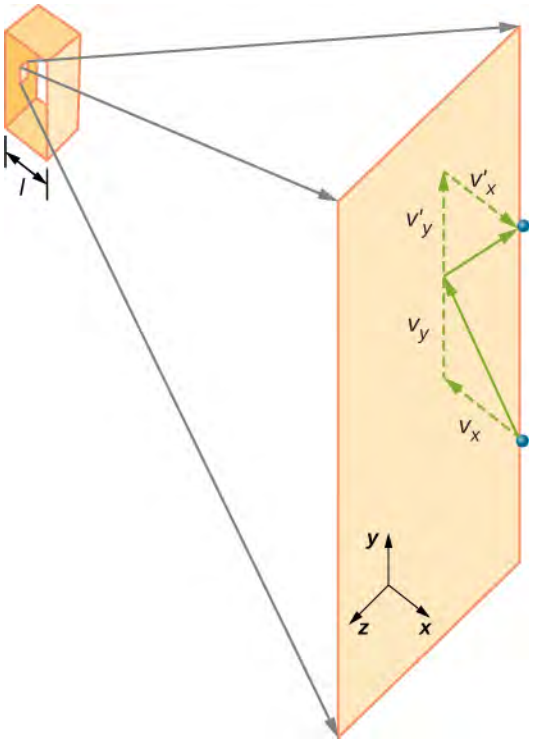


Figure 2.10 Gas in a box exerts an outward pressure on its walls. A molecule colliding with a rigid wall has its velocity and momentum in the *x*-direction reversed. This direction is perpendicular to the wall. The components of its velocity momentum in the *y*- and *z*-directions are not changed, which means there is no force parallel to the wall.

If the molecule's velocity changes in the *x*-direction, its momentum changes from $-mv_x$ to $+mv_x$. Thus, its change in momentum is $\Delta mv = +mv_x - (-mv_x) = 2mv_x$. According to the impulse-momentum theorem given in the chapter on linear momentum and collisions, the force exerted on the *i*th molecule, where *i* labels the molecules from 1 to *N*, is given by

$$F_i = \frac{\Delta p_i}{\Delta t} = \frac{2mv_{ix}}{\Delta t}.$$

(In this equation alone, *p* represents momentum, not pressure.) There is no force between the wall and the molecule except while the molecule is touching the wall. During the short time of the collision, the force between the molecule and wall is relatively large, but that is not the force we are looking for. We are looking for the average force, so we take Δt to be the average time between collisions of the given molecule with this wall, which is the time in which we expect to find one collision. Let *l* represent the length of the box in the *x*-direction. Then Δt is the time the molecule would take to go across the box and back, a distance 2*l*, at a speed of v_x. Thus $\Delta t = 2l/v_x$, and the expression for the force becomes

$$F_i = \frac{2mv_{ix}}{2l/v_{ix}} = \frac{mv_{ix}^2}{l}.$$

This force is due to *one* molecule. To find the total force on the wall, *F*, we need to add the contributions of all *N* molecules:

$$F = \sum_{i=1}^{N} F_i = \sum_{i=1}^{N} \frac{mv_{ix}^2}{l} = \frac{m}{l} \sum_{i=1}^{N} v_{ix}^2.$$

We now use the definition of the average, which we denote with a bar, to find the force:

$$F = N\frac{m}{l}\left(\frac{1}{N}\sum_{i=1}^{N} v_{ix}^2\right) = N\frac{m\overline{v_x^2}}{l}.$$

We want the force in terms of the speed *v*, rather than the *x*-component of the velocity. Note that the total velocity squared is the sum of the squares of its components, so that

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}.$$

With the assumption of isotropy, the three averages on the right side are equal, so

$$\overline{v^2} = 3\overline{v_{ix}^2}.$$

Substituting this into the expression for *F* gives

$$F = N\frac{m\overline{v^2}}{3l}.$$

The pressure is *F*/*A*, so we obtain

$$p = \frac{F}{A} = N\frac{m\overline{v^2}}{3Al} = \frac{Nm\overline{v^2}}{3V},$$

where we used $V = Al$ for the volume. This gives the important result

$$pV = \frac{1}{3}Nm\overline{v^2}. \tag{2.5}$$

Combining this equation with $pV = Nk_\text{B}T$ gives

$$\frac{1}{3}Nm\overline{v^2} = Nk_\text{B}T.$$

We can get the average kinetic energy of a molecule, $\frac{1}{2}m\overline{v^2}$, from the left-hand side of the equation by dividing out *N* and multiplying by 3/2.

Average Kinetic Energy per Molecule

The average kinetic energy of a molecule is directly proportional to its absolute temperature:

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_\text{B}T. \tag{2.6}$$

The equation $\overline{K} = \frac{3}{2}k_\text{B}T$ is the average kinetic energy per molecule. Note in particular that nothing in this equation depends on the molecular mass (or any other property) of the gas, the pressure, or anything but the temperature. If samples of helium and xenon gas, with very different molecular masses, are at the same temperature, the molecules have the same average kinetic energy.

The **internal energy** of a thermodynamic system is the sum of the mechanical energies of all of the molecules in it. We can now give an equation for the internal energy of a monatomic ideal gas. In such a gas, the molecules' only energy is their translational kinetic energy. Therefore, denoting the internal energy by E_int, we simply have $E_\text{int} = N\overline{K}$, or

$$E_\text{int} = \frac{3}{2}Nk_\text{B}T. \tag{2.7}$$

Often we would like to use this equation in terms of moles:

$$E_\text{int} = \frac{3}{2}nRT.$$

We can solve $\bar{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$ for a typical speed of a molecule in an ideal gas in terms of temperature to determine what is known as the *root-mean-square* (*rms*) *speed* of a molecule.

RMS Speed of a Molecule

The **root-mean-square (rms) speed** of a molecule, or the square root of the average of the square of the speed $\overline{v^2}$, is

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}. \tag{2.8}$$

The rms speed is not the average or the most likely speed of molecules, as we will see in **Distribution of Molecular Speeds**, but it provides an easily calculated estimate of the molecules' speed that is related to their kinetic energy. Again we can write this equation in terms of the gas constant R and the molar mass M in kg/mol:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{2.9}$$

We digress for a moment to answer a question that may have occurred to you: When we apply the model to atoms instead of theoretical point particles, does rotational kinetic energy change our results? To answer this question, we have to appeal to quantum mechanics. In quantum mechanics, rotational kinetic energy cannot take on just any value; it's limited to a discrete set of values, and the smallest value is inversely proportional to the rotational inertia. The rotational inertia of an atom is tiny because almost all of its mass is in the nucleus, which typically has a radius less than $10^{-14}\ \text{m}$. Thus the minimum rotational energy of an atom is much more than $\frac{1}{2}k_B T$ for any attainable temperature, and the energy available is not enough to make an atom rotate. We will return to this point when discussing diatomic and polyatomic gases in the next section.

Example 2.4

Calculating Kinetic Energy and Speed of a Gas Molecule

(a) What is the average kinetic energy of a gas molecule at $20.0\,^\circ\text{C}$ (room temperature)? (b) Find the rms speed of a nitrogen molecule (N_2) at this temperature.

Strategy

(a) The known in the equation for the average kinetic energy is the temperature:

$$\bar{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T.$$

Before substituting values into this equation, we must convert the given temperature into kelvin: $T = (20.0 + 273)\ \text{K} = 293\ \text{K}.$ We can find the rms speed of a nitrogen molecule by using the equation

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}},$$

but we must first find the mass of a nitrogen molecule. Obtaining the molar mass of nitrogen N_2 from the periodic table, we find

$$m = \frac{M}{N_A} = \frac{2\,(14.0067) \times 10^{-3}\ \text{kg/mol})}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 4.65 \times 10^{-26}\ \text{kg}.$$

Solution

a. The temperature alone is sufficient for us to find the average translational kinetic energy. Substituting the temperature into the translational kinetic energy equation gives

$$\bar{K} = \frac{3}{2}k_B T = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = 6.07 \times 10^{-21} \text{ J}.$$

b. Substituting this mass and the value for k_B into the equation for v_{rms} yields

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{4.65 \times 10^{-26} \text{ kg}}} = 511 \text{ m/s}.$$

Significance

Note that the average kinetic energy of the molecule is independent of the type of molecule. The average translational kinetic energy depends only on absolute temperature. The kinetic energy is very small compared to macroscopic energies, so that we do not feel when an air molecule is hitting our skin. On the other hand, it is much greater than the typical difference in gravitational potential energy when a molecule moves from, say, the top to the bottom of a room, so our neglect of gravitation is justified in typical real-world situations. The rms speed of the nitrogen molecule is surprisingly large. These large molecular velocities do not yield macroscopic movement of air, since the molecules move in all directions with equal likelihood. The *mean free path* (the distance a molecule moves on average between collisions, discussed a bit later in this section) of molecules in air is very small, so the molecules move rapidly but do not get very far in a second. The high value for rms speed is reflected in the speed of sound, which is about 340 m/s at room temperature. The higher the rms speed of air molecules, the faster sound vibrations can be transferred through the air. The speed of sound increases with temperature and is greater in gases with small molecular masses, such as helium (see **Figure 2.11**).

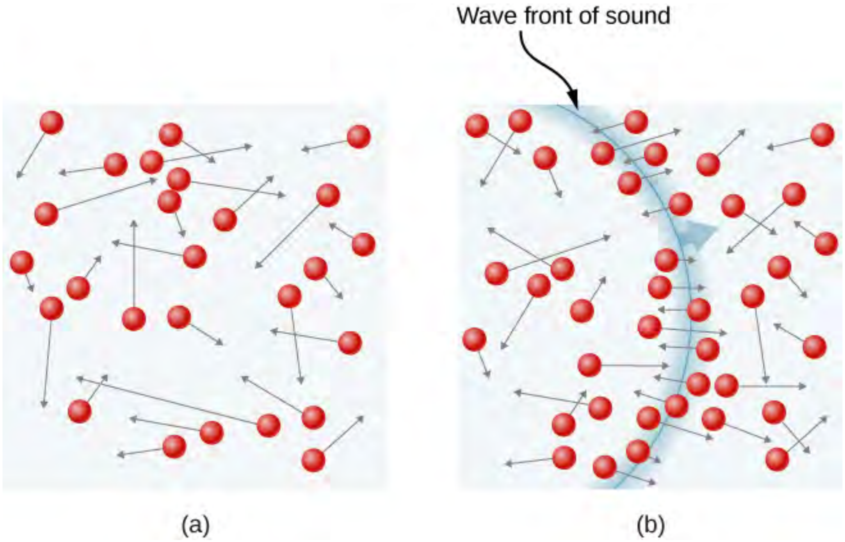


Figure 2.11 (a) In an ordinary gas, so many molecules move so fast that they collide billions of times every second. (b) Individual molecules do not move very far in a small amount of time, but disturbances like sound waves are transmitted at speeds related to the molecular speeds.

