

At the same temperature, the He, O₂, and Xe molecules all have the same average kinetic energy; lighter molecules move faster to compensate for their smaller masses. These rms speeds convert to 3050, 1080, and 532 mph, respectively. The average molecule moves along quite rapidly at room temperature!

Related Problems: 41, 42, 43, 44

It is useful to have a complete picture of the entire distribution of molecular speeds. This turns out to be important when we study chemical kinetics (see Chapter 18), where we will need to know what fraction of a sample of molecules has kinetic energy above the minimum necessary for a chemical reaction. In particular, we would like to know what fraction of molecules, $\Delta N/N$, have speeds between u and $u + \Delta u$. This fraction gives the speed distribution function $f(u)$:

$$\frac{\Delta N}{N} = f(u) \Delta u$$

The speed distribution of the molecules in a gas has been measured experimentally by an apparatus sketched in Figure 9.13. The entire apparatus is enclosed in a large vacuum chamber. The molecules leak out of their container to form a *molecular beam*, which passes into a speed analyzer. The analyzer consists of two rotating plates, each with a notch in its edge, separated by the fixed distance L . The plates are rotated so the notches align and permit molecules to pass through both to reach the detector only for a short time interval, $\Delta\tau$. Only those molecules with speeds in the range $\Delta u = L/\Delta\tau$ reach the detector and are counted. The entire speed distribution can be mapped out by progressively varying the duration of the measurement time interval, $\Delta\tau$.

The function $f(u)$ was predicted theoretically by Maxwell and Boltzmann about 60 years before it was first measured. It is called the **Maxwell-Boltzmann speed distribution** for a gas of molecules of mass m at temperature T and it has the following form:

$$f(u) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 \exp(-mu^2/2k_B T) \quad [9.17]$$

where Boltzmann's constant k_B was defined in Equation 9.14. This distribution is plotted in Figure 9.14 for several temperatures. As the temperature is raised, the entire distribution of molecular speeds shifts toward higher values. Few molecules

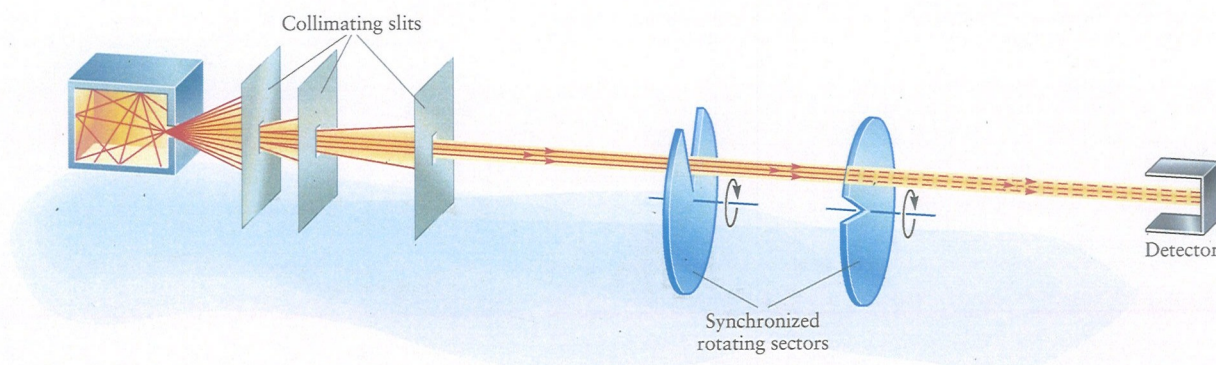
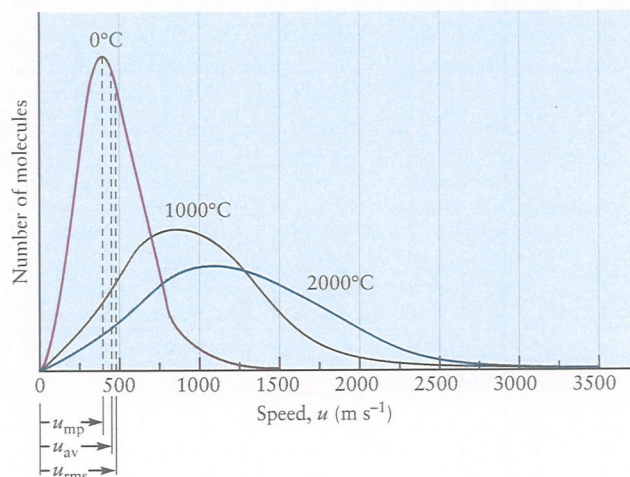


