

scale Θ (capital theta). Temperature ratios on the thermodynamic scale are thus defined by

$$\frac{\Theta_C}{\Theta_H} \equiv \frac{-q_C}{q_H} \quad (3.44)$$

Equation (3.44) fixes only the ratio Θ_C/Θ_H . We complete the definition of the Θ scale by choosing the temperature of the triple point of water as $\Theta_{\text{tr}} = 273.16^\circ$.

To measure the thermodynamic temperature Θ of an arbitrary body, we use it as one of the heat reservoirs in a Carnot cycle and use a body composed of water at its triple point as the second reservoir. We then put any system through a Carnot cycle between these two reservoirs and measure the heat q exchanged with the reservoir at Θ and the heat q_{tr} exchanged with the reservoir at 273.16° . The thermodynamic temperature Θ is then calculated from (3.44) as

$$\Theta = 273.16^\circ \frac{|q|}{|q_{\text{tr}}|} \quad (3.45)$$

Since the heat ratio in (3.45) is independent of the nature of the system put through the Carnot cycle, the Θ scale does not depend on the properties of any kind of substance.

How is the thermodynamic scale Θ related to the ideal-gas scale T ? We proved in Sec. 3.2 that, on the ideal-gas temperature scale, $T_C/T_H = -q_C/q_H$ for any system that undergoes a Carnot cycle; see Eq. (3.16). Moreover, we chose the ideal-gas temperature at the water triple point as 273.16 K . Hence for a Carnot cycle between an arbitrary temperature T and the triple-point temperature, we have

$$T = 273.16 \text{ K} \frac{|q|}{|q_{\text{tr}}|} \quad (3.46)$$

where q is the heat exchanged with the reservoir at T . Comparison of (3.45) and (3.46) shows that *the ideal-gas temperature scale and the thermodynamic temperature scale are numerically identical*. We will henceforth use the same symbol T for each scale. The thermodynamic scale is the fundamental scale of science, but as a matter of practical convenience, extrapolated measurements on gases, rather than Carnot-cycle measurements, are used to measure temperatures accurately.

3.7 WHAT IS ENTROPY?

Each of the first three laws of thermodynamics leads to the existence of a state function. The zeroth law leads to temperature. The first law leads to internal energy. The second law leads to entropy. It is not the business of thermodynamics, which is a macroscopic science, to explain the microscopic nature of these state functions. Thermodynamics need only tell us how to measure T , ΔU , and ΔS . Nevertheless it is nice to have a molecular picture of the macroscopic thermodynamic state functions.

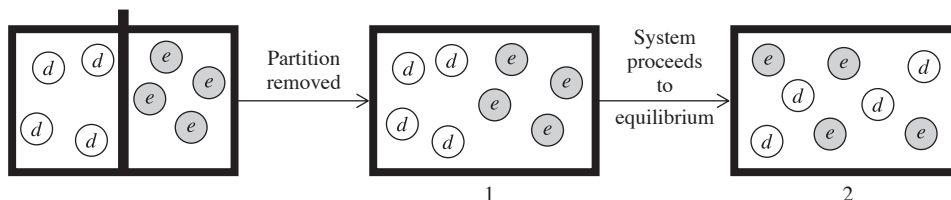
Temperature is readily interpreted as some sort of measure of the average molecular energy. Internal energy is interpreted as the total molecular energy. Although we have shown how ΔS can be calculated for various processes, the reader may feel frustrated at not having any clear picture of the physical nature of entropy. Although entropy is not as easy a concept to grasp as temperature or internal energy, we can get some understanding of its physical nature.

Molecular Interpretation of Entropy

We saw in Sec. 3.5 that the entropy S of an isolated system is maximized at equilibrium. We therefore now ask: What else is maximized at equilibrium? In other words,

Figure 3.12

Irreversible mixing of perfect gases at constant T and P .



what really determines the equilibrium position of an isolated thermodynamic system? To answer this, consider a simple example, the mixing at constant temperature and pressure of equal volumes of two different inert perfect gases d and e in an isolated system (Fig. 3.12). The motion of the gas molecules is completely random, and the molecules do not interact with one another. What then makes 2 in Fig. 3.12 the equilibrium state and 1 a nonequilibrium state? Why is the passage from the unmixed state 1 to the mixed state 2 irreversible? (From 2, an isolated system will never go back to 1.)