Example 2.5

Calculating Temperature: Escape Velocity of Helium Atoms

To escape Earth's gravity, an object near the top of the atmosphere (at an altitude of 100 km) must travel away from Earth at 11.1 km/s. This speed is called the *escape velocity*. At what temperature would helium atoms have an rms speed equal to the escape velocity?

Strategy

Identify the knowns and unknowns and determine which equations to use to solve the problem.

Solution

1. Identify the knowns: v is the escape velocity, 11.1 km/s.

2. Identify the unknowns: We need to solve for temperature, T. We also need to solve for the mass m of the helium atom.
3. Determine which equations are needed.
    - To get the mass m of the helium atom, we can use information from the periodic table:
    $$m = \frac{M}{N_A}.$$
    - To solve for temperature T, we can rearrange
    $$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_\text{B}T$$
    to yield
    $$T = \frac{m\overline{v^2}}{3k_\text{B}}.$$
4. Substitute the known values into the equations and solve for the unknowns,
$$m = \frac{M}{N_A} = \frac{4.0026 \times 10^{-3}\ \text{kg/mol}}{6.02 \times 10^{23}\ \text{mol}} = 6.65 \times 10^{-27}\ \text{kg}$$
and
$$T = \frac{(6.65 \times 10^{-27}\ \text{kg})\left(11.1 \times 10^3\ \text{m/s}\right)^2}{3\,(1.38 \times 10^{-23}\ \text{J/K})} = 1.98 \times 10^4\ \text{K}.$$

Significance

This temperature is much higher than atmospheric temperature, which is approximately 250 K $(-25\ °\text{C or } -10\ °\text{F})$ at high elevation. Very few helium atoms are left in the atmosphere, but many were present when the atmosphere was formed, and more are always being created by radioactive decay (see the chapter on nuclear physics). The reason for the loss of helium atoms is that a small number of helium atoms have speeds higher than Earth’s escape velocity even at normal temperatures. The speed of a helium atom changes from one collision to the next, so that at any instant, there is a small but nonzero chance that the atom’s speed is greater than the escape velocity. The chance is high enough that over the lifetime of Earth, almost all the helium atoms that have been in the atmosphere have reached escape velocity at high altitudes and escaped from Earth’s gravitational pull. Heavier molecules, such as oxygen, nitrogen, and water, have smaller rms speeds, and so it is much less likely that any of them will have speeds greater than the escape velocity. In fact, the likelihood is so small that billions of years are required to lose significant amounts of heavier molecules from the atmosphere. **Figure 2.12** shows the effect of a lack of an atmosphere on the Moon. Because the gravitational pull of the Moon is much weaker, it has lost almost its entire atmosphere. The atmospheres of Earth and other bodies are compared in this chapter’s exercises.

Figure 2.12 This photograph of Apollo 17 Commander Eugene Cernan driving the lunar rover on the Moon in 1972 looks as though it was taken at night with a large spotlight. In fact, the light is coming from the Sun. Because the acceleration due to gravity on the Moon is so low (about 1/6 that of Earth), the Moon's escape velocity is much smaller. As a result, gas molecules escape very easily from the Moon, leaving it with virtually no atmosphere. Even during the daytime, the sky is black because there is no gas to scatter sunlight. (credit: Harrison H. Schmitt/NASA)

2.4 Check Your Understanding If you consider a very small object, such as a grain of pollen, in a gas, then the number of molecules striking its surface would also be relatively small. Would you expect the grain of pollen to experience any fluctuations in pressure due to statistical fluctuations in the number of gas molecules striking it in a given amount of time?

Vapor Pressure, Partial Pressure, and Dalton's Law

The pressure a gas would create if it occupied the total volume available is called the gas's **partial pressure**. If two or more gases are mixed, they will come to thermal equilibrium as a result of collisions between molecules; the process is analogous to heat conduction as described in the chapter on temperature and heat. As we have seen from kinetic theory, when the gases have the same temperature, their molecules have the same average kinetic energy. Thus, each gas obeys the ideal gas law separately and exerts the same pressure on the walls of a container that it would if it were alone. Therefore, in a mixture of gases, *the total pressure is the sum of partial pressures of the component gases*, assuming ideal gas behavior and no chemical reactions between the components. This law is known as **Dalton's law of partial pressures**, after the English scientist John Dalton (1766–1844) who proposed it. Dalton's law is consistent with the fact that pressures add according to Pascal's principle.

In a mixture of ideal gases in thermal equilibrium, the number of molecules of each gas is proportional to its partial pressure. This result follows from applying the ideal gas law to each in the form $p/n = RT/V$. Because the right-hand side is the same for any gas at a given temperature in a container of a given volume, the left-hand side is the same as well.

- Partial pressure is the pressure a gas would create if it existed alone.
- Dalton's law states that the total pressure is the sum of the partial pressures of all of the gases present.
- For any two gases (labeled 1 and 2) in equilibrium in a container, $\frac{p_1}{n_1} = \frac{p_2}{n_2}$.

An important application of partial pressure is that, in chemistry, it functions as the concentration of a gas in determining the rate of a reaction. Here, we mention only that the partial pressure of oxygen in a person's lungs is crucial to life and health. Breathing air that has a partial pressure of oxygen below 0.16 atm can impair coordination and judgment, particularly in people not acclimated to a high elevation. Lower partial pressures of O_2 have more serious effects; partial pressures below 0.06 atm can be quickly fatal, and permanent damage is likely even if the person is rescued. However, the sensation of needing to breathe, as when holding one's breath, is caused much more by high concentrations of carbon dioxide in the blood than by low concentrations of oxygen. Thus, if a small room or closet is filled with air having a low concentration of oxygen, perhaps because a leaking cylinder of some compressed gas is stored there, a person will not feel any "choking" sensation and may go into convulsions or lose consciousness without noticing anything wrong. Safety engineers give considerable attention to this danger.

Another important application of partial pressure is **vapor pressure**, which is the partial pressure of a vapor at which it is in equilibrium with the liquid (or solid, in the case of sublimation) phase of the same substance. At any temperature, the partial pressure of the water in the air cannot exceed the vapor pressure of the water at that temperature, because whenever the partial pressure reaches the vapor pressure, water condenses out of the air. Dew is an example of this condensation. The temperature at which condensation occurs for a sample of air is called the *dew point*. It is easily measured by slowly cooling a metal ball; the dew point is the temperature at which condensation first appears on the ball.

The vapor pressures of water at some temperatures of interest for meteorology are given in Table 2.2.

T (°C)	Vapor Pressure (Pa)
0	610.5
3	757.9
5	872.3
8	1073
10	1228
13	1497
15	1705
18	2063
20	2338
23	2809
25	3167
30	4243
35	5623
40	7376

Table 2.2 Vapor Pressure of Water at Various Temperatures

The *relative humidity* (R.H.) at a temperature *T* is defined by

$$\text{R.H.} = \frac{\text{Partial pressure of water vapor at } T}{\text{Vapor pressure of water at } T} \times 100\%.$$

A relative humidity of 100% means that the partial pressure of water is equal to the vapor pressure; in other words, the air is saturated with water.

Example 2.6

Calculating Relative Humidity

What is the relative humidity when the air temperature is $25\,°\text{C}$ and the dew point is $15\,°\text{C}$?

Strategy

We simply look up the vapor pressure at the given temperature and that at the dew point and find the ratio.

Solution

$$\text{R.H.} = \frac{\text{Partial pressure of water vapor at 15 °C}}{\text{Partial pressure of water vapor at 25 °C}} \times 100\% = \frac{1705\ \text{Pa}}{3167\ \text{Pa}} \times 100\% = 53.8\%.$$

Significance

R.H. is important to our comfort. The value of 53.8% is within the range of 40% to 60% recommended for comfort indoors.

As noted in the chapter on temperature and heat, the temperature seldom falls below the dew point, because when it reaches the dew point or frost point, water condenses and releases a relatively large amount of latent heat of vaporization.

Mean Free Path and Mean Free Time

We now consider collisions explicitly. The usual first step (which is all we'll take) is to calculate the **mean free path**, λ, the average distance a molecule travels between collisions with other molecules, and the *mean free time* τ, the average time between the collisions of a molecule. If we assume all the molecules are spheres with a radius r, then a molecule will collide with another if their centers are within a distance $2r$ of each other. For a given particle, we say that the area of a circle with that radius, $4\pi r^2$, is the "cross-section" for collisions. As the particle moves, it traces a cylinder with that cross-sectional area. The mean free path is the length λ such that the expected number of other molecules in a cylinder of length λ and cross-section $4\pi r^2$ is 1. If we temporarily ignore the motion of the molecules other than the one we're looking at, the expected number is the number density of molecules, N/V, times the volume, and the volume is $4\pi r^2 \lambda$, so we have $(N/V)4\pi r^2 \lambda = 1$, or

$$\lambda = \frac{V}{4\pi r^2 N}.$$

Taking the motion of all the molecules into account makes the calculation much harder, but the only change is a factor of $\sqrt{2}$. The result is

$$\lambda = \frac{V}{4\sqrt{2}\pi r^2 N}. \tag{2.10}$$

In an ideal gas, we can substitute $V/N = k_B T/p$ to obtain

$$\lambda = \frac{k_B T}{4\sqrt{2}\pi r^2 p}. \tag{2.11}$$

The **mean free time** τ is simply the mean free path divided by a typical speed, and the usual choice is the rms speed. Then

$$\tau = \frac{k_B T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}}. \tag{2.12}$$

Example 2.7

Calculating Mean Free Time

Find the mean free time for argon atoms $(M = 39.9\text{ g/mol})$ at a temperature of $0\,°\text{C}$ and a pressure of 1.00 atm. Take the radius of an argon atom to be 1.70×10^{-10} m.

Solution

1. Identify the knowns and convert into SI units. We know the molar mass is 0.0399 kg/mol, the temperature is 273 K, the pressure is 1.01×10^{5} Pa, and the radius is 1.70×10^{-10} m.
2. Find the rms speed: $v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = 413\,\frac{\text{m}}{\text{s}}$.
3. Substitute into the equation for the mean free time:

$$\tau = \frac{k_{\text{B}}T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}} = \frac{(1.38 \times 10^{-23}\text{ J/K})\,(273\text{ K})}{4\sqrt{2}\pi(1.70 \times 10^{-10}\text{ m})^2(1.01 \times 10^{5}\text{ Pa})(413\text{ m/s})} = 1.76 \times 10^{-10}\text{ s}.$$

Significance

We can hardly compare this result with our intuition about gas molecules, but it gives us a picture of molecules colliding with extremely high frequency.