FIGURE 9.13 A device for measuring the distribution of molecular speeds. Only those molecules with the correct velocity to pass through *both* rotating sectors will reach the detector, where they will be counted. Changing the rate of rotation of the sectors allows the speed distribution to be determined.

FIGURE 9.14 The Maxwell–Boltzmann distribution of molecular speeds in nitrogen at three temperatures. The peak in each curve gives the most probable speed, u_{mp} , which is slightly smaller than the root-mean-square speed, u_{rms} . The average speed u_{av} (obtained simply by adding the speeds and dividing by the number of molecules in the sample) lies in between. All three measures give comparable estimates of typical molecular speeds and show how these speeds increase with temperature.



have either very low or very high speeds; thus, $f(u)$ is small in these limits and has a maximum at some intermediate speed.

An alternative interpretation of the Maxwell–Boltzmann speed distribution is helpful in statistical analysis of the experiment. Experimentally, the probability that a molecule selected from the gas will have speed in the range Δu is defined as the fraction $\Delta N/N$ discussed earlier. Because $\Delta N/N$ is equal to $f(u) \Delta u$, we interpret this product as the probability predicted from theory that any molecule selected from the gas will have speed between u and $u + \Delta u$. In this way we think of the Maxwell–Boltzmann speed distribution $f(u)$ as a *probability distribution*. It is necessary to restrict Δu to very small ranges compared with u to make sure the probability distribution is a continuous function of u . An elementary introduction to probability distributions and their applications is given in Appendix C.6. We suggest you review that material now.

A probability distribution gives a quick visual indication of the likely outcome of the experiment it describes. The **most probable speed** u_{mp} is the speed at which $f(u)$ has its maximum. For the Maxwell–Boltzmann distribution function, this is

$$u_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}} \quad [9.18]$$

A probability distribution enables us to calculate the average of the values obtained in several repetitions of the experiment it describes. The procedure is described in Appendix C.6. For the Maxwell–Boltzmann distribution, this calculation gives the **average speed** \bar{u} , which is

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad [9.19]$$

If a probability distribution is symmetrical about its maximum, like the familiar “bell curve,” the most probable value and the average value are the same. The Maxwell–Boltzmann distribution is not symmetrical; the area under the curve to the right of the maximum is somewhat larger than the area under the curve to the left of the maximum. (The next paragraphs use the mathematical form of the distribution to explain this fact.) Consequently, \bar{u} will be larger than the most probable value of u .

The root-mean-square value can be calculated from the probability distribution, as shown in Appendix C.6. For a symmetrical distribution, this would be

equal to the average value. For the Maxwell–Boltzmann distribution, we have already seen that

$$u_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} = \sqrt{\frac{3RT}{\pi M}}$$

which verifies that $\bar{u} < u_{\text{rms}}$.

There are several possible ways to characterize a non-symmetrical probability distribution by a single number. The three different speeds discussed above serve this purpose for the Maxwell–Boltzmann distribution. Because the distribution is non-symmetrical, they are close to each other but are not equal. They stand in the ratio:

$$u_{\text{mp}} : \bar{u} : u_{\text{rms}} = 1.000 : 1.128 : 1.1225$$

It is not important for you to memorize these ratios. But you should understand that each quantity is a measure of the “average” speed of the molecules described by the distribution. Different applications require different choices among these quantities. You will learn how to make these connections in more advanced work.