Clearly the answer is *probability*. If the molecules move at random, any d molecule has a 50% chance of being in the left half of the container. The probability that all the d molecules will be in the left half and all the e molecules in the right half (state 1) is extremely small. The most probable distribution has d and e molecules each equally distributed between the two halves of the container (state 2). An analogy to the spatial distribution of 1 mole of d molecules would be tossing a coin 6×10^{23} times. The chance of getting 6×10^{23} heads is extremely tiny. The most probable outcome is 3×10^{23} heads and 3×10^{23} tails, and only outcomes with a very nearly equal ratio of heads to tails have significant probabilities. The probability maximum is extremely sharply peaked at 50% heads. (For example, Fig. 3.13 shows the probabilities for obtaining various numbers of heads for 10 tosses of a coin and for 100 tosses. As the number of tosses increases, the probability of significant deviations from 50% heads diminishes.) Similarly, any spatial distribution of the d molecules that differs significantly from 50% d in each container has an extremely small probability because of the large number of d molecules; similarly for the e molecules.

It seems clear that *the equilibrium thermodynamic state of an isolated system is the most probable state*. The increase in S as an isolated system proceeds toward equilibrium is directly related to the system's going from a state of low probability to one of high probability. We therefore postulate that the entropy S of a system is a function of the probability p of the system's thermodynamic state:

$$S = f(p) \quad (3.47)$$

Amazingly, use of the single fact that entropy is an extensive state function allows us to find the function f in our postulate (3.47). To do this, we consider a system composed of two independent, noninteracting parts, 1 and 2, separated by a rigid, impermeable, adiabatic wall that prevents flow of heat, work, and matter between them. Entropy is an extensive property, so the entropy of the composite system 1 + 2 is $S_{1+2} = S_1 + S_2$, where S_1 and S_2 are the entropies of parts 1 and 2. Substitution of (3.47) into this equation gives

$$h(p_{1+2}) = f(p_1) + g(p_2) \quad (3.48)$$

where f , g , and h are three functions. Since systems 1, 2, and 1 + 2 are not identical, the functions f , g , and h are not necessarily identical. What is the relation between the probability p_{1+2} of the composite system's thermodynamic state and the probabilities p_1 and p_2 of the states of parts 1 and 2? The probability that two independent events will both happen is shown in probability theory to be the product of the probabilities for each event. For example, the probability of getting two heads when two coins are

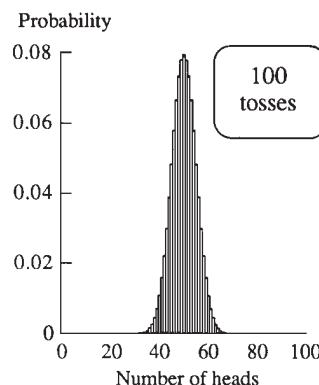
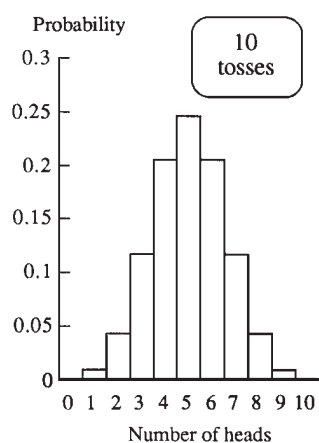


Figure 3.13

Probabilities for various numbers of heads when a coin is tossed 10 times and 100 times.

tossed is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. Since parts 1 and 2 behave independently of each other, we have $p_{1+2} = p_1 p_2$. Equation (3.48) becomes

$$h(p_1 p_2) = f(p_1) + g(p_2) \quad (3.49)$$

Our task is to find the functions that satisfy

$$h(xy) = f(x) + g(y) \quad (3.50)$$

Before reading ahead, you might try to guess a solution for h .