2.5 **Check Your Understanding** Which has a longer mean free path, liquid water or water vapor in the air?

2.3 | Heat Capacity and Equipartition of Energy

Learning Objectives

By the end of this section, you will be able to:

- Solve problems involving heat transfer to and from ideal monatomic gases whose volumes are held constant
- Solve similar problems for non-monatomic ideal gases based on the number of degrees of freedom of a molecule
- Estimate the heat capacities of metals using a model based on degrees of freedom

In the chapter on temperature and heat, we defined the specific heat capacity with the equation $Q = mc\Delta T$, or $c = (1/m)Q/\Delta T$. However, the properties of an ideal gas depend directly on the number of moles in a sample, so here we define specific heat capacity in terms of the number of moles, not the mass. Furthermore, when talking about solids and liquids, we ignored any changes in volume and pressure with changes in temperature—a good approximation for solids and liquids, but for gases, we have to make some condition on volume or pressure changes. Here, we focus on the heat capacity with the volume held constant. We can calculate it for an ideal gas.

Heat Capacity of an Ideal Monatomic Gas at Constant Volume

We define the *molar heat capacity at constant volume* C_V as

$$C_V = \frac{1}{n}\frac{Q}{\Delta T},\text{ with }V\text{ held constant.}$$

This is often expressed in the form

$$Q = nC_V \Delta T. \tag{2.13}$$

If the volume does not change, there is no overall displacement, so no work is done, and the only change in internal energy is due to the heat flow $\Delta E_{\text{int}} = Q$. (This statement is discussed further in the next chapter.) We use the equation $E_{\text{int}} = 3nRT/2$ to write $\Delta E_{\text{int}} = 3nR\Delta T/2$ and substitute ΔE for Q to find $Q = 3nR\Delta T/2$, which gives the following simple result for an ideal monatomic gas:

$$C_V = \frac{3}{2}R.$$

It is independent of temperature, which justifies our use of finite differences instead of a derivative. This formula agrees well with experimental results.

In the next chapter we discuss the molar specific heat at constant pressure C_p, which is always greater than C_V.

Example 2.8

Calculating Temperature

A sample of 0.125 kg of xenon is contained in a rigid metal cylinder, big enough that the xenon can be modeled as an ideal gas, at a temperature of $20.0\,°\text{C}$. The cylinder is moved outside on a hot summer day. As the xenon comes into equilibrium by reaching the temperature of its surroundings, 180 J of heat are conducted to it through the cylinder walls. What is the equilibrium temperature? Ignore the expansion of the metal cylinder.

Solution

1. Identify the knowns: We know the initial temperature T_1 is $20.0\,°\text{C}$, the heat Q is 180 J, and the mass m of the xenon is 0.125 kg.
2. Identify the unknown. We need the final temperature, so we'll need ΔT.
3. Determine which equations are needed. Because xenon gas is monatomic, we can use $Q = 3nR\Delta T/2$. Then we need the number of moles, $n = m/M$.
4. Substitute the known values into the equations and solve for the unknowns.
   The molar mass of xenon is 131.3 g, so we obtain

$$n = \frac{125\text{ g}}{131.3\text{ g/mol}} = 0.952\text{ mol},$$

$$\Delta T = \frac{2Q}{3nR} = \frac{2(180\text{ J})}{3(0.952\text{ mol})(8.31\text{ J/mol}\cdot°\text{C})} = 15.2\,°\text{C}.$$

Therefore, the final temperature is $35.2\,°\text{C}$. The problem could equally well be solved in kelvin; as a kelvin is the same size as a degree Celsius of temperature change, you would get $\Delta T = 15.2\text{ K}$.

Significance

The heating of an ideal or almost ideal gas at constant volume is important in car engines and many other practical systems.

2.6 Check Your Understanding Suppose 2 moles of helium gas at 200 K are mixed with 2 moles of krypton gas at 400 K in a calorimeter. What is the final temperature?

We would like to generalize our results to ideal gases with more than one atom per molecule. In such systems, the molecules can have other forms of energy beside translational kinetic energy, such as rotational kinetic energy and vibrational kinetic and potential energies. We will see that a simple rule lets us determine the average energies present in these forms and solve problems in much the same way as we have for monatomic gases.

Degrees of Freedom

In the previous section, we found that $\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$ and $\overline{v^2} = 3\overline{v_x^2}$, from which it follows that $\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_B T$. The same equation holds for $\overline{v_y^2}$ and for $\overline{v_z^2}$. Thus, we can look at our energy of $\frac{3}{2}k_B T$ as the sum of contributions of $\frac{1}{2}k_B T$ from each of the three dimensions of translational motion. Shifting to the gas as a whole, we see that the 3 in the formula $C_V = \frac{3}{2}R$ also reflects those three dimensions. We define a **degree of freedom** as an independent possible motion of a molecule, such as each of the three dimensions of translation. Then, letting *d* represent the number of degrees of freedom, the molar heat capacity at constant volume of a monatomic ideal gas is $C_V = \frac{d}{2}R,\quad \text{where } d = 3$.

The branch of physics called *statistical mechanics* tells us, and experiment confirms, that C_V of any ideal gas is given by this equation, regardless of the number of degrees of freedom. This fact follows from a more general result, the **equipartition theorem**, which holds in classical (non-quantum) thermodynamics for systems in thermal equilibrium under technical conditions that are beyond our scope. Here, we mention only that in a system, the energy is shared among the degrees of freedom by collisions.

Equipartition Theorem

The energy of a thermodynamic system in equilibrium is partitioned equally among its degrees of freedom. Accordingly, the molar heat capacity of an ideal gas is proportional to its number of degrees of freedom, *d*:

$$C_V = \frac{d}{2}R. \tag{2.14}$$

This result is due to the Scottish physicist James Clerk Maxwell (1831−1871), whose name will appear several more times in this book.

For example, consider a diatomic ideal gas (a good model for nitrogen, N_2, and oxygen, O_2). Such a gas has more degrees of freedom than a monatomic gas. In addition to the three degrees of freedom for translation, it has two degrees of freedom for rotation perpendicular to its axis. Furthermore, the molecule can vibrate along its axis. This motion is often modeled by imagining a spring connecting the two atoms, and we know from simple harmonic motion that such motion has both kinetic and potential energy. Each of these forms of energy corresponds to a degree of freedom, giving two more.

We might expect that for a diatomic gas, we should use 7 as the number of degrees of freedom; classically, if the molecules of a gas had only translational kinetic energy, collisions between molecules would soon make them rotate and vibrate. However, as explained in the previous module, quantum mechanics controls which degrees of freedom are active. The result is shown in **Figure 2.13**. Both rotational and vibrational energies are limited to discrete values. For temperatures below about 60 K, the energies of hydrogen molecules are too low for a collision to bring the rotational state or vibrational state of a molecule from the lowest energy to the second lowest, so the only form of energy is translational kinetic energy, and $d = 3$ or $C_V = 3R/2$ as in a monatomic gas. Above that temperature, the two rotational degrees of freedom begin to contribute, that is, some molecules are excited to the rotational state with the second-lowest energy. (This temperature is much lower than that where rotations of monatomic gases contribute, because diatomic molecules have much higher rotational inertias and hence much lower rotational energies.) From about room temperature (a bit less than 300 K) to about 600 K, the rotational degrees of freedom are fully active, but the vibrational ones are not, and $d = 5$. Then, finally, above about 3000 K, the vibrational degrees of freedom are fully active, and $d = 7$ as the classical theory predicted.

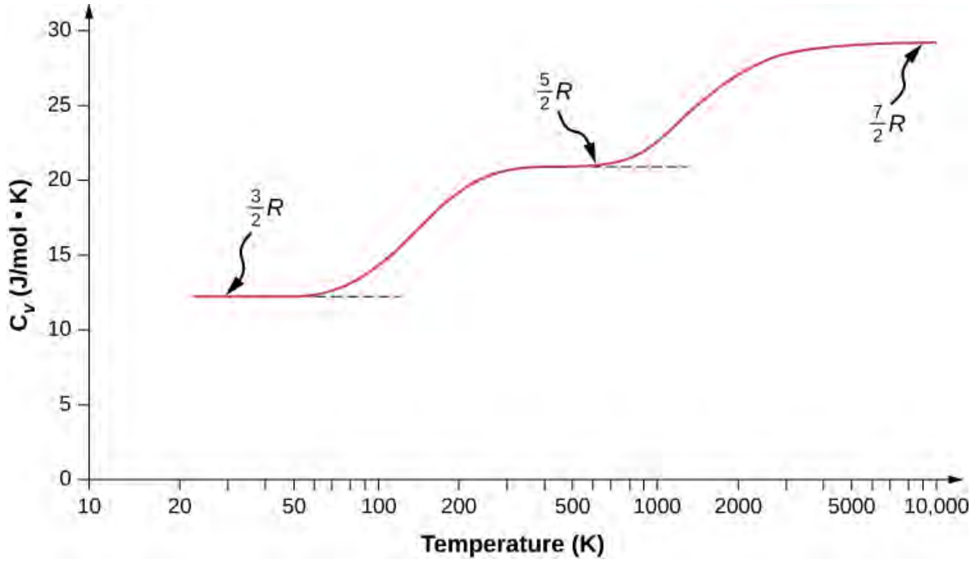


Figure 2.13 The molar heat capacity of hydrogen as a function of temperature (on a logarithmic scale). The three "steps" or "plateaus" show different numbers of degrees of freedom that the typical energies of molecules must achieve to activate. Translational kinetic energy corresponds to three degrees of freedom, rotational to another two, and vibrational to yet another two.

Polyatomic molecules typically have one additional rotational degree of freedom at room temperature, since they have comparable moments of inertia around any axis. Thus, at room temperature, they have $d = 6,$ and at high temperature, $d = 8.$ We usually assume that gases have the theoretical room-temperature values of d.

As shown in **Table 2.3**, the results agree well with experiments for many monatomic and diatomic gases, but the agreement for triatomic gases is only fair. The differences arise from interactions that we have ignored between and within molecules.

Gas	C_V/R at $25\,°\text{C}$ and 1 atm
Ar	1.50
He	1.50
Ne	1.50
CO	2.50
H_2	2.47
N_2	2.50
O_2	2.53
F_2	2.8
CO_2	3.48
H_2S	3.13
N_2O	3.66

Table 2.3 C_V/R **for Various Monatomic, Diatomic, and Triatomic Gases**

What about internal energy for diatomic and polyatomic gases? For such gases, C_V is a function of temperature (**Figure 2.13**), so we do not have the kind of simple result we have for monatomic ideal gases.