The Maxwell–Boltzmann distribution is not symmetrical because it has the following mathematical form

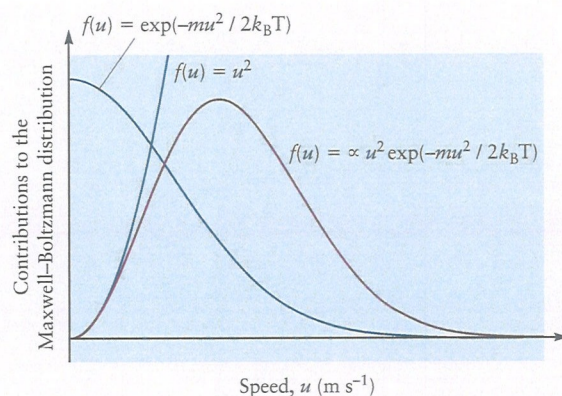
$$f(u) \propto u^2 \exp(-mu^2/2k_{\text{B}}T)$$

which describes a competition between the two factors that depend on u^2 . The competition arises because these factors behave oppositely, for physical reasons, as the value of u changes. We can get a great deal of physical insight into the distribution by studying the behavior of these factors separately while T is held constant.

The exponential factor can be viewed graphically as the right half of a bell curve with its maximum at $u = 0$ (Fig. 9.15). At low values of u , this factor behaves as $\exp(-mu^2/2k_{\text{B}}T) \rightarrow \exp(-0) = 1$. At very large values of u , this factor behaves as $\exp(-mu^2/2k_{\text{B}}T) = 1/[\exp(mu^2/2k_{\text{B}}T)] \rightarrow 1/\infty = 0$. The role of this factor is to describe the statistical weight given to each value of u in relation to T . The limits we have just examined shows this factor gives large statistical weight to small values of u , and increasingly small weight to large values of u , eventually forcing the distribution to fall off to zero at extremely high values of u . This is exactly what we expect on physical grounds.

The factor u^2 can be viewed as the right half of a parabola with its minimum at $u = 0$ (see Fig. 9.15). The value of this factor approaches zero as u decreases towards 0, and it grows without bound as u becomes extremely large. Although we do not provide all the details, the role of this factor is to count the number of different ways molecules in the gas can achieve a particular value of the speed, u . With Avogadro’s number of molecules moving around the vessel, it is physically sensible that many different combinations of velocity vectors correspond to a

FIGURE 9.15 Mathematical form of the Maxwell–Boltzmann speed distribution. The factor u^2 cuts off the distribution at small values of u , whereas the exponential factor causes it to die off at large values of u . The competition between these effects causes the distribution to achieve its maximum value at intermediate values of u .



given value of the speed. And, we expect the number of such combinations to increase as the value of the speed increases. The shape of this factor strongly favors molecules with large values of u and it rapidly cuts off the distribution for small values of u .

The net result of these two competing factors is to keep the probability small for both extremely large and extremely small values of u . The probability will have a maximum at some intermediate value of u where the increasing effect of u^2 is just balanced by the decreasing effect of the exponential factor (see Fig. 9.15). This is the *most probable* value of u , denoted by u_{mp} , and it can be identified by setting to zero the derivative of the curve with respect to u . Because u^2 approaches zero for small values of u more rapidly than the exponential factor approaches zero for large values of u , the probability is larger to the right side of the maximum. The area under the curve to the right of the maximum is somewhat larger than the area under the curve to the left of the maximum. Consequently, the average value of u denoted by \bar{u} will be larger than the most probable value of u . This is illustrated in Figure 9.14, which shows that $u_{\text{mp}} < \bar{u} < u_{\text{rms}}$.