It isn't hard to prove that the only way to satisfy (3.50) is with logarithmic functions. Problem 14.54 shows that the functions in (3.50) must be

$$f(x) = k \ln x + a, \quad g(y) = k \ln y + b, \quad h(xy) = k \ln(xy) + c \quad (3.51)$$

where k is a constant and a , b , and c are constants such that $c = a + b$. The constant k must be the same for all systems [otherwise, (3.50) would not be satisfied], but the additive constant (a , b , or c) differs for different systems.

Since we postulated $S = f(p)$ in Eq. (3.47), we have from (3.51) that

$$S = k \ln p + a \quad (3.52)$$

where k and a are constants and p is the probability of the system's thermodynamic state. Since the second law allows us to calculate only *changes* in entropy, we cannot use thermodynamics to find a . We can, however, evaluate k as follows.

Consider again the spontaneous mixing of equal volumes of two different perfect gases (Fig. 3.12). State 1 is the unmixed state of the middle drawing of Fig. 3.12, and state 2 is the mixed state. Equation (3.52) gives for the process $1 \rightarrow 2$:

$$\begin{aligned} \Delta S &= S_2 - S_1 = k \ln p_2 + a - k \ln p_1 - a \\ S_2 - S_1 &= k \ln (p_2/p_1) \end{aligned} \quad (3.53)$$

(Don't confuse the probabilities p_1 and p_2 with pressures.) We want p_2/p_1 . The probability that any particular d molecule is in the left half of the container is $\frac{1}{2}$. Since the perfect-gas molecules move independently of one another, the probability that every d molecule is in the left half of the container is the product of the independent probabilities for each d molecule, namely, $(\frac{1}{2})^{N_d}$, where N_d is the number of d molecules. Likewise, the probability that all the e molecules are in the right half of the container is $(\frac{1}{2})^{N_e}$. Since d and e molecules move independently, the simultaneous probability that all d molecules are in the left half of the box and all e molecules are in the right half is the product of the two separate probabilities, namely,

$$p_1 = (\frac{1}{2})^{N_d} (\frac{1}{2})^{N_e} = (\frac{1}{2})^{N_d + N_e} = (\frac{1}{2})^{2N_d} \quad (3.54)$$

since $N_d = N_e$. (We took equal volumes of d and e at the same T and P .)

State 2 is the thermodynamic state in which, to within the limits of macroscopic measurement, the gases d and e are uniformly distributed through the container. As noted, the probability of any departure from a uniform distribution that is large enough to be directly detectable is vanishingly small because of the large number of molecules composing the system. Hence the probability of the final state 2 is only "infinitesimally" less than one and can be taken as one: $p_2 = 1$. Therefore, for the mixing, (3.53) and (3.54) give

$$S_2 - S_1 = k \ln (1/p_1) = k \ln 2^{2N_d} = 2N_d k \ln 2 \quad (3.55)$$

However, in Sec. 3.4 we used thermodynamics to calculate ΔS for the constant- T -and- P irreversible mixing of two perfect gases; Eq. (3.33) with mole fractions set equal to one-half gives

$$S_2 - S_1 = 2n_d R \ln 2 \quad (3.56)$$

Equating the thermodynamic ΔS of (3.56) to the statistical-mechanical ΔS of (3.55), we get $n_d R = N_d k$ and $k = R n_d / N_d = R / N_A$, where $N_A = N_d / n_d$ [Eq. (1.5)] is the Avogadro constant. Thus

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K} \quad (3.57)$$

We have evaluated k in the statistical-mechanical formula $S = k \ln p + a$. The fundamental physical constant k , called **Boltzmann's constant**, plays a key role in statistical mechanics. The connection between entropy and probability was first recognized in the 1870s by the physicist Ludwig Boltzmann. The application of $S = k \ln p + a$ to situations more complicated than the mixing of perfect gases requires knowledge of quantum and statistical mechanics. In Chapter 21 we shall obtain an equation that expresses the entropy of a system in terms of its quantum-mechanical energy levels. Our main conclusion for now is that *entropy is a measure of the probability of a state*. Apart from an additive constant, the entropy is proportional to the log of the probability of the thermodynamic state.