Molar Heat Capacity of Solid Elements

The idea of equipartition leads to an estimate of the molar heat capacity of solid elements at ordinary temperatures. We can model the atoms of a solid as attached to neighboring atoms by springs (**Figure 2.14**).

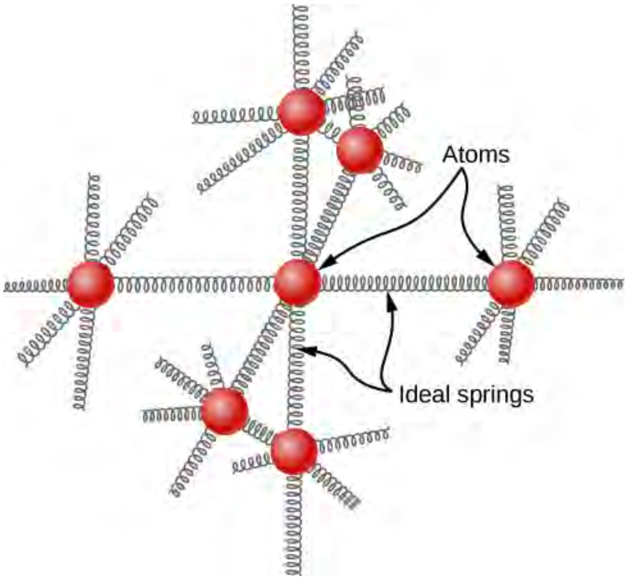


Figure 2.14 In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. Thus $d = 6$.

Analogously to the discussion of vibration in the previous module, each atom has six degrees of freedom: one kinetic and one potential for each of the x-, y-, and z-directions. Accordingly, the molar specific heat of a metal should be $3R$. This result, known as the Law of Dulong and Petit, works fairly well experimentally at room temperature. (For every element, it fails at low temperatures for quantum-mechanical reasons. Since quantum effects are particularly important for low-mass particles, the Law of Dulong and Petit already fails at room temperature for some light elements, such as beryllium and carbon. It also fails for some heavier elements for various reasons beyond what we can cover.)

Problem-Solving Strategy: Heat Capacity and Equipartition

The strategy for solving these problems is the same as the one in **Phase Changes** for the effects of heat transfer. The only new feature is that you should determine whether the case just presented—ideal gases at constant volume—applies to the problem. (For solid elements, looking up the specific heat capacity is generally better than estimating it from the Law of Dulong and Petit.) In the case of an ideal gas, determine the number d of degrees of freedom from the number of atoms in the gas molecule and use it to calculate C_V (or use C_V to solve for d).

Example 2.9

Calculating Temperature: Calorimetry with an Ideal Gas

A 300-g piece of solid gallium (a metal used in semiconductor devices) at its melting point of only $30.0\,°\text{C}$ is in contact with 12.0 moles of air (assumed diatomic) at $95.0\,°\text{C}$ in an insulated container. When the air reaches equilibrium with the gallium, 202 g of the gallium have melted. Based on those data, what is the heat of fusion of gallium? Assume the volume of the air does not change and there are no other heat transfers.

Strategy

We'll use the equation $Q_{\text{hot}} + Q_{\text{cold}} = 0.$ As some of the gallium doesn't melt, we know the final temperature is still the melting point. Then the only Q_{hot} is the heat lost as the air cools, $Q_{\text{hot}} = n_{\text{air}} C_V \Delta T,$ where $C_V = 5R/2.$ The only Q_{cold} is the latent heat of fusion of the gallium, $Q_{\text{cold}} = m_{\text{Ga}} L_{\text{f}}.$ It is positive because heat flows into the gallium.

Solution

1. Set up the equation:

$$n_{\text{air}} C_V \Delta T + m_{\text{Ga}}\, L_{\text{f}} = 0.$$

2. Substitute the known values and solve:

$$(12.0\text{ mol})\left(\frac{5}{2}\right)\left(8.31\frac{\text{J}}{\text{mol}\cdot{}^\circ\text{C}}\right)(30.0\,{}^\circ\text{C} - 95.0\,{}^\circ\text{C}) + (0.202\text{ kg})\text{L}_{\text{f}} = 0.$$

We solve to find that the heat of fusion of gallium is 80.2 kJ/kg.

2.4 | Distribution of Molecular Speeds

Learning Objectives

By the end of this section, you will be able to:

- Describe the distribution of molecular speeds in an ideal gas
- Find the average and most probable molecular speeds in an ideal gas

Particles in an ideal gas all travel at relatively high speeds, but they do not travel at the same speed. The rms speed is one kind of average, but many particles move faster and many move slower. The actual distribution of speeds has several interesting implications for other areas of physics, as we will see in later chapters.

The Maxwell-Boltzmann Distribution

The motion of molecules in a gas is random in magnitude and direction for individual molecules, but a gas of many molecules has a predictable distribution of molecular speeds. This predictable distribution of molecular speeds is known as the **Maxwell-Boltzmann distribution**, after its originators, who calculated it based on kinetic theory, and it has since been confirmed experimentally (**Figure 2.15**).

To understand this figure, we must define a distribution function of molecular speeds, since with a finite number of molecules, the probability that a molecule will have exactly a given speed is 0.

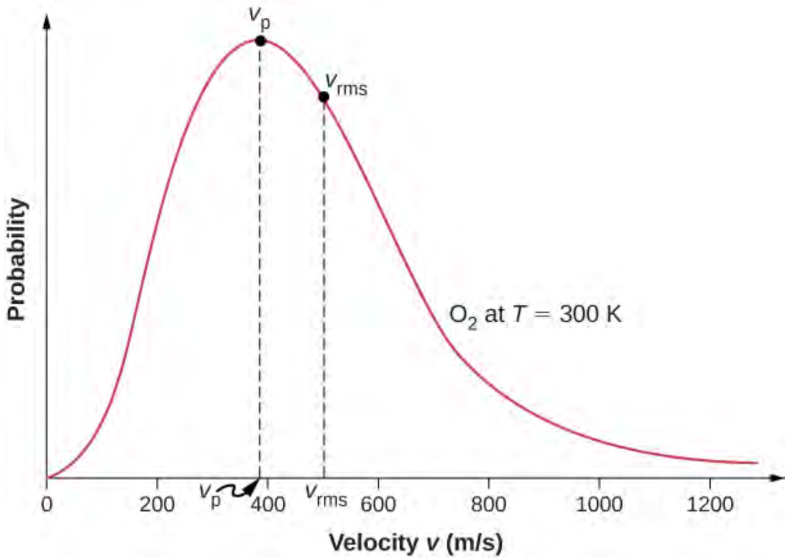


Figure 2.15 The Maxwell-Boltzmann distribution of molecular speeds in an ideal gas. The most likely speed v_p is less than the rms speed v_{rms}. Although very high speeds are possible, only a tiny fraction of the molecules have speeds that are an order of magnitude greater than v_{rms}.

We define the distribution function $f(v)$ by saying that the expected number $N(v_1, v_2)$ of particles with speeds between v_1 and v_2 is given by

$$N(v_1, v_2) = N\int_{v_1}^{v_2} f(v)dv.$$

[Since *N* is dimensionless, the unit of *f*(*v*) is seconds per meter.] We can write this equation conveniently in differential form:

$$dN = Nf(v)dv.$$

In this form, we can understand the equation as saying that the number of molecules with speeds between *v* and $v + dv$ is the total number of molecules in the sample times *f*(*v*) times *dv*. That is, the probability that a molecule's speed is between *v* and $v + dv$ is *f*(*v*)*dv*.

We can now quote Maxwell's result, although the proof is beyond our scope.

Maxwell-Boltzmann Distribution of Speeds

The distribution function for speeds of particles in an ideal gas at temperature *T* is

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}. \tag{2.15}$$

The factors before the v^2 are a normalization constant; they make sure that $N(0, \infty) = N$ by making sure that $\int_0^\infty f(v)dv = 1.$ Let's focus on the dependence on *v*. The factor of v^2 means that $f(0) = 0$ and for small *v*, the curve looks like a parabola. The factor of $e^{-m_0 v^2/2k_B T}$ means that $\lim_{v \to \infty} f(v) = 0$ and the graph has an exponential tail, which indicates that a few molecules may move at several times the rms speed. The interaction of these factors gives the function the single-peaked shape shown in the figure.

Example 2.10

Calculating the Ratio of Numbers of Molecules Near Given Speeds

In a sample of nitrogen $(N_2,$ with a molar mass of 28.0 g/mol) at a temperature of $273\ °C$, find the ratio of the number of molecules with a speed very close to 300 m/s to the number with a speed very close to 100 m/s.

Strategy

Since we're looking at a small range, we can approximate the number of molecules near 100 m/s as $dN_{100} = f(100\ \text{m/s})dv$. Then the ratio we want is

$$\frac{dN_{300}}{dN_{100}} = \frac{f(300\ \text{m/s})dv}{f(100\ \text{m/s})dv} = \frac{f(300\ \text{m/s})}{f(100\ \text{m/s})}.$$

All we have to do is take the ratio of the two *f* values.

Solution

1. Identify the knowns and convert to SI units if necessary.

$$T = 300\ \text{K},\ \ k_{\text{B}} = 1.38 \times 10^{-23}\ \text{J/K}$$

$$M = 0.0280\ \text{kg/mol so } m = 4.65 \times 10^{-26}\ \text{kg}$$

2. Substitute the values and solve.

$$\begin{aligned}\frac{f(300\ \text{m/s})}{f(100\ \text{m/s})} &= \frac{\frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_{\text{B}}T}\right)^{3/2}(300\ \text{m/s})^2\ \exp[-m(300\ \text{m/s})^2/2k_{\text{B}}T]}{\frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_{\text{B}}T}\right)^{3/2}(100\ \text{m/s})^2\ \exp[-m(100\ \text{m/s})^2/2k_{\text{B}}T]} \\ &= \frac{(300\ \text{m/s})^2\ \exp[-(4.65\times10^{-26}\ \text{kg})(300\ \text{m/s})^2/2(1.38\times10^{-23}\ \text{J/K})(300\ \text{K})]}{(100\ \text{m/s})^2\ \exp[-(4.65\times10^{-26}\ \text{kg})(100\ \text{m/s})^2/2(1.38\times10^{-23}\ \text{J/K})(300\ \text{K})]} \\ &= 3^2\ \exp\left[-\frac{(4.65\times10^{-26}\ \text{kg})[(300\ \text{m/s})^2-(100\ \text{ms})^2]}{2(1.38\times10^{-23}\ \text{J/K})(300\ \text{K})}\right] \\ &= 5.74\end{aligned}$$

Figure 2.16 shows that the curve is shifted to higher speeds at higher temperatures, with a broader range of speeds.