The behavior of these competing factors also explains why the distribution becomes broader and its maximum moves to a higher value of u as the temperature increases (see Fig. 9.14). The maximum increases because the value of u at which the parabolic factor u^2 is cut off by the exponential factor increases as T increases. This happens because a particular value of u that would make $\exp(-mu^2/2k_B T) \ll 1$ at low T will now make $\exp(-mu^2/2k_B T) \rightarrow \exp(-0) = 1$ at higher T . The distribution broadens because the falloff after the maximum is slower at high T than at low T . The reason is that as T increases, the value of u at which $\exp(-mu^2/2k_B T) \rightarrow 0$ also increases. The net effect at higher T is that larger values of u become accessible, so the molecules are spread over a broader range of speeds.

The Maxwell–Boltzmann speed distribution defines temperature in the kinetic theory of gases as proportional to the average kinetic energy per molecule through Equation 9.14. Unless the molecular speed distribution for a given gas corresponds to the Maxwell–Boltzmann distribution, temperature has no meaning for the gas. Temperature describes a system of gaseous molecules only when their speed distribution is represented by the Maxwell–Boltzmann function. Consider a closed container filled with molecules whose speed distribution is not “Maxwellian.” Such a situation is possible (for example, just after an explosion), but it cannot persist for long. Any distribution of molecular speeds other than a Maxwell–Boltzmann distribution quickly becomes Maxwellian through molecular collisions that exchange energy. Once attained, the Maxwell–Boltzmann distribution persists indefinitely (or at least until some new disturbance is applied). The gas molecules have come to **thermal equilibrium** with one another, and we can speak of a system as having a temperature only if the condition of thermal equilibrium exists.

A DEEPER LOOK

9.6 Distribution of Energy among Molecules

The kinetic molecular theory of gases relates the macroscopic properties of a gas to the structure of the constituent molecules, the forces between them, and their motions. Because the number

of molecules in a sample of gas is so incredibly large—28 g nitrogen contains 6.02×10^{23} molecules—we give up the idea of following the detailed motions of any one molecule and rely on a statistical description that gives the *probability* of finding a molecule in the gas at a certain position, with a certain speed, with a certain value of energy, and so on. Treating the molecules as point masses obeying classical mechanics and using simple statistical arguments, the kinetic theory shows that the temperature of the

gas is proportional to the average kinetic energy per molecule. This relation not only provides a microscopic interpretation of the concept of temperature, but it also indicates the typical values of molecular kinetic energy that occur in a gas at a particular temperature.

Now we want to determine the relation between temperature and the energy involved in other kinds of molecular motions that depend on molecular structure, not just the translation of the molecule. This relation is provided by the *Boltzmann energy distribution*, which relies on the quantum description of molecular motions. This section defines the Boltzmann distribution and uses it to describe the vibrational energy of diatomic molecules in a gas at temperature T .

The Boltzmann energy distribution is one of the most widely used relations in the natural sciences, because it provides a reliable way to interpret experimental results in terms of molecular behavior. You should become skilled in its applications.

The Boltzmann Energy Distribution

Just as in the previous section, we start with a model system in which gaseous molecules move around inside a container held at temperature T . The molecules collide with the container walls but not with one another. We can achieve this condition by setting up the experiment with sufficiently low pressure in the system. But this time we assume that the molecules have quantum states described by a quantum number n and represented on an energy level diagram where the energy of each state is labeled ε_n . After the system has settled down to equilibrium, how many of the molecules are in their ground state? To what extent are the excited states populated? The answers depend on the probability that a molecule in the gas is in the quantum state n , which is given by the **Boltzmann energy distribution**:

$$P(n) = C \exp(-\varepsilon_n/k_B T) \quad [9.20]$$

where C is a normalization factor and k_B is Boltzmann's constant. This equation was derived for classical systems by Ludwig Boltzmann even before quantum mechanics had been invented. Max Planck used a version of the Boltzmann distribution in formulating his theory of blackbody radiation (see Section 4.2) to obtain the probability that his quantized oscillators would radiate energy when the blackbody was at temperature T . We do not derive the distribution, but illustrate its application and interpretation.