Equation (3.52) reads $S = (R/N_A) \ln p + a$. This relation is valid for any system, not just an ideal gas. The occurrence of R in this general equation shows that the constant R is more universal and fundamental than one might suspect from its initial occurrence in the ideal-gas law. (The same is true of the ideal-gas absolute temperature T .) We shall see in Chapter 21 that R/N_A , the gas constant per molecule (Boltzmann's constant), occurs in the fundamental equations governing the distribution of molecules among energy levels and thermodynamic systems among quantum states.

Disordered states generally have higher probabilities than ordered states. For example, in the mixing of two gases, the disordered, mixed state is far more probable than the ordered, unmixed state. Hence it is often said that entropy is a measure of the molecular *disorder* of a state. Increasing entropy means increasing molecular disorder. However, order and disorder are subjective concepts, whereas probability is a precise quantitative concept. It is therefore preferable to relate S to probability rather than to disorder.

For mixing two different gases, the connection between probability and entropy is clear. Let us examine some other processes. If two parts of a system are at different temperatures, heat flows spontaneously and irreversibly between the parts, accompanied by an increase in entropy. How is probability involved here? The heat flow occurs via collisions between molecules of the hot part with molecules of the cold part. In such collisions, it is more probable for the high-energy molecules of the hot part to lose some of their energy to the low-energy molecules of the cold part than for the reverse to happen. Thus, internal energy is transferred from the hot body to the cold until thermal equilibrium is attained, at which point it is equally probable for molecular collisions to transfer energy from one part to the second part as to do the opposite. It is therefore more probable for the internal molecular translational, vibrational, and rotational energies to be spread out among the parts of the system than for there to be an excess of such energy in one part.

Now consider an isolated reaction mixture of H_2 , Br_2 , and HBr gases. During molecular collisions, energy transfers can occur that break bonds and allow the formation of new chemical species. There will be a probability for each possible outcome of each possible kind of collision, and these probabilities, together with the numbers of molecules of each species present, determine whether there is a net reaction to give more HBr or more H_2 and Br_2 . When equilibrium is reached, the system has attained the most probable distribution of the species present over the available energy levels of H_2 , Br_2 , and HBr .

These last two examples indicate that entropy is related to the distribution or spread of energy among the available molecular energy levels. The total energy of an

isolated system is conserved, and it is the *distribution* of energy (which is related to the entropy) that determines the direction of spontaneity. The equilibrium position corresponds to the most probable distribution of energy.

We shall see in Sec. 21.6 that the greater the number of energy levels that have significant occupation, the larger the entropy is. Increasing a system's energy (for example by heating it) will increase its entropy because this allows higher energy levels to be significantly occupied, thereby increasing the number of occupied levels. It turns out that increasing the volume of a system at constant energy also allows more energy levels to be occupied, since it lowers the energies of many of the energy levels. (In the preceding discussion, the term "energy levels" should be replaced by "quantum states" but we won't worry about this point now.)

The website www.entropysite.com contains several articles criticizing the increasing-disorder interpretation of entropy increase and promoting the increasing-dispersal-of-energy interpretation.

Fluctuations

What light does this discussion throw on the second law of thermodynamics, which can be formulated as $\Delta S \geq 0$ for an isolated system (where $dS = dq_{\text{rev}}/T$)? The reason S increases is because an isolated system tends to go to a state of higher probability. *However*, it is not absolutely impossible for a macroscopic isolated system to go spontaneously to a state of lower probability, but such an occurrence is highly unlikely. Hence the second law is only a law of probability. There is an extremely small, but nonzero, chance that it might be violated. For example, there is a possibility of observing the spontaneous unmixing of two mixed gases, but because of the huge numbers of molecules present, the probability that this will happen is fantastically small. There is an extremely tiny probability that the random motions of oxygen molecules in the air around you might carry them all to one corner of the room, causing you to die for lack of oxygen, but this possibility is nothing to lose any sleep over. The mixing of gases is irreversible because the mixed state is far, far more probable than any state with significant unmixing.