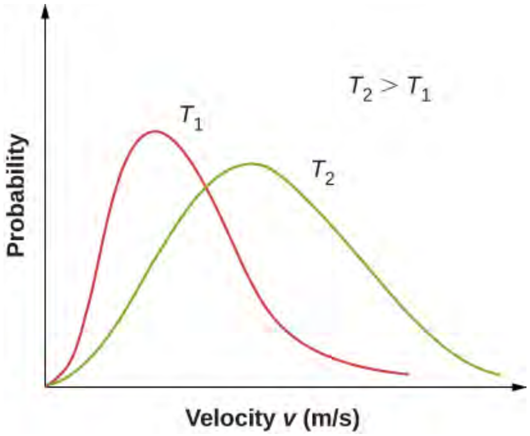


Figure 2.16 The Maxwell-Boltzmann distribution is shifted to higher speeds and broadened at higher temperatures.

With only a relatively small number of molecules, the distribution of speeds fluctuates around the Maxwell-Boltzmann distribution. However, you can view this **simulation (https://openstaxcollege.org/l/21maxboltzdisim)** to see the essential features that more massive molecules move slower and have a narrower distribution. Use the set-up “2 Gases, Random Speeds”. Note the display at the bottom comparing histograms of the speed distributions with the theoretical curves.

We can use a probability distribution to calculate average values by multiplying the distribution function by the quantity to be averaged and integrating the product over all possible speeds. (This is analogous to calculating averages of discrete distributions, where you multiply each value by the number of times it occurs, add the results, and divide by the number of values. The integral is analogous to the first two steps, and the normalization is analogous to dividing by the number of values.) Thus the average velocity is

$$\bar{v} = \int_0^\infty v f(v)dv = \sqrt{\frac{8}{\pi}\frac{k_\text{B} T}{m}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}}. \tag{2.16}$$

Similarly,

$$v_\text{rms} = \sqrt{\overline{v^2}} = \sqrt{\int_0^\infty v^2 f(v)dv} = \sqrt{\frac{3k_\text{B} T}{m}} = \sqrt{\frac{3RT}{M}}$$

as in **Pressure, Temperature, and RMS Speed**. The **most probable speed**, also called the **peak speed** v_p, is the speed at the peak of the velocity distribution. (In statistics it would be called the mode.) It is less than the rms speed v_rms. The most probable speed can be calculated by the more familiar method of setting the derivative of the distribution function, with respect to *v*, equal to 0. The result is

$$v_p = \sqrt{\frac{2k_\text{B} T}{m}} = \sqrt{\frac{2RT}{M}}, \tag{2.17}$$

which is less than v_rms. In fact, the rms speed is greater than both the most probable speed and the average speed.

The peak speed provides a sometimes more convenient way to write the Maxwell-Boltzmann distribution function:

$$f(v) = \frac{4v^2}{\sqrt{\pi}v_p^3}e^{-v^2/v_p^2} \tag{2.18}$$

In the factor $e^{-mv^2/2k_\text{B} T}$, it is easy to recognize the translational kinetic energy. Thus, that expression is equal to $e^{-K/k_\text{B} T}$. The distribution *f*(*v*) can be transformed into a kinetic energy distribution by requiring that $f(K)dK = f(v)dv$. Boltzmann showed that the resulting formula is much more generally applicable if we replace the kinetic energy of translation with the total mechanical energy *E*. Boltzmann’s result is

$$f(E) = \frac{2}{\sqrt{\pi}}(k_\text{B} T)^{-3/2}\sqrt{E}e^{-E/k_\text{B} T} = \frac{2}{\sqrt{\pi}(k_\text{B} T)^{3/2}}\frac{\sqrt{E}}{e^{E/k_\text{B} T}}.$$

The first part of this equation, with the negative exponential, is the usual way to write it. We give the second part only to remark that $e^{E/k_\text{B} T}$ in the denominator is ubiquitous in quantum as well as classical statistical mechanics.

Problem-Solving Strategy: Speed Distribution

Step 1. Examine the situation to determine that it relates to the distribution of molecular speeds.

Step 2. Make a list of what quantities are given or can be inferred from the problem as stated (identify the known quantities).

Step 3. Identify exactly what needs to be determined in the problem (identify the unknown quantities). A written list is useful.

Step 4. Convert known values into proper SI units (K for temperature, Pa for pressure, m^3 for volume, molecules for *N*, and moles for *n*). In many cases, though, using *R* and the molar mass will be more convenient than using k_B and the molecular mass.

Step 5. Determine whether you need the distribution function for velocity or the one for energy, and whether you are using a formula for one of the characteristic speeds (average, most probably, or rms), finding a ratio of values of the distribution function, or approximating an integral.

Step 6. Solve the appropriate equation for the ideal gas law for the quantity to be determined (the unknown quantity). Note that if you are taking a ratio of values of the distribution function, the normalization factors divide out. Or if approximating an integral, use the method asked for in the problem.

Step 7. Substitute the known quantities, along with their units, into the appropriate equation and obtain numerical solutions complete with units.

We can now gain a qualitative understanding of a puzzle about the composition of Earth’s atmosphere. Hydrogen is by far the most common element in the universe, and helium is by far the second-most common. Moreover, helium is constantly produced on Earth by radioactive decay. Why are those elements so rare in our atmosphere? The answer is that gas molecules that reach speeds above Earth’s escape velocity, about 11 km/s, can escape from the atmosphere into space. Because of the lower mass of hydrogen and helium molecules, they move at higher speeds than other gas molecules, such as nitrogen and oxygen. Only a few exceed escape velocity, but far fewer heavier molecules do. Thus, over the billions of years that Earth has existed, far more hydrogen and helium molecules have escaped from the atmosphere than other molecules, and hardly any of either is now present.

We can also now take another look at evaporative cooling, which we discussed in the chapter on temperature and heat. Liquids, like gases, have a distribution of molecular energies. The highest-energy molecules are those that can escape from the intermolecular attractions of the liquid. Thus, when some liquid evaporates, the molecules left behind have a lower average energy, and the liquid has a lower temperature.

CHAPTER 2 REVIEW

KEY TERMS

Avogadro's number N_A, the number of molecules in one mole of a substance; $N_A = 6.02 \times 10^{23}$ particles/mole

Boltzmann constant k_B, a physical constant that relates energy to temperature and appears in the ideal gas law; $k_B = 1.38 \times 10^{-23}$ J/K

critical temperature T_c at which the isotherm has a point with zero slope

Dalton's law of partial pressures physical law that states that the total pressure of a gas is the sum of partial pressures of the component gases

degree of freedom independent kind of motion possessing energy, such as the kinetic energy of motion in one of the three orthogonal spatial directions

equipartition theorem theorem that the energy of a classical thermodynamic system is shared equally among its degrees of freedom

ideal gas gas at the limit of low density and high temperature

ideal gas law physical law that relates the pressure and volume of a gas, far from liquefaction, to the number of gas molecules or number of moles of gas and the temperature of the gas

internal energy sum of the mechanical energies of all of the molecules in it

kinetic theory of gases theory that derives the macroscopic properties of gases from the motion of the molecules they consist of

Maxwell-Boltzmann distribution function that can be integrated to give the probability of finding ideal gas molecules with speeds in the range between the limits of integration

mean free path average distance between collisions of a particle

mean free time average time between collisions of a particle

mole quantity of a substance whose mass (in grams) is equal to its molecular mass

most probable speed speed near which the speeds of most molecules are found, the peak of the speed distribution function

partial pressure pressure a gas would create if it occupied the total volume of space available

peak speed same as "most probable speed"

***pV* diagram** graph of pressure vs. volume

root-mean-square (rms) speed square root of the average of the square (of a quantity)

supercritical condition of a fluid being at such a high temperature and pressure that the liquid phase cannot exist

universal gas constant R, the constant that appears in the ideal gas law expressed in terms of moles, given by $R = N_A k_B$

van der Waals equation of state equation, typically approximate, which relates the pressure and volume of a gas to the number of gas molecules or number of moles of gas and the temperature of the gas

vapor pressure partial pressure of a vapor at which it is in equilibrium with the liquid (or solid, in the case of sublimation) phase of the same substance

KEY EQUATIONS

Ideal gas law in terms of molecules	$pV = Nk_B T$

Ideal gas law ratios if the amount of gas is constant	$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$
Ideal gas law in terms of moles	$pV = nRT$
Van der Waals equation	$\left[p + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT$
Pressure, volume, and molecular speed	$pV = \frac{1}{3}Nm\overline{v^2}$
Root-mean-square speed	$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$
Mean free path	$\lambda = \frac{V}{4\sqrt{2}\pi r^2 N} = \frac{k_B T}{4\sqrt{2}\pi r^2 p}$
Mean free time	$\tau = \frac{k_B T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}}$

The following two equations apply only to a monatomic ideal gas:

Average kinetic energy of a molecule	$\bar{K} = \frac{3}{2}k_B T$
Internal energy	$E_{\text{int}} = \frac{3}{2}Nk_B T.$
Heat in terms of molar heat capacity at constant volume	$Q = nC_V \Delta T$
Molar heat capacity at constant volume for an ideal gas with *d* degrees of freedom	$C_V = \frac{d}{2}R$
Maxwell–Boltzmann speed distribution	$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}$
Average velocity of a molecule	$\bar{v} = \sqrt{\frac{8}{\pi}\frac{k_B T}{m}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}}$
Peak velocity of a molecule	$v_p = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$

SUMMARY

2.1 Molecular Model of an Ideal Gas

- The ideal gas law relates the pressure and volume of a gas to the number of gas molecules and the temperature of the gas.
- A mole of any substance has a number of molecules equal to the number of atoms in a 12-g sample of carbon-12. The number of molecules in a mole is called Avogadro's number N_A,

$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}.$$

- A mole of any substance has a mass in grams numerically equal to its molecular mass in unified mass units, which can be determined from the periodic table of elements. The ideal gas law can also be written and solved in terms of the number of moles of gas:

$$pV = nRT,$$

where n is the number of moles and R is the universal gas constant,

$$R = 8.31\ \text{J/mol} \cdot \text{K}.$$

- The ideal gas law is generally valid at temperatures well above the boiling temperature.
- The van der Waals equation of state for gases is valid closer to the boiling point than the ideal gas law.
- Above the critical temperature and pressure for a given substance, the liquid phase does not exist, and the sample is "supercritical."

2.2 Pressure, Temperature, and RMS Speed

- Kinetic theory is the atomic description of gases as well as liquids and solids. It models the properties of matter in terms of continuous random motion of molecules.
- The ideal gas law can be expressed in terms of the mass of the gas's molecules and $\overline{v^2}$, the average of the molecular speed squared, instead of the temperature.
- The temperature of gases is proportional to the average translational kinetic energy of molecules. Hence, the typical speed of gas molecules v_{rms} is proportional to the square root of the temperature and inversely proportional to the square root of the molecular mass.
- In a mixture of gases, each gas exerts a pressure equal to the total pressure times the fraction of the mixture that the gas makes up.
- The mean free path (the average distance between collisions) and the mean free time of gas molecules are proportional to the temperature and inversely proportional to the molar density and the molecules' cross-sectional area.