VIBRATIONAL ENERGY DISTRIBUTION

We apply the Boltzmann distribution to describe the probability of finding molecules in each of the vibrational states in a sample of CO held at temperature T . We describe the vibrational motions using the harmonic oscillator model, for which the allowed energy levels are

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu$$

where $n = 0, 1, 2, 3, \dots$ and the vibrational frequency is related to the force constant by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

and μ is the reduced mass. These equations define the energy level diagram, which has uniformly spaced levels separated by

$$h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad [9.21]$$

We calculate the reduced mass of $^{12}\text{C}^{16}\text{O}$ using the isotopic masses in Table 19.1 to be

$$\begin{aligned} \mu &= \frac{m_{\text{C}}m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} \\ &= \frac{(12.00)(15.99)\text{amu}}{27.99} \left(\frac{1\text{ g}}{6.02 \times 10^{23}\text{ amu}}\right) \left(\frac{1\text{ kg}}{10^3\text{ g}}\right) \\ \mu &= 1.14 \times 10^{-26}\text{ kg} \end{aligned}$$

The value of the force constant for CO is 1902 N m^{-1} , as measured in vibrational spectroscopy. The value of the energy level separation is then

$$\begin{aligned} h\nu &= \left(\frac{6.63 \times 10^{-34}\text{ J s}}{2\pi}\right) \left(\frac{1.902 \times 10^3\text{ N m}^{-1}}{1.14 \times 10^{-26}\text{ kg}}\right)^{1/2} \\ h\nu &= 4.52 \times 10^{-20}\text{ J} \end{aligned}$$

The relative probability of finding molecules in the excited state n and in the ground state $n = 0$ is given by

$$\frac{P(n)}{P(0)} = \frac{C \exp(-\varepsilon_n/k_B T)}{C \exp(-\varepsilon_0/k_B T)} = \exp(-[\varepsilon_n - \varepsilon_0]/k_B T) \quad [9.22]$$

Inserting the energy level expression for the harmonic oscillator gives

$$\frac{P(n)}{P(0)} = \exp\left[-\left(n + \frac{1}{2}\right)h\nu - \frac{1}{2}h\nu\right]/k_B T = \exp(-nh\nu/k_B T) \quad [9.23]$$

The relative populations of the first excited state $n = 1$ and the ground state are determined by the ratio $h\nu/k_B T$. We know from Chapter 4 that $h\nu$ is the quantum of vibrational energy needed to put a CO molecule in its first excited state, and we have calculated that value to be $h\nu = 4.52 \times 10^{-20}\text{ J}$. From Section 9.5 we know that the average kinetic energy of a molecule in the gas is $(3/2)k_B T$, which is $(1/2)k_B T$ for each of the x , y , and z directions of motion. Therefore, we interpret $k_B T$ as a measure of the average energy available to each molecule in a gas at temperature T . So, the ratio $h\nu/k_B T$ determines whether there is sufficient energy in the gas to put the molecules into excited states. At 300 K, the value of $k_B T$ is $4.14 \times 10^{-21}\text{ J}$, which is a factor of 10 smaller than the vibrational quantum of CO. Inserting these numbers into Equation 9.23 gives the relative probability as 3.03×10^{-5} . This means that only 3 molecules in a group of 100,000 are in the first excited state at 300 K. At 1000 K, the value of $k_B T$ is $1.38 \times 10^{-20}\text{ J}$, which is closer to the value of the CO vibrational quantum and gives a relative population of 4.41×10^{-2} .

This case study shows that CO molecules do not have significant vibrational energy unless the temperature is quite high. This happens because CO has a triple bond and, therefore, a large force constant ($k = 1902\text{ N m}^{-1}$). The correlation between force constant and bond order in diatomic molecules is explained by molecular orbital theory, and is summarized in Figure 6.20. Other diatomic molecules will behave differently, as determined by their structure and the Boltzmann distribution.