To show the extremely small probability of significant macroscopic deviations from the second law, consider the mixed state of Fig. 3.12. Let there be $N_d = 0.6 \times 10^{24}$ molecules of the perfect gas d distributed between the two equal volumes. The most likely distribution is one with 0.3×10^{24} molecules of d in each half of the container, and similarly for the e molecules. (For simplicity we shall consider only the distribution of the d molecules, but the same considerations apply to the e molecules.) The probability that each d molecule will be in the left half of the container is $\frac{1}{2}$.

Probability theory (*Sokolnikoff and Redheffer*, p. 645) shows that the standard deviation of the number of d molecules in the left volume equals $\frac{1}{2}N_d^{1/2} = 0.4 \times 10^{12}$. The *standard deviation* is a measure of the typical deviation that is observed from the most probable value, 0.3×10^{24} in this case. Probability theory shows that, when many observations are made, 68% of them will lie within 1 standard deviation from the most probable value. (This statement applies whenever the distribution of probabilities is a normal, or gaussian, distribution. The gaussian distribution is the familiar bell-shaped curve at the upper left in Fig. 17.18.)

In our example, we can expect that 68% of the time the number of d molecules in the left volume will lie in the range $0.3 \times 10^{24} \pm 0.4 \times 10^{12}$. Although the standard deviation 0.4×10^{12} molecules is a very large number of molecules, it is negligible compared with the total number of d molecules in the left volume, 0.3×10^{24} . A deviation of 0.4×10^{12} out of 0.3×10^{24} would mean a fluctuation in gas density of 1 part in 10^{12} , which is much too small to be directly detectable experimentally. A directly detectable density fluctuation might be 1 part in 10^6 , or 0.3×10^{18} molecules out of 0.3×10^{24} .

This is a fluctuation of about 10^6 standard deviations. The probability of a fluctuation this large or larger is found (Prob. 3.26) to be approximately $1/10^{200,000,000,000}$. The age of the universe is about 10^{10} years. If we measured the density of the gas sample once every second, it would take (Prob. 3.27) about

$$\frac{0.7 \times 10^{200,000,000,000}}{3 \times 10^7} \approx 10^{200,000,000,000} \quad (3.58)$$

years of measurements for the probability of finding a detectable density fluctuation of 1 part in 10^6 to reach 50%. For all practical purposes, such a fluctuation in a macroscopic system is “impossible.”

Probability theory shows that we can expect fluctuations about the equilibrium number density to be on the order of \sqrt{N} , where N is the number of molecules per unit volume. These fluctuations correspond to continual fluctuations of the entropy about its equilibrium value. Such fluctuations are generally unobservable for systems of macroscopic size but can be detected in special situations (see below). If a system had 100 molecules, we would get fluctuations of about 10 molecules, which is an easily detectable 10% fluctuation. A system of 10^6 molecules would show fluctuations of 0.1%, which is still significant. For 10^{12} molecules ($\approx 10^{-12}$ mole), fluctuations are 1 part per million, which is perhaps the borderline of detectability. The validity of the second law is limited to systems where N is large enough to make fluctuations essentially undetectable.

In certain situations, fluctuations about equilibrium are experimentally observable. For example, tiny (but still macroscopic) dust particles or colloidal particles suspended in a fluid and observed through a microscope show a ceaseless random motion (Fig. 3.14), called **Brownian motion** (after its discoverer, the botanist Robert Brown). These motions are due to collisions with the molecules of the fluid. If the fluid pressure on all parts of the colloidal particle were always the same, the particle would remain at rest. (More accurately, it would sink to the bottom of the container because of gravity.) However, tiny fluctuations in fluid pressures on the colloidal particle cause the random motion. Such motion can be regarded as a small-scale violation of the second law.

Similarly, random fluctuations in electron densities in an electrical resistor produce tiny internal currents, which, when amplified, give the “noise” that is always present in an electronic circuit. This noise limits the size of a detectable electronic signal, since amplification of the signal also amplifies the noise.