2.3 Heat Capacity and Equipartition of Energy

- Every degree of freedom of an ideal gas contributes $\frac{1}{2}k_{\text{B}}T$ per atom or molecule to its changes in internal energy.
- Every degree of freedom contributes $\frac{1}{2}R$ to its molar heat capacity at constant volume C_V.
- Degrees of freedom do not contribute if the temperature is too low to excite the minimum energy of the degree of freedom as given by quantum mechanics. Therefore, at ordinary temperatures, $d = 3$ for monatomic gases, $d = 5$ for diatomic gases, and $d \approx 6$ for polyatomic gases.

2.4 Distribution of Molecular Speeds

- The motion of individual molecules in a gas is random in magnitude and direction. However, a gas of many molecules has a predictable distribution of molecular speeds, known as the Maxwell-Boltzmann distribution.
- The average and most probable velocities of molecules having the Maxwell-Boltzmann speed distribution, as well as the rms velocity, can be calculated from the temperature and molecular mass.

CONCEPTUAL QUESTIONS

2.1 Molecular Model of an Ideal Gas

1. Two H_2 molecules can react with one O_2 molecule to produce two H_2O molecules. How many moles of hydrogen molecules are needed to react with one mole of oxygen molecules?

2. Under what circumstances would you expect a gas to behave significantly differently than predicted by the ideal gas law?

3. A constant-volume gas thermometer contains a fixed amount of gas. What property of the gas is measured to indicate its temperature?

4. Inflate a balloon at room temperature. Leave the inflated balloon in the refrigerator overnight. What happens to the balloon, and why?

5. In the last chapter, free convection was explained as the result of buoyant forces on hot fluids. Explain the upward motion of air in flames based on the ideal gas law.

2.2 Pressure, Temperature, and RMS Speed

6. How is momentum related to the pressure exerted by a gas? Explain on the molecular level, considering the behavior of molecules.

7. If one kind of molecule has double the radius of another and eight times the mass, how do their mean free paths under the same conditions compare? How do their mean free times compare?

8. What is the average *velocity* of the air molecules in the room where you are right now?

9. Why do the atmospheres of Jupiter, Saturn, Uranus, and Neptune, which are much more massive and farther from the Sun than Earth is, contain large amounts of hydrogen and helium?

10. Statistical mechanics says that in a gas maintained at a constant temperature through thermal contact with a bigger system (a "reservoir") at that temperature, the fluctuations in internal energy are typically a fraction $1/\sqrt{N}$ of the internal energy. As a fraction of the total internal energy of a mole of gas, how big are the fluctuations in the internal energy? Are we justified in ignoring them?

11. Which is more dangerous, a closet where tanks of nitrogen are stored, or one where tanks of carbon dioxide are stored?

2.3 Heat Capacity and Equipartition of Energy

12. Experimentally it appears that many polyatomic molecules' vibrational degrees of freedom can contribute to some extent to their energy at room temperature. Would you expect that fact to increase or decrease their heat capacity from the value R? Explain.

13. One might think that the internal energy of diatomic gases is given by $E_{\text{int}} = 5RT/2$. Do diatomic gases near room temperature have more or less internal energy than that? *Hint:* Their internal energy includes the total energy added in raising the temperature from the boiling point (very low) to room temperature.

14. You mix 5 moles of H_2 at 300 K with 5 moles of He at 360 K in a perfectly insulated calorimeter. Is the final temperature higher or lower than 330 K?

2.4 Distribution of Molecular Speeds

15. One cylinder contains helium gas and another contains krypton gas at the same temperature. Mark each of these statements true, false, or impossible to determine from the given information. (a) The rms speeds of atoms in the two gases are the same. (b) The average kinetic energies of atoms in the two gases are the same. (c) The internal energies of 1 mole of gas in each cylinder are the same. (d) The pressures in the two cylinders are the same.

16. Repeat the previous question if one gas is still helium but the other is changed to fluorine, F_2.

17. An ideal gas is at a temperature of 300 K. To double the average speed of its molecules, what does the temperature need to be changed to?

PROBLEMS

2.1 Molecular Model of an Ideal Gas

18. The gauge pressure in your car tires is $2.50 \times 10^5\ \text{N/m}^2$ at a temperature of $35.0\ °\text{C}$ when you drive it onto a ship in Los Angeles to be sent to Alaska. What is their gauge pressure on a night in Alaska when their temperature has dropped to $-40.0\ °\text{C}$? Assume the tires have not gained or lost any air.

19. Suppose a gas-filled incandescent light bulb is manufactured so that the gas inside the bulb is at atmospheric pressure when the bulb has a temperature of $20.0\ °\text{C}$. (a) Find the gauge pressure inside such a bulb when it is hot, assuming its average temperature is $60.0\ °\text{C}$ (an approximation) and neglecting any change in volume due to thermal expansion or gas leaks. (b) The actual final pressure for the light bulb will be less than calculated in part (a) because the glass bulb will expand. Is this effect significant?

20. People buying food in sealed bags at high elevations often notice that the bags are puffed up because the air inside has expanded. A bag of pretzels was packed at a pressure of 1.00 atm and a temperature of $22.0\ °\text{C}$. When opened at a summer picnic in Santa Fe, New Mexico, at a temperature of $32.0\ °\text{C}$, the volume of the air in the bag is 1.38 times its original volume. What is the pressure of the air?

21. How many moles are there in (a) 0.0500 g of N_2 gas $(M = 28.0\ \text{g/mol})$? (b) 10.0 g of CO_2 gas $(M = 44.0\ \text{g/mol})$? (c) How many molecules are present in each case?

22. A cubic container of volume 2.00 L holds 0.500 mol of nitrogen gas at a temperature of $25.0\,°\text{C}$. What is the net force due to the nitrogen on one wall of the container? Compare that force to the sample's weight.

23. Calculate the number of moles in the 2.00-L volume of air in the lungs of the average person. Note that the air is at $37.0\,°\text{C}$ (body temperature) and that the total volume in the lungs is several times the amount inhaled in a typical breath as given in **Example 2.2**.

24. An airplane passenger has $100\,\text{cm}^3$ of air in his stomach just before the plane takes off from a sea-level airport. What volume will the air have at cruising altitude if cabin pressure drops to $7.50 \times 10^4\ \text{N/m}^2$?

25. A company advertises that it delivers helium at a gauge pressure of $1.72 \times 10^7\ \text{Pa}$ in a cylinder of volume 43.8 L. How many balloons can be inflated to a volume of 4.00 L with that amount of helium? Assume the pressure inside the balloons is $1.01 \times 10^5\ \text{Pa}$ and the temperature in the cylinder and the balloons is $25.0\,°\text{C}$.

26. According to http://hyperphysics.phy-astr.gsu.edu/hbase/solar/venusenv.html, the atmosphere of Venus is approximately $96.5\%\ \text{CO}_2$ and $3.5\%\ \text{N}_2$ by volume. On the surface, where the temperature is about 750 K and the pressure is about 90 atm, what is the density of the atmosphere?

27. An expensive vacuum system can achieve a pressure as low as $1.00 \times 10^{-7}\ \text{N/m}^2$ at $20.0\,°\text{C}$. How many molecules are there in a cubic centimeter at this pressure and temperature?

28. The number density *N*/*V* of gas molecules at a certain location in the space above our planet is about $1.00 \times 10^{11}\ \text{m}^{-3}$, and the pressure is $2.75 \times 10^{-10}\ \text{N/m}^2$ in this space. What is the temperature there?

29. A bicycle tire contains 2.00 L of gas at an absolute pressure of $7.00 \times 10^5\ \text{N/m}^2$ and a temperature of $18.0\,°\text{C}$. What will its pressure be if you let out an amount of air that has a volume of $100\,\text{cm}^3$ at atmospheric pressure? Assume tire temperature and volume remain constant.

30. In a common demonstration, a bottle is heated and stoppered with a hard-boiled egg that's a little bigger than the bottle's neck. When the bottle is cooled, the pressure difference between inside and outside forces the egg into the bottle. Suppose the bottle has a volume of 0.500 L and the temperature inside it is raised to $80.0\,°\text{C}$ while the pressure remains constant at 1.00 atm because the bottle is open. (a) How many moles of air are inside? (b) Now the egg is put in place, sealing the bottle. What is the gauge pressure inside after the air cools back to the ambient temperature of $25\,°\text{C}$ but before the egg is forced into the bottle?

31. A high-pressure gas cylinder contains 50.0 L of toxic gas at a pressure of $1.40 \times 10^7\ \text{N/m}^2$ and a temperature of $25.0\,°\text{C}$. The cylinder is cooled to dry ice temperature $(-78.5\,°\text{C})$ to reduce the leak rate and pressure so that it can be safely repaired. (a) What is the final pressure in the tank, assuming a negligible amount of gas leaks while being cooled and that there is no phase change? (b) What is the final pressure if one-tenth of the gas escapes? (c) To what temperature must the tank be cooled to reduce the pressure to 1.00 atm (assuming the gas does not change phase and that there is no leakage during cooling)? (d) Does cooling the tank as in part (c) appear to be a practical solution?

32. Find the number of moles in 2.00 L of gas at $35.0\,°\text{C}$ and under $7.41 \times 10^7\ \text{N/m}^2$ of pressure.

33. Calculate the depth to which Avogadro's number of table tennis balls would cover Earth. Each ball has a diameter of 3.75 cm. Assume the space between balls adds an extra 25.0% to their volume and assume they are not crushed by their own weight.

34. (a) What is the gauge pressure in a $25.0\,°\text{C}$ car tire containing 3.60 mol of gas in a 30.0-L volume? (b) What will its gauge pressure be if you add 1.00 L of gas originally at atmospheric pressure and $25.0\,°\text{C}$? Assume the temperature remains at $25.0\,°\text{C}$ and the volume remains constant.

2.2 Pressure, Temperature, and RMS Speed

In the problems in this section, assume all gases are ideal.

35. A person hits a tennis ball with a mass of 0.058 kg against a wall. The average component of the ball's velocity perpendicular to the wall is 11 m/s, and the ball hits the wall every 2.1 s on average, rebounding with the opposite perpendicular velocity component. (a) What is the average force exerted on the wall? (b) If the part of the wall the person hits has an area of $3.0\,\text{m}^2$, what is the average pressure on that area?