In 1993, several workers derived the *fluctuation theorem*, which gives the probability that the second law is violated in a very small system. The fluctuation theorem was verified in an experiment that observed the motions of colloidal latex particles of 6300-nm diameter suspended in water and subject to tiny forces due to a laser beam [G. M. Wang et al., *Phys. Rev. Lett.*, **89**, 050601 (2002)].

Thermal fluctuations impose limitations on the operations of proposed nanoscale machines and engines. Molecular machines in biological cells operate at the nanoscale level and so are subject to large thermal fluctuations. Therefore “many central cell processes, such as protein synthesis, energy generation, and catalysis are inherently noisy. That the cell somehow manages to coordinate these noisy processes is one of the remarkable, and still poorly understood, facts of complex biological systems. How is it that the cell is capable of coordinating all these processes in which the signals are essentially buried in noise is one of the remarkable facts of complex biological systems that are still not well understood” (C. Bustamente et al., arxiv.org/abs/cond-mat/0511629).

The realization that the second law is not an absolute law but only one for which observation of macroscopic violations is in general overwhelmingly improbable need

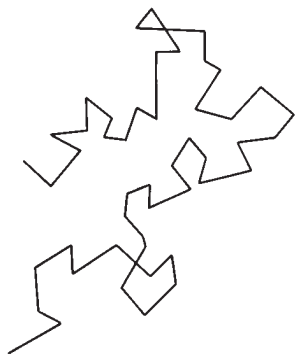


Figure 3.14

A particle undergoing Brownian motion.

not disconcert us. Most laws dealing with the macroscopic behavior of matter are really statistical laws whose validity follows from the random behavior of huge numbers of molecules. For example, in thermodynamics, we refer to the pressure P of a system. The pressure a gas exerts on the container walls results from the collisions of molecules with the walls. There is a possibility that, at some instant, the gas molecules might all be moving inward toward the interior of the container, so that the gas would exert zero pressure on the container. Likewise, the molecular motion at a given instant might make the pressure on some walls differ significantly from that on other walls. However, such situations are so overwhelmingly improbable that we can with complete confidence ascribe a single uniform pressure to the gas.

3.8 ENTROPY, TIME, AND COSMOLOGY

In the spontaneous mixing of two different gases, the molecules move according to Newton's second law, $\mathbf{F} = m d^2\mathbf{r}/dt^2 = m d\mathbf{v}/dt$. This law is symmetric with respect to time, meaning that, if t is replaced by $-t$ and \mathbf{v} by $-\mathbf{v}$, the law is unchanged. Thus, a reversal of all particle motions gives a set of motions that is also a valid solution of Newton's equation. It is therefore possible for the molecules to become spontaneously unmixed, and this unmixing does not violate the law of motion $\mathbf{F} = m\mathbf{a}$. However, as noted in the previous section, motions that correspond to a detectable degree of unmixing are extremely improbable (even though not absolutely impossible). Although Newton's laws of motion (which govern the motion of individual molecules) do not single out a direction of time, when the behavior of a very large number of molecules is considered, the second law of thermodynamics (which is a statistical law) tells us that states of an isolated system with lower entropy must precede in time states with higher entropy. The second law is not time-symmetric but singles out the direction of increasing time; we have $dS/dt > 0$ for an isolated system, so the signs of dS and dt are the same.

If someone showed us a film of two gases mixing spontaneously and then ran the film backward, we would not see any violations of $\mathbf{F} = m\mathbf{a}$ in the unmixing process, but the second law would tell us which showing of the film corresponded to how things actually happened. Likewise, if we saw a film of someone being spontaneously propelled out of a swimming pool, with the concurrent subsidence of waves in the pool, we would know that we were watching a film run backward. Although tiny pressure fluctuations in a fluid can propel colloidal particles about, Brownian motion of an object the size of a person is too improbable to occur.