36. A person is in a closed room (a racquetball court) with $V = 453\ \text{m}^3$ hitting a ball $(m = 42.0\ \text{g})$ around at random without any pauses. The average kinetic energy of the ball is 2.30 J. (a) What is the average value of v_x^2? Does it matter which direction you take to be x? (b) Applying the methods of this chapter, find the average pressure on the walls? (c) Aside from the presence of only one "molecule" in this problem, what is the main assumption in **Pressure, Temperature, and RMS Speed** that does not apply here?

37. Five bicyclists are riding at the following speeds: 5.4 m/s, 5.7 m/s, 5.8 m/s, 6.0 m/s, and 6.5 m/s. (a) What is their average speed? (b) What is their rms speed?

38. Some incandescent light bulbs are filled with argon gas. What is v_{rms} for argon atoms near the filament, assuming their temperature is 2500 K?

39. Typical molecular speeds (v_{rms}) are large, even at low temperatures. What is v_{rms} for helium atoms at 5.00 K, less than one degree above helium's liquefaction temperature?

40. What is the average kinetic energy in joules of hydrogen atoms on the $5500\ °\text{C}$ surface of the Sun? (b) What is the average kinetic energy of helium atoms in a region of the solar corona where the temperature is $6.00 \times 10^5\ \text{K}$?

41. What is the ratio of the average translational kinetic energy of a nitrogen molecule at a temperature of 300 K to the gravitational potential energy of a nitrogen-molecule−Earth system at the ceiling of a 3-m-tall room with respect to the same system with the molecule at the floor?

42. What is the total translational kinetic energy of the air molecules in a room of volume $23\ \text{m}^3$ if the pressure is $9.5 \times 10^4\ \text{Pa}$ (the room is at fairly high elevation) and the temperature is $21\ °\text{C}$? Is any item of data unnecessary for the solution?

43. The product of the pressure and volume of a sample of hydrogen gas at $0.00\ °\text{C}$ is 80.0 J. (a) How many moles of hydrogen are present? (b) What is the average translational kinetic energy of the hydrogen molecules? (c) What is the value of the product of pressure and volume at $200\ °\text{C}$?

44. What is the gauge pressure inside a tank of $4.86 \times 10^4\ \text{mol}$ of compressed nitrogen with a volume of $6.56\ \text{m}^3$ if the rms speed is 514 m/s?

45. If the rms speed of oxygen molecules inside a refrigerator of volume $22.0\ \text{ft.}^3$ is 465 m/s, what is the partial pressure of the oxygen? There are 5.71 moles of oxygen in the refrigerator, and the molar mass of oxygen is 32.0 g/mol.

46. The escape velocity of any object from Earth is 11.1 km/s. At what temperature would oxygen molecules (molar mass is equal to 32.0 g/mol) have root-mean-square velocity v_{rms} equal to Earth's escape velocity of 11.1 km/s?

47. The escape velocity from the Moon is much smaller than that from the Earth, only 2.38 km/s. At what temperature would hydrogen molecules (molar mass is equal to 2.016 g/mol) have a root-mean-square velocity v_{rms} equal to the Moon's escape velocity?

48. Nuclear fusion, the energy source of the Sun, hydrogen bombs, and fusion reactors, occurs much more readily when the average kinetic energy of the atoms is high—that is, at high temperatures. Suppose you want the atoms in your fusion experiment to have average kinetic energies of $6.40 \times 10^{-14}\ \text{J}$. What temperature is needed?

49. Suppose that the typical speed (v_{rms}) of carbon dioxide molecules (molar mass is 44.0 g/mol) in a flame is found to be 1350 m/s. What temperature does this indicate?

50. (a) Hydrogen molecules (molar mass is equal to 2.016 g/mol) have v_{rms} equal to 193 m/s. What is the temperature? (b) Much of the gas near the Sun is atomic hydrogen (H rather than H_2). Its temperature would have to be $1.5 \times 10^7\ \text{K}$ for the rms speed v_{rms} to equal the escape velocity from the Sun. What is that velocity?

51. There are two important isotopes of uranium, ^{235}U and ^{238}U; these isotopes are nearly identical chemically but have different atomic masses. Only ^{235}U is very useful in nuclear reactors. Separating the isotopes is called uranium enrichment (and is often in the news as of this writing, because of concerns that some countries are enriching uranium with the goal of making nuclear weapons.) One of the techniques for enrichment, gas diffusion, is based on the different molecular speeds of uranium hexafluoride gas, UF_6. (a) The molar masses of ^{235}U and $^{238}\text{UF}_6$ are 349.0 g/mol and 352.0 g/mol, respectively. What is the ratio of their typical speeds v_{rms}? (b) At what temperature would their typical speeds differ by 1.00 m/s? (c) Do your answers in this problem imply that this technique may be difficult?

52. The partial pressure of carbon dioxide in the lungs is about 470 Pa when the total pressure in the lungs is 1.0 atm. What percentage of the air molecules in the lungs is carbon dioxide? Compare your result to the percentage of carbon dioxide in the atmosphere, about 0.033%.

53. Dry air consists of approximately 78% nitrogen, 21% oxygen, and 1% argon by mole, with trace amounts of other gases. A tank of compressed dry air has a volume of 1.76 cubic feet at a gauge pressure of 2200 pounds per square inch and a temperature of 293 K. How much oxygen does it contain in moles?

54. (a) Using data from the previous problem, find the mass of nitrogen, oxygen, and argon in 1 mol of dry air. The molar mass of N_2 is 28.0 g/mol, that of O_2 is 32.0 g/mol, and that of argon is 39.9 g/mol. (b) Dry air is mixed with pentane $(C_5H_{12},$ molar mass 72.2 g/mol), an important constituent of gasoline, in an air-fuel ratio of 15:1 by mass (roughly typical for car engines). Find the partial pressure of pentane in this mixture at an overall pressure of 1.00 atm.

55. (a) Given that air is 21% oxygen, find the minimum atmospheric pressure that gives a relatively safe partial pressure of oxygen of 0.16 atm. (b) What is the minimum pressure that gives a partial pressure of oxygen above the quickly fatal level of 0.06 atm? (c) The air pressure at the summit of Mount Everest (8848 m) is 0.334 atm. Why have a few people climbed it without oxygen, while some who have tried, even though they had trained at high elevation, had to turn back?

56. (a) If the partial pressure of water vapor is 8.05 torr, what is the dew point? $(760\ \text{torr} = 1\ \text{atm} = 101,\ 325\ \text{Pa})$ (b) On a warm day when the air temperature is $35\ °\text{C}$ and the dew point is $25\ °\text{C}$, what are the partial pressure of the water in the air and the relative humidity?

2.3 Heat Capacity and Equipartition of Energy

57. To give a helium atom nonzero angular momentum requires about 21.2 eV of energy (that is, 21.2 eV is the difference between the energies of the lowest-energy or ground state and the lowest-energy state with angular momentum). The electron-volt or eV is defined as 1.60×10^{-19} J. Find the temperature T where this amount of energy equals $k_B T/2$. Does this explain why we can ignore the rotational energy of helium for most purposes? (The results for other monatomic gases, and for diatomic gases rotating around the axis connecting the two atoms, have comparable orders of magnitude.)

58. (a) How much heat must be added to raise the temperature of 1.5 mol of air from $25.0\ °\text{C}$ to $33.0\ °\text{C}$ at constant volume? Assume air is completely diatomic. (b) Repeat the problem for the same number of moles of xenon, Xe.

59. A sealed, rigid container of 0.560 mol of an unknown ideal gas at a temperature of $30.0\ °\text{C}$ is cooled to $-40.0\ °\text{C}$. In the process, 980 J of heat are removed from the gas. Is the gas monatomic, diatomic, or polyatomic?

60. A sample of neon gas (Ne, molar mass $M = 20.2\ \text{g/mol})$ at a temperature of $13.0\ °\text{C}$ is put into a steel container of mass 47.2 g that's at a temperature of $-40.0\ °\text{C}$. The final temperature is $-28.0\ °\text{C}$. (No heat is exchanged with the surroundings, and you can neglect any change in the volume of the container.) What is the mass of the sample of neon?

61. A steel container of mass 135 g contains 24.0 g of ammonia, NH_3, which has a molar mass of 17.0 g/mol. The container and gas are in equilibrium at $12.0\ °\text{C}$. How much heat has to be removed to reach a temperature of $-20.0\ °\text{C}$? Ignore the change in volume of the steel.

62. A sealed room has a volume of $24\ \text{m}^3$. It's filled with air, which may be assumed to be diatomic, at a temperature of $24\ °\text{C}$ and a pressure of 9.83×10^4 Pa. A 1.00-kg block of ice at its melting point is placed in the room. Assume the walls of the room transfer no heat. What is the equilibrium temperature?

63. Heliox, a mixture of helium and oxygen, is sometimes given to hospital patients who have trouble breathing, because the low mass of helium makes it easier to breathe than air. Suppose helium at $25\ °\text{C}$ is mixed with oxygen at $35\ °\text{C}$ to make a mixture that is 70% helium by mole. What is the final temperature? Ignore any heat flow to or from the surroundings, and assume the final volume is the sum of the initial volumes.

64. Professional divers sometimes use heliox, consisting of 79% helium and 21% oxygen by mole. Suppose a perfectly rigid scuba tank with a volume of 11 L contains heliox at an absolute pressure of 2.1×10^7 Pa at a temperature of $31\ °\text{C}$. (a) How many moles of helium and how many moles of oxygen are in the tank? (b) The diver goes down to a point where the sea temperature is $27\ °\text{C}$ while using a negligible amount of the mixture. As the gas in the tank reaches this new temperature, how much heat is removed from it?

65. In car racing, one advantage of mixing liquid nitrous oxide (N_2O) with air is that the boiling of the “nitrous” absorbs latent heat of vaporization and thus cools the air and ultimately the fuel-air mixture, allowing more fuel-air mixture to go into each cylinder. As a very rough look at this process, suppose 1.0 mol of nitrous oxide gas at its boiling point, $-88\,°\text{C}$, is mixed with 4.0 mol of air (assumed diatomic) at $30\,°\text{C}$. What is the final temperature of the mixture? Use the measured heat capacity of N_2O at $25\,°\text{C}$, which is $30.4\ \text{J/mol}\,°\text{C}$. (The primary advantage of nitrous oxide is that it consists of 1/3 oxygen, which is more than air contains, so it supplies more oxygen to burn the fuel. Another advantage is that its decomposition into nitrogen and oxygen releases energy in the cylinder.)