The second law of thermodynamics singles out the direction of increasing time. The astrophysicist Eddington stated that "entropy is time's arrow." The fact that $dS/dt > 0$ for an isolated system gives us the *thermodynamic arrow* of time. Besides the thermodynamic arrow, there is a *cosmological arrow* of time. Spectral lines in light reaching us from other galaxies show wavelengths that are longer than the corresponding wavelengths of light from objects at rest (the famous red shift). This red shift indicates that all galaxies are moving away from us. (The frequency shift results from the Doppler effect.) Thus the universe is expanding with increasing time, and this expansion gives the cosmological arrow. Many physicists believe that the thermodynamic and the cosmological arrows are directly related, but this question is still undecided. [See T. Gold, *Am. J. Phys.*, **30**, 403 (1962); S. F. Savitt (ed.), *Time's Arrows Today*, Cambridge University Press, 1997.]

The currently accepted cosmological model is the Big Bang model: Much evidence indicates that about 13.7 billion (13.7×10^9) years ago, the universe began in an extraordinarily dense and hot state and has been expanding ever since. It was formerly believed that the rate of expansion of the universe was slowing down due to

gravitational attractions. There was a possibility that gravitational attractions might eventually overcome the expansion, thereby causing the universe to begin to contract, ultimately bringing all matter together again. Perhaps a new Big Bang would then initiate a new cycle of expansion and contraction. An alternative possibility was that there was not enough matter to prevent the expansion from continuing forever.

If the cyclic expansion–contraction cosmological model is correct, what will happen in the contraction phase of the universe? If the universe returns to a state essentially the same as the initial state that preceded the Big Bang, then the entropy of the universe would decrease during the contraction phase. This expectation is further supported by the arguments for a direct connection between the thermodynamic and cosmological arrows of time. But what would a universe with decreasing entropy be like? Would time run backward in a contracting universe? What is the meaning of the statement that “time runs backward”?

Astronomical observations made in 1998 and subsequent years have shown the startling fact that the rate of expansion of the universe is increasing with time, rather than slowing down as formerly believed. The accelerated expansion is driven by a mysterious entity called dark energy, hypothesized to fill all of space. Observations indicate that ordinary matter constitutes only about 4% of the mass–energy of the universe. Another 22% is dark matter, whose nature is unknown (but might be as yet undiscovered uncharged elementary particles). The existence of dark matter is inferred from its observed gravitational effects. The remaining 74% of the universe is dark energy, whose nature is unknown. The ultimate fate of the universe depends on the nature of dark energy, and what is now known about it seems to indicate that the expansion will likely continue forever, but this is not certain. For discussion of the possibilities for the ultimate fate of the universe and how these possibilities depend on the properties of dark energy, see R. Vaas, “*Dark Energy and Life’s Ultimate Future*,” arxiv.org/abs/physics/0703183.

3.9 SUMMARY

We assumed the truth of the Kelvin–Planck statement of the second law of thermodynamics, which asserts the impossibility of the complete conversion of heat to work in a cyclic process. From the second law, we proved that dq_{rev}/T is the differential of a state function, which we called the entropy S . The entropy change in a process from state 1 to state 2 is $\Delta S = \int_1^2 dq_{\text{rev}}/T$, where the integral must be evaluated using a reversible path from 1 to 2. Methods for calculating ΔS were discussed in Sec. 3.4.

We used the second law to prove that the entropy of an isolated system must increase in an irreversible process. It follows that thermodynamic equilibrium in an isolated system is reached when the system’s entropy is maximized. Since isolated systems spontaneously change to more probable states, increasing entropy corresponds to increasing probability p . We found that $S = k \ln p + a$, where the Boltzmann constant k is $k = R/N_A$ and a is a constant.

Important kinds of calculations dealt with in this chapter include:

- Calculation of ΔS for a reversible process using $dS = dq_{\text{rev}}/T$.
- Calculation of ΔS for an irreversible process by finding a reversible path between the initial and final states (Sec. 3.4, paragraphs 5, 7, and 9).
- Calculation of ΔS for a reversible phase change using $\Delta S = \Delta H/T$.
- Calculation of ΔS for constant-pressure heating using $dS = dq_{\text{rev}}/T = (C_p/T) dT$.
- Calculation of ΔS for a change of state of a perfect gas using Eq. (3.30).
- Calculation of ΔS for mixing perfect gases at constant T and P using Eq. (3.33).