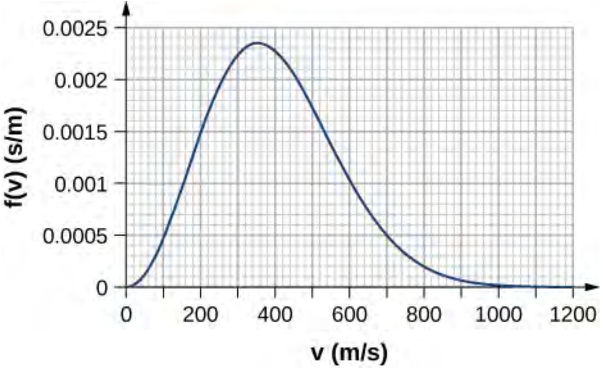
2.4 Distribution of Molecular Speeds

66. In a sample of hydrogen sulfide $(M = 34.1\ \text{g/mol})$ at a temperature of $3.00 \times 10^2\ \text{K}$, estimate the ratio of the number of molecules that have speeds very close to v_{rms} to the number that have speeds very close to $2v_{\text{rms}}$.

67. Using the approximation $\int_{v_1}^{v_1+\Delta v} f(v)dv \approx f(v_1)\Delta v$ for small Δv, estimate the fraction of nitrogen molecules at a temperature of $3.00 \times 10^2\ \text{K}$ that have speeds between 290 m/s and 291 m/s.

68. Using the method of the preceding problem, estimate the fraction of nitric oxide (NO) molecules at a temperature of 250 K that have energies between $3.45 \times 10^{-21}\ \text{J}$ and $3.50 \times 10^{-21}\ \text{J}$.

69. By counting squares in the following figure, estimate the fraction of argon atoms at $T = 300\ \text{K}$ that have speeds between 600 m/s and 800 m/s. The curve is correctly normalized. The value of a square is its length as measured on the *x*-axis times its height as measured on the *y*-axis, with the units given on those axes.



70. Using a numerical integration method such as Simpson's rule, find the fraction of molecules in a sample of oxygen gas at a temperature of 250 K that have speeds between 100 m/s and 150 m/s. The molar mass of oxygen (O_2) is 32.0 g/mol. A precision to two significant digits is enough.

71. Find (a) the most probable speed, (b) the average speed, and (c) the rms speed for nitrogen molecules at 295 K.

72. Repeat the preceding problem for nitrogen molecules at 2950 K.

73. At what temperature is the average speed of carbon dioxide molecules $(M = 44.0\ \text{g/mol})$ 510 m/s?

74. The most probable speed for molecules of a gas at 296 K is 263 m/s. What is the molar mass of the gas? (You might like to figure out what the gas is likely to be.)

75. a) At what temperature do oxygen molecules have the same average speed as helium atoms $(M = 4.00\ \text{g/mol})$ have at 300 K? b) What is the answer to the same question about most probable speeds? c) What is the answer to the same question about rms speeds?

ADDITIONAL PROBLEMS

76. In the deep space between galaxies, the density of molecules (which are mostly single atoms) can be as low as $10^6\ \text{atoms/m}^3$, and the temperature is a frigid 2.7 K. What is the pressure? (b) What volume (in m^3) is occupied by 1 mol of gas? (c) If this volume is a cube, what is the length of its sides in kilometers?

77. (a) Find the density in SI units of air at a pressure of 1.00 atm and a temperature of $20\,°\text{C}$, assuming that air is $78\%\ \text{N}_2,\ 21\%\ \text{O}_2,$ and $1\%\ \text{Ar}$, (b) Find the density of the atmosphere on Venus, assuming that it's $96\%\ \text{CO}_2$ and $4\%\ \text{N}_2$, with a temperature of 737 K and a pressure of 92.0 atm.

78. The air inside a hot-air balloon has a temperature of 370 K and a pressure of 101.3 kPa, the same as that of the air outside. Using the composition of air as $78\%\ \text{N}_2,\ 21\%\text{O}_2,$ and $1\%\ \text{Ar}$, find the density of the air inside the balloon.

79. When an air bubble rises from the bottom to the top of a freshwater lake, its volume increases by 80%. If the temperatures at the bottom and the top of the lake are 4.0 and 10 $°\text{C}$, respectively, how deep is the lake?

80. (a) Use the ideal gas equation to estimate the temperature at which 1.00 kg of steam (molar mass $M = 18.0\ \text{g/mol}$) at a pressure of $1.50 \times 10^6\ \text{Pa}$ occupies a volume of $0.220\ \text{m}^3$. (b) The van der Waals constants for water are $a = 0.5537\ \text{Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 3.049 \times 10^{-5}\ \text{m}^3/\text{mol}$. Use the Van der Waals equation of state to estimate the temperature under the same conditions. (c) The actual temperature is 779 K. Which estimate is better?

81. One process for decaffeinating coffee uses carbon dioxide $(M = 44.0\ \text{g/mol})$ at a molar density of about $14{,}600\ \text{mol/m}^3$ and a temperature of about $60\ °\text{C}$. (a) Is CO_2 a solid, liquid, gas, or supercritical fluid under those conditions? (b) The van der Waals constants for carbon dioxide are $a = 0.3658\ \text{Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 4.286 \times 10^{-5}\ \text{m}^3/\text{mol}.$ Using the van der Waals equation, estimate the pressure of CO_2 at that temperature and density.

82. On a winter day when the air temperature is $0\ °\text{C},$ the relative humidity is 50%. Outside air comes inside and is heated to a room temperature of $20\ °\text{C}$. What is the relative humidity of the air inside the room. (Does this problem show why inside air is so dry in winter?)

83. On a warm day when the air temperature is $30\ °\text{C}$, a metal can is slowly cooled by adding bits of ice to liquid water in it. Condensation first appears when the can reaches $15\ °\text{C}$. What is the relative humidity of the air?

84. (a) People often think of humid air as "heavy." Compare the densities of air with 0% relative humidity and 100% relative humidity when both are at 1 atm and $30\ °\text{C}$. Assume that the dry air is an ideal gas composed of molecules with a molar mass of 29.0 g/mol and the moist air is the same gas mixed with water vapor. (b) As discussed in the chapter on the applications of Newton's laws, the air resistance felt by projectiles such as baseballs and golf balls is approximately $F_\text{D} = C\rho A v^2/2$, where ρ is the mass density of the air, *A* is the cross-sectional area of the projectile, and *C* is the projectile's drag coefficient. For a fixed air pressure, describe qualitatively how the range of a projectile changes with the relative humidity. (c) When a thunderstorm is coming, usually the humidity is high and the air pressure is low. Do those conditions give an advantage or disadvantage to home-run hitters?

85. The mean free path for helium at a certain temperature and pressure is 2.10×10^{-7} m. The radius of a helium atom can be taken as $1.10 \times 10^{-11}\ \text{m}$. What is the measure of the density of helium under those conditions (a) in molecules per cubic meter and (b) in moles per cubic meter?

86. The mean free path for methane at a temperature of 269 K and a pressure of $1.11 \times 10^5\ \text{Pa}$ is 4.81×10^{-8} m. Find the effective radius *r* of the methane molecule.

87. In the chapter on fluid mechanics, Bernoulli's equation for the flow of incompressible fluids was explained in terms of changes affecting a small volume *dV* of fluid. Such volumes are a fundamental idea in the study of the flow of compressible fluids such as gases as well. For the equations of hydrodynamics to apply, the mean free path must be much less than the linear size of such a volume, $a \approx dV^{1/3}$. For air in the stratosphere at a temperature of 220 K and a pressure of 5.8 kPa, how big should *a* be for it to be 100 times the mean free path? Take the effective radius of air molecules to be 1.88×10^{-11} m, which is roughly correct for N_2.

88. Find the total number of collisions between molecules in 1.00 s in 1.00 L of nitrogen gas at standard temperature and pressure ($0\ °\text{C}$, 1.00 atm). Use 1.88×10^{-10} m as the effective radius of a nitrogen molecule. (The number of collisions per second is the reciprocal of the collision time.) Keep in mind that each collision involves two molecules, so if one molecule collides once in a certain period of time, the collision of the molecule it hit cannot be counted.

89. (a) Estimate the specific heat capacity of sodium from the Law of Dulong and Petit. The molar mass of sodium is 23.0 g/mol. (b) What is the percent error of your estimate from the known value, $1230\ \text{J/kg} \cdot °\text{C}$?

90. A sealed, perfectly insulated container contains 0.630 mol of air at $20.0\ °\text{C}$ and an iron stirring bar of mass 40.0 g. The stirring bar is magnetically driven to a kinetic energy of 50.0 J and allowed to slow down by air resistance. What is the equilibrium temperature?

91. Find the ratio $f(v_\text{p})/f(v_\text{rms})$ for hydrogen gas $(M = 2.02\ \text{g/mol})$ at a temperature of 77.0 K.

92. **Unreasonable results**. (a) Find the temperature of 0.360 kg of water, modeled as an ideal gas, at a pressure of 1.01×10^5 Pa if it has a volume of $0.615\ \text{m}^3$. (b) What is unreasonable about this answer? How could you get a better answer?

93. **Unreasonable results**. (a) Find the average speed of hydrogen sulfide, H_2S, molecules at a temperature of 250 K. Its molar mass is 31.4 g/mol (b) The result isn't *very* unreasonable, but why is it less reliable than those for, say, neon or nitrogen?

CHALLENGE PROBLEMS

94. An airtight dispenser for drinking water is $25\ \text{cm} \times 10\ \text{cm}$ in horizontal dimensions and 20 cm tall. It has a tap of negligible volume that opens at the level of the bottom of the dispenser. Initially, it contains water to a level 3.0 cm from the top and air at the ambient pressure, 1.00 atm, from there to the top. When the tap is opened, water will flow out until the gauge pressure at the bottom of the dispenser, and thus at the opening of the tap, is 0. What volume of water flows out? Assume the temperature is constant, the dispenser is perfectly rigid, and the water has a constant density of $1000\ \text{kg/m}^3$.

95. Eight bumper cars, each with a mass of 322 kg, are running in a room 21.0 m long and 13.0 m wide. They have no drivers, so they just bounce around on their own. The rms speed of the cars is 2.50 m/s. Repeating the arguments of **Pressure, Temperature, and RMS Speed**, find the average force per unit length (analogous to pressure) that the cars exert on the walls.

96. Verify that $v_p = \sqrt{\frac{2k_B T}{m}}$.

97. Verify the normalization equation $\int_0^\infty f(v)dv = 1$. In doing the integral, first make the substitution $u = \sqrt{\frac{m}{2k_B T}}v = \frac{v}{v_p}$. This "scaling" transformation gives you all features of the answer except for the integral, which is a dimensionless numerical factor. You'll need the formula

$$\int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}$$

to find the numerical factor and verify the normalization.

98. Verify that $\bar{v} = \sqrt{\frac{8}{\pi}\frac{k_B T}{m}}$. Make the same scaling transformation as in the preceding problem.

99. Verify that $v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$.